Rheology and Polymer Characterization

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20 Sep 2010

http://pioneer.netserv.chula.ac.th/~sanongn1/course.html
Fundamentals:

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

• Why Rheology?
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A Rheological Paradox

Sometimes it does ____    Sometimes it doesn’t ____
If a material is pumped, sprayed, extended, extruded, molded, coated, mixed, chewed, swallowed, rubbed, transported, stored, heated, cooled, aged …

RHEOLOGY is important …!!
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“παντα ρει” (everything flows ...) 

- Heraclito de Samos (500 A.C.)

Time Scale in Rheology

Deborah Number \[ \text{De} = \frac{\lambda}{t_{\text{exp}}} \]

Judges 5:5
Definition of Rheology

Rheology is the science of ___flow___ and ____deformation____ of matter under controlled testing conditions.

• flow
• deformation
Definition of Rheology

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

- Flow is a special case of deformation
- Deformation is a special case of flow
Simple Shear Deformation and Shear Flow

Shear Deformation

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

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

Viscosity, \( \eta = \frac{\tau}{\dot{\gamma}} \)

Shear Modulus, \( G = \frac{\tau}{\gamma} \)
Range of Rheological Material Behavior

Rheology: The study of deformation and flow of matter \textit{at specified conditions}.

Range of material behavior

Solid Like \hspace{1cm} \textarrow{\longrightarrow} \hspace{1cm} Liquid Like

(Ideal Solid \hspace{1cm} \textarrow{\longrightarrow} \hspace{1cm} Ideal Fluid)

Classical Extremes
Classical Extremes: Elasticity

1678: Robert Hooke develops his “True Theory of Elasticity”

- “The power of any spring is in the same proportion with the tension thereof.”
- Hooke’s Law: $\tau = G \gamma$ or (Stress = $G \times$ Strain)

where $G$ is the RIGIDITY MODULUS
Linear and Non-Linear Stress-Strain Behavior of Solids

Linear Region
G is constant

Non-Linear Region
G = f(\gamma)

G' (Pa)
osc. stress (Pa)

% strain
1687: Isaac Newton addresses liquids and steady simple shearing flow in his "Principia"

“The resistance which arises from the lack of slipperiness of the parts of the liquid, other things being equal, is proportional to the velocity with which the parts of the liquid are separated from one another.”

Newton’s Law: \( \tau = \eta \dot{\gamma} \)

where \( \eta \) is the Coefficient of Viscosity
Newtonian and Non-Newtonian Behavior of Fluids

Newtonian Region
\( \eta \) Independent of \( \dot{\gamma} \)

Non-Newtonian Region
\( \eta = f(\dot{\gamma}) \)

\( \eta \) (Pa.s)

shear rate (1/s) \( \dot{\gamma} \)

\( \tau \) (Pa)
PARAMETERS for Rheological Properties

Classical Extremes

**Ideal Solid**
- Strong Structure
- Rigidity
- Deformation
- Retains/recovers form
- Stores Energy
  
  (Purely Elastic – R. Hooke, 1678)

**Ideal Fluid**
- Weak Structure
- Fluidity
- Flow
- Losses form
- Dissipates Energy
  
  (Purely Viscous – I. Newton, 1687)

**REAL Behavior**

**Apparent Solid**
- [Energy + time]

**Apparent Fluid**
- viscoelastic materials
Types of non-Newtonian fluids

- Deformation rate dependent viscosity
- Yield Stress (plasticity)
- Elasticity
- Thixotropy
- Transient behaviour
Dilatancy (shear thickening)
Plastic and Pseudoplastic (shear thinning)
apparent viscosity as a function of time

- Thixotropy: apparent viscosity decreases over time.
- Rheopexy: apparent viscosity increases over time.
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Viscometer vs. Rheometer

- **Viscometer**: instrument that measures the viscosity of a fluid over a limited shear rate range.

- **Rheometer**: instrument that measures:
  - Viscosity over a wide range of shear rates, and...
  - Viscoelasticity of fluids, semi-solids and solids.
Frame of Reference…

• Recognize that a rheometer is a highly sensitive device used to quantify viscoelastic properties of the *molecular structure* of materials.

• A rheometer can not always mimic the conditions of a process, application or use.

• Rheometers determine apparent properties under a wide range of testing conditions.

  – *The apparent behavior can be used as a “finger print” or “benchmark” of the material.*
Constitutive Relations

\[
\frac{\text{Stress}}{\text{Strain}} = \text{Modulus}
\]

\[
\frac{\text{Stress}}{\text{Shear rate}} = \text{Viscosity}
\]
Measuring Systems - Geometries

Concentric Cylinders: Very Low to Medium Viscosity
Cone and Plate: Very Low to High Viscosity
Parallel Plates: Low Viscosity to soft Solids
Rectangular Torsion: Soft to Rigid Solids

Decane → Water → Steel
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Dynamic Testing

- An oscillatory (sinusoidal) deformation (stress or strain) is applied to a sample.

- The material response (strain or stress) is measured.

- The phase angle $\delta$, or phase shift, between the deformation and response is measured.
Dynamic Viscoelastic Material Response

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

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

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

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

\[ G' = \text{Stress}^*/\text{strain}\cos\Theta \]

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

\[ G'' = \text{Stress}^*/\text{strain}\sin\Theta \]

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

\[ \tan \phi = \frac{G''}{G'} \]
Dynamic Time Sweep (Time Ramp)

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

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

• Why Rheology?
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• Fundamental Rheometry Concepts
• Viscosity, Viscoelasticity and the Storage Modulus
• The Linear Viscoelastic Region (LVR)
The material response to increasing deformation amplitude (stress or strain) is monitored at a constant frequency and temperature.

- **USES**
  - Identify Linear Viscoelastic Region
  - Strength of dispersion structure - settling stability
  - Resilience
Dynamic Strain Sweep: Material Response

Linear Region
G is constant

Non-Linear Region
G = f(γ)

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

- **USES**
  - Viscosity Information - Zero Shear $\eta$, shear thinning
  - Elasticity (reversible deformation) in materials
  - MW & MWD differences Polymer Melts and Polymer solutions.
  - Finding Yield in gelled dispersions
  - High and Low Rate (short and long time) modulus properties.
  - Extend time or frequency range with TTS
Time Sweep on Latex

Structural Recovery after Preshear

G' (Pa) vs. time (s)
Dynamic Strain Sweep: Material Response

Linear Region
G is constant

Non-Linear Region
\( G = f(\gamma) \)

Critical Strain \( \gamma_c \)
Oscillation Model Fitting for Classic Polymer Data [Polyacrylamide Soln.]

Polyacrylamide Solution 20 C

TA Instruments

Slope = 0.97

Slope = 1.96

4 Element Maxwell Fit

Straight Line Fit to Terminal Region of Data

G'

G''

n'

n' (Pa.s)
## Defining Shear Rate Ranges

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

Response of Viscoelastic Material

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

- For small deformations (strains within the linear region), the ratio of stress to strain is a function of time only.
- This function is a material property known as the STRESS RELAXATION MODULUS, $G(t)$
  
  \[ G(t) = \frac{s(t)}{\gamma} \]
Creep Recovery Experiment

Response of Classical Extremes

**Elastic**
- Stain for $t > t_1$ is constant
- Strain for $t > t_2$ is 0

**Viscous**
- Stain rate for $t > t_1$ is constant
- Strain for $t > t_1$ increase with time
- Strain rate for $t > t_2$ is 0
Creep Recovery Experiment: Response of Viscoelastic Material

Strain rate decreases with time in the creep zone, until finally reaching a steady state. In the recovery zone, the viscoelastic fluid recoils, eventually reaching an equilibrium at some small total strain relative to the strain at unloading.

Polyethylene Rheology @ 150 C

The chart illustrates the viscosity (Pa.s) as a function of shear rate (1/s) for HDPE, LLDPE, and LDPE. The data points and lines represent the rheological behavior of these polyethylenes at 150°C.
Polydimethylsiloxane - Cox-Merz Data

Creep or Equilibrium Flow

Dynamic Frequency Sweep

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

Dynamic data gives high shear rates unattainable in flow
Dynamic Temperature Ramp or Step and Hold: 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 $G''$)
Molecular Structure - Effect of Molecular Weight

MW has practically no effect on the modulus below Tg.
Effect of Heating Rate on Temperature of Cold Crystallization in PET

Heating Rate After Quench Cooling

Crystallization [kinetic event]

T_g

melt
PET Bottle Resin – Cold Crystallization

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

$G'$

$G''$

$\tan\delta$

$\alpha$- transition
$T_g = 88.0°C$

$\beta$- transition
$-56.62°C$

Cold Crystallization
PET Bottle Resin – Before and After DMA Scan

Pressed PET Bottle Resin

PET After Temperature Ramp Scan (Cold Crystallization)
PET Bottle Resin - Repeat Run After Cold Crystallization

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

Melt
$T_m = 240°C$

$\alpha$-transition
$T_g = 103°C$

$G'$

$G''$

$\tan \delta$
PET Bottle Resin - Comparison of G’

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

Repeat Run After Cold Crystallization
Initial Scan on Pressed Resin
Cold Crystallization
BECAUSE ... Typical DSC Transitions

Describe Thermal Transitions of the Materials Structure

Quantitative Description of Consistency (structure)?
BECAUSE ...

- Thermal Analysis describes thermal transitions

NEED to quantify ...

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

and because ...

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

Flexure
Tension

Compression
Creep
Stress
relaxation

Creep
Stress relaxation

Constant stressing rate

Creep
Stress system

(a) Constant stressing rate

(b) Stress relaxation

(c) Constant straining rate

(d) Constant straining rate
Acknowledgements

Abel Gaspar-Rosas, Ph.D.
TA Instruments – Waters, Inc
For graphs and figures