Rheology: An Introduction

Rheology: The study of stress-deformation relationships

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

\[
\text{Stress} \quad \text{Strain} = \text{Modulus}
\]
Shear Flow in Parallel Plates

Stress ($\sigma$)  \[ \sigma = \frac{2}{\pi r^2} \times M \]

Strain ($\gamma$)  \[ \gamma = \frac{r}{h} \times \theta \]

Strain rate ($\dot{\gamma}$)  \[ \dot{\gamma} = \frac{r}{h} \times \Omega \]

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

Open Boundary Rotational Rheometer

**ARES G2**

- Measured Torque (Stress)
- Sample
- Direct Drive Motor
- Transducer
- Controlled Strain
- Applied Strain or Rotation
Viscoelasticity

- Viscoelasticity: Having both Viscous and Elastic properties.

- Elastic Behavior: Stress is dependent on Strain
  - Hooke’s Law of Elasticity: Modulus = Stress/Strain
- Viscous Behavior: Stress is dependent on Strain Rate
  - Newton’s Law of Viscosity: Viscosity = Stress/Strain Rate

- Viscoelastic materials cannot be fully understood using only one of these relationships. Oscillation measurements are able to measure stress as a function of both strain and strain rate.
Hooke’s Law of Elasticity

- For an Elastic Solid, Stress and Strain have a constant proportionality $\sigma = E*\varepsilon$
- If the material follows Hooke’s Law, the deformation will be reversible when the stress is removed
- The modulus of a Hookean solid will not show any time dependence - the stress depends on the strain, but not the strain rate

Newton’s Law of Viscosity

- For a Viscous Liquid, Stress is proportional to Strain Rate $d\varepsilon/dt$ by a coefficient of Viscosity $\eta$
  \[ \sigma = \eta \frac{d\varepsilon}{dt} \]
- The deformation of a liquid is non-reversible
Viscoelastic Behavior

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

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

Time-Dependent Viscoelastic Behavior

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

- T is short [< 1s]
- T is long [24 hours]
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

- Silly Putties have different characteristic relaxation times
- Dynamic (oscillatory) testing can measure time-dependent viscoelastic properties more accurately and efficiently by varying frequency (deformation time)
**Frequency Sweep - Time Dependent Viscoelastic Properties**

- Frequency crossover correlates with Relaxation Time.

**Storage and Loss of a Viscoelastic Material**

- Storage $(G')$ and Loss $(G'')$ in different materials.
Oscillation Testing

• The motor applies an oscillating deformation to the sample at a set Amplitude and Frequency.
  - Amplitude: Degree of Arc, or % Strain
  - Frequency: Hz (cycles per second) or CPM (cycles per minute)

• The torque transducer measures the response of the sample.
  - Amplitude: Torque (S*), or Stress

• The phase lag between the deformation and the torque is used to determine the Elastic and Viscous response.

---

Oscillation Testing

In a purely Elastic material, Stress is in phase with the Strain

Phase angle= 0°

In a purely Viscous material, Stress is out of phase with the Strain

Phase angle= 90°

Viscoelastic material

0° < Phase angle< 90°
Oscillation Testing - Lissajous-Bowditch Plots

Elastic Material

Viscoelastic material

Viscous Material

Raw oscillation data can also be plotted as stress vs. strain. An elliptical shape represents a viscoelastic response.

Oscillation Testing

The Phase Angle can be used to separate the stress signal into the elastic and viscous components:

- **G'**: Storage Modulus
  - Measure of elasticity, or the ability to store energy
  - \( G' = \frac{\text{Stress}}{\text{Strain}} \times \cos(\delta) \)

- **G'': Loss Modulus
  - Measure of viscosity, or the ability to lose energy
  - \( G'' = \frac{\text{Stress}}{\text{Strain}} \times \sin(\delta) \)

- **Tan Delta**
  - Measure of dampening properties
  - \( \tan(\delta) = \frac{G''}{G'} \)

- **G*: Complex Modulus**
  - Measure of resistance to deformation
  - \( G* = \frac{\text{Stress}}{\text{Strain}} \)

- **η*: Complex Viscosity**
  - Measure of resistance to flow
  - \( \eta* = \frac{\text{Stress}}{\text{Strain Rate}} \)
PDMS Frequency Sweep Comparison Overlay

Frequency Sweeps on Solids

- Happy & Unhappy Balls
- Modulus is the same
- tan δ is very different
Apart from chemical nature, tacticity and microstructure, polymers have 3 major characteristics which affect processability:

1. Average molecular weight
2. Molecular weight distribution
3. Branching (Type and architecture)
Long Chain Branching: Improving Processability

- Long Chain Branching (LCB) provides Shear Thinning, Strain Hardening and Melt Strength
- Very effective only one per 10000C needed.
- Difficult to fully characterize length of branches, number per chain and distribution.

Common Characterization Techniques

Chromatography (SEC)

FTIR

NMR

**Influence of Molecular Weight on G’ and G”**

The G’ and G” curves are shifted to lower frequency (longer time) with increasing molecular weight.

**Influence of MW on Viscosity**

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.
Materials Evaluated: Polyolefin Elastomers

<table>
<thead>
<tr>
<th>POE</th>
<th>Co-Monomer</th>
<th>Density (g/cm³)</th>
<th>Long Chain Branching</th>
</tr>
</thead>
<tbody>
<tr>
<td>EB-1</td>
<td>Butene</td>
<td>0.901</td>
<td>High</td>
</tr>
<tr>
<td>EB-2</td>
<td>Butene</td>
<td>0.870</td>
<td>Medium</td>
</tr>
<tr>
<td>EB-3</td>
<td>Butene</td>
<td>0.870</td>
<td>High</td>
</tr>
<tr>
<td>EO-1</td>
<td>Octene</td>
<td>0.870</td>
<td>Medium</td>
</tr>
</tbody>
</table>

- The level of Long Chain Branching (LCB) is difficult to directly measure in POEs
  - Amount and length of short chain branching interferes with NMR
  - Characterize differences in LCB using rheology

Conventional Rheology of Polyolefin Elastomers

Viscosity (poise) vs. Angular Frequency (rad/sec)

- EB-1: High LCB
- EB-2: Med LCB
- EB-3: High LCB
- EO-1: Med LCB
Conventional Rheology of Polyolefin Elastomers

Tan Delta vs. Angular Frequency (rad/sec)

Extensional Viscosity of Polyolefin Elastomers

Extensional Viscosity vs. Time (s)
In the Linear Viscoelastic Region, the Stress signal is a sine wave, and meaningful rheology measurements can be made.

At higher strains, stress becomes non-sinusoidal. Modulus is an approximation.
Linear Viscoelasticity

![Graph showing shear modulus vs strain for linear viscoelasticity]

Non-Linear Viscoelasticity - Higher Harmonics

**SAOS**

\[ \gamma(t) = \gamma_0 \sin(\omega t) \]
\[ \tau(t) = \tau_0 \sin(\omega t + \delta) \]

**LAOS**

\[ \gamma(t) = \gamma_0 \sin(\omega t) \]
\[ \tau(t) = \tau_1 \sin(\omega_1 t + \phi_1) + \tau_3 \sin(3\omega_1 t + \phi_3) + \tau_5 \sin(5\omega_1 t + \phi_5) + \ldots \]
\[ = \sum_{n=1}^{\infty} \tau_n \sin(n\omega_1 t + \phi_n) \]
Non-Linear Viscoelasticity - Higher Harmonics

Sample Response

Fundamental + 3rd Harmonic + 5th Harmonic

Large Amplitude Oscillatory Shear (LAOS)

"The potential of large amplitude oscillatory shear to gain an insight into the long-chain branching structure of polymers"
ACS Meeting 2008, Florian J. Stadler, Sunil Dhole, Adrien Leygue, Christian Bailly – Université Catholique de Louvain (UCL)
Large Amplitude Oscillatory Shear (LAOS)

"The potential of large amplitude oscillatory shear to gain an insight into the long-chain branching structure of polymers"
ACS Meeting 2008, Florian J. Stadler, Sunil Dhole, Adrien Leygue, Christian Bailly – Université Catholique de Louvain (UCL)

---

Long Chain Branching Index

"The potential of large amplitude oscillatory shear to gain an insight into the long-chain branching structure of polymers"
ACS Meeting 2008, Florian J. Stadler, Sunil Dhole, Adrien Leygue, Christian Bailly – Université Catholique de Louvain (UCL)
Long Chain Branching

Shear stress (Pa)

High visc. PP
Low visc. PP
95% Low visc. PP+5% high visc. PP
50% Low visc. PP+50% high visc. PP

Secondary loops not affected by AMW and MWD

• Secondary loops can be associated with linear polymer architecture
• There has to be a mathematical condition to account for loops

Lissajous-Bowditch Plots

Rheological characterization of EPDMs

ML(1+4) at 125°C

Mooney shear rate range

Angular frequency (Hz/s)

Rheological characterization of EPDMs

Extensional viscosity (Pa·s)

Angular frequency (Hz/s)

Burhin, Henri G.  Polymer Process Consult

Burhin, Henri G.  Polymer Process Consult
LAOS testing of EPDMs

Long Chain Branching Index - EPDMs
Dynamic Mechanical Analysis

- Is DMA Rheology, or Thermal Analysis?
- Oscillation measurements- $E'$, $E''$, Tan Delta
- Characterize viscoelastic materials as a function of time, temperature, stress and strain.

Glass Transition of PSA measured by DMA

![Graph showing Glass Transition of PSA measured by DMA](image)
Effect of Crosslinking

\[ M_c = \text{MW between crosslinks} \]

Effect of Aging on Elastomer O Rings
Conclusions

- Closed-Die RPA rheometer can match the viscoelastic measurements of the ARES
- Rheological measurements within the linear viscoelastic region can be used to compare MW for non-branched polymers
- Effects of branching are seen in linear, small-amplitude rheology measurements, especially at low frequency
- Large Amplitude Oscillatory Shear (LAOS) clearly differentiates linear and branched polymers.
- DMA measurements also show differences in viscoelastic properties. These can indicate differences in chemistry or molecular structure, but also relate to bulk properties.

Thank You

The World Leader in Thermal Analysis, Rheology, and Microcalorimetry