MICROMECHANICS OF POLYMERS

Electron Microscopic Methods to Investigate Micro- and Nanoscopic Processes of Deformation and Fracture

25\textsuperscript{th} Short Course on Polymer Characterization

\begin{center}
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Outline

1. Micromechanics: Imaging of Micro- and Nanoscopic Processes of Deformation and Fracture
2. Preparation
3. Examples
   - semicrystalline polymers
   - toughness enhancement
   - thin layer yielding
   - nanocomposites of carbon based nanofillers: CB and CNT
4. Summary
1. Micromechanics: Imaging of Micro- and Nanoscopic Processes of Deformation and Fracture

Probe types for microscopic investigations of morphology and micromechanics

<table>
<thead>
<tr>
<th>light</th>
<th>electron beam</th>
<th>mechanical</th>
</tr>
</thead>
<tbody>
<tr>
<td>light optical microscopy</td>
<td>scanning electron microscopy (SEM)</td>
<td>transmission electron microscopy (TEM)</td>
</tr>
<tr>
<td><img src="image1.png" alt="Light microscopy image" /></td>
<td><img src="image2.png" alt="SEM image" /></td>
<td><img src="image3.png" alt="TEM image" /></td>
</tr>
</tbody>
</table>

- **SFM imaging**
- **micro- and nano-indentation**

![Additional images](image4.png)
1. Micromechanics: Imaging of Micro- and Nanoscopic Processes of Deformation and Fracture

Comparison of probe design and bulk sample preparation strategies for different microscopic techniques

→ Morphology
1. Micromechanics: Imaging of Micro- and Nanoscopic Processes of Deformation and Fracture

Comparison of sample preparation strategies for different microscopic techniques

→ Micromechanics
1. Micromechanics: Imaging of Micro- and Nanoscopic Processes of Deformation and Fracture

- Determination of local mechanical properties
  - Defined microscopic sample region, microscopic probe

- Mechanical testing of miniaturized samples
  - Microscopic specimens, miniature testing equipment

- Fracture surface analysis
  - Failure analysis, interpretation of micromechanical processes of fracture, defects, loading conditions

- Estimation of mechanical properties from small amounts of materials
  - High throughput characterization, screening

- Imaging of microscopic processes of deformation and fracture
  - Analysis of structure-property relations and tailored material design

  - In situ-techniques: Deformation under microscopic observation
    - Tensile and bending experiments in LOM, SEM, TEM, AFM

  - Preparation and investigation of deformation zones of deformed samples
    - LOM, SEM, TEM, AFM investigations after mechanical testing
1. Micromechanics: Imaging of Micro- and Nanoscopic Processes of Deformation and Fracture

- Polymerization
- Processing
- Loading Conditions

Molecular (Chemical) Structure → Supermolecular Structures (Morphology) → Micromechanical Processes of Deformation and Fracture → Mechanical Properties

Mechanical load

polymer specific material laws
elastic/viscous/viscoelastic/plastic behaviour

deformation and fracture
1. Micromechanics: Imaging of Micro- and Nanoscopic Processes of Deformation and Fracture

Micromechanics:
Examples for micro- and nanoscopic processes during deformation and fracture

<table>
<thead>
<tr>
<th>scale</th>
<th>processes</th>
</tr>
</thead>
<tbody>
<tr>
<td>nm</td>
<td>stretching of chain segments,</td>
</tr>
<tr>
<td></td>
<td>reptation movements,</td>
</tr>
<tr>
<td></td>
<td>chain scission</td>
</tr>
<tr>
<td>μm</td>
<td>microvoid formation</td>
</tr>
<tr>
<td></td>
<td>microyielding</td>
</tr>
<tr>
<td></td>
<td>crazing</td>
</tr>
<tr>
<td></td>
<td>shear band formation</td>
</tr>
<tr>
<td></td>
<td>micro flow</td>
</tr>
<tr>
<td>mm</td>
<td>crack initiation &amp; propagation</td>
</tr>
<tr>
<td></td>
<td>fracture</td>
</tr>
</tbody>
</table>
1. Micromechanics: Imaging of Micro- and Nanoscopic Processes of Deformation and Fracture

Deformation mechanisms:
Schematic illustration of the features of typical deformation zones in polymers

**Left:** macroscopic appearance of the deformation zones in tensile bars

**Center:** Microstructure of the deformation zone

**Right:** Examples with the corresponding entanglement molecular weight $M_e$

<table>
<thead>
<tr>
<th>Type</th>
<th>Orientation of the length compared to principal stress direction</th>
<th>Structure inside</th>
<th>Volume-change $\Delta V/V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shear band</td>
<td>$\approx 45^\circ$</td>
<td>Homogeneous</td>
<td>0</td>
</tr>
<tr>
<td>Craze</td>
<td>$\perp$</td>
<td>Nano-voids, fibrillated</td>
<td>$\sim 1$</td>
</tr>
<tr>
<td>Crack</td>
<td>$\perp$</td>
<td></td>
<td>$\gg 0$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Deformation / band</th>
<th>Example $M_e$ [kg/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Fibrillated craze</td>
<td>PS 18.7</td>
</tr>
<tr>
<td>b) Homogeneous craze (homogeneous deformation band)</td>
<td>PMMA 9.2</td>
</tr>
<tr>
<td>c) Shear bands</td>
<td>PVC 5.6</td>
</tr>
<tr>
<td>d) Broad shear bands</td>
<td>PC 2.5</td>
</tr>
</tbody>
</table>
1. Micromechanics: Imaging of Micro- and Nanoscopic Processes of Deformation and Fracture

Deformation mechanisms:

Different deformation zones in polymers under tensile loading

**Left:** macroscopic appearance of the tensile bars after loading

**Center:** Light microscopic appearance of the deformation zones

**Right:** micromechanical processes

- micro plastic zone: stretching of molecules
  - chain-scission
- crazes: nanovoid formation
  - stretching of molecules
- shear bands: gliding of molecules
  - multiple crazing
  - multiple shearing
1. Micromechanics: Imaging of Micro- and Nanoscopic Processes of Deformation and Fracture

Defects:
Schematic representation of defects which can reduce the strength of polymers

**Left**: macroscopic appearance of the tensile bars after loading

**Right**: supramolecular (structural) defects
2. Preparation

Preparation of Electron Transparent Samples: (Cryo-)Ultramicrotomy

- Preparation of electron transparent samples from bulk materials
  - at room temperature for hard samples
  - under cryo conditions for soft materials \( (T_{\text{cut}} < T_g) \)
  - using glass or diamond knives
2. Preparation

Preparation of Electron Transparent Samples: (Cryo-)Ultramicrotomy

→ ultra- and semithin thin sections for TEM
→ smooth surfaces for AFM and SEM

A - specimen is cut with controlled speed (downward stroke)
B - retraction
C - advance of specimen arm determines the specimen thickness
2. Preparation

Sample preparation for micromechanical *in situ* testing: (Cryo-)Ultramicrotomy
2. Preparation

- **In situ-investigations:**
  - Instrumentation

- different straining devices for LOM, SEM, TEM and AFM
2. Preparation

Sample preparation for micromechanical \textit{ex situ} testing: (Cryo-)Ultramicrotomy

Transfer of the section to formvar coated ductile copper grids

Deformation under light optical control: Cracks in the support film induce localized deformation in the ultrathin section
2. Preparation

Sample preparation for micromechanical analyses using deformed specimen **after mechanical testing**:

- Ultrathin sections (+ staining): TEM
- Block faces: (+ etching) SEM, AFM
2. Preparation

Sample preparation for micromechanical analyses using deformed specimen after mechanical testing:

- Block faces + etching: SEM
- Preparation of flat surfaces from internal regions of deformed tensile bars by microtomy
- Permanganic etching
- SEM observation of deformation structures
2. Preparation

Sample preparation: Fixation and staining

- Polymer samples are too soft for sectioning at RT?
- Polymer samples are sensitive to electron beam irradiation?
  → Chemical or physical treatment for hardening („Fixation“)
- Polymer samples very often do not show sufficient contrast (similar electron densities of the elements that are present)
  → Heavy elements can be placed selectively into one or more phases of the material giving contrast („Staining“)
- Staining procedures can be applied prior to sectioning (staining of a trimmed block) or after ultramicrotomy (staining of ultrathin sections).
- Staining can be performed by immersion of the sample in the staining agent or in vapour.
- There are one-step procedures and more complex procedures with two or more steps.
2. Preparation

Sample preparation: Fixation and staining

Polyolefines:
- chlorosulfonic acid + osmium tetroxide
- chlorosulfonic acid + uranyl acetate
- ruthenium tetroxide

Polyamides:
- formalin + osmium tetroxide
- tungstophosphoric acid + osmium tetroxide
- ruthenium tetroxide

Styrol-Butadiene-Copolymers:
- osmium tetroxide
- ruthenium tetroxide

Polyurethanes:
- chlorosulfonic acid + osmium tetroxide
- ruthenium tetroxide
2. Preparation

Sample preparation: Fixation and staining

Example: semicrystalline morphology of $\alpha$- and $\beta$- modification of polypropylene

One-step staining with ruthenium tetroxide, ultramicrotome sections
2. Preparation

Sample preparation: Fixation and staining

Example: Styrene-butadiene blockcopolymers

One-step staining with osmium tetroxide, ultramicrotome sections

<table>
<thead>
<tr>
<th>Linear asymmetric tapered</th>
<th>Star shaped asymmetric tapered</th>
<th>Star shaped asymmetric PS-co-PB mid-block</th>
<th>Linear symmetric PS-co-PB mid-block</th>
</tr>
</thead>
<tbody>
<tr>
<td>lamellae</td>
<td>lamellae</td>
<td>co-continuous</td>
<td>PS domains</td>
</tr>
</tbody>
</table>

200 nm
2. Preparation

Sample preparation: Etching

Example for permanganic etching:
Development of a topography at the surface of a polypropylene sample; SEM-SE images

Literature on permanganic etching:
e.g. Olley et al., J. Mat. Sci. 28 (1993), 1102-1112

Preparation from a deformed sample (bulk)

Mixture of sulfuric acid, orthophosphoric acid, water, potassium permanganate

Etching time (15...30)min
23°C
Ultrasonic bath
Rinsing, drying

Transformation of morphological features to topography
2. Preparation

Sample preparation: Etching

Example: semicrystalline morphology of $\alpha$- and $\beta$- modification of polypropylene
3. Examples

Semicrystalline Polymers
3. Examples

Semicrystalline Polymers

- Comparison of mechanical properties and micromechanical mechanisms in two different crystalline modifications of Polypropylene

![Graph showing comparison of mechanical properties between beta PP and alpha PP](image)
3. Examples
Semicrystalline Polymers

- Comparison of mechanical properties and micromechanical mechanisms in two different crystalline modifications of Polypropylene
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Semicrystalline Polymers

- Comparison of mechanical properties and micromechanical mechanisms in two different crystalline modifications of Polypropylene
3. Examples
Semicrystalline Polymers

- PP parts from micro injection moulding

Illustration of morphology formation of PP with different molecular weights by injection moulding

31 [Frick, Stern, Michler, Henning, Ruff. in: Layered Nanostructures. Macromolecular Symposia 294-II]
3. Examples
Semicrystalline Polymers

- PP parts from micro injection moulding

Light optical images (polarized light) of cross sections of the miniature tensile bars: spherulitic morphology

From a to f: Increasing molecular weight

With increasing molecular weight, the skin layer becomes more and more dominant

[Frick, Stern, Michler, Henning, Ruff. in: Layered Nanostructures. Macromolecular Symposia 294-I]

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3. Examples
Semicrystalline Polymers

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3. Examples

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Semicrystalline Polymers

- PP parts from micro injection moulding

\[ M_w = 837 \text{ kg/mol} \]

[Image of graph showing stress-strain relationship with labels: Stress (MPa) on the y-axis and Deformation (%) on the x-axis, with a peak at around 90 MPa for a deformation of 300%.

[Graph depicting a curve representing the relationship between stress and strain, with labels for stress in MPa on the y-axis and deformation in % on the x-axis, showing a steep rise to peak stress at about 90 MPa at 300% deformation.]
3. Examples

Semicrystalline Polymers

- PP parts from micro injection moulding
3. Examples

Semicrystalline Polymers

- PP parts from micro injection moulding
3. Examples
Toughness Enhancement

- Micromechanical principles of toughness enhancement

*bulk PS homopolymer*

- amorphous, hard at RT ($T_g \approx 103^\circ$C)
- high strength and stiffness:
  - $\sigma_B \approx 40 \ldots 50$ MPa,
  - $E \approx 3.5$ GPa
- transparent
- *brittle: $\varepsilon_B \approx 3\%$*
- *micromechanical mechanism: crazing*
3. Examples
Toughness Enhancement

- Micromechanical principles of toughness enhancement

rubber toughening of PS

deflection structures in HIPS

(G.H. Michler: Electron Microscopy of Polymers; Springer 2008)

micromechanical mechanisms of toughening with dispersed rubber particles: multiple crazing, crack stop, crack bridging

3. Examples

Toughness Enhancement

- deformation of PP-EPR at low temperature (-20 °C)
3. Examples

Thin layer yielding

- Special effects in block copolymers, layered structures and nanofibers
3. Examples

Thin layer yielding

- Special effects in block copolymers, layered structures and nanofibers

- Thin layer yielding in lamellar SBS block copolymers

![Diagram showing deformation and stress-strain curve for SBS block copolymers with different PS domain sizes.](image)
3. Examples

**Thin layer yielding**

- Special effects in block copolymers, *layered structures* and nanofibers
  - Thin layer yielding in layered structures of PET and PC produced by forced assembly
3. Examples

Thin layer yielding

- Special effects in block copolymers, layered structures and nanofibers
  - Thin layer yielding: brittle to ductile transition in nanofibers
3. Examples

Thin layer yielding

- Special effects in block copolymers, layered structures and nanofibers
  - Thin layer yielding: brittle to ductile transition in nanofibers
3. Examples
Nanocomposites

Micromechanics of nanocomposites: Principles

- Increasing influence of the interface/interphase with decreasing particle size
3. Examples
Nanocomposites

- Micromechanics of nanocomposites: Problems
  - large aggregates/agglomerates are supercritical defects
  - Aggregates/agglomerates bind the majority of the filler reducing the filler effective in the matrix
3. Examples
Nanocomposites

- Micromechanics of nanocomposites
3. Examples
Nanocomposites: CB-filled rubber blends

Comfort
Noise
Feel
Price

Green Tyres
Fuel Saver Tyres
Low-Rolling Resistance Tyres

Puncture Resistance

Wear
Chip/Chunk

Grip / Wet Grip
Grip is best served by rubber compounds which absorb high levels of energy (high hysteresis compounds).

Winter Performance
Compounds using silica are more elastic and flexible at lower temperatures allowing better grip and braking during wintry weather.

Rolling resistance is the amount of energy a tyre absorbs as it revolves and deflects. It requires compounds which absorb low quantities of energy (low hysteresis compounds).

[pictures and schematic modified using: www.tyres-online.co.uk/technology/silica.asp]
3. Examples

Nanocomposites: CB-filled rubber blends

- Morphology of CB-filled SBR/NR rubber blends
  - Sample: 70phr SBR / 30phr NR / 50phr CB

Ultrathin section, TEM

UM block face, AFM tapping mode (2,5x2,5 µm)
3. Examples

Nanocomposites: CB-filled rubber blends

- Micromechanical mechanisms in CB-filled SBR/NR rubber blends
  - TEM images of a deformed ultrathin section
  - Sample: 70phr SBR / 30phr NR / 50phr CB

![TEM images of a deformed ultrathin section](image1.jpg)
![TEM images of a deformed ultrathin section](image2.jpg)
3. Examples
Nanocomposites: CB-filled rubber blends

- Micromechanical mechanisms in a CB-filled SBR/NR rubber blends
  - Cryo-ESEM images of cryo-fracture surfaces

50phr SBR / 50phr NR / 50phr Silica

SBR / 30phr CB
4. Summary

- Aims of the analysis of morphology and micromechanics
  - understanding of structure-property correlations
  - formulation of material laws
  - fundament of morphology control
  - design of micromechanical mechanisms
  - detection and elimination of (critical) defects

Improvement of mechanical properties
Materials design for tailored properties
Further reading