Notes about this lecture:

- There is a lot of stuff on the following slides!!!

- Make sure you can explain what the following mean:
  - Viscous material and elastic material; viscoelastic
  - Flow curve
  - Newtonian and non-newtonian fluid
  - Pseudoplastic
  - WLF equation
  - Time-temperature superposition
  - Mechanical models of viscoelastic behaviour
  - Typical stress-strain curves for polymers in solid state
Viscoelasticity
Viscoelastic behaviour

- Viscoelastic materials simultaneously exhibit a combination of elastic and viscous behaviour.
- Viscoelasticity refers to both the time- and temperature dependence of mechanical behaviour.
- Typical for polymers.
- Viscoelastic properties as a function of temperature and time (frequency) are commonly studied with dynamic mechanical analysis.
  - Stress response to sinusoidal strain.
Ideal viscous and elastic materials

- **Ideal elastic material:**
  - Reversible shape change, all energy is preserved
  - Final deformation state
  - Hooke’s material

- **Ideal viscous material:**
  - Irreversible shape change, all energy is lost as heat
  - Final shape will equal the shape of the container
  - Newtonian fluid
The elastic limit: Hooke’s Law

Strain increases with increasing stress

\[
\text{Slope} = k
\]
The viscous limit: Newtonian behaviour

The speed at which the fluid flows through the holes (the strain rate) increases with stress!!!
Effect of stress

Figure 4-23 Response of different idealized materials to an instantaneous application of a stress at $t = 0$. A. Elastic. B. Viscous. C. Viscoelastic.
General concepts

- Rheology is the science of deformation and flow of matter
- Provides information about the mechanical response to a dynamic stress or strain
- Polymer rheology involves the melt flow properties of polymers and also mechanical properties of solid polymer materials
- Rheology of polymer melts is more complicated than solution rheology; the melts are viscoelastic
- Rheological properties depend on shear rate, molecular weight, polymer structure, amount of additives and temperature
- Practical applications of rheological property characterization are in polymer processing
Flow curve
Flow curve concepts

- Polymer behaviour is both dependent on time and temperature.
- The flow curve can be measured for both amorphous or partly crystalline polymers, as a function of time or temperature.
- Polymer flow is affected by molecular motions.
- For linear amorphous polymers five regions of viscoelastic behaviour can be observed:
  - Glassy region
  - Glass transition ($T_g$)
  - Rubbery plateau
  - Rubbery-flow region
  - Liquid-flow region
Flow curve

- Typical curve for amorphous polymer as a function of $T$
Flow curve components
Components of a flow curve (Mod. Vs. Temp.)

1. Glassy region
   - The polymer is glassy and brittle
   - Below $T_g$, the modulus approximately 1 GPa for many glassy polymers
   - Molecular motions are restricted to vibrations and short range rotational motions

2. Glass transition
   - Typically the modulus drops a factor of about 1000 across a 20-30 °C range
   - For high molecular weight polymers modulus drops to a secondary plateau region, i.e. rubbery plateau

3. Rubbery plateau
   - Results from the formation of entanglements in high molecular weight polymers
   - Modulus is inversely proportional to the molecular weight between entanglements $M_e$
   - For semi-crystalline materials the modulus is higher

4. Rubbery-flow region
   - Combines the rubber elasticity and flow properties
   - Depends on the time-scale of experiment
   - Does not occur for cross-linked materials

5. Liquid flow region - polymer flows readily
Melt and solution viscosity
Basic concepts

- Stress = Force / Area [Pa]
  - $\sigma$ = tensile stress, $\tau$ = shear stress
- Strain = Geometric shape change [no units, usually % or mm·mm]
  - $\varepsilon$ = tensile strain, $\gamma$ = shear strain
- Strain or shear rate = velocity gradient or $d$(strain) / $dt$ [1/s]
  - $\dot{\varepsilon}$ = tensile strain rate, $\dot{\gamma}$ = shear strain rate
- Modulus = Stress / strain [Pa]
  - $E$ = Young’s or tensile, $G$ = shear modulus
- Compliance = Strain / stress [1/Pa]
  - typically denoted by $J$
- Viscosity = Stress / strain rate [Pa·s or poise]
  - denoted by $\eta$
Viscosity

- Measure of resistance to deformation by shear stress or tensile strength
  - ‘thickness’ of liquids
  - resistance to flow
- SI unit for viscosity is Pa·s
- Old unit is poise (P) dyn·s·cm²
  - 1 P = 0.1 Pa·s
- Polymer viscosity is usually between \(10^1\text{-}10^{10}\) Pa·s

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<thead>
<tr>
<th>Materiaali</th>
<th>Viskositeetti (Pa·s) 20°C</th>
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<td>Glass</td>
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Viscosity: Steady simple shear flow

- Fluid confined between two parallel plates
- Upper plate moves at a constant velocity while the lower plate is at rest
- The force needed to move the upper plate is \( F \) and the contact area of the upper plate to the liquid is \( A \)
- The shear stress is \( \sigma = F/A \)
**Shear viscosity**

Shear stress

\[ \tau = \frac{F}{A} \quad \text{(Pa)} \]

Shear deformation

\[ \gamma = \frac{S}{D} = \tan \theta \]

Viscosity

\[ \eta = \frac{\tau}{\frac{d\gamma}{dt}} = \frac{\tau}{\xi} \quad \text{(Pa·s)} \]
Tensile deformation

- Stress – strain
- Tensile or compression

\[ E = \frac{\sigma}{\varepsilon} \]

\[ G = \frac{\tau}{\gamma} \]
Viscosity

- Tensile stress
  \[ \sigma = \frac{F}{A} \] (Pa)

- Tensile strain
  \[ \varepsilon = \frac{l - l_0}{l_0} \]

- Strain viscosity
  \[ \eta_t = \frac{\sigma}{d\varepsilon/dt} \]
Stress-strain

The area under the curve to this line is the energy needed to break the material.

Brittle materials
Tough materials with yield point
Tough materials without yield point

The points for the calculation of Young's modulus $E_t$ according to 10.3 are indicated by $(\sigma_1, \epsilon_1)$ and $(\sigma_2, \epsilon_2)$, shown only for curve $d$ ($\epsilon_1 = 0.005$; $\epsilon_2 = 0.0025$).

Figure 1 — Typical stress/strain curves
Parameters affecting viscosity

- Shear dependence

- Polymer melts, polymer solutions and dispersions have different relations between shear rate and stress
  - Newtonian
  - Pseudoplastic
  - Dilatant
  - Bingham
Newtonian fluid (black line)

- Viscosity does not depend on shear rate
- Fluids are almost always Newtonian
**Pseudoplastic (green line)**

- Viscosity is lowered as shear rate increases
- Polymer chains are oriented in the flow
- Exhibit shear thinning without the initial resistance to deformation
- Like plastic materials, they also show linear (Newtonian) behaviour at the highest levels of stress and shear rate
Dilatant (red line)

- Viscosity increases as shear rate increases
- Resists deformation more than in proportion to the applied force
- For example, the more effort you put into stirring a dilatant material, the more resistant it becomes to stirring
- Indication that the applied force is causing the material to adopt a more ordered structure
- Rare in polymers
Bingham (blue line)

- Substance shows first elastic and then viscous transition
- Flow will only start when shear stress is at critical value $s_0$
  - Above this it can be either Newtonian or other
Apparent viscosity

- For Newtonian fluids, viscosity is not dependent on shear rate or stress whereas for pseudoplastic or dilatant fluid the viscosity depends on the shear rate
- Apparent viscosity is obtained from steady shear measurement

- Increasing shear rate:
  - Reduces viscosity of pseudoplastic fluids
  - Increases viscosity of dilatant fluids
- Properties of pseudoplastic and dilatant fluids are independent of time
  - With constant shear rate or shear stress the apparent viscosity stays constant
Polymer melts and polymer solutions depending on shear rate

- Logarithmic change

![Graph showing changes in polymer properties with shear rate](graph.png)
Polymer melts and solutions-flow properties

1. First the flow is Newtonian (lower Newtonian region)
   - Shear-stress is increasing steadily and viscosity is constant ($\eta_0$)

2. As shear rate increases, the pseudoplasctic region starts where viscosity is reduced

3. At very high shear rates the flow becomes Newtonian again (upper Newtonian region) where the viscosity then remains constant ($\eta_\infty$)
   - Usually only for solutions, rarely observed in polymer melts since the shear rates required for chain orientation are so high that chains can actually be broken

- Changes in viscosity are due to changes in polymer molecule orientation and entanglements (disentanglement)
Time dependent viscosity

- For some fluids, the apparent viscosity depends on the shear time even when shear rate and stress are kept constant

- **Thixotropic fluid**
  - Apparent viscosity lowers with time with mixing but returns when mixing is stopped

- **Rheopectic fluid**
  - Apparent viscosity increases with mechanical treatment but returns when stopped
Time dependent viscosity

\[ \eta_a \]

\begin{align*}
\text{Reopektinen} \\
\text{Tiksotrooppinen}
\end{align*}

\text{Aika} / t
Pseudoplastic versus Thixotropic

- Most polymers are pseudoplastic and thixotropic, which is generally desired
Viscosity of pseudoplastic material is affected by:

When adding or increasing;

(a) Pressure
(b) Temperature
(c) Molecular weight
(d) Fillers and
(e) Plasticizers
Effect of temperature on viscosity

- Effect of temperature on viscosity of polymer melt can be estimated with several different models. **Arrhenius** and **WLF** equations

- Small molecule liquids and several polymer melts follow the **Arrhenius-equation**

\[ \eta = A e^{E/RT} \]

- \( E \) = Activation energy for viscous flow (kJ/mol)
- \( A \) = constant
Effect of temperature on viscosity

<table>
<thead>
<tr>
<th>Polymeeri</th>
<th>$E$ (kJ/mol)</th>
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<tbody>
<tr>
<td>PDMS</td>
<td>17</td>
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<tr>
<td>HDPE</td>
<td>26 - 29</td>
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<tr>
<td>LDPE</td>
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<td>PP</td>
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<td>PIB</td>
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<td>PC</td>
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<td>SAN</td>
<td>104 - 125</td>
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</tbody>
</table>
Effect of temperature on viscosity

- Viscosities of amorphous polymers follow Williams, Landel and Ferry (WLF) equation above glass transition temperature:

\[\log \frac{\eta}{\eta_s} = \frac{-8.86(T - T_s)}{101.6 + T - T_s} = \log a_T\]

- \(\eta_s\) = viscosity of polymer in standard temperature
- \(T_s\) = standard (reference) temperature (K)
- Equation is applicable in \(T\) range \(T_s = \pm 50\) °C
Effect of temperature on viscosity

Considering the $T_g$ as the standard temperature, the equation is:

- $C_1$ and $C_2$ = constants (depend on polymer)
- $h_{T_g}$ = viscosity of polymer at glass transition temperature

- If $T_g$ is reference temperature, then:
  - $C_1 = 17.44$
  - $C_2 = 51.6$

$$\log \frac{\eta}{\eta_{T_g}} = \frac{-C_1 \times (T - T_g)}{C_2 + (T - T_g)}$$

Equation is applicable in the T range $T_g... (T_g + 100 \, ^\circ C)$,
If polymer specific values for constants C are not known, values $C_1=8.86$ and $C_2=101.6$ can be used
Effect of temperature on viscosity

some $T_g$ and $T_s$ –values for polymers:

<table>
<thead>
<tr>
<th>Polymeeri</th>
<th>$T_s$ (K)</th>
<th>$T_g$ (K)</th>
<th>$T_s - T_g$ (K)</th>
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<tbody>
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<td>polyisobuteeni</td>
<td>243</td>
<td>197</td>
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<td>37</td>
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Effect of pressure on viscosity

• Significant effect on polymer viscosity
• Some processing techniques, for example injection moulding, have high pressures
• When T is constant the effect of pressure on viscosity can be estimated with the equation:

\[
\ln\left(\frac{\eta}{\eta_r}\right) = \beta(p - p_r)
\]

\(\eta_r\) = reference viscosity at reference pressure \(p_r\)
\(\beta\) = pressure constant
Effect of molecular weight on viscosity

- Molecular weight and structure (branching)

- Viscosity follows experimental correlation:

\[
\eta_0 = k \cdot \overline{M}_w^\alpha
\]

- Equation is valid at very low shear rates where viscosity is not dependent on shear rate (\(\eta=\eta_0=\text{constant}\)). \(k\) is an experimentally measured coefficient which is dependent on T. \(\alpha\) is 1 or 3.4 (see next slide)
Effect of molecular weight on viscosity
Effect of molecular weight on viscosity

\[ \bar{M}_{wc} \] = critical molecular weight (depends on polymer structure and is between 2000 - 60 000 g/mol)

\[ Z_c \] = critical value for atomic number in polymer chain

<table>
<thead>
<tr>
<th>Polymeeri</th>
<th>( \bar{M}_{wc} )</th>
<th>( Z_c )</th>
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</table>
Other effects on viscosity

- Entanglements
- Long chain branching (LCB)
- Solvents lower viscosity

- Effect of fillers on viscosity can be estimated using Mooney correlation:

\[
\ln\left(\frac{\eta}{\eta^0}\right) = \frac{k_E \phi}{1 - \phi/\phi_m}
\]

\(\phi_m\) = maximum packing (volume) fraction
\(k_E\) = Einstein coefficient
Measurement of viscosity
Measurement of viscosity

- Rheological properties are measured as a function of temperature and shear rate

- Methods are divided:
  1. Static shear strain methods
     - Capillary rheometry
     - Couette rheometry (Concentric cylinder)
     - Parallel plate
     - Cone and plate
  2. Dynamic shear strain methods
     - Dynamic rheometers
Measuring methods

a) capillary  
b) cylinder  
c) cone
Capillary rheometer

- The measurement of volumetric flow rate, \( Q \), as a function of \( \Delta P \) through a capillary of known dimensions. The capillary is attached to a reservoir containing the polymer solution or melt. Pressuration of the reservoir forces the fluid through the capillary:

\[
\eta = \frac{\pi R^4 P}{8 L Q}
\]

- \( R \) = radius of capillary (m)
- \( L \) = length of capillary (m)
- \( P \) = pressure drop across the capillary (Pa)
- \( Q \) = volumetric flow rate (m\(^3\)/s)
Capillary viscometry

• Advantages:
  – Easy to fill
  – Temperature and shear rate easy to change
  – Relevant to most polymer processing operations
    • Shear rate 1-10^{-5} \text{ s}^{-1}
  – Easy to study different flow phenomena (flow fracture etc.)

• Challenges:
  – Shear rate can vary
  – Measuring accurate values can be difficult
Cylinder viscometer

- Inner cylinder is driven at constant angular velocity within an outer cylinder, liquid is placed in the space between the cylinders. Torque is measured; assuming the cylinders have infinite length and the edge effects can be neglected, viscosity can be calculated from

\[
\eta = \frac{M}{4\pi \omega (h + h_0)} \left( \frac{1}{R_1^2} - \frac{1}{R_2^2} \right)
\]

- **Pros**: shear rate nearly uniform in the device
- **Cons**: filling the apparatus with the viscous fluid can be challenging

\( M \) = torque  
\( h \) = length of the inner cylinder (m)  
\( \omega \) = angular velocity (rad/s)  
\( R_1 \) = radius of inner cylinder (m)  
\( R_2 \) = radius of outer cylinder (m)  
\( h_0 \) = length
Cone-and-plate rheometer

- Steady shear or dynamic viscosity
- Fluid is in between the plate and cone:

\[ \eta = \frac{3\alpha M}{2\pi R^3 \omega} \]

\( \alpha \) = cone angle (rad)
\( M \) = measured torque
\( \omega \) = angular velocity of the cone
\( R \) = radius of the cone (m)

- **Pros**: shear rate steady for solution, small sample size
- **Cons**: only slow shear rates can be measured

Figure: Fried
Shear rates

- Melt flow index and capillary rheometer near real life applications
Dynamic or oscillatory rheometers

- Principle of the measurement

\[ \tau_t = \tau_0 \sin(\omega t) \]

\[ \gamma_t = \gamma_0 \sin(\omega t - \delta) \]

\( \gamma_0 = \text{Amplitude} \)
Dynamic parameters

- Dynamic viscosity: $\eta^*$
- Storage modulus: $G'$
- Loss modulus: $G''$
- $\tan \delta$: $G''(\omega)/G'(\omega)$
- Zero viscosity: $\eta_0$ – dynamic viscosity at zero frequency
- $E_a$ – Activation energy of flow according to Arrhenius equation
  
  $$\eta = Ae^{Ea/RT}$$
Dynamic viscometer testing

In dynamic testing, the stress is measured as a function of strain that is in periodic function of time, usually a sine wave. For a strain $\gamma$ that is a function of time, the strain function can be written:

$$\gamma(t) = \gamma_0 \sin(\omega \cdot t)$$

where $\gamma_0$ is amplitude and $\omega$ the angular frequency of oscillation.

The stress resulting from the applied sinusoidal strain can be written:

$$\tau(t) = \tau_0 \sin(\omega t + \delta)$$

where $\tau_0$ is amplitude and $\delta$ the phase angle.

Ideal elastic: stress is in phase with strain $\delta=0$

Ideal viscous fluid: always 90° out of phase $\delta=\pi/2$
Dynamic viscometer principles

- The phase lag will be $0^\circ$ for purely elastic materials and $90^\circ$ for purely viscous materials
  - Viscoelastic materials (e.g. polymers) will exhibit an intermediate phase difference
Dynamic viscometer

• Manipulating equation (2) using trigonometry we get:

\[
\tau(t) = \gamma_0 (G'(\omega)\sin(\omega \cdot t) + G''(\omega)\cos(\omega \cdot t))
\]  

(3)

Where \(G'(\omega)\) is the storage modulus and \(G''(\omega)\) is the loss modulus. Using these the dynamic modulus can be expressed in complex number notation

\[
G*(\omega) = G'(\omega) + iG''(\omega)
\]  

(4)

Further the dynamic modulus is:

\[
|G*(\omega)| = \sqrt{(G')^2 + (G'')^2}
\]  

(5)
Dynamic viscometer

- Storage and loss modulus can be written:

\[ G' = \left| G^*(\omega) \right| \cos(\delta) \]  \hspace{1cm} (5)

\[ G'' = \left| G^*(\omega) \right| \sin(\delta) \]  \hspace{1cm} (6)

- \( \tan \delta \) is the ratio of loss modulus to storage modulus. It can be used to estimate changes in material behaviour.

\[ \tan \delta = \frac{G''(\omega)}{G'(\omega)} \]  \hspace{1cm} (7)
Dynamic viscometer

- The dynamic viscosity consists of storage and loss parts:

\[ \eta^*(\omega) = \eta'(\omega) + i\eta''(\omega) \quad (8) \]

- Dynamic viscosity parts as function of modulus:

\[ \eta' = \frac{G''}{\omega} \quad (9) \quad \eta'' = \frac{G'}{\omega} \quad (10) \]

- Temperature and shear rate affect the complex modulus significantly
Dynamic viscometer

- Complex modulus \((E' + iE'')\) as a function of frequency or temperature

![Diagram showing complex modulus as a function of frequency or temperature.](image)
Dynamic viscometer

- Complex compliance \((J' - iJ'')\) as a function of frequency (or temperature):
Rotation rheometer

- Shear measurement
- Dynamic measurement
- Creep/recovery measurement

Levy/levy  Kartio/levy  Sylinteri
Strain sweep, PE, 190°C

Strain [%]

$G'$ ([Pa])

$G''$ ([Pa])

$\tan\ delta (G''/G')$

Strain sweep
Frequency sweep

HDPE2 frequency sweep 190°C

- Complex viscosity, $\eta^*$
- Loss modulus, $G''$
- Storage modulus, $G'$
- Complex modulus, $G^*$
- Tan delta ($G''/G'$)
Time sweep

Time sweep, 2h, 210°C, stable sample

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

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

\[ \tan \delta \]
Time-temperature superposition (TTS)

- With viscoelastic materials, time and temperature are equivalent to the extent that data at one temperature can be superimposed on data at another temperature by shifting the curves along the log time axis.

- Enables evaluating long time behaviour by measuring stress-relaxation or creep data over a shorter period of time but at several different temperatures.

- Information from each temperature curve is combined to yield a master curve at a single T.
Time-temperature superposition (TTS)

- Why is it used?
  - To determine the temperature dependence of the rheological behaviour of a polymer liquid.
  - To expand the time or frequency at a temperature at which the material is being characterised

- Low temperature corresponds to a high frequency response and vice-versa

![Diagram showing the relationship between temperature, frequency, and material behavior]
Analysis of polystyrene

- Temperature range: 30 to 150 °C
  - (10 °C interval, 5 min soak time)
- 12 frequencies:
  - 0.01, 0.02, 0.05,
  - 0.1, 0.2, 0.5,
  - 1, 2, 5,
  - 10, 20, 50 Hz
- From the resulting isothermal curves, a reference curve was selected. All remaining curves were shifted horizontally and vertically to superimpose on the reference curve
E’ mastercurve of polystyrene

Vertical shift factors
\[ \alpha_v = \frac{T_g \rho_g}{T_\rho} \]

Horizontal shift factors
Williams-Landel-Ferry (WLF) equation
\[ \log(\alpha_T) = \frac{-C_1(T - T_r)}{C_2 + (T - T_r)} \]
Master curve

A) Modulus of PV as a function of time and temperature from stress-relaxation

B) Resulting master curve obtained by shifting data at ref. T=150°C
Time-temperature superposition (TTS)
Melt instabilities
Melt fracture

- During polymer extrusion, the surface of the product is uneven above a critical shear stress (or shear rate)
  - Critical shear stress value for most polymers ~20 N/cm²
- Distortions can take the form of spirals or “sharkskin”
- The general phenomenon of distorted extrudate is called **melt fracture**
- Factors contributing to higher shear stress increase the tendency for melt fracture
  - Higher shear rate
  - Higher molecular weight
  - Lower temperature
## Melt fracture

- Shear rates in different processing methods:

<table>
<thead>
<tr>
<th>Muovausmenetelmä</th>
<th>$\dot{\gamma}$ (s$^{-1}$)</th>
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<tbody>
<tr>
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<td>geeliytymisajan määritys</td>
<td>1 - 10</td>
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<td>puristusmuovaus</td>
<td>1 - 10</td>
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<tr>
<td>kalanterointi</td>
<td>$10 - 10^2$</td>
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<td>suulakepuristus</td>
<td>$10^2 - 10^3$</td>
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<td>ruiskupuristus</td>
<td>$10^3 - 10^4$</td>
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<tr>
<td>kehruu</td>
<td>$10^4 - 10^5$</td>
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Gel time

Calendering

Extrusion

Injection molding
Die swell

- Related to entropy and relaxation of polymer chains
- Chain entanglements act as temporary crosslinks and outside the die the release of axial stress causes an axial shrinkage and a transverse expansion
- Chain disentanglement is a kinetic process
  - The longer the die is, the more time is given for the physical entanglements within the polymer stream to disentangle
  - With a longer die and a slower polymer flow stream, less pronounced die swell will be observed
  - This characteristic relaxation time determines the length of time the polymer must spend inside the die to minimize die swell
Die swell

Pre-entrance to die, slow flow rate, polymers have a roughly spherically conformation in order to minimize entropy.

Narrow die causes flow rate to increase, polymer conformations begin to length in response to this increase in flow rate. Physical entanglements begin to disentangle proportional to time of polymer in this condition over relaxation time.

Flow returns to slow flow rate after exiting die, polymers regain a roughly spherically conformation again in order to minimize entropy; magnitude of die swell is inversely related to number of disentanglements within the die.
Die swell

The diameter of the extruded fiber is larger than the diameter of capillary:

\[ B_{ex} = \frac{D_e}{R} \]

Where \( D_e \) is the diameter of extrudate and \( R \) is the diameter of capillary

Can be determined when measuring melt flow index
Melt flow index (MFI)

- Melt index refers to the weight (in grams) of polymer extruded over a specified time interval and temperature through an extrusion die in a plastometer that is fitted with a standard dead-weight piston and cylinder.
Mechanical models of viscoelastic behaviour
Mechanical models of viscoelastic behaviour

- Stress–induced deformation of materials is a time dependent phenomena, particularly in polymers
- These phenomena can be modelled by combining two elements: elastic and viscous
- Viscoelastic properties of polymers can be obtained by analysing the stress or strain response of mechanical models using an ideal spring as the Hookean (elastic) element and a dashpot as the viscous element
  - A dashpot can be viewed as a shock absorber consisting of a piston in a cylinder filled with a Newtonian fluid
Mechanical models of viscoelastic behaviour

- Elastic component modelled by a string
Mechanical models of viscoelastic behaviour

- Viscous flow modelled by a dashpot:
Mechanical models of viscoelastic behaviour

The strain rate of an ideal elastic spring can be written according to Hooke’s law:

\[ \gamma = \frac{1}{G} \cdot S \]

\( S = \) stress
\( G = \) modulus
\( \gamma = \) strain

The strain rate for the dashpot is obtained by rearranging Newton’s law

\[ \frac{d\gamma}{dt} = \frac{1}{\eta} \cdot s \]

\( \gamma = \) strain
\( \eta = \) viscosity
\( s = \) stress
Mechanical models – Maxwell element

Series combination of a spring and dashpot

Limitation:
- Sharp corners produced at region changes and continued deformation as long as stress is applied make it unsuitable for describing creep.
Mechanical models – Maxwell element

The total strain is the sum of the individual strains of the spring and the dashpot

When load is removed, the spring will recover immediately but the dashpot won’t move and thus there is permanent strain

The stress relaxation:

\[ s = s_0 e^{-\frac{Gt}{\eta}} = s_0 e^{-t/\tau} \]

\( \tau = \text{relaxation time (} \eta/G \text{)} \)
Mechanical models – Voigt element

Parallel combination of a spring and dashpot
Also referred to as ‘Kelvin-Voigt’ model

Limitation:
- It fails to show instantaneous response or continued flow under equilibrium stress
Mechanical models – Voigt element

Parallel combination of a spring and dashpot - Voigt element
The strain on each element must be equal while the stress is additive

\[ s = G\gamma + \eta \frac{d\gamma}{dt} \]
Model for amorphous polymer

Polymer deformation consists of Hooke´s elasticity, viscoelasticity and viscous flow. These can be represented with a model where both the Maxwell and Voigt elements are combined in series:

Referred to as the ‘4-element model’ or ‘Maxwell-Voigt model’

Utilised for creep-recovery
Creep-recovery of an amorphous polymer

- Hooke elasticity
- Viscoelastic recovery
- Permanent change

Graph showing the creep-recovery process with time as the x-axis and strain (γ) as the y-axis.
What happens during a creep-recovery experiment

OA: Instantaneous extension (Maxwell element, E1)

AB: Creep Kelvin element

BC: Creep Maxwell element

CD: Instantaneous recovery (Maxwell element, E1)

DE: Delayed recovery (Kelvin element)
The retardation time ($\tau$) is the time required for the Voigt element to recover to 63.21 % (or $1-1/e$) of its total deformation.
Modelling Recovery – KWW stretched exponential function

• Of the numerous models available to explain recovery, the stretched exponential function of Kohlrausch, Williams and Watts (KWW) is one of the most suitable, fitting experimental recovery data well

• $\Phi = A \exp\left(\frac{t}{\tau}\right)^{\beta}$

where $A$ is the pre-exponential coefficient, $t$ is time, $\tau$ is the retardation time and $\beta$ is the non-linearity coefficient ($0 < \beta < 1$)
Next week

- Polymer dissolution
- Fractionation
- Gas permeation