Performance polymers, fibres and textiles
Overview

1. Mechanics properties
2. Composite
   1. Rubber toughening
   2. Short fibre composites
3. Polymers for demanding environments
What relates these two objects?

Tesco and Asda bags “flimsiest on High Street”
The Telegraph, 24/9/2010

Body armour comprised Dyneema fibres and ceramic plates.
Polyethylene

Degree of crystallinity > 85 %
Highly orientated.

Semi-crystalline system
Part 1: Mechanical Properties

- Introduction
- Elastic deformation
  - Deformation of a polymer chain
  - Polymer Crystal Moduli
  - Elastic deformation of semi-crystalline polymers
- Phenomenology of Yield
  - High-Strain Deformation
  - Necking and the Considère construction
- Deformation Mechanisms
  - Theoretical shear stress
  - Shear yielding in glassy polymers
  - Plastic Deformation of Polymer Crystals
  - Plastic deformation of semi-crystalline polymers
- Fracture
  - Crazing
Laboratory experiments

• You tested the following samples
  – PS
  – HIPS
  – HDPE
  – LDPE
Deformation of polymers

Schematic tensile stress-strain curves

Initial slope gives $E$

Note wide range of possible $E$

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Modulus (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastomer</td>
<td>$\sim 10^6 - 10^7$</td>
</tr>
<tr>
<td>Semicrystalline Polymer</td>
<td>$\sim 10^8 - 10^9$</td>
</tr>
<tr>
<td>Glassy polymer</td>
<td>$\sim 10^9$</td>
</tr>
<tr>
<td>Polymer Fibre ($\perp$ to axis)</td>
<td>$\sim 10^9$</td>
</tr>
<tr>
<td></td>
<td>$\sim 10^{11}$</td>
</tr>
</tbody>
</table>
Notes on graph on previous slide:

• **Elastomers**
  - Tend to have very low Young’s moduli of the order of $10^6$ Pa.
  - Deformation consists essentially of uncoiling the molecules in a crosslinked network

• **Semi-crystalline polymers**
  - Young’s modulus of the order of $10^8 - 10^9$ Pa
  - Composite consisting of polymer crystals distributed in a rubbery matrix

• **Polymer glasses**
  - Young’s modulus of the order of $10^9$ Pa
  - Hard to model deformation which is a mixture of bending and stretching of the strong covalent bonds on the polymer backbone and displacement of adjacent molecules which is opposed by relatively weak secondary bonds

• **Polymer fibres**
  - Very anisotropic. E parallel to the chain direction are $\sim 10^{11}$ Pa which is similar to E found for metals (e.g. steel, $E \approx 2.1 \times 10^{11}$ Pa).
  - E perpendicular to the chain axes is only $10^9$ Pa.
  - Along fibre stretch covalent bonds, across chain breaking secondary bonds
We will focus on the mechanical properties of the crystalline, semi-crystalline and glass polymers for this course. This systems include:

- **Epoxy resins** – for composites (Glassy)
- **High impact polystryene** (Glassy)
- **Poly(aramid)**
e.g. Kevlar™ and Twaron™
- **Poly(ethylene)**

![Diagram of polymer structures]
• We will split the behaviour into 3 sections:
  Elastic deformation
  Yield
  Plastic deformation
Part 1: Mechanical Properties

- **Introduction**
- **Elastic deformation**
  - Deformation of a polymer chain
  - Polymer Crystal Moduli
  - Elastic deformation of semi-crystalline polymers
- **Phenomenology of Yield**
  - High-Strain Deformation
  - Necking and the Considère construction
- **Deformation Mechanisms**
  - Theoretical shear stress
  - Shear yielding in glassy polymers
  - Plastic Deformation of Polymer Crystals
  - Plastic deformation of semi-crystalline polymers
- **Fracture**
  - Crazing
Theoretical elastic deformation of single polymer crystal: the maximum performance

- High anisotropy of the bonding in polymer crystals allow you to calculate theoretical moduli for polymer crystal
- Originally done by Treloar, 1960

Assume:
1. Polymer that crystallizes with its backbone in the form of a planar zig-zag
2. Deformation involves only the bending and stretching of the bonds along the molecular backbone

Backbone consists of $n$ rods of length, $l$, which are capable of being stretched along their lengths but not of bending, and are joined together by torsional springs.
Bond angles are taken initially to be $\Theta$
Change in polymer chain length with force

- Change in overall polymer chain length
  Initial chain length, $L = n l \cos \alpha$
- Apply force, $f$, at an angle $\alpha$ to the initial bond position
- The change in length $\delta L$ upon deformation:

  $\delta L = n \delta (l \cos \alpha) = n (\delta l \cos \alpha - l \delta \alpha \sin \alpha)$

- Bond stretching, $\delta l$:
  - Component of force in the length direction = $f \cos \alpha$
  - Related to force constant, $k_i$, for bond (i.e. Hooke’s constant for spring bond):

  $\delta l = \frac{f \cos \alpha}{k_1}$
Change in polymer chain length with force

- **Change in bond angle, \( \delta \alpha \)**
- Torque on bond angles:
  - Angular deformation force constant \( k_\Theta \)
  - Torque = moment of the applied force about the angular vertices
    \[ = \frac{1}{2} f l \sin \alpha \]
  - Change in angle of bonds given by:
    \[ \delta \Theta = \frac{\text{Torque}}{\text{Force constant}} = \frac{(fl \sin \alpha)}{2k_\Theta} \]

- However, \( \alpha = 90^\circ - \Theta/2 \) so \( \delta \alpha = -\delta \Theta/2 \)

\[ \delta \alpha = -\frac{(fl \sin \alpha)}{4k_\Theta} \]
Calculation of $E$

\[
\delta L = n(\delta l \cos \alpha - l \delta \alpha \sin \alpha)
\]

\[
\delta \alpha = -\frac{(fl \sin \alpha)}{4k_{\Theta}}
\]

\[
\delta l = \frac{f \cos \alpha}{k_1}
\]

Substitute all above:

\[
\frac{\delta L}{f} = n \left[ \frac{\cos^2 \alpha}{k_1} + \frac{l^2 \sin^2 \alpha}{4k_{\Theta}} \right]
\]

Chain-direction modulus is given by:

\[
E = \frac{\text{Stress}}{\text{Strain}} = \left( \frac{f}{A} \right) / \left( \frac{\delta L}{L} \right) = \frac{fL}{A\delta L}
\]

Substituting $L = nl\cos\alpha$ and $\delta L/f$ from above

\[
E = \frac{l \cos \alpha}{A} \left[ \frac{\cos^2 \alpha}{k_1} + \frac{l^2 \sin^2 \alpha}{4k_{\Theta}} \right]^{-1}
\]

\[
E = \frac{l \sin(\Theta/2)}{A} \left[ \frac{\sin^2(\Theta/2)}{k_1} + \frac{l^2 \cos^2(\Theta/2)}{4k_{\Theta}} \right]^{-1}
\]

as $\alpha = 90^\circ - \Theta/2$
Deformation of a Polymer Chain

\[ E = \frac{l \sin(\Theta/2)}{A} \left[ \frac{\sin^2(\Theta/2)}{k_l} + \frac{l^2 \cos^2(\Theta/2)}{4k_\theta} \right]^{-1} \]

- \( k_1, k_\theta \) can be determined by Raman or IR spectroscopy
- Crystal structure gives \( A, l \) and \( \Theta \)

- Predicts a value of \( E \) for polyethylene of ~ 180 GPa
  - Rather lower than values obtained from more sophisticated calculations
  - We have not allowed for intramolecular interactions

- Also the chain direction modulus calculated here does not completely describe the behaviour of polymer crystal.

*In this model, does PE or PP have the highest modulus?*
Polymer Crystal Moduli

- Estimates of chain-direction moduli can be made experimentally using an X-ray diffraction method.
- Use fibres in which the molecules are aligned parallel to the fibre axis or mechanically draw an isotropic polymer into a filament or a tape.
- Measure the relative change under an applied stress in the position of any \((hkl)\) Bragg reflection that has a component of the chain-direction repeat (usually indexed \(c\)).
- The axial crystal strain, \(e_c\), can be determined from:

\[
    e_c = \frac{c_\sigma - c_0}{c_0}
\]

where:
- \(c_\sigma\) is the value of lattice parameter under stress.
- \(c_0\) is its value before deformation.
- Assume that the stress on the crystal, \(\sigma_f\), is equal to that on the whole fibre, filament or tape.

\[
    E_c = \frac{\sigma_f}{e_c}
\]
Example PBO fibres

Reciprocal space, hence as strain increases, $g$, gets smaller.
## Theory vs experimental

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Calculated</th>
<th>Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E$/GPa</td>
<td>method</td>
</tr>
<tr>
<td>Polyethylene (PE)</td>
<td>182</td>
<td>VFF</td>
</tr>
<tr>
<td></td>
<td>340</td>
<td>UBFF</td>
</tr>
<tr>
<td></td>
<td>257</td>
<td>UBFF</td>
</tr>
<tr>
<td>Polypropylene (PP)</td>
<td>49</td>
<td>UBFF</td>
</tr>
<tr>
<td>Polyoxymethylene (POM)</td>
<td>150</td>
<td>UBFF</td>
</tr>
<tr>
<td>Polytetrafluoroethylene PTFE</td>
<td>160</td>
<td>UBFF</td>
</tr>
<tr>
<td>Substituted polydiacetylenes</td>
<td>(i) 49</td>
<td>VFF</td>
</tr>
<tr>
<td></td>
<td>(ii) 65</td>
<td>VFF</td>
</tr>
<tr>
<td>PPTA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBO</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

VFF — Valence force field (e.g. Treloar’s method).
UBFF — Urey-Bradley force field

(i) Phenyl urethane derivative.
(ii) Ethyl urethane derivative.
General Considerations

• **Moduli higher for planar zig-zag molecules than rather than a helix.**
  – PE (zigzag) is stiffer than POM and PFTE (Helical)
  – The helices can be extended more easily than planar zig-zag.
  – Large side groups tends to reduce the modulus because they increase the separation of molecules in the crystal. This causes an increase in the area supported by each chain.

• **The potential unidirectional moduli are relatively high.**
  – Utilized to a limited extent in conventional polymer fibres.
  – Stiff and inflexible polymer molecules (PPTA and PBO) have led to very high modulus polymer fibres such as ‘kevlar’ being produced by the spinning of liquid crystalline solutions.

• **Specific modulus** that is important, especially when light high-stiffness materials are required:
  – Polymers tend to have low specific gravities, typically 0.8-1.5 compared with 7.9 for steel,
  ⇒ specific stiffnesses compare even more favourably with metals.
Semi-crystalline polymer c moduli

- Chain-direction modulus, $E_c$, is always greater than the Young’s modulus, $E_f$, of the fibre, filament or tape.

- Crystals and lower-modulus amorphous material are lined up in parallel in the fibre microstructure.

- Although they are subjected to the same level of stress, the strain in the amorphous material is higher than that in the crystals leading to $E_f < E_c$.

- Highly oriented semi-crystalline polymers tend to have moduli of < 50% of the theoretical values.
  - Presence of amorphous phase tends to cause a significant reduction in modulus.
Elastic deformation of semi-crystalline polymers

The presence of crystals in a polymer has a profound effect upon its mechanical behaviour.

NATURAL RUBBER
- Crystallization of rubber occurs during prolonged storage of the material at low temperature
- Increased crystallinity from 0 to 25% increases modulus x 100

(Data of Leitner reported by Treloar)
Elastic deformation of semi-crystalline polymers: PE

LINEAR POLYETHYLENE

- Usually crystallinity is >60%
- Can extrapolate to 100% crystallinity:

\[ E = 5 \text{ GPa for 100\% crystalline material} \]

Sample has randomly orientated crystals – how does that affect \( E \)?
Elastic deformation of semi-crystalline polymers

- **Semi-crystalline polymers are essentially two-phase materials**
  - Increase in modulus due to presence of crystals
  - Polymer is effectively a composite of amorphous and crystalline material
  - Observed modulus is a combination of the separate moduli for these two regions

- **Mathematically predicting behaviour is not trivial**
  
  *E.g. Spherulitic polymers have elastically isotropic elastic properties but the crystals in the spherulites themselves are highly anisotropic.*

  ⇒ Have to calculate an effective modulus for the particular type of morphology considered
  ⇒ Degree of crystallinity and size, shape and distribution of the crystals all effect the modulus
  ⇒ Reliable estimates can only be made for specific well-defined morphologies.
Part 1: Mechanical Properties

• Introduction
• Elastic deformation of polymers
  – Deformation of a polymer chain
  – Polymer Crystal Moduli
  – Elastic deformation of semi-crystalline polymers
• Phenomenology of Yield
  – High-Strain Deformation
  – Necking and the Considère construction
• Deformation Mechanisms
  – Theoretical shear stress
  – Shear yielding in glassy polymers
  – Plastic Deformation of Polymer Crystals
  – Plastic deformation of semi-crystalline polymers
• Fracture
  – Crazing
Ideal stress–strain curve for a ductile polymer sample

- **Yield point**
- **Strain hardening**
- **Fracture**
- **Necking**
  - Neck runs along whole sample

\[ \sigma_n = \frac{\text{Force divided by original cross-section area}}{\text{original cross-section area}} \]
Notes on ideal stress-strain curve

1. Elastic behaviour, where Hooke’s Law is obeyed
   • Tensile modulus taken from slope
   • Cross-sectional area of the specimen decreases uniformly as length increases

2. Yield point where the yield stress and yield strain are $\sigma_y$ and $e_y$
   • Should correspond to the point at which permanent plastic deformation takes place
   • In some polymers, though, inelastic behaviour occurs before maximum
   • In practice, exact position of the yield point is not important, so we define:
     Yield as maximum point on the curve
     • Yield strain for polymers is typically 5–10%
     • Yield strain for metals < 0.1%.
Notes on ideal stress-strain curve

3. Formation of a neck
   - Past the yield point, the cross-sectional area starts to decrease more rapidly at one particular point along the gauge length
   - This narrow region is called a neck
   - The nominal stress falls after yield and settles at a constant value as the neck extends along the specimen.
   - Extension of neck is called **cold drawing**
   - Polymers differ in their ability to form a stable neck and some do not neck at all.
   - Degree of necking depends on conditions

   ![Diagram of drawing](image)

   \[ \text{Draw ratio} = \frac{\text{Length of necked sample}}{\text{Length of original sample}} \]

   - Draw ratio = ratio of original specimen cross-sectional area to that of the drawn specimen.

4. Strain hardening
   - Eventually neck goes entire gauge length, at which point strain hardening starts and the stress rises

5. Fracture
Necking and drawing

- Material outside the neck is less deformed than in the neck
  - Material in neck is strain hardened
  - Outside material is ‘softer’
  ⇒ Outside material continues to deform even though it has a larger cross-sectional area and lower true stress.

- Strain-hardening in polymers due to the effects of orientation.
  - X-ray diffraction shows that the molecules are aligned parallel to the stretching direction in the cold-drawn regions of both amorphous and crystalline polymers.
  - Anisotropic nature of the chemical bonding in the molecules causes an oriented polymer to be very much stronger and stiffer than an isotropic one
  ⇒ Material in the necked region is capable of supporting a much higher true stress than that outside the neck.
  ⇒ Polymers tend to form stable necks and undergo cold-drawing if they do not first undergo brittle fracture.
Part 1: Mechanical Properties

- Introduction
- Elastic deformation of polymers
  - Deformation of a polymer chain
  - Polymer Crystal Moduli
  - Elastic deformation of semi-crystalline polymers
- Phenomenology of Yield
  - High-Strain Deformation
  - Necking and the Considère construction
- Deformation Mechanisms
  - Theoretical shear stress
  - Shear yielding in glassy polymers
  - Plastic Deformation of Polymer Crystals
  - Plastic deformation of semi-crystalline polymers
- Fracture
  - Crazing
Slip processes

• Deformation of metal crystals predominantly through slip processes:
  • Sliding of one layer of atoms over another through the motion of dislocations.
  • Ductility of metals stems from there normally being a large number of slip systems (i.e. slip planes and directions) available.

• Slip is also important in the deformation of polymer crystals:
  • The need to avoid molecular fracture limits the number of slip systems available.
  • Slip planes are limited to those which contain the chain direction i.e. \((hk0)\) planes when \([001]\) is the chain direction.

• Slip directions can in general be any direction which lies in these planes.
• Slip in any general direction in a \((hk0)\) plane will have components of these two specific types.
• *Chain direction slip* is illustrated schematically below. The molecules slide over each other in the direction parallel to the molecular axis.
Change in spherulite morphology during the cold-drawing

- Melt-crystallized polymers have a complex structure consisting of amorphous and crystalline regions in a spherulitic microstructure.
- Display most useful properties in the temperature range $T_g < T < T_m$
  - Below the $T_g$ they are brittle
  - Above $T_m$ they behave as viscous liquids or rubbers.

- Beyond yield point, the spherulites become elongated parallel to the stretching direction.
- At high strains the spherulitic microstructure breaks up and a fibre-like morphology is obtained.
From spherulite to fibrillar structure

Possible mechanism for last stage in previous graph

A) Idealized representation of undeformed structure
B) Crystals deforming by slip, twinning and martensitic transformations
C) Crystals break up and molecules are pulled out
D) Fibrillar structure forms.
Orientated, drawn polymers

- Polymers oriented by drawing are of considerable practical importance:
  - Can display up to 50% of the theoretical chain direction modulus of the crystals.
  - This short-fall in modulus is caused by imperfections within the crystals and the presence of folds and non-crystalline material.
  - The value of modulus obtained depends principally upon the crystal structure of the polymer and the extent to which a sample is drawn (i.e. the draw ratio).
  - Maximum draw ratio that can be obtained depends upon:
    - Temperature of drawing
    - Average molar mass
    - Molar mass distribution of the polymer.

There is now considerable interest in optimizing these variables to obtain ultra-high modulus, oriented polymers.

e.g. Dyneema (Highly orientated polyethylene)
Temperature and time dependence

- Modulus increases as temperature reduced
- Ductile-to-brittle transition
  - Ductility of the polymer decreases with temperature
  - < 320 K the polymer does not draw and behaves in a brittle manner
- Exact temperature of transition depends upon the rate of testing
- Similar behaviour with rate and temperature as with viscoelasticity
- Effect of increasing the rate of testing upon properties such as the Young’s modulus or yield stress is the same as reducing the testing temperature.

Stress–strain curves for poly(methyl methacrylate)
(Tg ~ 125 °C)
Glassy polymers do show plastic deformation in compression

- Glassy polymers are capable of displaying a considerable amount of ductility below $T_g$ in compression.
  - Brittle when tested in tension
  - Considerable ductility in compression and undergo shear yielding
  - Tend to show ‘strain softening’, where true stress drops after yielding due to inherent softening of the material, rather than necking.

Cross-linked epoxy resin ($T_g = 100 ^\circ C$) deformed in tension or compression at $\sim 20 ^\circ C$
Effect of temperature

Effect of temperature on the Young Modulus of amorphous and semi-crystalline polymers. (Tg is glass transition temperature and Tm is the melting temperature)
Part 1: Mechanical Properties

- Introduction
- Elastic deformation of polymers
  - Deformation of a polymer chain
  - Polymer Crystal Moduli
  - Elastic deformation of semi-crystalline polymers
- Phenomenology of Yield
  - High-Strain Deformation
  - Necking and the Considère construction
- Deformation Mechanisms
  - Theoretical shear stress
  - Shear yielding in glassy polymers
  - Plastic Deformation of Polymer Crystals
  - Plastic deformation of semi-crystalline polymers
- Fracture
  - Crazing
Crazing

- Crazing is a localized form of plastic deformation
- Tends to occur in thermoplastics in the glassy state
- Crazes appear as small crack-like entities
  - Usually initiated on the specimen surface
  - Oriented perpendicular to the tensile axis.
- Crazes are regions of cavitated polymer and so not true cracks (cracks contain no polymer)
  - However cracks tend to nucleate within the crazes
- Crazes are very small, ~100 nm thick and several microns long
- Can see them since less dense that undeformed matrix
  $\Rightarrow$ Reflect and scatter light
- Crazing can be made easier by the presence of certain liquids (‘crazing agents’)
  - Use of some glassy polymers is limited by them undergoing crazing at relatively low stresses in the presence of crazing agents
Crazing

Craze nucleate at when local stresses are above the craze initiation stress

- Craze initiation stress drops as the testing temperature is increased and as the strain-rate is decreased
- The presence of crazing agents (e.g. finger grease or methanol with polystyrene) causes the craze initiation stress to drop further.

**Dependence of craze initiation stress upon temperature at different strain-rates for polystyrene**
Crazing in glassy polymers

- Crazes normally nucleate on the surface of a specimen, probably at flaws (e.g. scratches and imperfections)
- Flaws on the surface tend to raise the magnitude of the applied stress locally and allow craze initiation to occur.
- Crazes are:
  - Lamellar in shape
  - Grow into the bulk of the specimen from the surface
- Crazes contain polymer, typically
  ~ 50 vol% within their bulk
- Cracks do not contain any polymer in their bulk

TEM craze in a thin film of polystyrene

Kramer

50nm
Nano/Microstructure of a craze

At end, craze tapers gradually until it eventually consists of a row of voids and microfibrils on the 5 nm scale.

Sharp boundary between the craze and the polymer matrix.

TEM craze in a thin film of polystyrene.

Craze itself contains many cavities, bridged by dense network of fine fibrils ~ 20 nm in diameter.
Nucleation and growth of crazes

• Basic mechanism is thought to be a local-yielding and cold-drawing process which takes place in a constrained zone of material.

1. Craze nucleation
   • Local stresses at the tip of a surface flaw are higher than overall tensile stress applied to the specimen.
   • Yielding takes place locally at these stress concentrations

2. Fibril formation
   • Local yielding and cold-drawing of material in craze to form fibrils
   • Fibrils remain intact because they contain oriented molecules so have higher modulus than surrounding material.

3. Craze widening
   • Uncrazed material at the craze/matrix boundary being deformed into fibrils and thus incorporated in the craze.
   • Craze forms as very thin lamellae in a plane perpendicular to the tensile axis because the tensile stress is highest across this plane and the elastic constraint of the surrounding uncrazed material allows the craze to grow only laterally and thicken.
Reminder: Griffith Fracture Criteria

- Stress is concentrated at the sharp points of the defects.

- Energy consideration:
  - Strain energy stored around defect which is released upon fracture
  - Crack growth creates surface and hence costs energy.
\[ \sigma_f = \left( \frac{2E\gamma}{\pi a} \right)^{1/2} \]

\[ \sigma_f = \left( \frac{EG_c}{\pi a} \right)^{1/2} \]

\( G_c \) = fracture energy = total work of fracture

\[ K = \sigma \sqrt{\pi a} \]

\[ K_c = \sqrt{EG_c} \]

where \( K_c \) = fracture toughness

\[ \sigma \leq \frac{\sqrt{\pi a}}{K_c} \]

\( \sigma_f \) = Critical fracture stress

\( a \) = crack length

\( E \) = Modulus

\( G_c \) = Fracture energy

\( K \) = Fracture toughness

(ability of material to resist fracture)

Material will not fail when:
Examples of $\sigma_f$ vs crack length


- Clear dependence of $\sigma_f$ upon $a^{-1/2}$
- Rise in strength does not go on indefinitely
  - $\sigma_f$ becomes independent of flaw size.
  - Limit at $a = 1$ mm for PS and $a = 0.07$ mm for PMMA at room temperature
  - Materials behave as if they contain natural flaws of these critical sizes, so adding smaller cracks makes no difference

**Inherent flaws are crazes**, which appear during loadings and in which the crack nucleates. Crazes are smaller in PMMA than in PS