Shear rheology of polymer melts

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Outline

- Review of some basic rheological concepts (simple shear, elastic solid and viscous liquid, viscoelasticity).
- Some fundamentals about the structure of polymers.
- The Maxwell model and some phenomena related to the elasticity of polymer melts.
- The flow curve of polymer melts: the shear thinning.
- Some correlations between the features of the flow curve and some structural variables like molecular weight and polydispersity.
- Conclusions
simple shear

the flow generates a velocity gradient along the y axis

shear strain:

\[ \gamma = \frac{\Delta x}{\Delta y} = \tan \alpha \]

shear rate:

\[ \dot{\gamma} = \frac{d\gamma}{dt} = \frac{V}{h} \]

shear stress:

\[ \sigma = \frac{F}{S} \]

F is a shear force

moving surface of area S

surface at rest of area S

V = V_{\text{max}}
elastic body

\[ \sigma = G\gamma \]

viscous liquid

\[ \sigma = \eta \frac{d\gamma}{dt} = \eta \dot{\gamma} \]

constitutive equations

Robert Hooke (1678)

store elastic energy!

Isaac Newton (1687)

dissipates energy!

creep and creep recovery
viscoelastic body

James Clerk Maxwell (1868)

Stores and wastes at the same time elastic energy of deformation!

Deborah number:

\[ \text{De} = \frac{\tau_{\text{mat}}}{\tau_{\text{exp}}} \]

“…even the mountains flowed before the Lord…”
(Prophetess Deborah, Judges, 5:5)
Maxwell model

stress relaxation

A constant strain $\gamma_0$ is imposed and the evolution of the stress is followed.

\[
G(t) = G_0 \cdot e^{-(t/\tau)}
\]

stress relaxation modulus:

\[
G(t) = \frac{\sigma(t)}{\gamma_0}
\]

time constant:

\[
\tau = \frac{\eta}{G}
\]
The pitch drop experiment *(University of Queensland)*

9 drops since 1927!

low De
(viscous flow)

A hammer instead of gravity!

high De
(ductile fracture)

the sixth drop in 1979
What is a polymer?

molecular weight of a single chain:

\[ M = mp \]

PolyEthylene (PE)

\[ m = 28 \]

PolyStyrene (PS)

\[ m = 104 \]
The molecular architecture of polymers

PolyEthylene (PE)

- HDPE: $\rho = 0.94 \text{ g/cm}^3$
- LDPE: $\rho = 0.92 \text{ g/cm}^3$
- LLDPE: $\rho = 0.92 \div 0.93 \text{ g/cm}^3$

Some branched structures:
- random
- star
- H-shaped
- T-shaped
- comb-like
- crosslinked
The peculiar structure of macromolecules

(Random Coil)


$l_{C-C} = 4 \text{ mm}$

$\alpha = 109.5^\circ$

$R_{ee} = 20 \text{ cm}$

$L = 4 \text{ m}$
Critical molecular weight and entanglements

For polystyrene the mean molecular weight between entanglements is:

\[ M_e = 18,000 \]

The polymer chains are highly entangled:

\[ R (\text{cm}) = 2.75 \cdot 10^{-9} \sqrt{M} \]

If \( M_w = 1,000,000 \):

\[ R = 2.75 \cdot 10^{-6} \text{ cm} \]

\[ m = \frac{10^6}{N_A} = 1.66 \cdot 10^{-18} \text{ g} \]

\[ \rho_{\text{mol}} = \frac{m}{V} = 0.019 \text{ g/cm}^3 \]

\[ \rho_{\text{melt}} = 1.05 \text{ g/cm}^3 \]

Critical molecular weight:

\[ M_c = 2M_e = 36,000 \]
The most important average values of the molecular weight distribution (MWD)

**number average molecular weight:**

\[
M_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{N_1 M_1 + N_2 M_2 + \ldots}{N_1 + N_2 + \ldots}
\]

**weight average molecular weight:**

\[
M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{N_1 M_1^2 + N_2 M_2^2 + \ldots}{M_1 N_1 + M_2 N_2 + \ldots}
\]

\[
\begin{align*}
N_1 &= 5 \\
M_1 &= 10.000 \\
N_2 &= 5 \\
M_2 &= 1.000
\end{align*}
\]

\[
\begin{align*}
M_n &= \frac{5 \times 10^4 + 5 \times 10^3}{5 + 5} = 5.500 \\
M_w &= \frac{5 \times 10^8 + 5 \times 10^6}{50.000 + 5.000} = 9.182 \\
\frac{M_w}{M_n} &= 1.67
\end{align*}
\]

We always have:

\[
M_w \geq M_n
\]

polydispersity:

\[
\frac{M_w}{M_n}
\]
Molecular weight distribution of a commercial polystyrene

Polystyrene

$M_w = 180.000$

$M_n = 105.000$

$M_z = 280.000$

$M_w / M_n = 1.71$

Relative weight fraction

$\approx 100$ monomers

$\approx 10,000$ monomers
Methods to measure rheological properties

Steady state measurements

Characterization of polymer melts by means of:
- capillary rheometers
- rotational rheometers equipped with cone-plate geometry

Oscillatory regime measurements

Characterization of polymer melts or solids by means of:
- rotational rheometers equipped with parallel plate geometry
- rotational rheometers equipped with torsion rectangular geometry
some phenomena due to melt elasticity

Polymers show elastic components of the stress

rod climbing

die swell

\[ B = \frac{D}{D_0} \]
The normal stress can be greater than the shear stress!

Polystyrene

$M_w = 170,000$

$M_w/M_n = 1.71$

The shear stress is given by:

$$\tau = \frac{3M}{2\pi R^3}$$

The normal stress is given by:

$$N_1 = \frac{2F}{\pi R^2}$$

Shear rate ($s^{-1}$)

low De  high De
Nature of polymer melts elasticity and viscosity

The elasticity of polymer melts is of entropic nature.

The viscous contribution is mainly due to the friction between entanglements.

\[ R_g \]

\[ R'_g \]
Stress relaxation modulus of polymers at $T>T_g$

Segmental relaxation ($T_g$)

Monodisperse with $M_w < M_c$

Monodisperse with $M_w > M_c$

Polydispersed with $M_w > M_c$

$$G^0_N = \frac{\rho RT}{M_e}$$
$M_c$ is a signature of the chain flexibility

<table>
<thead>
<tr>
<th>polymer</th>
<th>$M_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>polyethylene</td>
<td>3.800</td>
</tr>
<tr>
<td>polybutadiene</td>
<td>5.600</td>
</tr>
<tr>
<td>polyisobutylene</td>
<td>17.000</td>
</tr>
<tr>
<td>polyvinylacetate</td>
<td>22.500</td>
</tr>
<tr>
<td>polymethylmetacrilate</td>
<td>27.500</td>
</tr>
<tr>
<td>polydimethylsiloxane</td>
<td>29.000</td>
</tr>
<tr>
<td>polystyrene</td>
<td>36.000</td>
</tr>
</tbody>
</table>
The flow curve of molten polymers: the shear thinning

\[ \eta(\dot{\gamma}) = \frac{\eta_0}{(1 + \lambda\dot{\gamma})^m} \]

Cross equation:

- \( \eta_0 = 7.000 \)
- \( \lambda = 0.14 \)
- \( m = 0.79 \)

Polystyrene
- \( M_w = 170 \text{ kDa} \)
- \( T = 200^\circ \text{C} \)

shear rate (s\(^{-1}\))

viscosity (Pa·s)

newtonian region

power law region

capillary data
cone-plate data

best fit with Cross equation

low De high De
Flow curve of a polyethylene and processing

- Injection molding
- Film extrusion
- Blow molding
- Thermoforming
- Fiber spinning
- Coating
- Compression molding
- Pipe extrusion
- Rotomolding
Rheology and processing
Non-newtonian behavior and processing

Shear rate (s$^{-1}$)
Viscosity (Pa·s)

$\text{PS } M_w=180000$
$T=200{^\circ}\text{C}$
Unrealistic non-newtonian behavior and processing
An important feature of high molecular weight polymer melts:

$$\eta_0 \propto M_w^{3.4}$$
The critical molecular weight divides two regimes

if \( M_w < M_c \):

\[ \eta_0 \propto M_w \]

if \( M_w > M_c \):

\[ \eta_0 \propto M_w^{3.4} \]

Adapted from:
G. C. Berry e T.G. Fox,
Can we explain the huge $M_w$ dependence of the viscosity for high molecular weight polymers?

**in solution**

$R'_g$

The random coil shape is recovered only after a certain «relaxation» time due to memory effects.

The relaxation time increases with increasing molecular weight and decreases with increasing temperature.

For melts the motion is essentially one-dimensional: reptation!

The chain takes a «disengagement» time to relax out of the tube:

$$D \propto M^{-1}$$  \hspace{1cm}  $$L \propto M$$

but

$$\tau_d = \frac{L^2}{D}$$

thus

$$\tau_d \propto M^3$$
The greater the polydispersity, the broader the flow curve.
The greater the molecular weight, the greater the viscosity
die swell

Polystyrene
$M_w = 170,000$

$B = \frac{D}{D_0}$

$T = 180^\circ C$

$T = 195^\circ C$

$T = 210^\circ C$

shear rate ($s^{-1}$)

low $De$

high $De$
Polymer melts and melt fracture

- sharkskin
- stick-slip transition
- gross melt fracture
- smooth

- LLDPE

Graph showing relationship between apparent shear stress (Pa) and apparent shear rate (s⁻¹) for LLDPE.
Conclusions

- Polymer melts are complex fluids exhibiting a significant degree of elasticity.
- The viscosity of polymer melts strongly depends on the strain history and generally exhibits shear thinning behavior.
- The structure of polymers is unique and allows us to describe their rheological behavior by rather simple scaling laws.
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