Notes on Polymer Rheology
Outline

• Why is rheology important?
• Examples of its importance
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• Description of the flow equations
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  - laminar vs. turbulent
  - Reynolds number
  - definition of viscosity
• Characterizing Viscosity
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  - pressure
  - molecular weight
  - structure
• How do we measure rheological properties?
  - melt index measurements
  - capillary rheometry
  - cone and plate rheometers
• Solution of flow equations for simple geometries
**Why is rheology important?**

In the making of plastic articles, the manufacturer often starts with pellets of the plastic and ends up with the finished article -- often both the starting point and the final article being in a 'solid' state. To make the finished article, we need to take the polymer into an intermediate state.

This intermediate step in the forming or shaping of plastic articles involves the passage of the polymer through either the viscous flow region or the rubbery region. In these regions the material can be deformed using relatively small forces. Of course, both these regions are above the glass transition temperature. After shaping and forming, the polymer is quenched to a temperature below the glass transition temperature where it will keep its new shape. Of course, there are a number of articles that are in the rubbery state after being formed but they still tend to be 'solid' in that they keep their shape.

You should all be familiar with the effect of temperature. That is, as temperature increases, the properties of a material will change. Sometimes the changes are small, sometimes they are large. For polymers, if we look at the mechanical properties as a function of temperature, we see a behavior similar to that on this graph.

![Diagram of Temperature vs. Log (Modulus)](image)

Rheology is the study of flow and deformation of materials and how that flow is affected by stresses, strains and time.
Examples of it's importance
- extrusion (e.g. extrusion blow molding)
  & die design
  to analyze, we may need to take into account
  high viscosities
  odd shaped flow channels
  other effects include sag, swell, and stretching
  We want to be able to :
  1) design a die head
     a) get correct thickness distribution
     b) get the correct diameter
     c) insure that shear stresses are not too large
  2) predict pressure drops
  3) multilayer dies -- need to study flow patterns in the die to
     insure that layers are of the correct thickness and evenly
     distributed.
- injection molding
  high injection pressures are due to :
  high viscosities
  long flow channels
  thin parts
  desire for tight tolerances
  We may want to be able to predict :
  1) pressures needed
  2) fill time of part
  3) temperature of the melt versus time
     a) mold cooling time
     b) shear heating
     c) melt degradation
- calendering
- quality control (calculation of MIV)
  Properties of a plastic article are dependent on the molecular weight of
  the polymer. It's rigidity, ability to resist fracture, and chemical
  resistance, just to name a few properties, can all be affected by changes
  in molecular weight. The polymer chains can 'break down' during
  processing resulting in a degraded polymer with a reduced molecular
  weight. As we will see later, the viscosity of a melt is a very sensitive
  indicator of the molecular weight of a polymer. A very simple test for
  viscosity is the melt flow indexer.

Thus rheology (particularly the study of the viscous flow of polymers) is very
important in processing and proves useful as a quality control tool.

Viscous properties determine processing issues such as
  form of the velocity profile
  magnitude of pressure drops or amount of heat generation
4.1 Main features of a single screw extruder.
**Extrusion**

- High viscosities
- Odd shaped flow channels
- Other effects include sag, swell and stretching by the mold

Want to be able to:

1) Design a die head
   a) Get correct thickness distribution
   b) Get the correct diameter
   c) Unsure that shear stresses are not too large

2) Predict pressure drops (cannot be too large)

3) Multilayer dies — need to study flow patterns in the die to insure that layers are of the correct thickness and evenly distributed
Injection Molding

- high viscosities
- long flow channels
- thin parts
- desire for tight tolerances

Want to be able to predict:
1) pressures needed
2) fill time of part
3) temperature of melt versus time
   a) mold cool time
   b) shear heating
   c) melt degradation

Figure 11.9. Simplified representation of a calendering process. (Adapted from J. M. McKelvey, Polymer Processing, John Wiley and Sons, New York, 1962. Courtesy of J. M. McKelvey.)

Calendering
Summary of important variables

viscosity
density
heat capacity, thermal conductivity

Description of the flow equations

If we wish to predict or analyze

- pressure drops or
- flow rates or
- velocity profiles

we need to solve the flow equations for the system

If we wish to compute

- temperature profiles or
- heat generated or transferred

we need to solve the thermal energy equations

The basic equations for flow usually include:

- equation of continuity
- momentum balance
  - pressure forces
  - viscous forces
  - inertial forces
  - gravitational forces

We also need a relationship to describe the behavior of viscosity as a function of

- stresses
- strain rates
- temperature
- pressure
Flow regimes

- laminar flow
- turbulent flow

The transition between these regimes is characterized by a quantity called the Reynolds Number

\[ N_{Re} = \frac{\rho V D}{\mu} \]

\( \rho \) density
\( \mu \) viscosity
\( V \) characteristic velocity
\( D \) characteristic length

Characterizing Viscosity

Often the definition of viscosity is explained by using a simple flow situation such as drag flow. No pressure gradients are present. Movement of the fluid contained between two plates is sustained by the motion of the top plate while the bottom plate is held stationary. A force \( F \) is necessary to maintain the motion where the top plate moves at a velocity \( V \).

![Drag flow diagram]

The shear stress \( \tau \) is given by:

\[ \tau = \frac{F}{A} \]

We can also show that the strain rate is proportional to the velocity gradient.

\[ \gamma = \frac{dV}{dy} \]

For many fluids, we assume that the shear stress is proportional to the strain rate -- so:

\[ \tau = -\eta \gamma \]

This equation defines the viscosity (even when the viscosity is not constant).
Units of viscosity

shear rate \( \text{sec}^{-1} \) or \( 1/\text{sec} \)
shear stress Newtons / meter\(^2\) (N / m\(^2\)) Pascals
viscosity Pa-sec

in CGS

viscosity is given in terms of poise

1 poise = 1 dyne / cm\(^2\) - sec = 1 gm/(cm-sec) = 1 gm cm\(^{-1}\) sec\(^{-1}\)

Note also that:
10 poise = 1 Pa-sec = 1 kg/(m-sec) = 1 N-sec/m\(^2\)
1 poise = 2.09 * 10\(^{-3}\) lbf/(ft\(^2\)-sec)

Conversion factors

Pascal (Pa) = Newton(N)/m\(^2\) Joule (J) = N m
N = kilogram - m/sec\(^2\) = kg-m/sec\(^2\)dyne = 10\(^{-5}\) N
1 MPa = 10\(^6\) Pa = 10\(^6\) N m\(^{-2}\) = 10.2 Kg cm\(^{-2}\) = 145 psi

Shear Rates of Different Processes

<table>
<thead>
<tr>
<th>process</th>
<th>shear rate (sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>compression molding</td>
<td>1 - 10</td>
</tr>
<tr>
<td>calendering</td>
<td>10 - 100</td>
</tr>
<tr>
<td>extrusion</td>
<td>100 - 1000</td>
</tr>
<tr>
<td>injection molding</td>
<td>10(^3) - 10(^5)</td>
</tr>
</tbody>
</table>

Viscosities of Various Materials

<table>
<thead>
<tr>
<th>substance</th>
<th>viscosity (Pa-sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>air</td>
<td>10(^{-5})</td>
</tr>
<tr>
<td>water</td>
<td>10(^{-3})</td>
</tr>
<tr>
<td>paint</td>
<td>10(^{-2}) to 10(^{-1})</td>
</tr>
<tr>
<td>glycerol</td>
<td>10</td>
</tr>
<tr>
<td>syrup</td>
<td>10(^2)</td>
</tr>
<tr>
<td>liquid polyurethane</td>
<td>10(^2) to 10(^3)</td>
</tr>
<tr>
<td>polymer melts</td>
<td>10(^2) to 10(^6)</td>
</tr>
<tr>
<td>pitch</td>
<td>10(^9)</td>
</tr>
<tr>
<td>glass</td>
<td>10(^{21})</td>
</tr>
</tbody>
</table>
Limitations of flow

At high enough stress levels or strain rates, the flow of polymer melts becomes unstable. Thus, turbulent flow is not generally possible. These instabilities limit flow rates.
**Viscosity models**

- **ideal fluid**
  
  the viscosity is zero, this is used for the analysis of potential flow problems such as found in aerodynamics

- **Newtonian fluid**

  a good viscosity model for gases and simple liquids such as water

- **non Newtonian fluid**

  the viscosity of the fluid changes with shear rate. For some fluids, it increases with shear rate (dilatant fluids) while for others it decreases with shear rate (pseudoplastic behavior). This pseudoplastic (or shear thinning) behavior is what we observe for polymers.

The most common model for shear thinning is the **power-law model**. This states that the viscosity is proportional to the shear rate raised to a power.

For a power-law fluid, 
\[
\tau = -\eta \dot{\gamma}
\]

where 
\[
\eta = m (-\dot{\gamma})^{n-1} \quad \text{or} \quad m |\dot{\gamma}|^{n-1}
\]

\(n\) is called the power-law index

This model will give a straight-line curve on a log-log plot.

\[
\log(\eta) = \log(m) + (n-1) \log(-\dot{\gamma})
\]

One can plot either shear stress versus shear rate or viscosity versus shear rate on the log-log plots.

**Factors affecting viscosity**

- pressure
- temperature
- molecular weight
- shear rate or shear stress
- branching
- side groups
- molecular weight
- pressure

Any factor which increases entanglements between chains increases the viscosity.

These factors affect the ability of the chains to slide past each other.
Figure 11.12. Typical dependence of apparent viscosity, $\eta$, of a polymeric melt on shear rate, $\dot{\gamma}$, showing the zero-shear viscosity, $\eta_0$, plateau. (Adapted from H. A. Barnes, J. F. Hutton, and K. Walters, An Introduction to Rheology, Elsevier, Amsterdam, 1989, with permission of the publisher.)

Fig. 2.5 Apparent viscosity vs. shear rate for some polymers.
Fig. 2.6 Effect of temperature on polymer viscosity.

Figure 8.15 Effect of chain branching on melt viscosity. Branched chains start shear-thinning at lower shear rates than linear chains. Branched chains tend to have higher limiting viscosities because branches tend to "stiffen" the macromolecule.
Polymer melts are:
- non-Newtonian
- usually shear thinning (decrease in viscosity with increasing shear rate)
- decrease in viscosity with increasing temperature
- increase in viscosity with increasing pressure
- increase in viscosity with increasing molecular weight

**Figure 8.16** Effects of processing variables on melt viscosity. The arrows show the direction the viscosity curve will be shifted by an increase in the variable.
Figure 8.12 Plot of the shear rate dependent viscosity of a narrow molecular weight distribution (PS)(■) at 180°C, showing the "Newtonian plateau" and the "power law" regions and a broad distribution PS (●) (Graessley et al., 1970).
Temperature Effects

WLF Equation  (Williams-Landel-Ferry)

This represents the temperature dependency of a response

\[
\log \left( \frac{\eta}{\eta_{T_g}} \right) = \frac{-a(T - T_g)}{b + (T - T_g)} \quad \text{for } T > T_g
\]

where the universal constants are

\[a = 17.44 \quad ; \quad b = 51.6\]

It can also be shown that the free volume at the glass transition temperature is about 2.5% of the total free volume.

Also, viscosity at the glass transition temperature (\(\eta_{T_g}\)) is about 10\(^{13}\) poise for most plastics.

Prediction of viscosity at any temperature

\[
\log (\eta) = 13 - \frac{17.44}{51.6} \left( \frac{T - T_g}{T - T_g} \right)
\]

Prediction of injection molding temperature

a) need to estimate required viscosity at molding conditions
   e.g. assume \(\eta = 7000\) poise

b) need to determine \(T_g\)
   e.g. for polystyrene \(T_g = 100\, ^\circ C\)

Then

\[
\log (7000) = 13 - \frac{17.44}{51.6} \left( \frac{T - T_g}{T - T_g} \right)
\]

or \(T = 157\, ^\circ C = 430\, ^\circ K\)
**Solution of flow equations for simple geometries**

The viscosity we are most familiar with is the shear viscosity.

Sometimes we need to be concerned with other material quantities

- **Bulk modulus** (which relates a volume change to applied pressure)
  \[ K \approx 10^9 \text{ Pa} \]

  \[ K = \frac{P}{\Delta V/V} \]

- Elongational viscosity which is important in
  - spinning of fibers
  - calendaring

**How do we measure rheological properties?**
- melt index measurements
  (for quality control)
- cone and plate rheometers
- capillary rheometry
  For the capillary tube, the momentum equation becomes a balance between the pressure forces and the viscous forces. If we know the viscosity function, we can then compute the velocity profile and from this get the shear rates.
Melt Flow Index (MFI)

To compute the melt flow index (MFI) of a polymer, the polymer is brought up to a specified melt temperature in a cylindrical chamber. A piston on top of the melt is loaded with a given weight, applying a specified pressure to the melt which is extruded through a given die. Sometimes this is also referred to as the melt index (MI).

For example, for polyethylene (PE) the melt flow index is equivalent to the grams of material extruded from the die in 10 minutes with the melt at 190 °C. Weight applied to the piston equates to 43.5 psi (or 300 kPa). For polypropylene, the melt temperature is 230 °C.

This test is just meant as a comparison between similar materials -- it does not compute a material property. It is mainly useful for quality control -- to see if the material has changed from batch to batch, or to compare the relative flow behavior of different materials.

Both the load and melt temperature may be different for different materials. More information can be obtained by either taking the Polymer Lab course or by referring to ASTM procedure D 1238.
11.4.3 Cone-and-Plate Rheometer

Another important method of measuring the rheological properties of polymer solutions and melts is the cone-and-plate rheometer, which is illustrated in Figure 11.27. Either steady-shear or dynamic-viscosity data (see Section 5.1.3) can be obtained by this method.

The cone angle, $\beta$, is typically very small (1 to 3 radians) — much smaller than suggested by Figure 11.27. At these low angles, the shear rate is given as

$$\dot{\gamma} = \frac{\Omega}{\beta}$$  \hspace{1cm} (11.46)

where $\Omega$ is the angular velocity of the cone. Dynamic viscosity can be obtained by applying an oscillatory shear on the cone. The shear stress, $\tau$, is determined as

$$\tau = \frac{3M}{2\pi R_c^3}$$  \hspace{1cm} (11.47)

where $M$ is the measured torque on the cone having radius $R_c$. The apparent viscosity is then obtained from steady-shear measurements as

$$\eta = \frac{\tau}{\dot{\gamma}}$$  \hspace{1cm} (11.48)

Figure 11.27. Idealized illustration of a cone-and-plate rheometer.
Capillary Rheometer

A force balance between the shear stress and the pressure drop results in

\[ \tau_w = \frac{R}{2L} \left(-\Delta P\right) \]

The apparent strain rate is given by

\[ \varphi = \dot{\gamma}_a = \frac{4Q}{\pi R^3} \]

* Note that often the minus sign is dropped but remember that for flow through a tube, strain rates are either zero or negative.

This is related to the actual strain rate by

\[ \dot{\gamma}_w = \left(\frac{3}{4} \frac{n'}{n} + \frac{1}{n'}\right) \varphi \]

Thus for capillary flow we can compute the shear stress and the actual strain rate and from these compute the viscosity.

\[ \eta = \frac{\tau_w}{\dot{\gamma}_w} \]

The variable \( n' \) is computed from a plot of the log(shear stress) versus log(strain rate). This index is the slope of the curve

\[ \log(\tau_w) \]

\[ \log(\varphi) \]

slope = n
The diagram shows a pressure distribution along a length $z$. The pressure $P_0$ is constant at the beginning, and it decreases linearly with $z$, as indicated by the slope $\frac{dP}{dz}$.
Equations for pressure flow of a power-law fluid in a tube

\[ u_z(r) = \left( \frac{nR}{1+n} \right) \left( \frac{R\Delta p}{2mL} \right)^{1/n} \left[ 1 - \left( \frac{r}{R} \right)^{(1+n)/n} \right] \]

\[ u_z^{\text{max}} = \left( \frac{nR}{1+n} \right) \left( \frac{R\Delta p}{2mL} \right)^{1/n} \]

power-law index, \( n \)

--- 0.2
------ 0.4
----- 1.0
### TABLE 11.3 DIE CHARACTERISTICS FOR A POWER-LAW FLUID IN PRESSURE FLOW

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Die Characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capillary</td>
<td>$Q = \left( \frac{n\pi R^3}{1+3n} \right) \left( \frac{R \Delta p}{2mL} \right)^{1/n}$</td>
</tr>
<tr>
<td>Annulus(^a)</td>
<td>$Q = \left( \frac{n\pi R_o}{1+2n} \right) \left( R_o - R_i \right)^{2+1/n} \left( \frac{\Delta p}{2mL} \right)^{1/n} F(n, \kappa)$</td>
</tr>
<tr>
<td>Parallel plates(^b)</td>
<td>$\frac{Q}{W} = \left[ \frac{nH^2}{2(1+2n)} \right] \left( \frac{H \Delta p}{2mL} \right)^{1/n}$</td>
</tr>
<tr>
<td>Rectangular duct(^c)</td>
<td>$Q = WH^2 \left( \frac{1}{2mL} \right)^{1/n} S_p$</td>
</tr>
</tbody>
</table>

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\(^a\) $R_i$, inner radius; $R_o$, outer radius; $F$ is a function of $n$ and the aspect ratio of the annulus, $\kappa = R_i/R_o$.

\(^b\) Infinitely wide parallel plates where $H$ represents the separation of plates and $W$ is unit width.

\(^c\) This is an example of a nonsimple flow geometry; $S_p$ is a shape factor that is a function of $n$ and the aspect ratio, $WH/W$. 