MICROMECHANICS OF POLYMERS

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

25th Short Course on Polymer Characterization

25th POLYCHAR 2017
World Forum on Advanced Materials

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IUPAC
INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

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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

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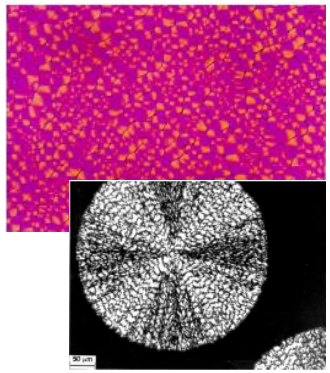
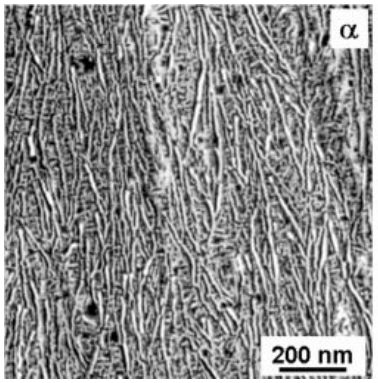
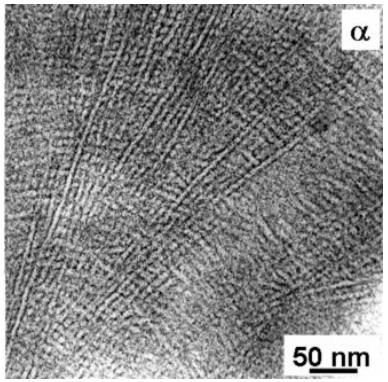
1. Micromechanics: Imaging of Micro- and Nanoscopic Processes of Deformation and Fracture

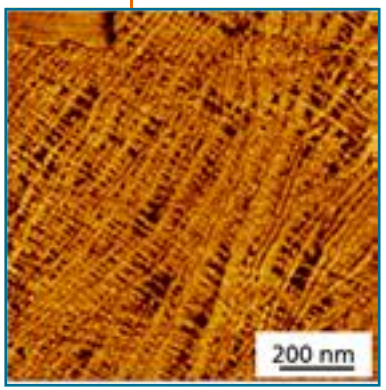
Probe types for microscopic investigations of morphology and micromechanics

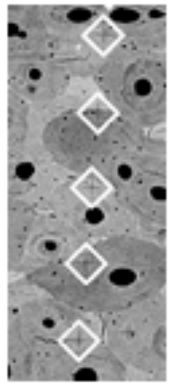
light	electron beam		mechanical	
light optical microscopy	scanning electron microscopy (SEM)	transmission electron microscopy (TEM)	SFM imaging	micro- and nano-indentation











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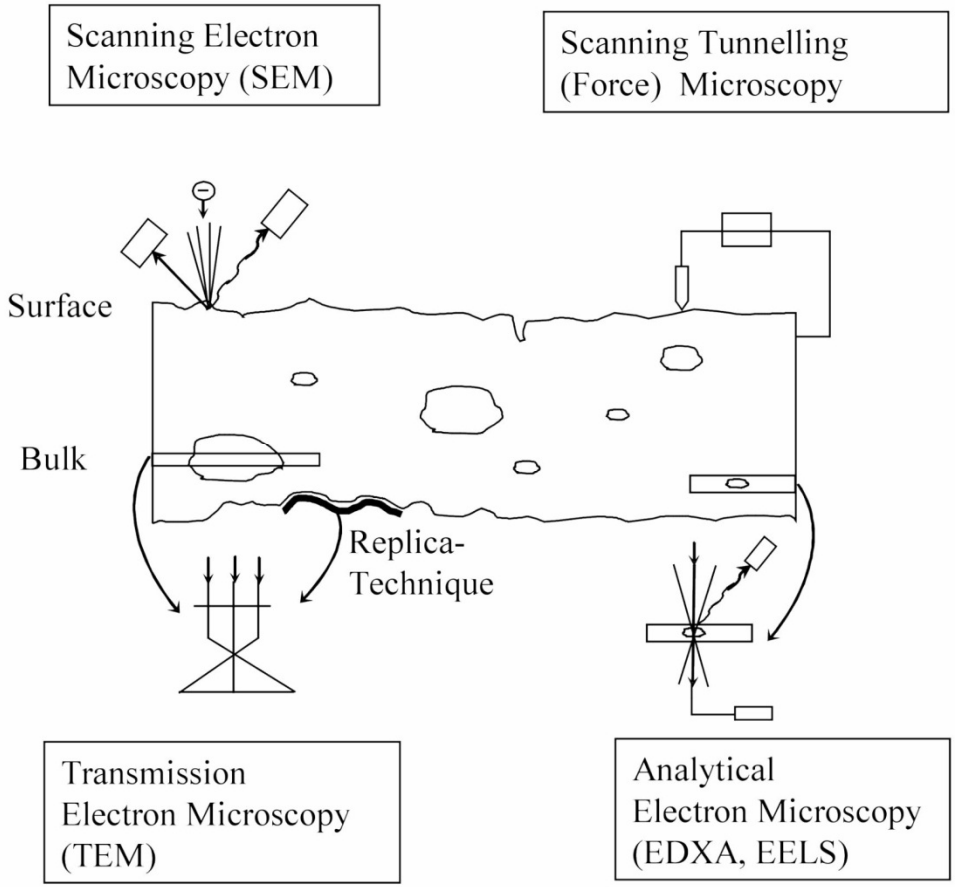
1. Micromechanics: Imaging of Micro- and Nanoscopic Processes of Deformation and Fracture

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

→ Morphology



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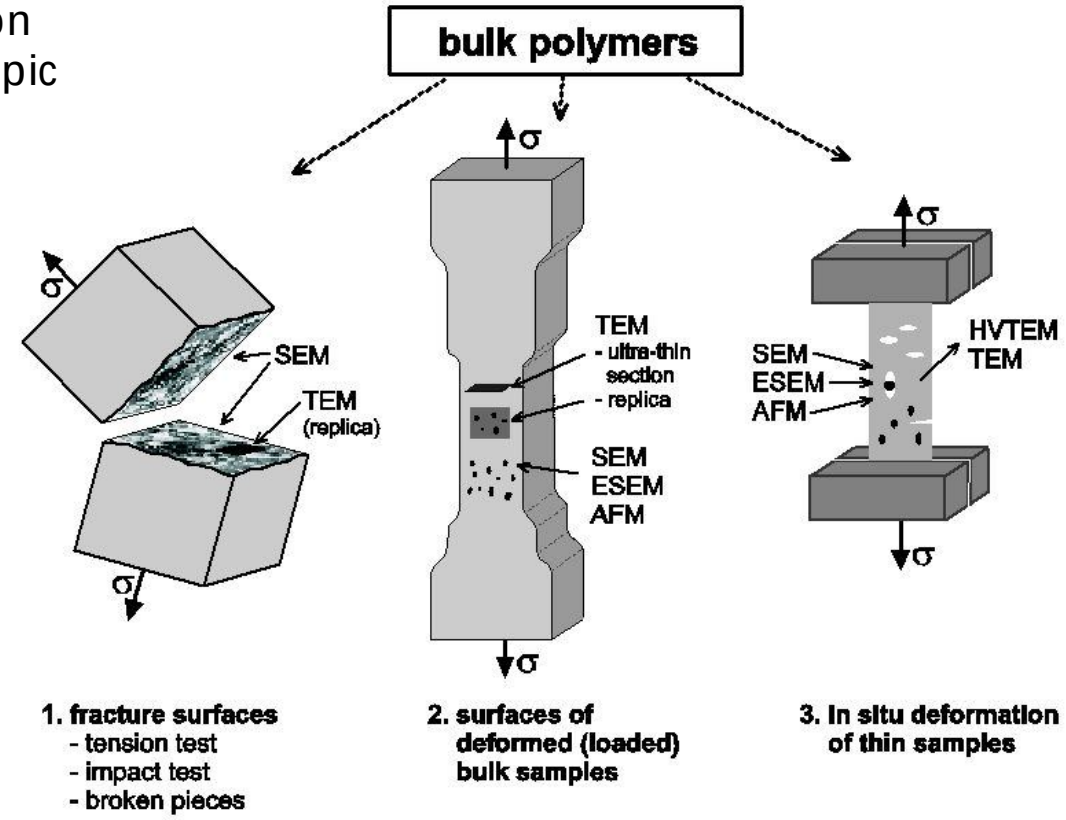
1. Micromechanics: Imaging of Micro- and Nanoscopic Processes of Deformation and Fracture

Comparison of sample preparation strategies for different micsroscopic techniques

→ Micromechanics



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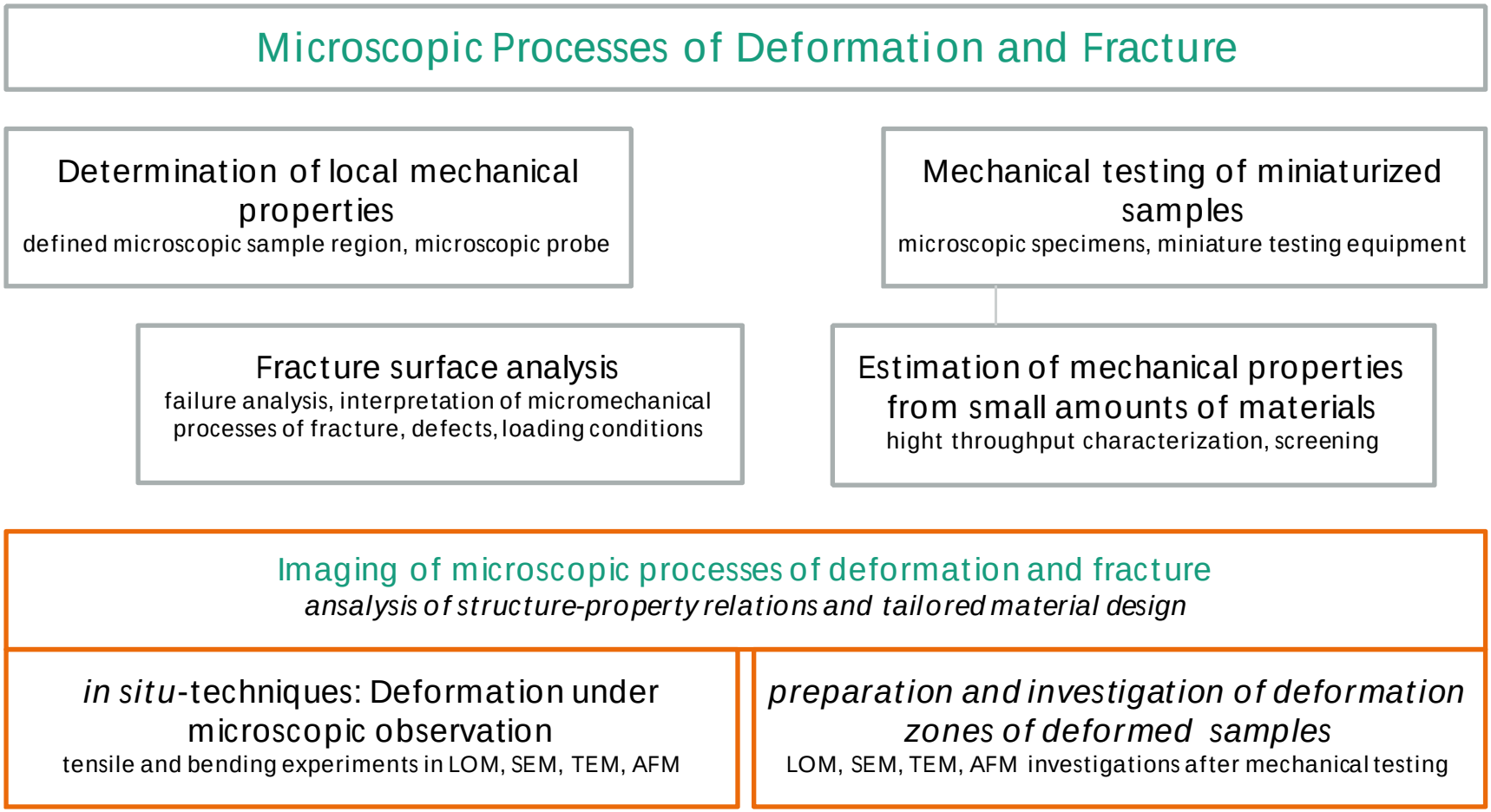

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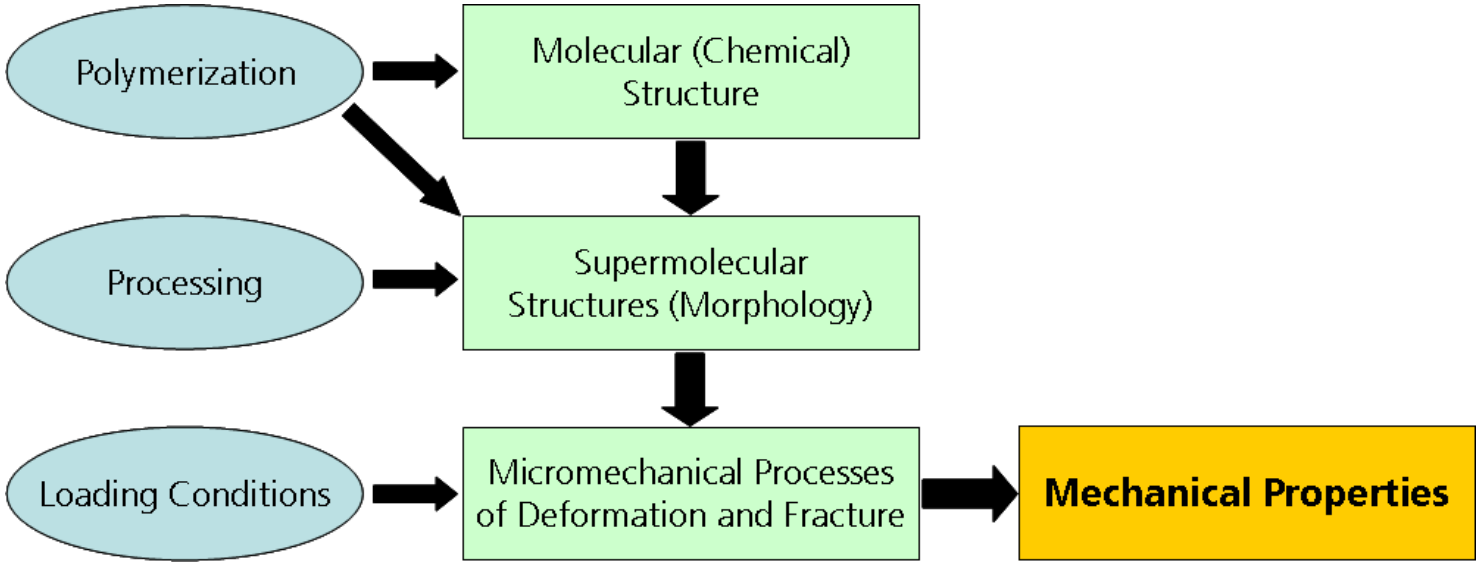

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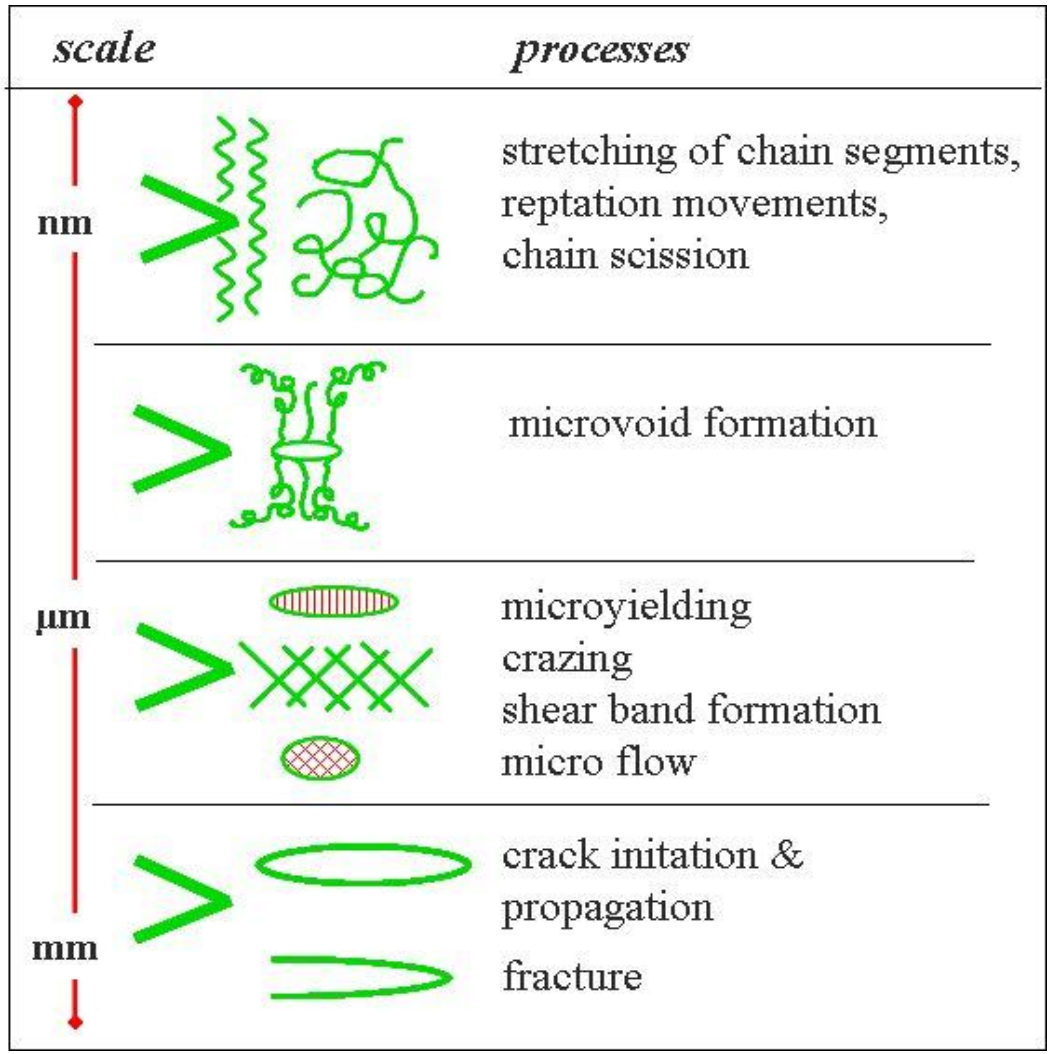
1. Micromechanics: Imaging of Micro- and Nanoscopic Processes of Deformation and Fracture

Micromechanics:

Examples for micro- and nanoscopic processes during deformation and fracture



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

Deformation mechanisms:

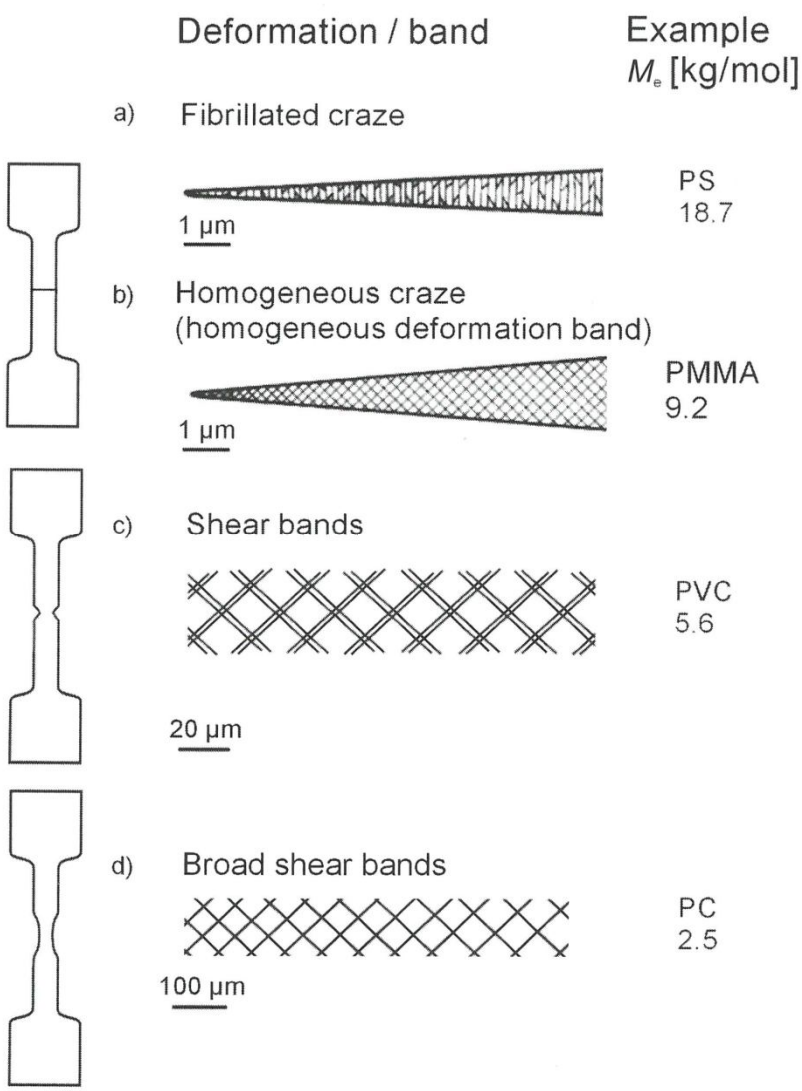
Schematic illustration of the features of typical deformation zones in polymers

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

Type	Orientation of the length compared to principal stress direction	Structure inside	Volume-change $\Delta V/V$
Shear band	≈ 45°	Homogeneous	0
Craze	⊥	Nano-voids, fibrillated	~ 1
Crack	⊥	-	≫ 0



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

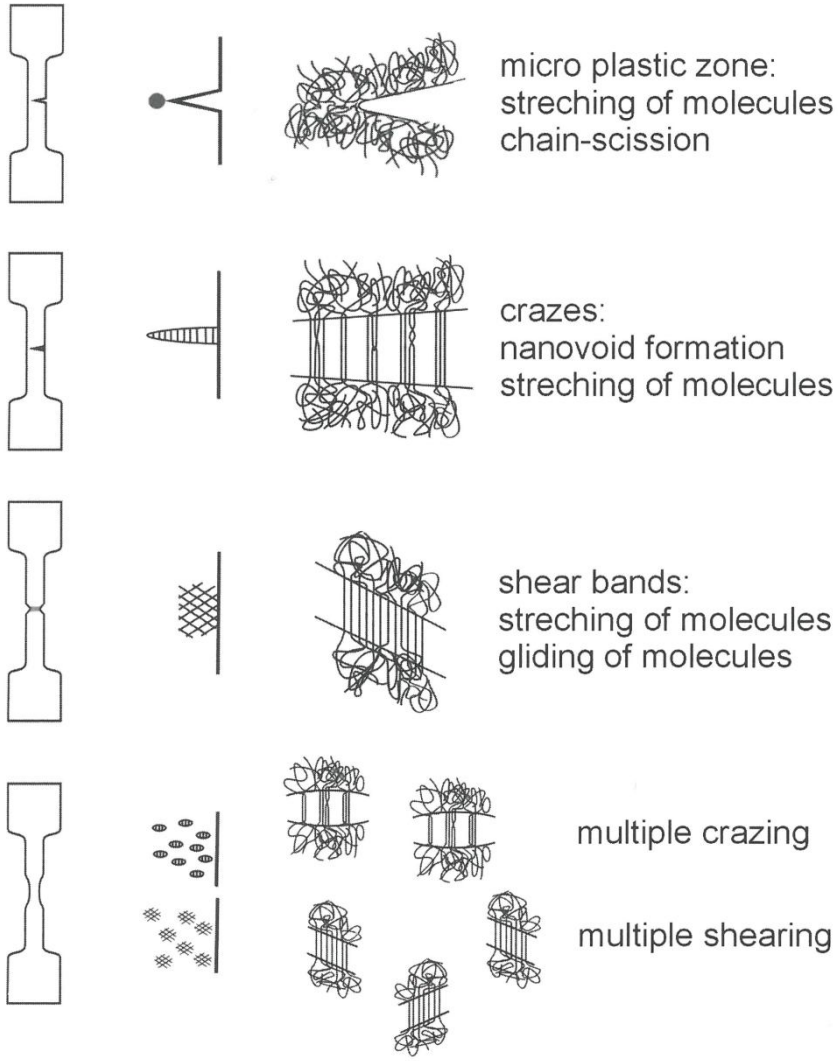
Deformation mechanisms:

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



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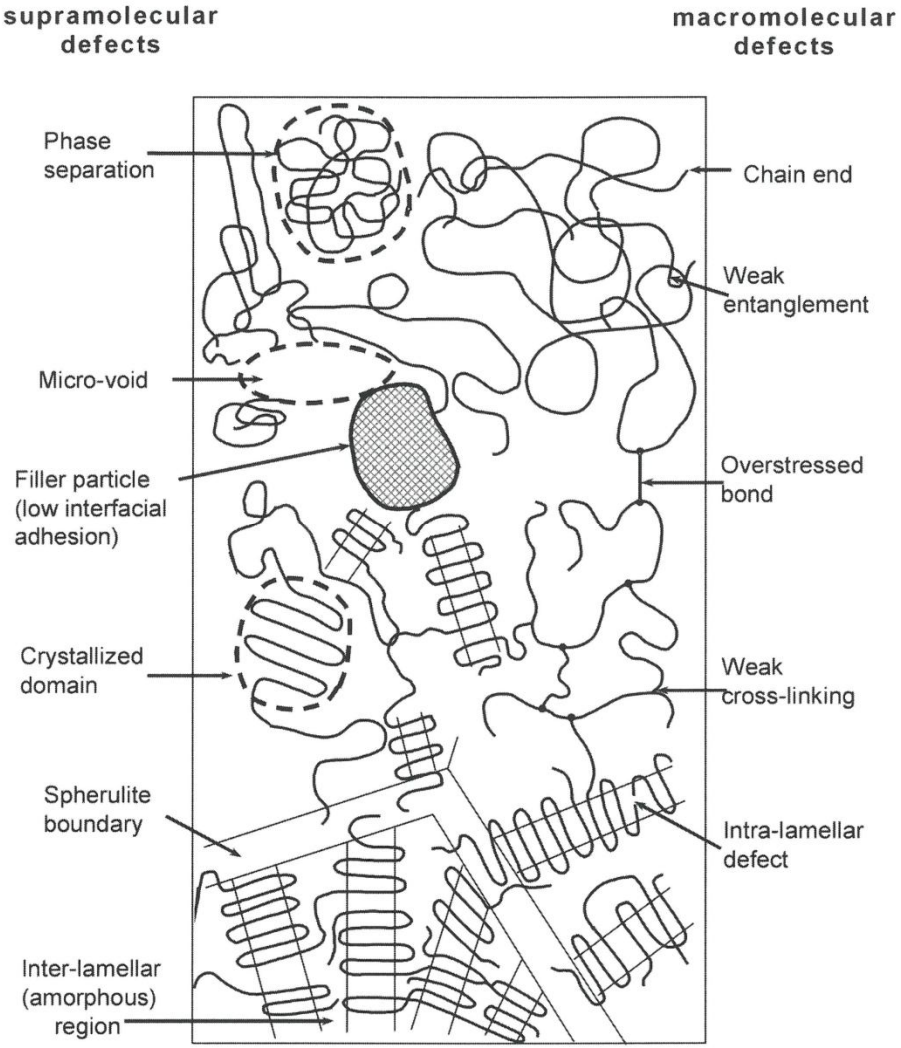
1. Micromechanics: Imaging of Micro- and Nanoscopic Processes of Deformation and Fracture

Defects:

Schematic repesentation of defects which can reduce the strength of polymers

Left: macroscopic appearance of the tensile bars after loading

Right: supermolecular (structural) defects



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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 ($T_{cut} < T_g$)
  - using glass or diamond knives

RMC PowerTome PT-PC with CRX cryo chamber

LEICA EM UC7 ultra-microtome

Diamond knives for dry, wet, and cry applications; different manufacturers

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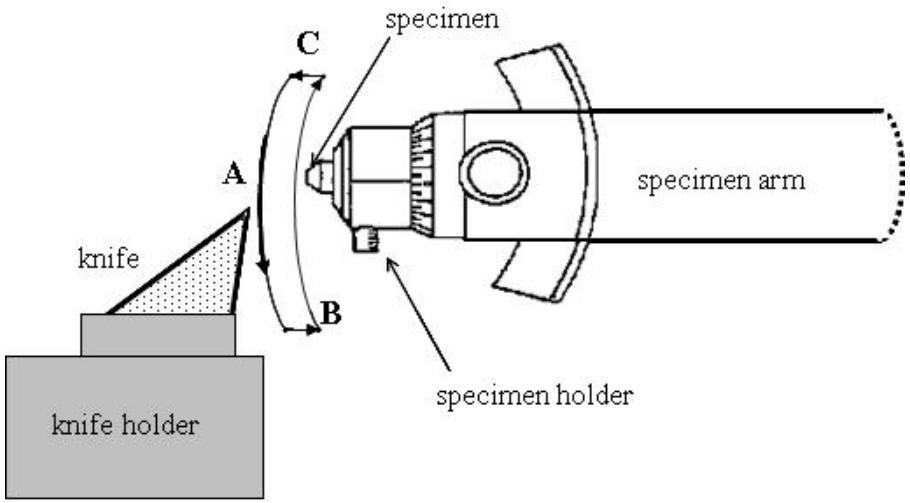
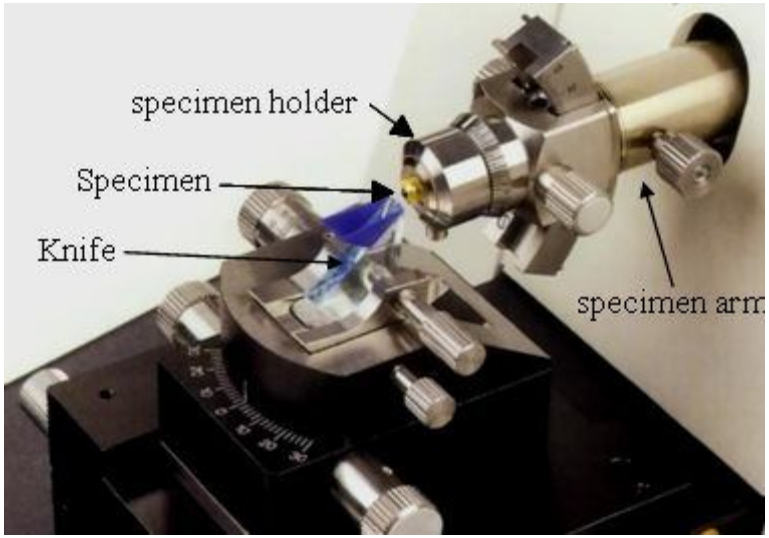
2. Preparation

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

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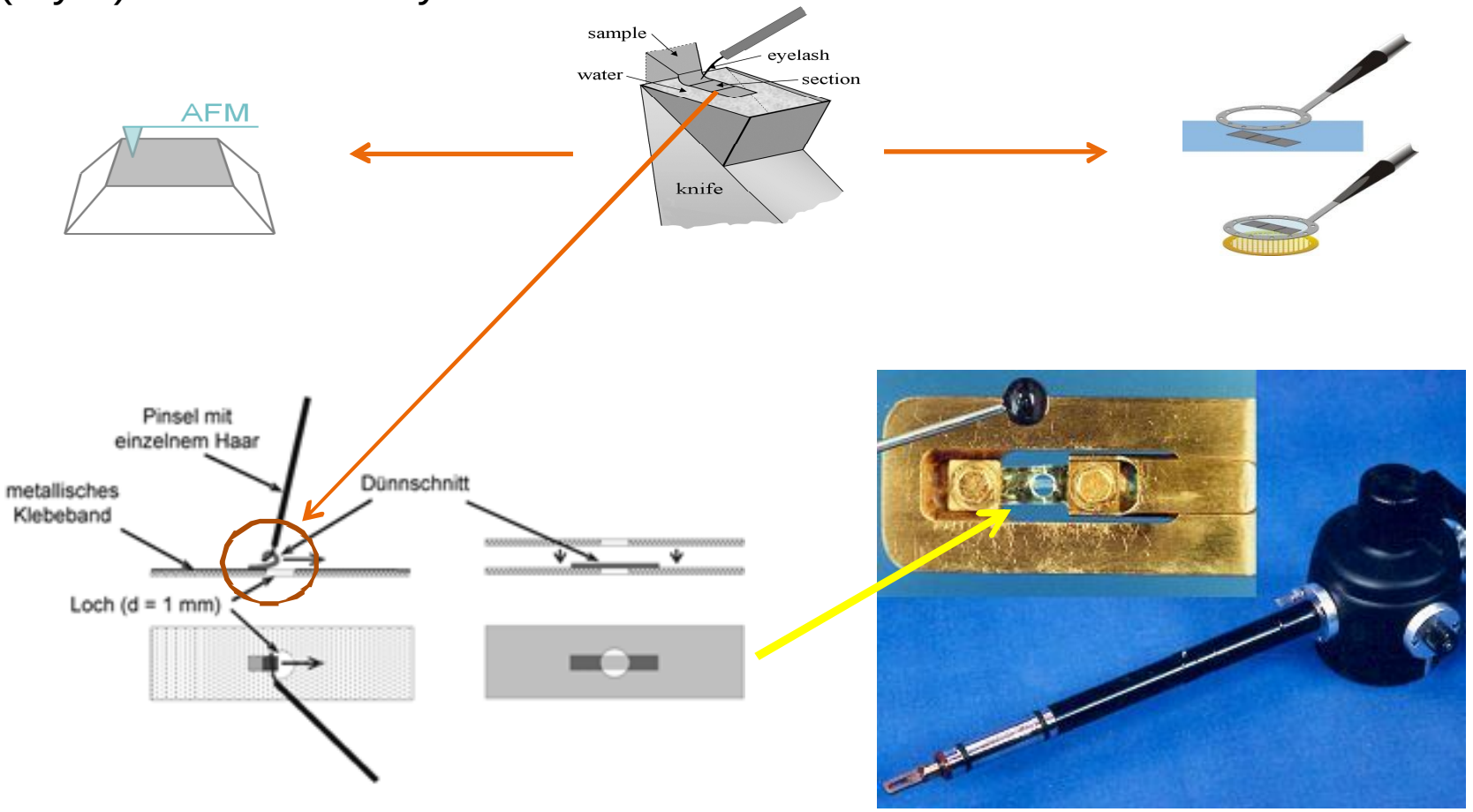
2. Preparation

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



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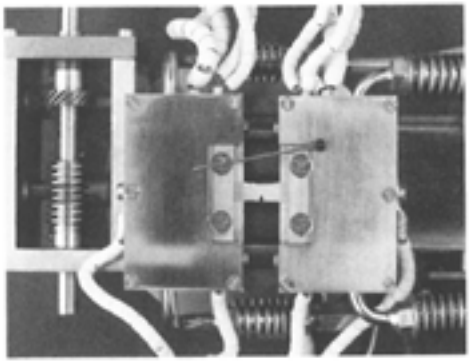
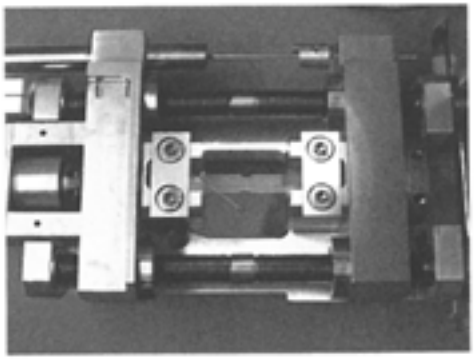
2. Preparation

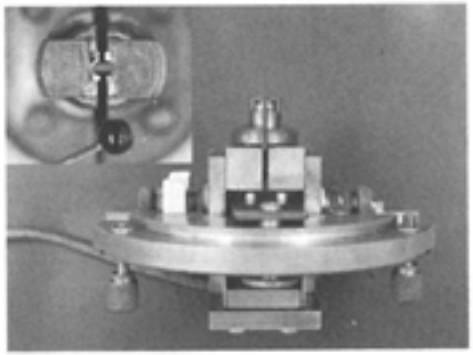
- *In situ*-investigations: Instrumentation
- different straining devices for LOM, SEM, TEM and AFM



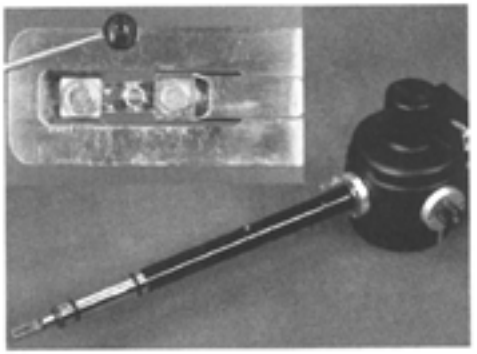
a) Scanning Electron Microscope
Tensile Stage B156 (Oxford Instruments)
Temperature: -180 °C ... 200 °C
Thickness: 0.5 µm ... 0.5 mm



b) Scanning Electron Microscope *and* **Atomic Force Microscope**
Tensile Module 1000 N (Kammrath &Weiss)
Temperature: Room Temperature
Thickness: 10 µm ... 5 mm



c) High Voltage Electron Microscope
Tensile Stage (Jeol)
Temperature: Room Temperature
Thickness: 100 nm ... 5 µm



d) Transmission Electron Microscope
Straining Holder Model 671 (Gatan)
Temperature: -180 °C ... 120 °C
Thickness: 100 nm ... 0.5 µm

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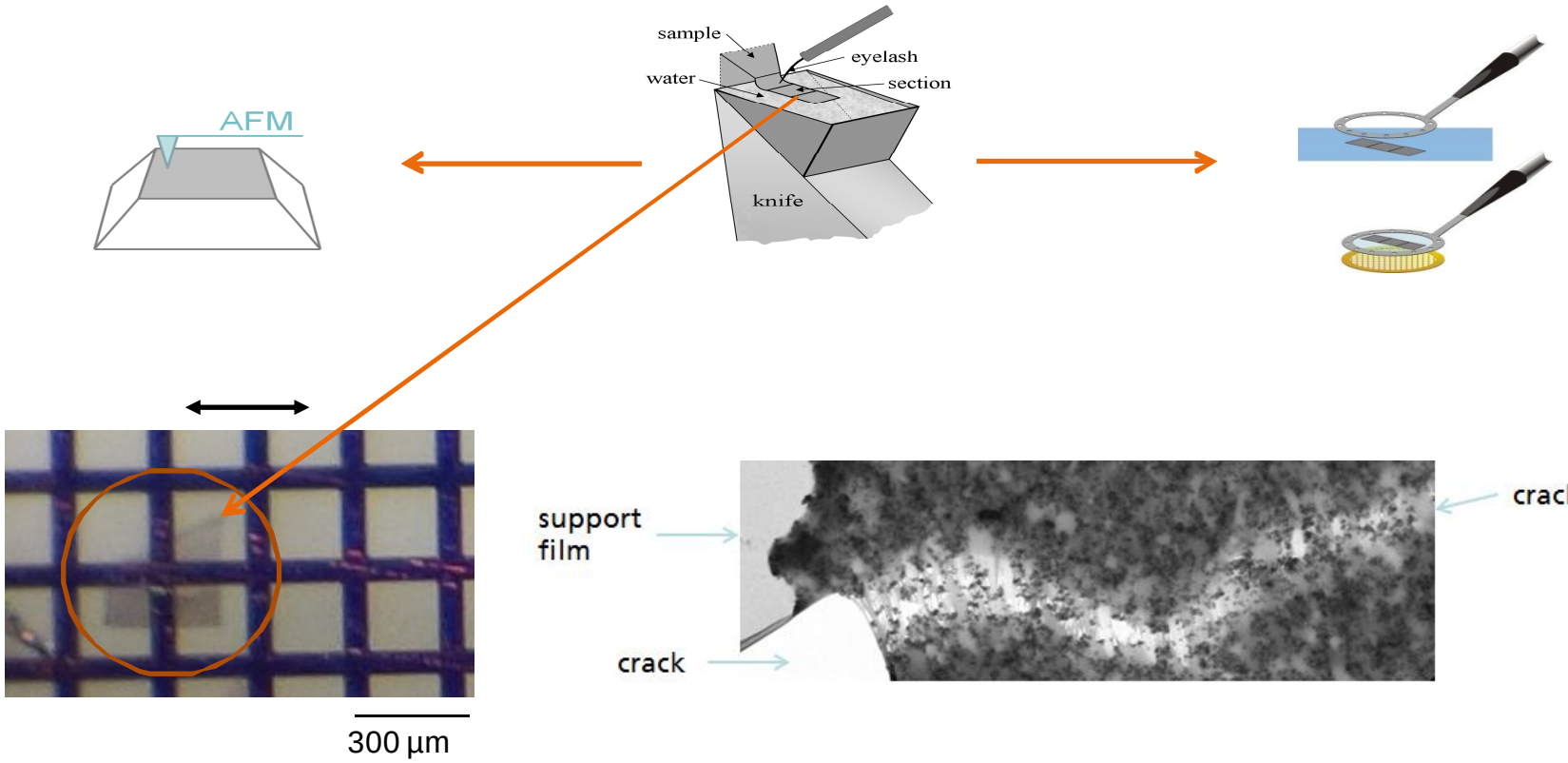
2. Preparation

Sample preparation for micromechanical *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

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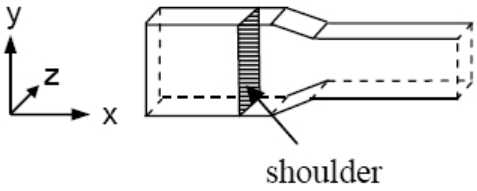
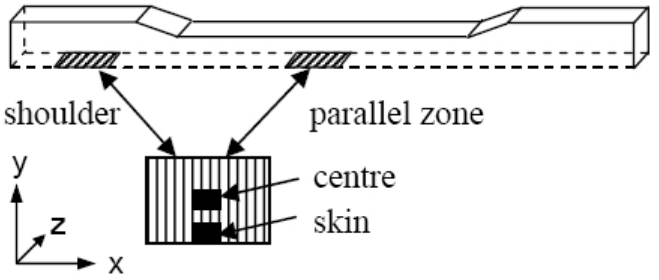
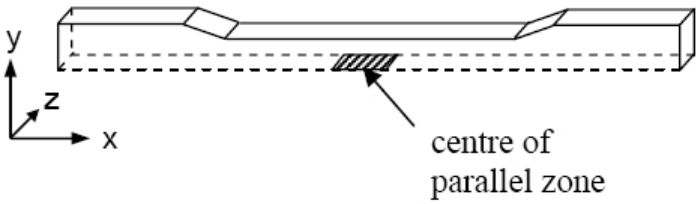
2. Preparation

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

- *Ultrathin sections (+ staining): TEM*
- *Block faces: (+ etching) SEM, AFM*







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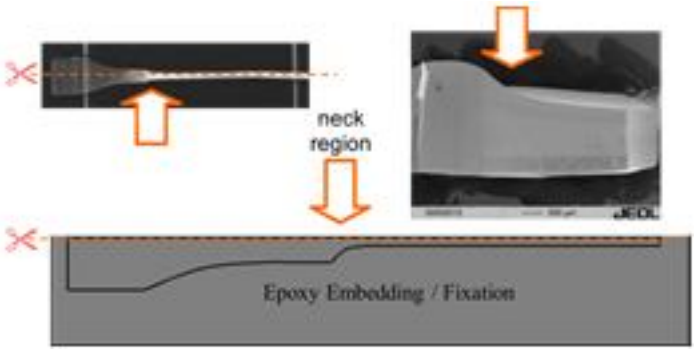
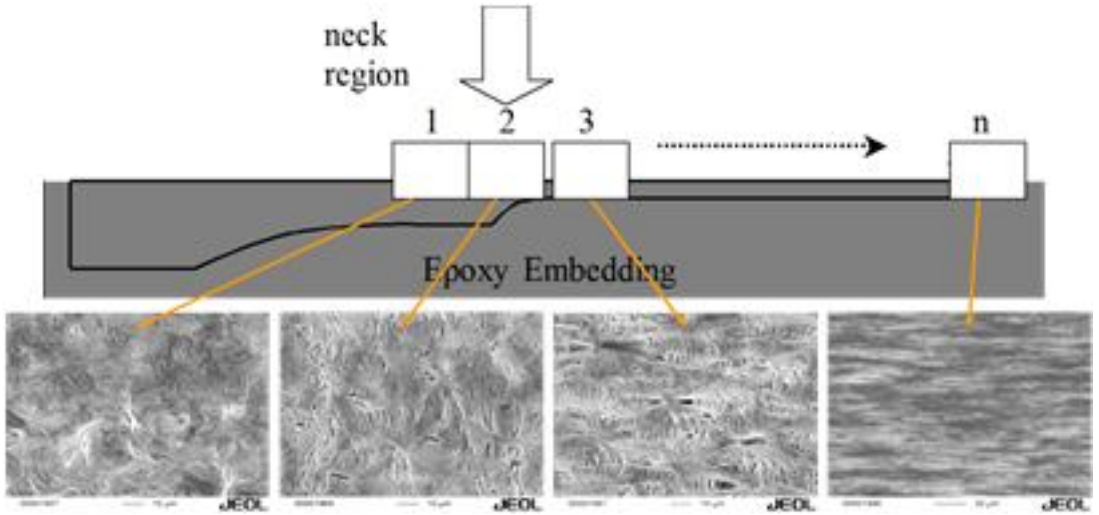
2. Preparation

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





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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.

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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

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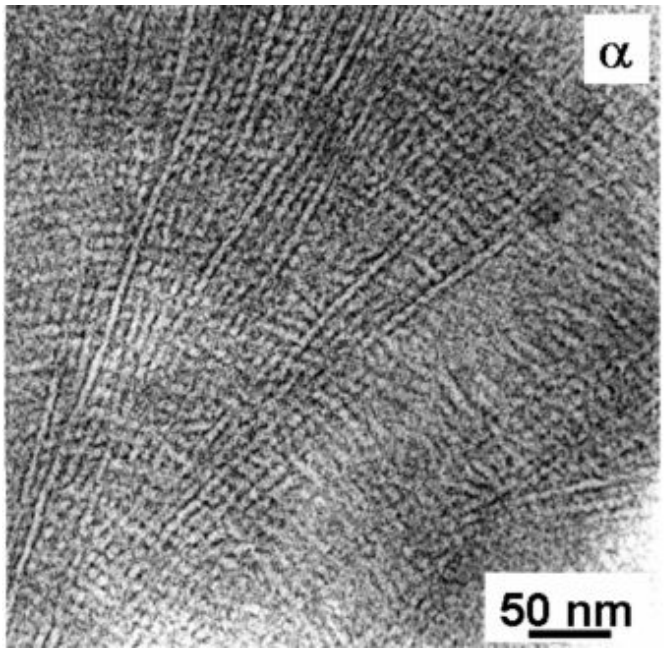
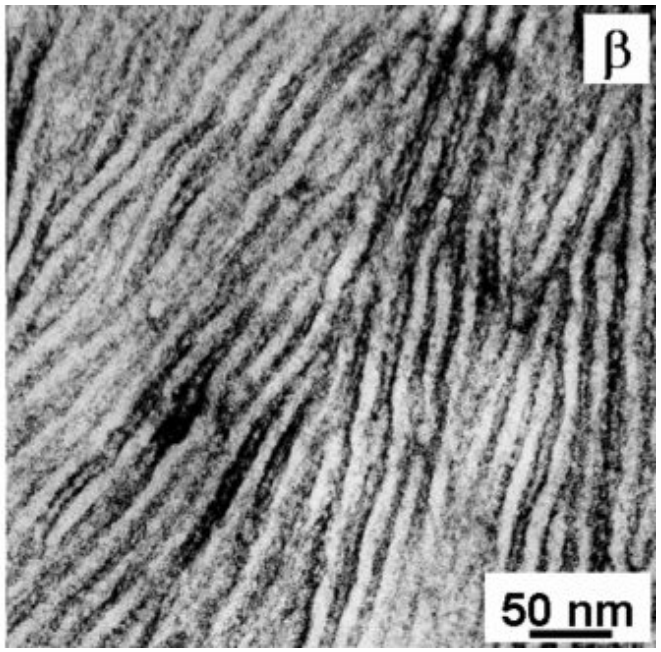
2. Preparation

Sample preparation: Fixation and staining

Example: semicrystalline morphology of α- and β- modification of polypropylene

One-step staining with ruthenium tetroxide, ultramicrotome sections





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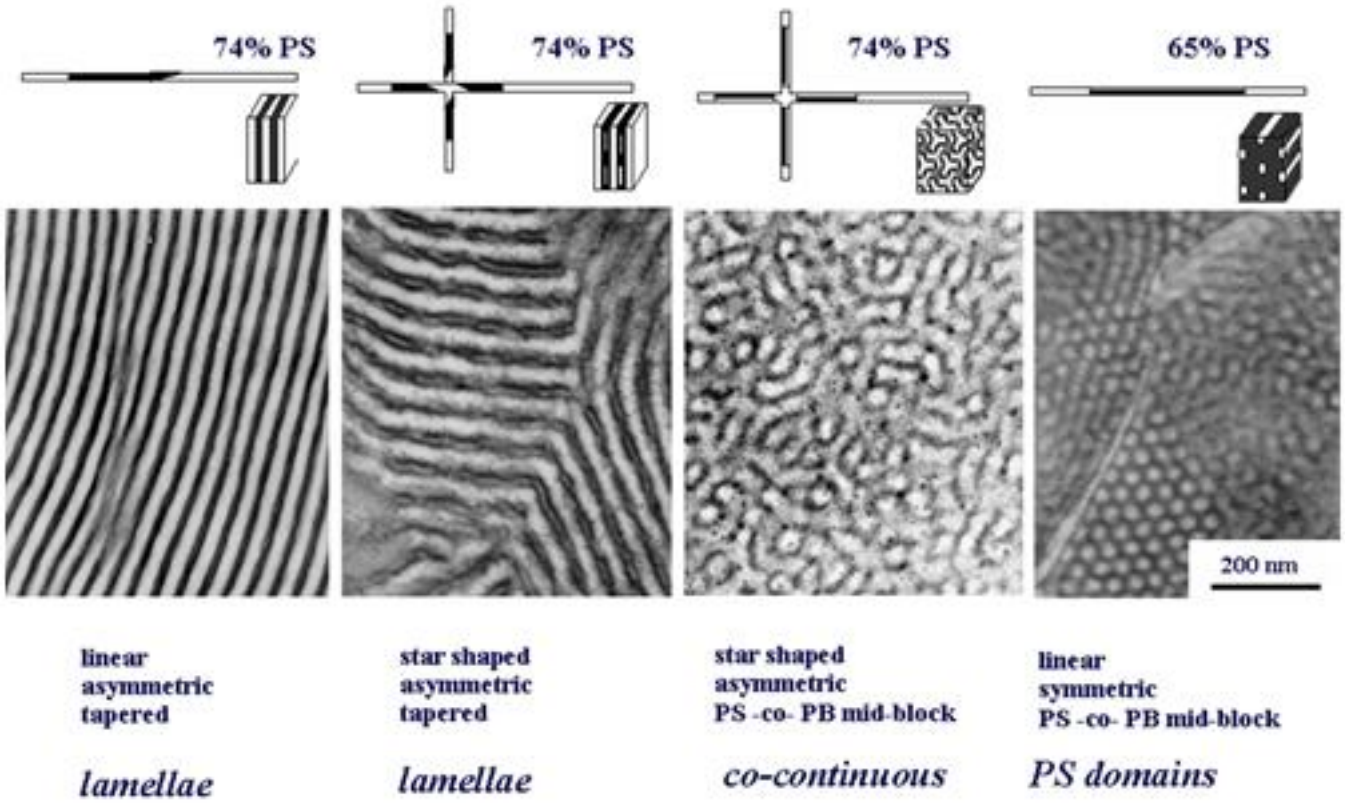
2. Preparation

Sample preparation: Fixation and staining

Example: Styrene-butadiene blockcopolymers

One-step staining with osmium tetroxide, ultramicrotome sections



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

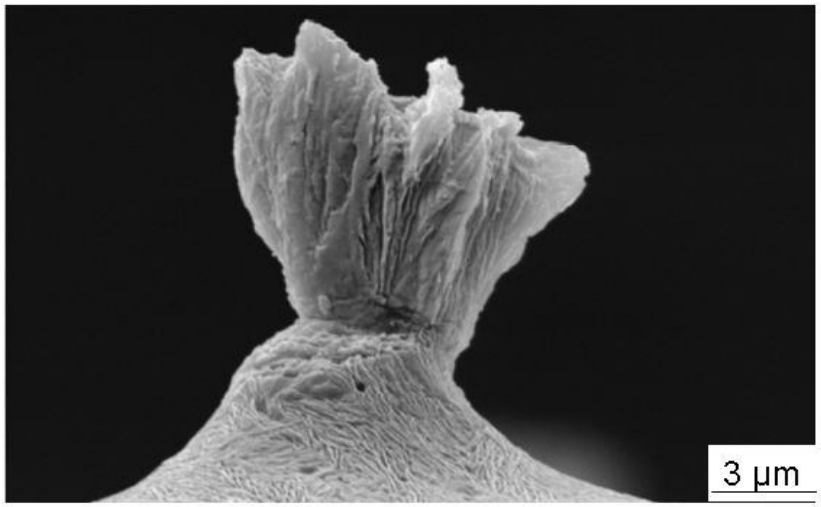
preparation from a deformed sample (bulk)

↓

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

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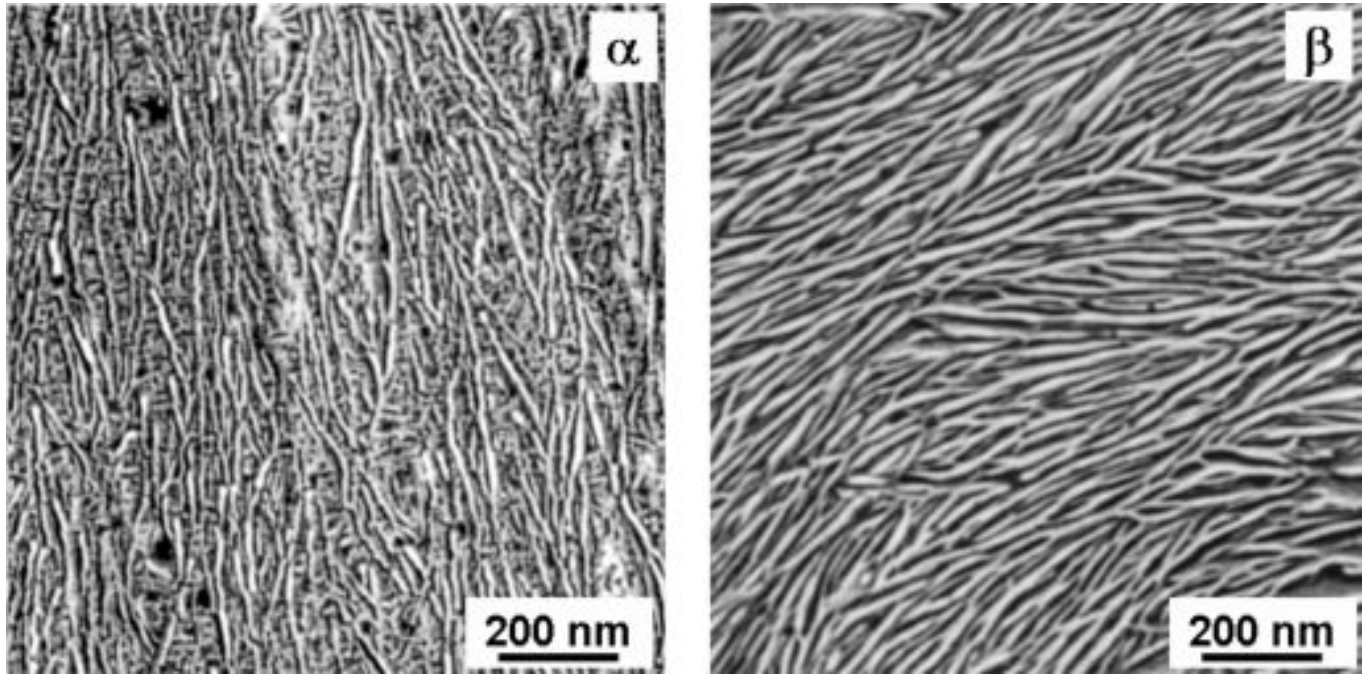
2. Preparation

Sample preparation: Etching

Example: semicrystalline morphology of α- and β- modification of polypropylene



Comparison of lamellar structures after permanganic etching;

SEM-SE images

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3. Examples

Semicrystalline Polymers

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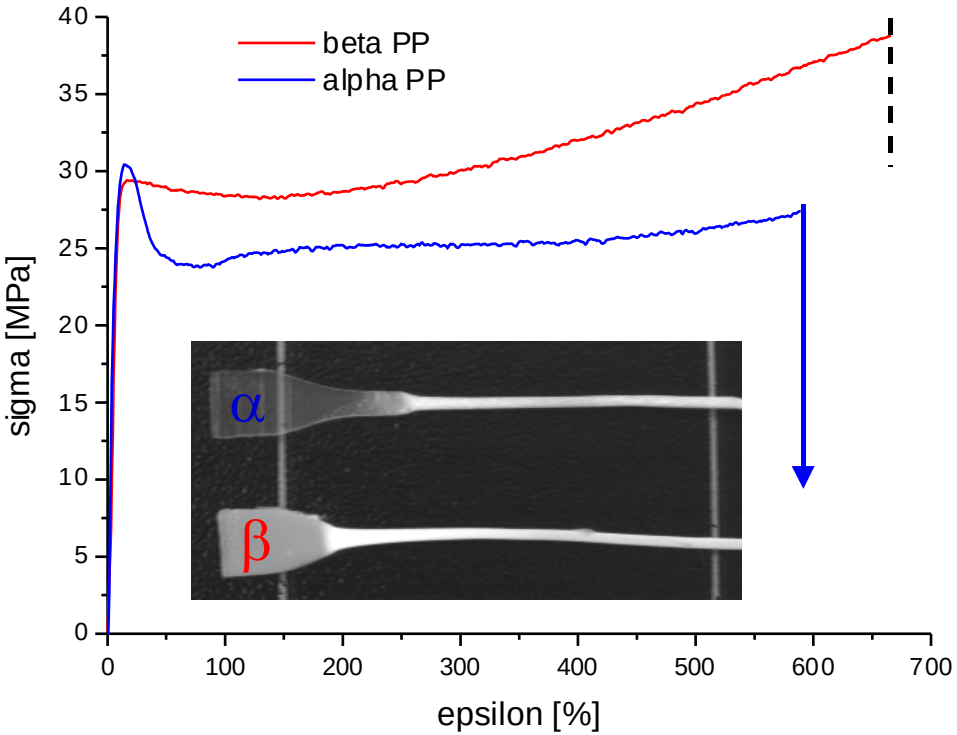
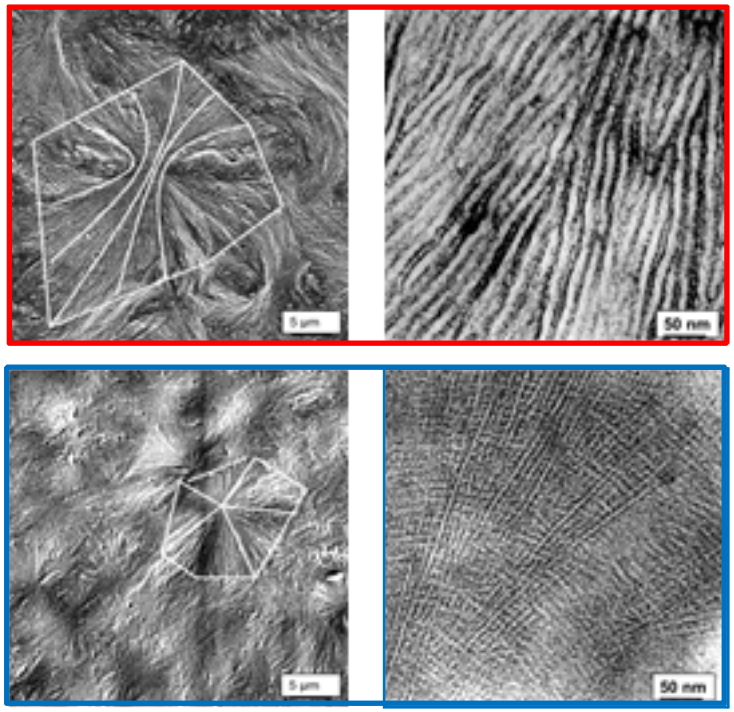
3. Examples

Semicrystalline Polymers

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





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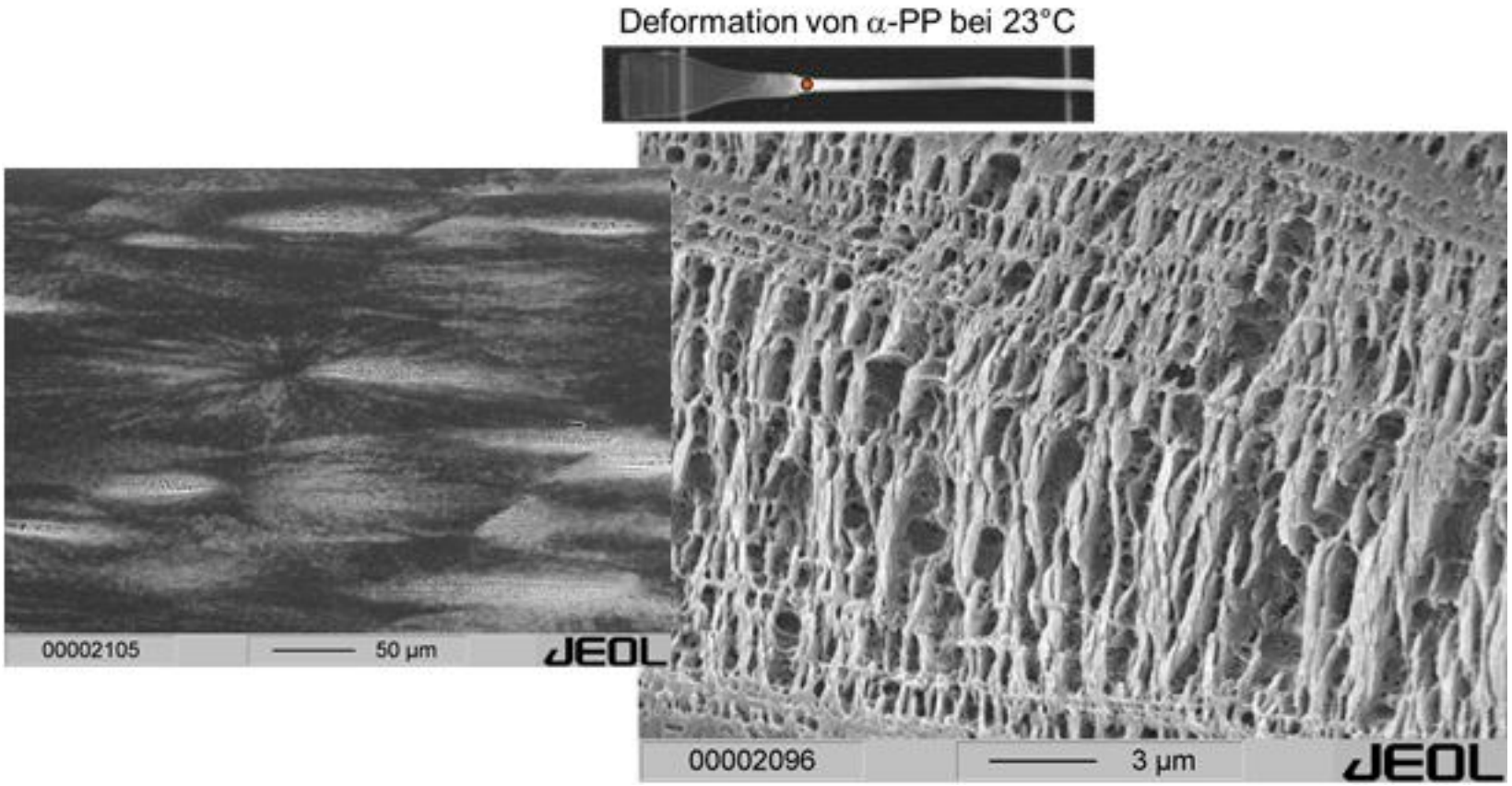
3. Examples

Semicrystalline Polymers

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



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3. Examples

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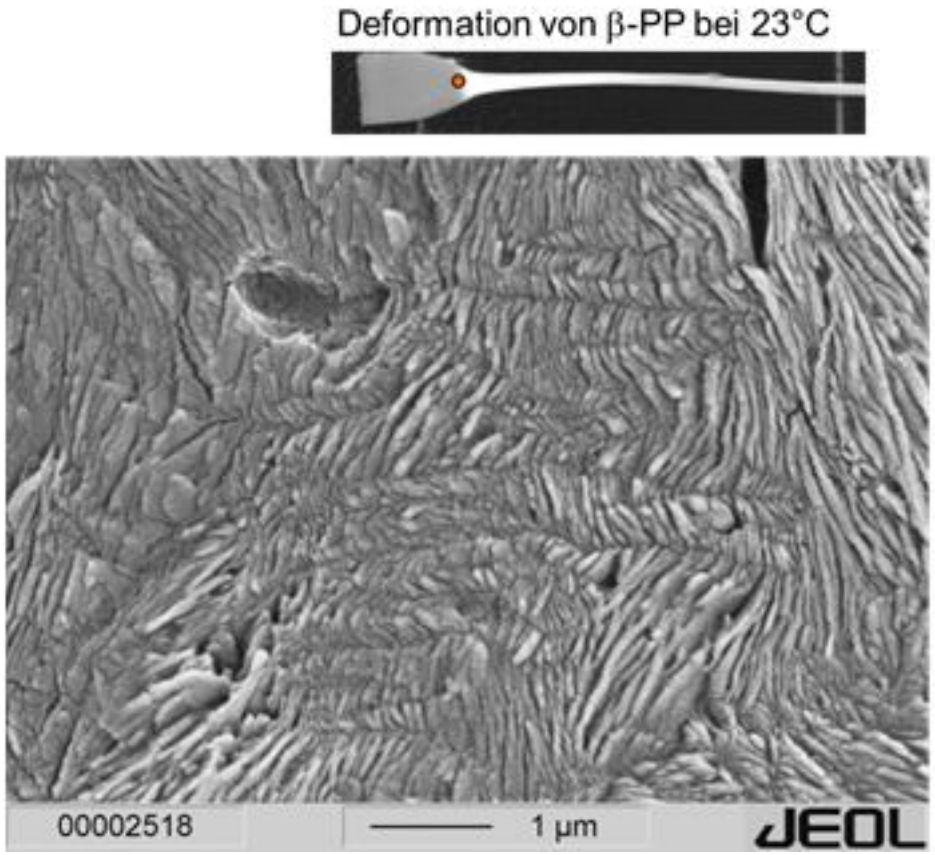

Morphologie der deformierten Probe

$\lambda_{local} = 1.18$

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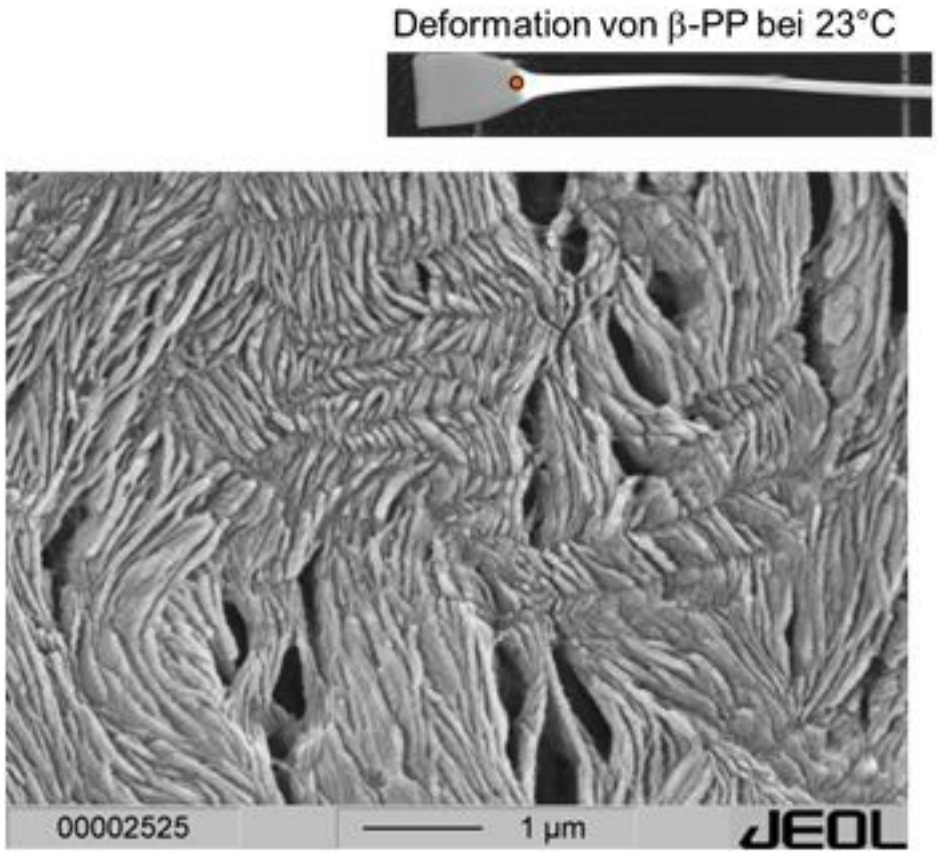
3. Examples

Semicrystalline Polymers

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



Morphologie der deformierten Probe

$\lambda_{local} = 1.3$

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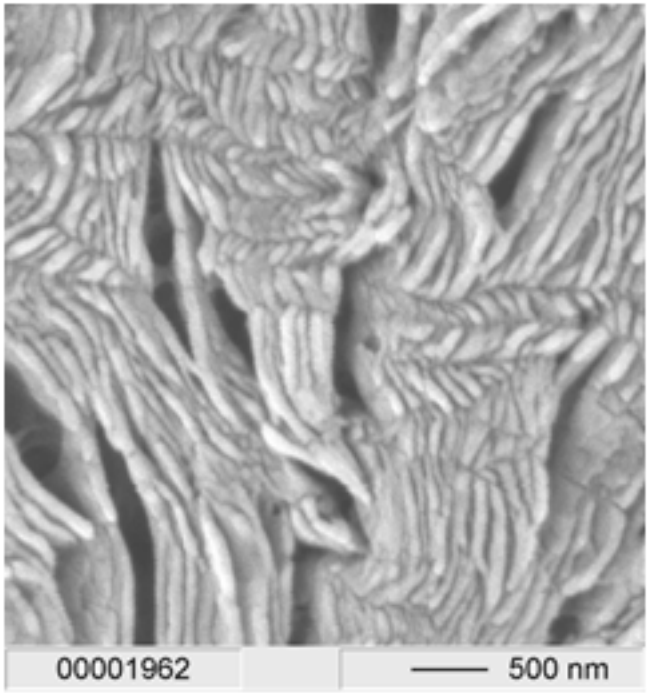
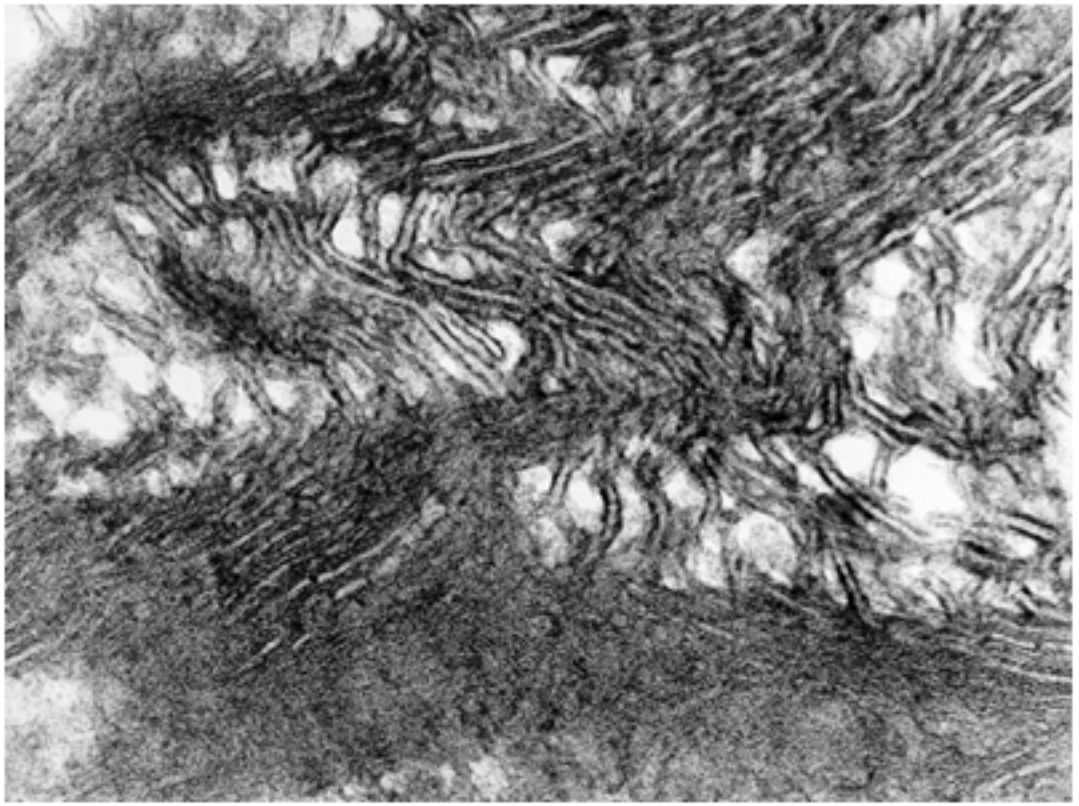
3. Examples

Semicrystalline Polymers

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





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3. Examples

Semicrystalline Polymers

- PP parts from micro injection moulding

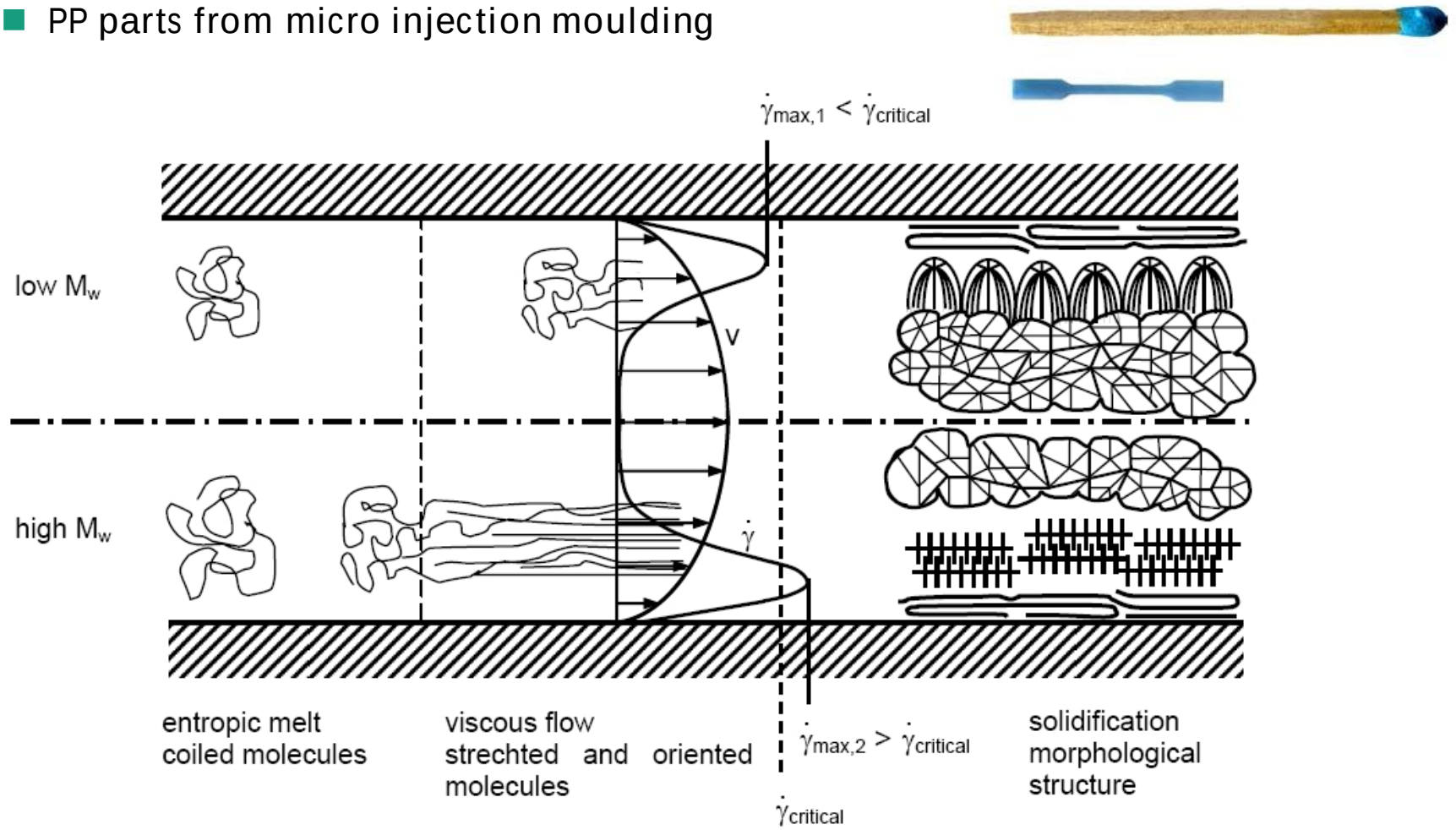

Illustration of morphology formation of PP with different molecular weights by injection moulding

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

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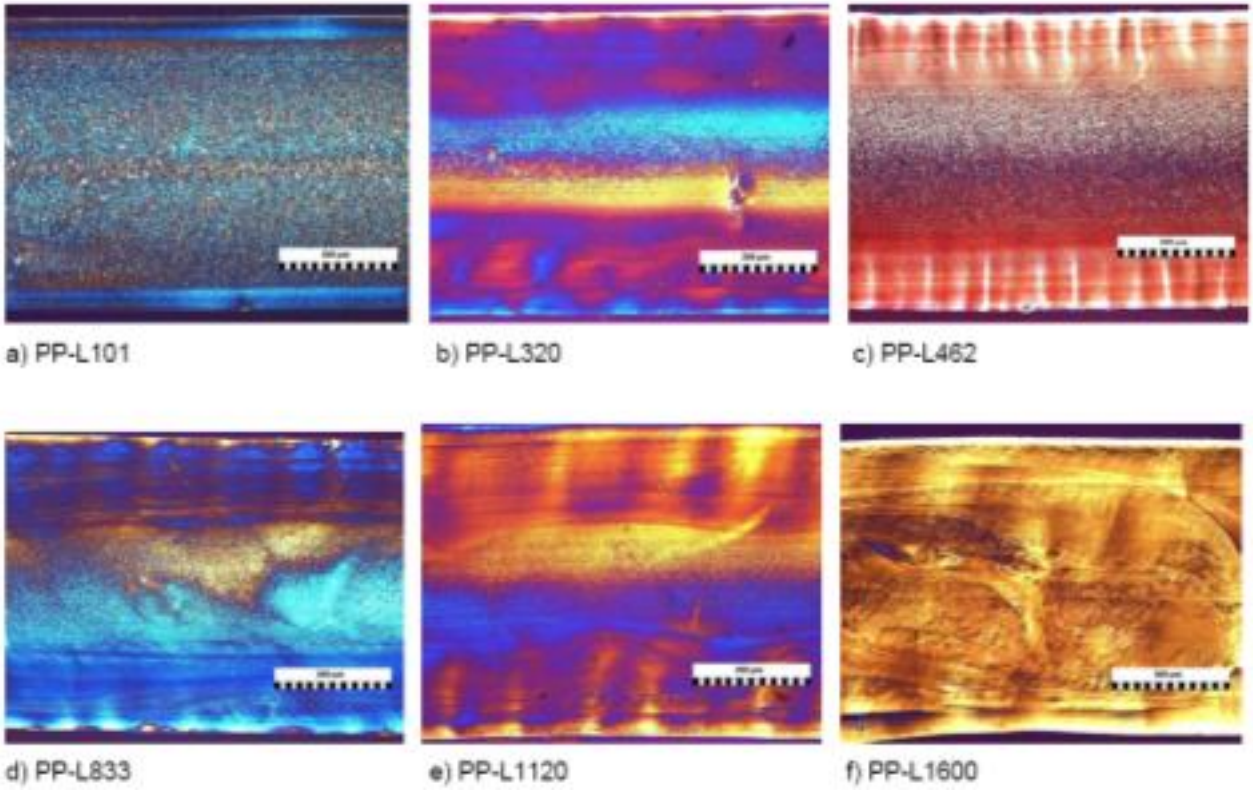
3. Examples

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 weigt

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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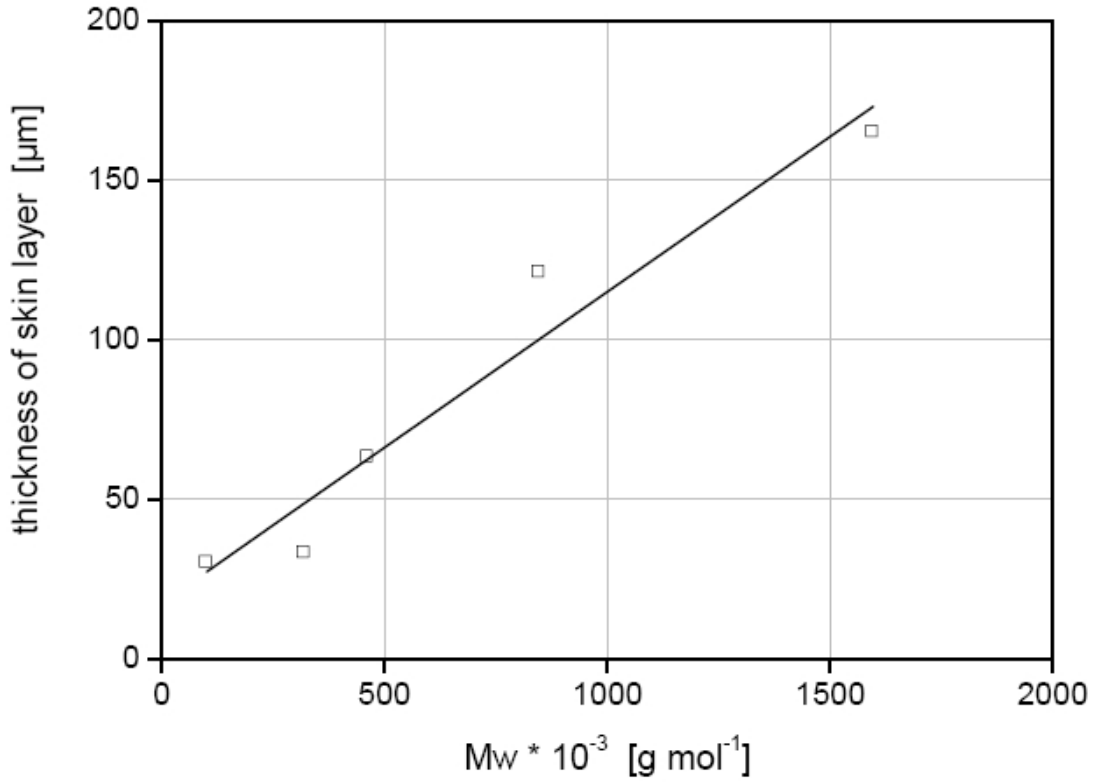
3. Examples

Semicrystalline Polymers

- PP parts from micro injection moulding



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

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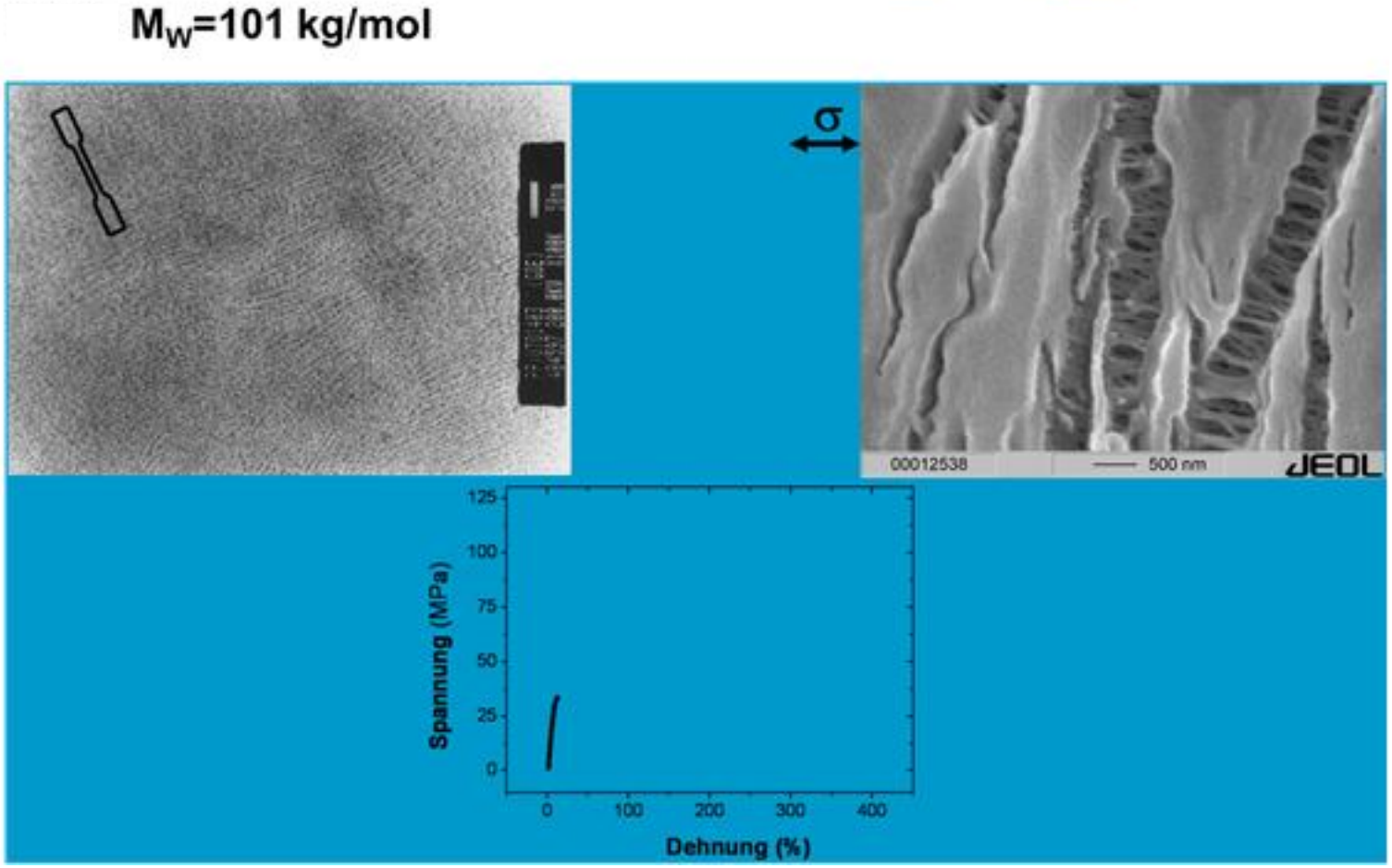
3. Examples

Semicrystalline Polymers

- PP parts from micro injection moulding



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

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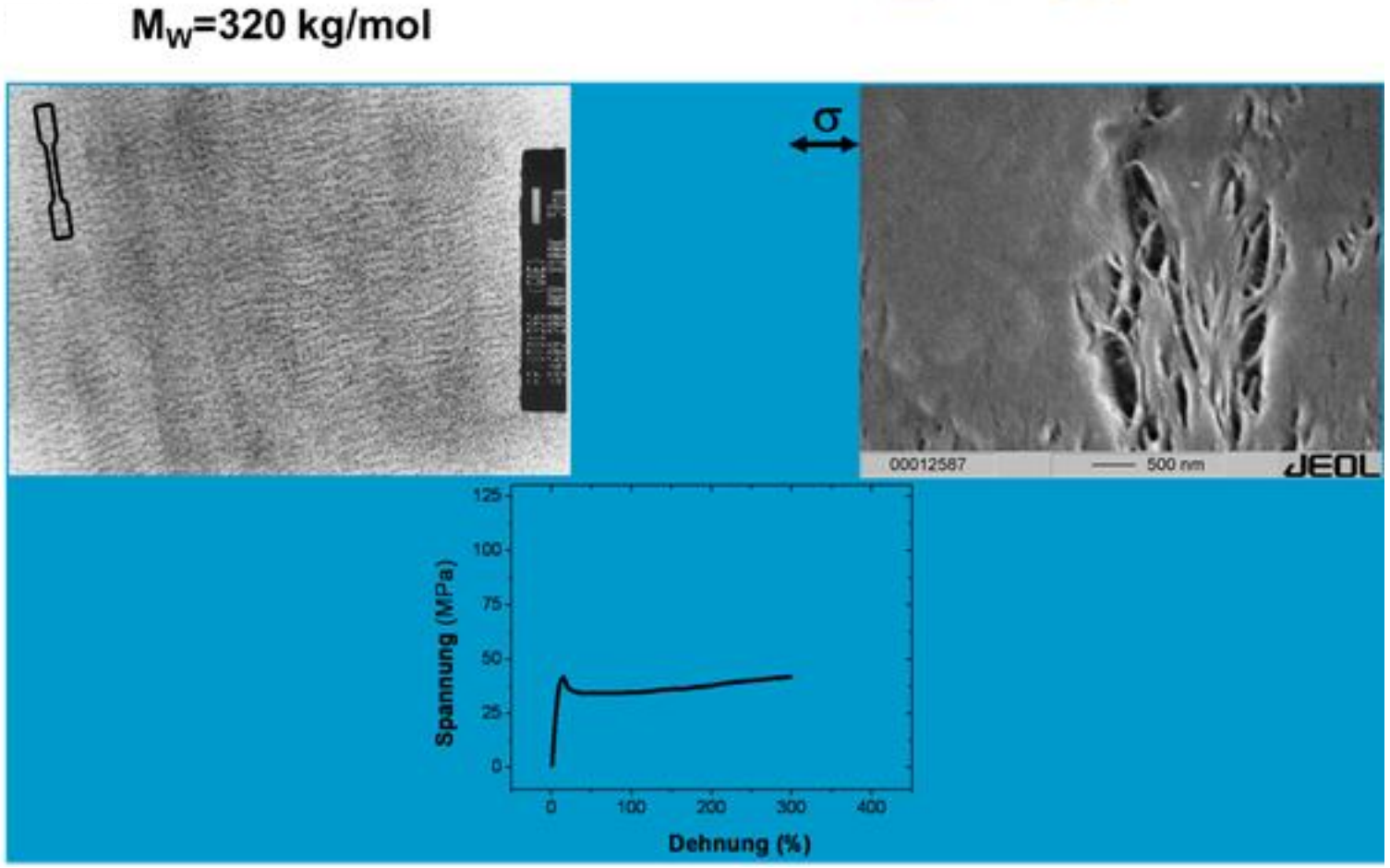
3. Examples

Semicrystalline Polymers

- PP parts from micro injection moulding



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

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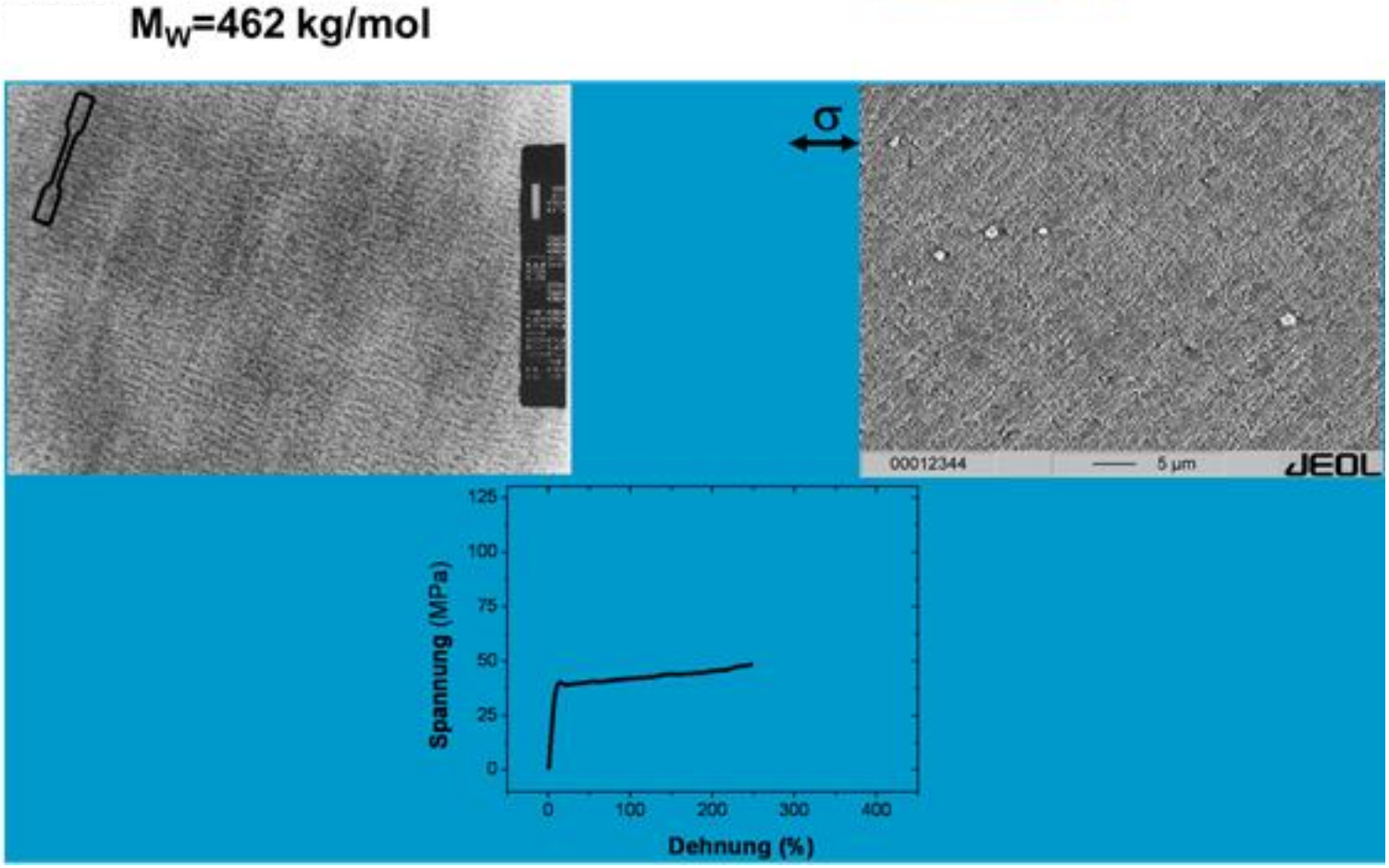
3. Examples

Semicrystalline Polymers

- PP parts from micro injection moulding



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

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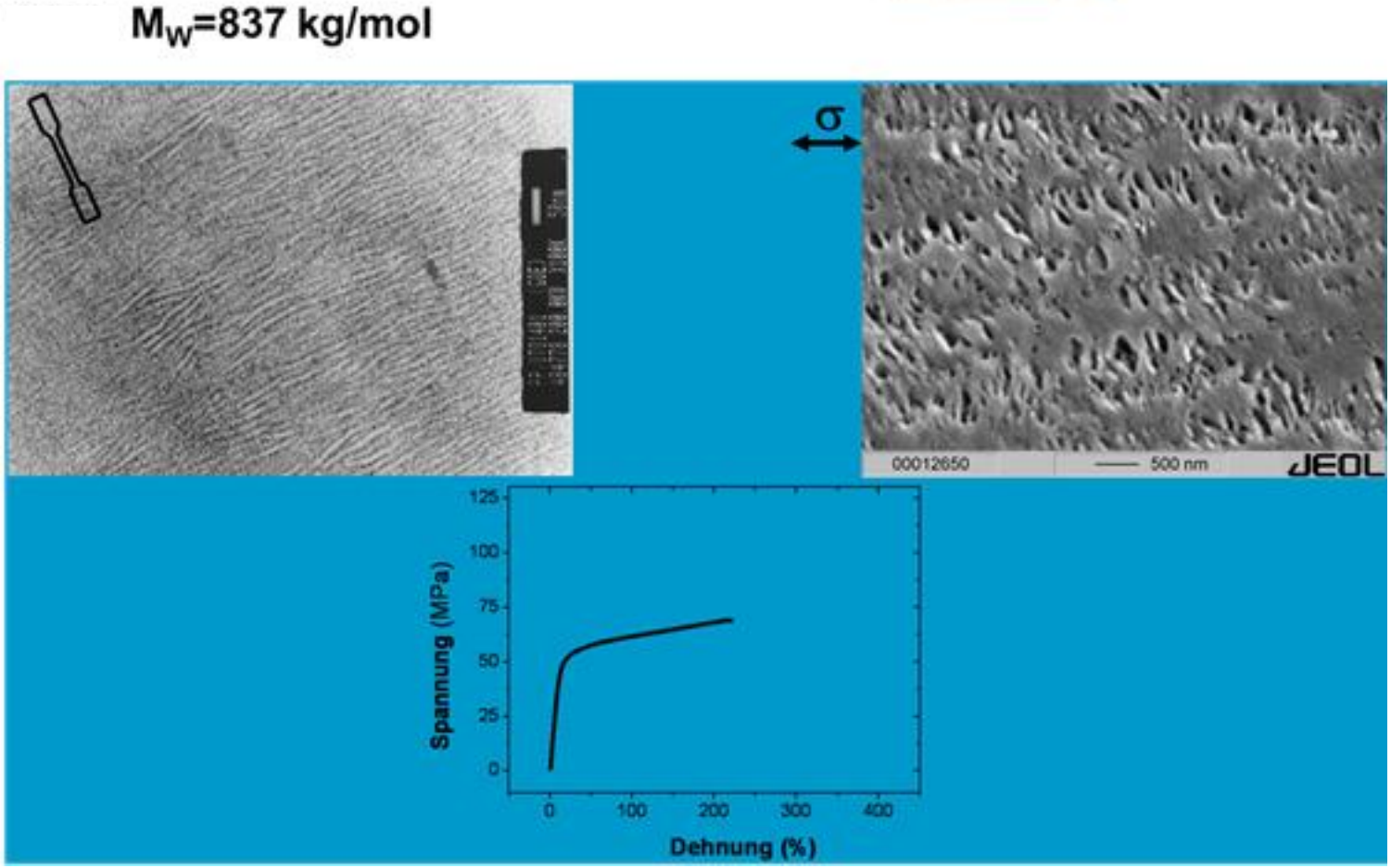
3. Examples

Semicrystalline Polymers

- PP parts from micro injection moulding



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

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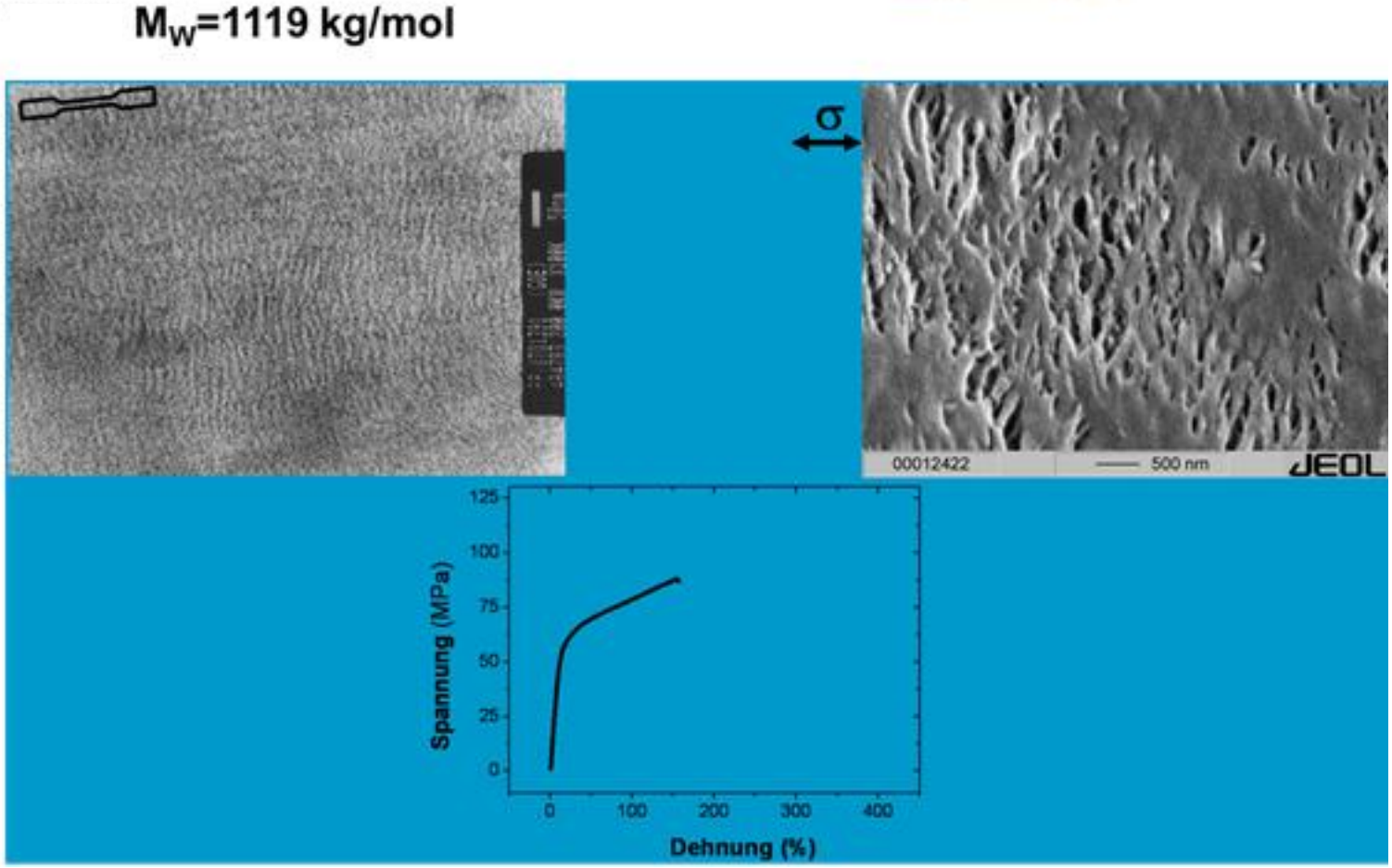
3. Examples

Semicrystalline Polymers

- PP parts from micro injection moulding



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

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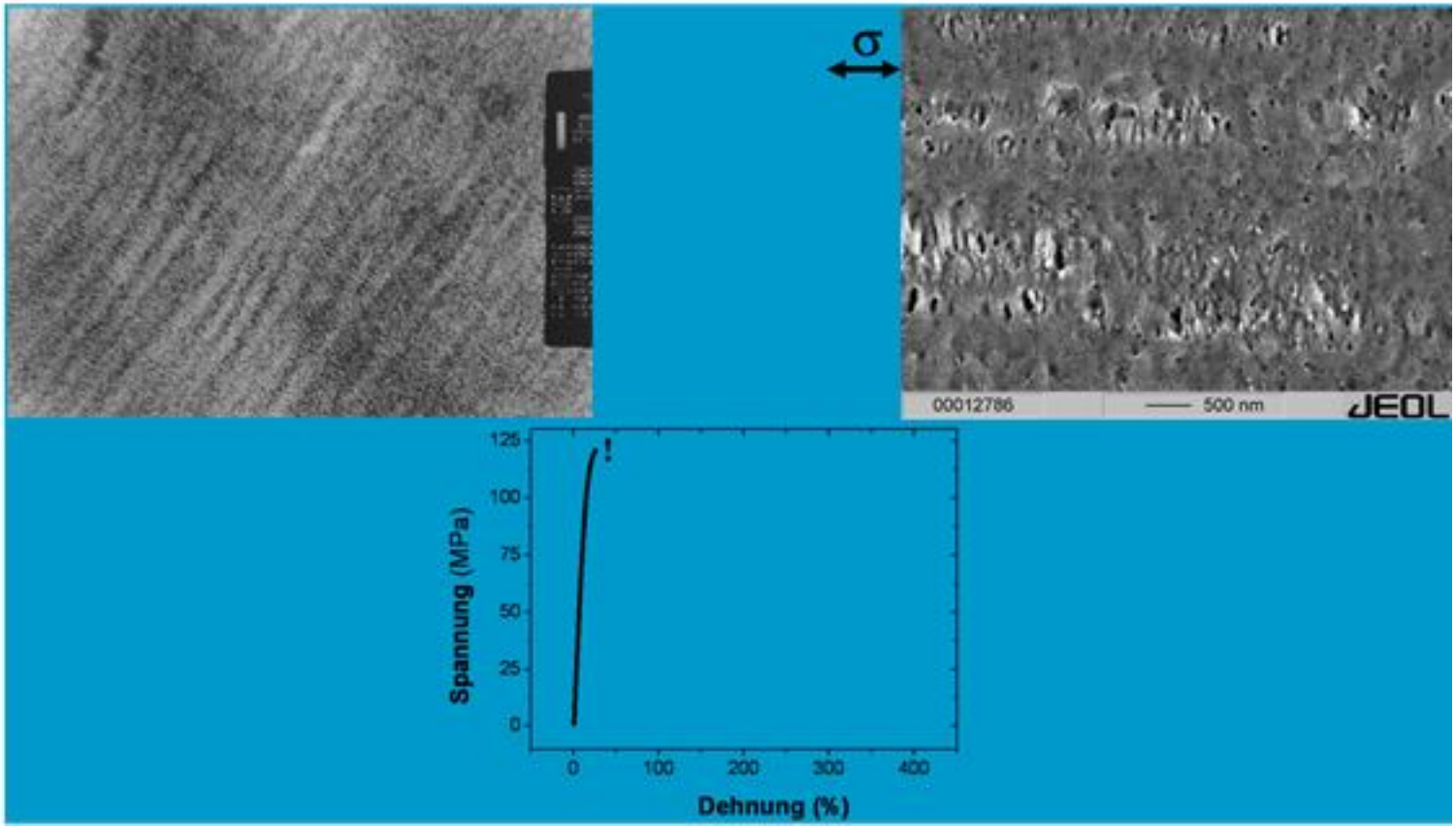
3. Examples

Semicrystalline Polymers

- PP parts from micro injection moulding



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

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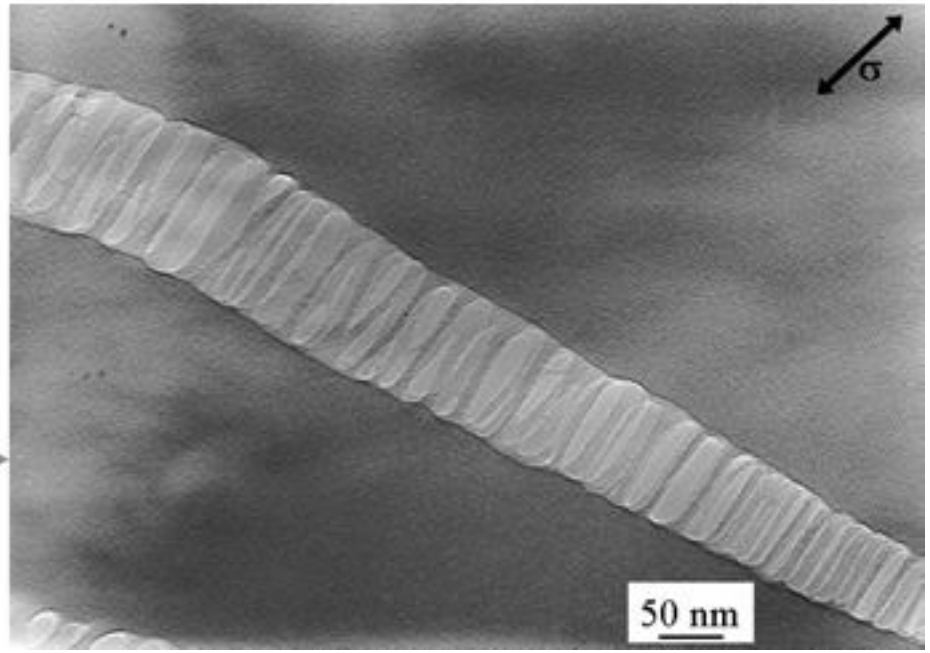
3. Examples
Toughness Enhancement

- Micromechanical principles of toughness enhancement

bulk PS homopolymer

- amorphous, hard at RT ($T_g \cong 103°C$)
- high strength and stiffness:
  $\sigma_B \cong 40 \ldots 50$ MPa,
  $E \cong 3.5$ GPa
- transparent
- *brittle: $\varepsilon_B \cong 3\%$*
- *micromechanical mechanism: crazing*



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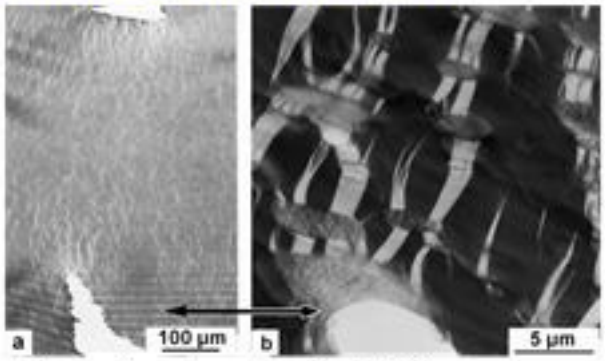
3. Examples

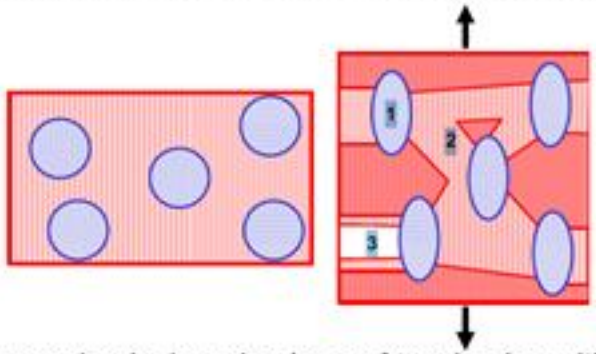
Toughness Enhancement

- Micromechanical principles of toughness enhancement

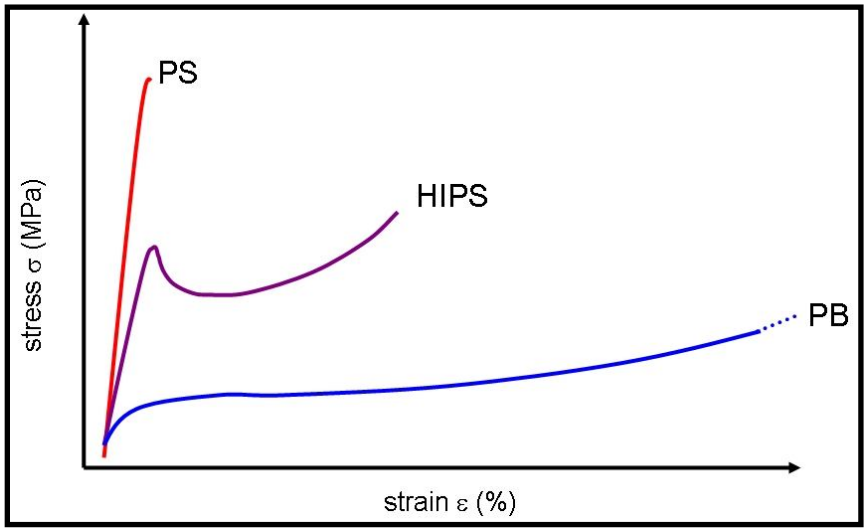
rubber toughening of PS



deformation 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
(M. Buschnakowski: PhD thesis, Halle 2008; redrawn after G.H. Michler: Kunststoff-Mikromechanik; Hanser 1992))



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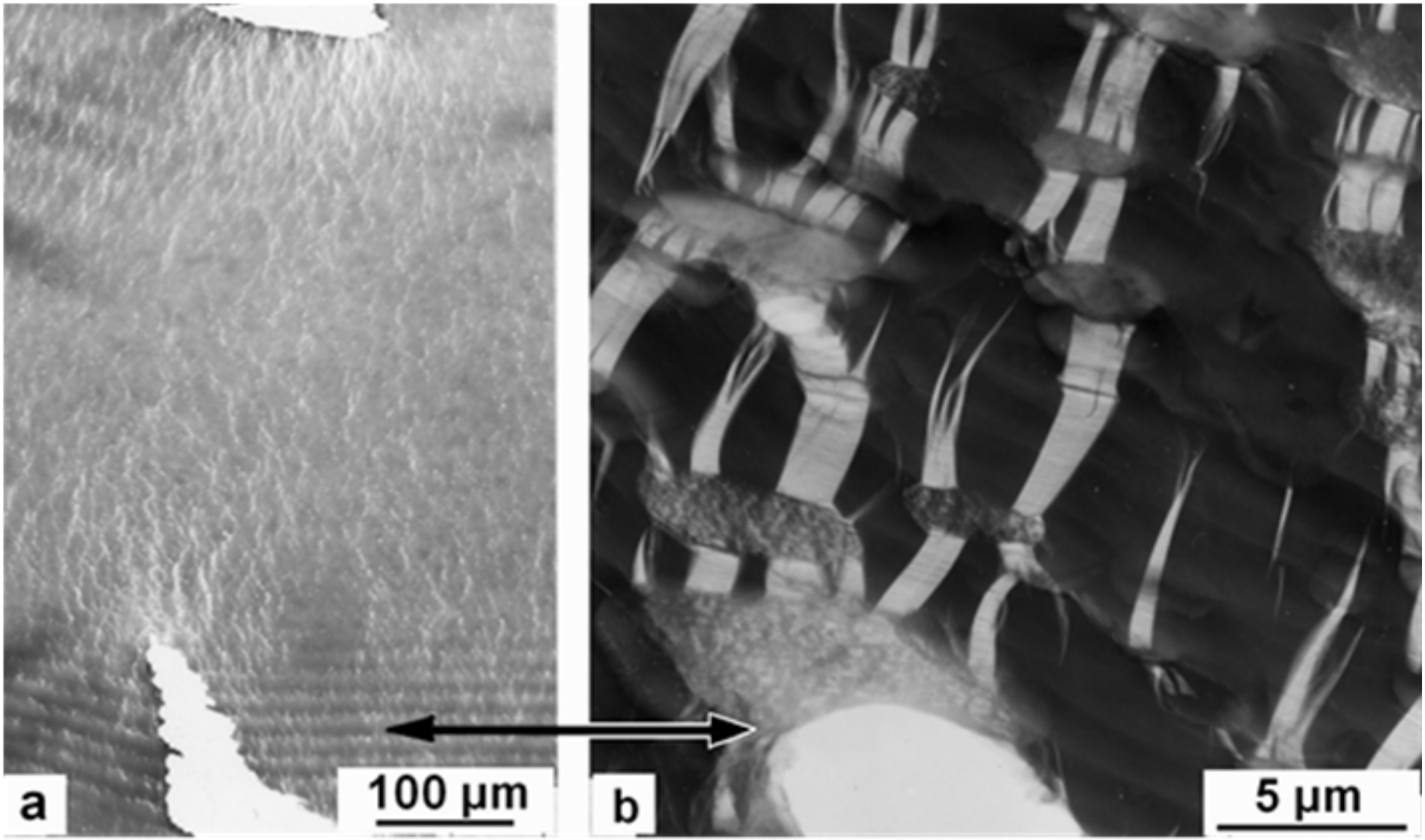

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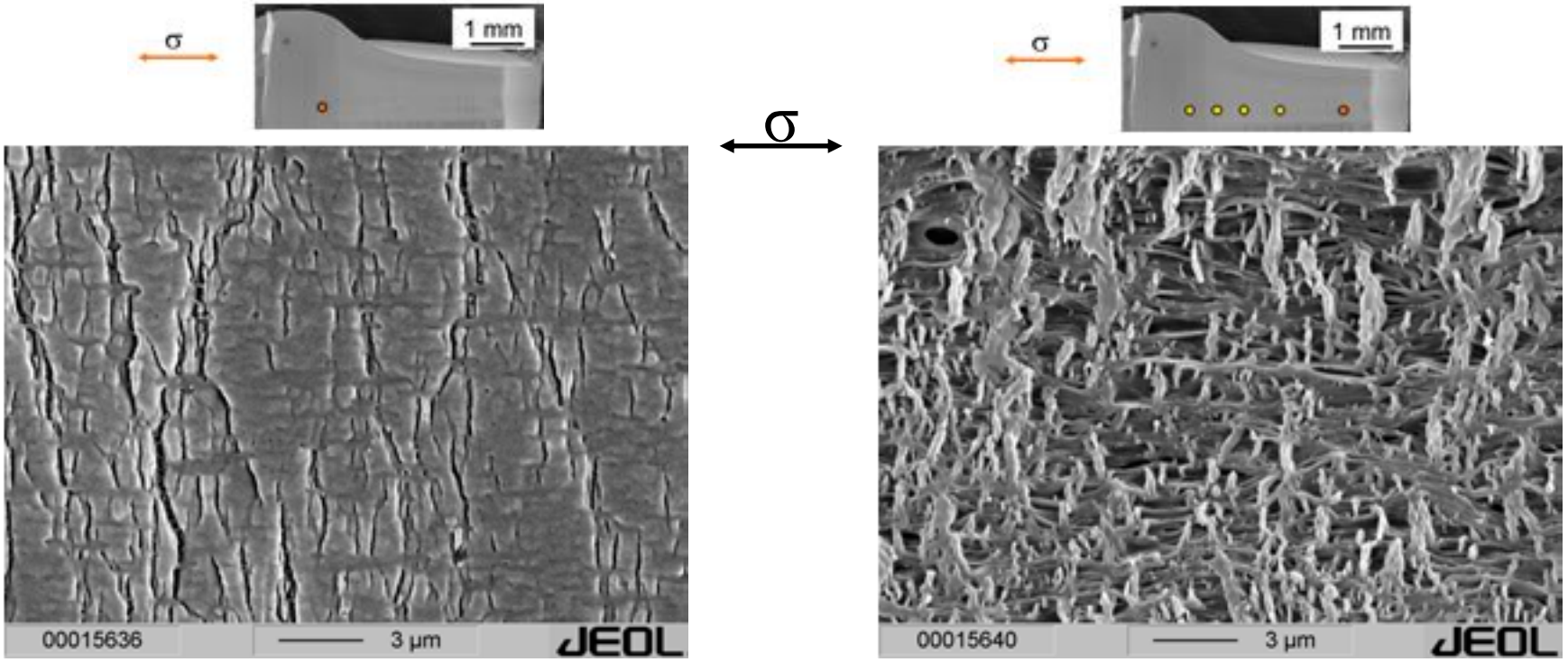
3. Examples

Toughness Enhancement

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



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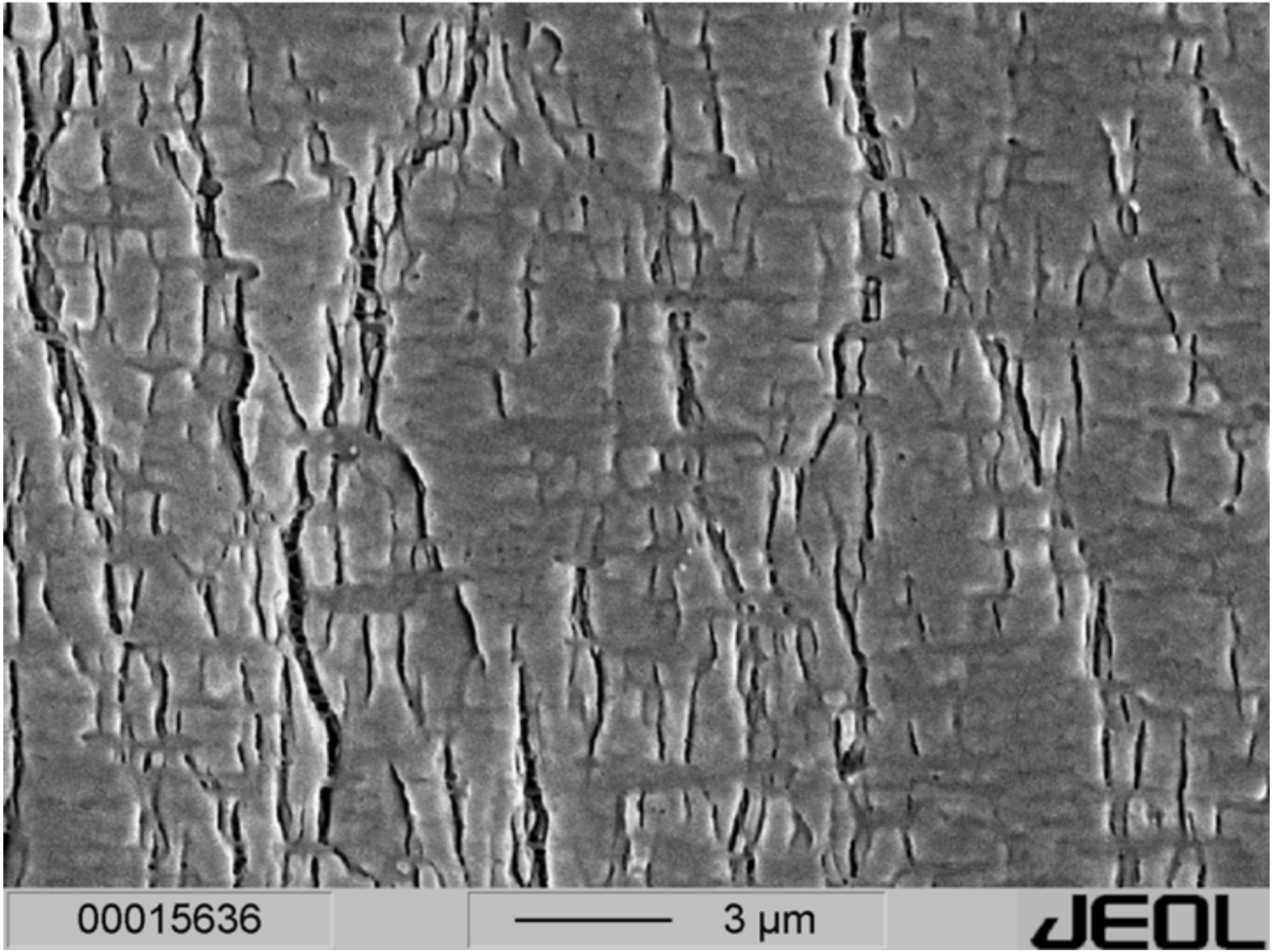
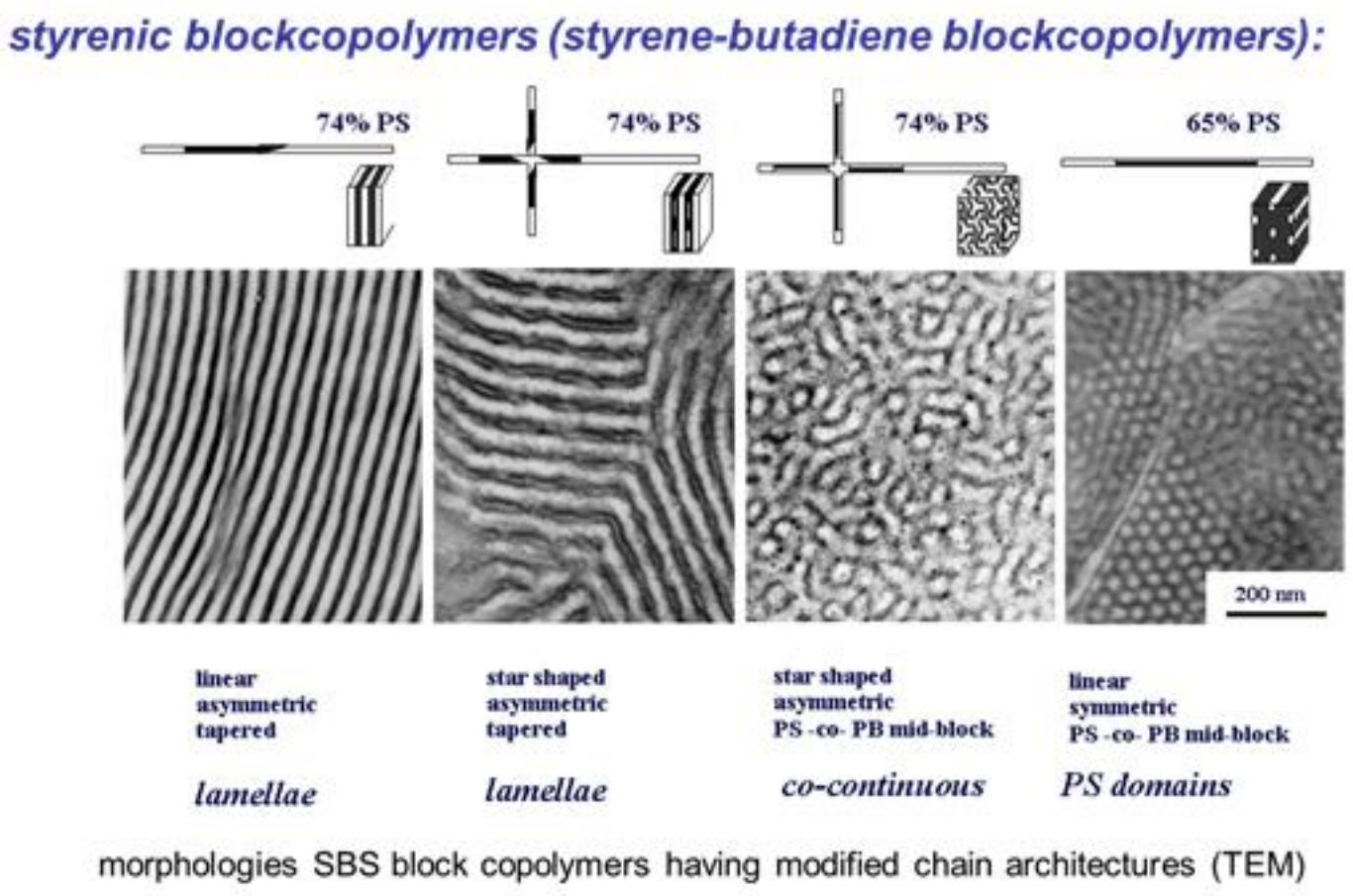

00015636
3 µm
JEOL

3. Examples
Thin layer yielding

- Special effects in block copolymers, layered structures and nanofibers



morphologies SBS block copolymers having modified chain architectures (TEM)

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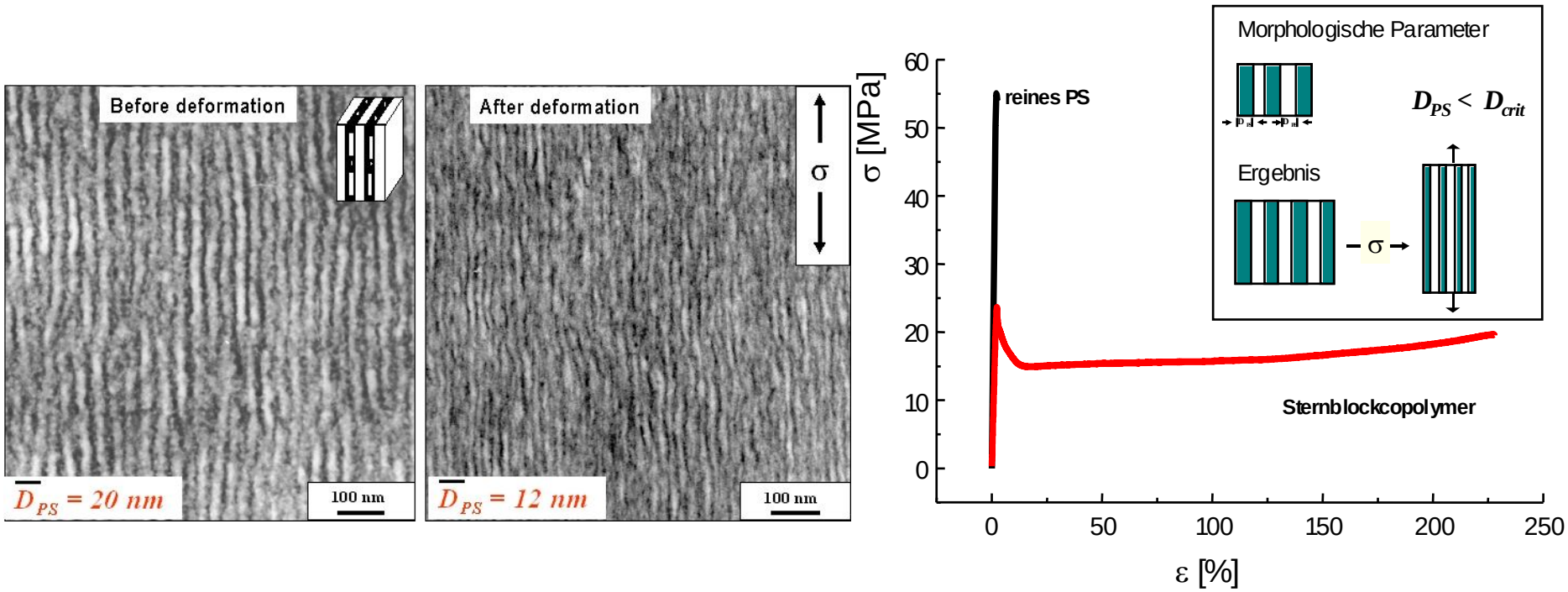
3. Examples

Thin layer yielding

- Special effects in block copolymers, layered structures and nanofibers
  - Thin layer yielding in lamellar SBS block copolymers



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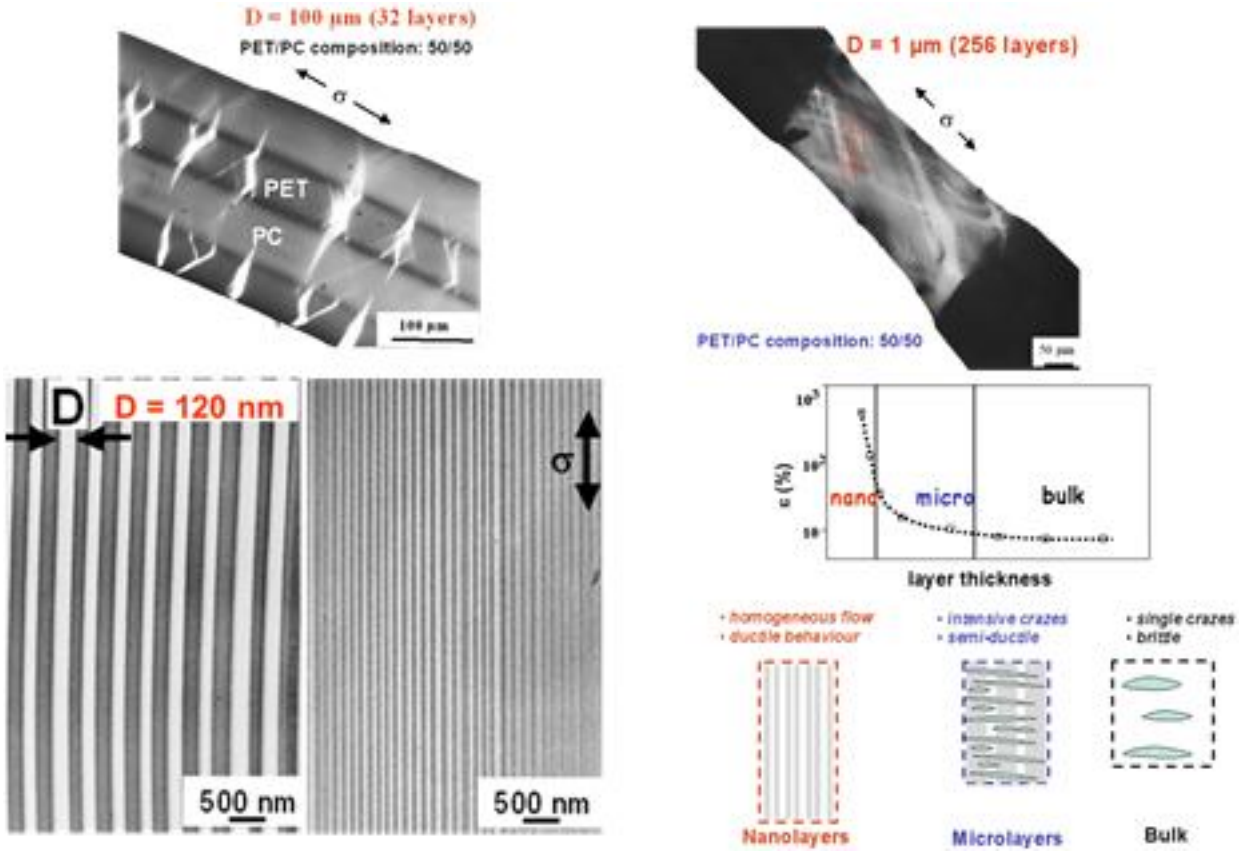
3. Examples
Thin layer yielding

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



47 [sample preparation e.g.: Ponting, Hiltner, Baer: Macromol. Symp. 294-I, 2010]

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3. Examples
Thin layer yielding

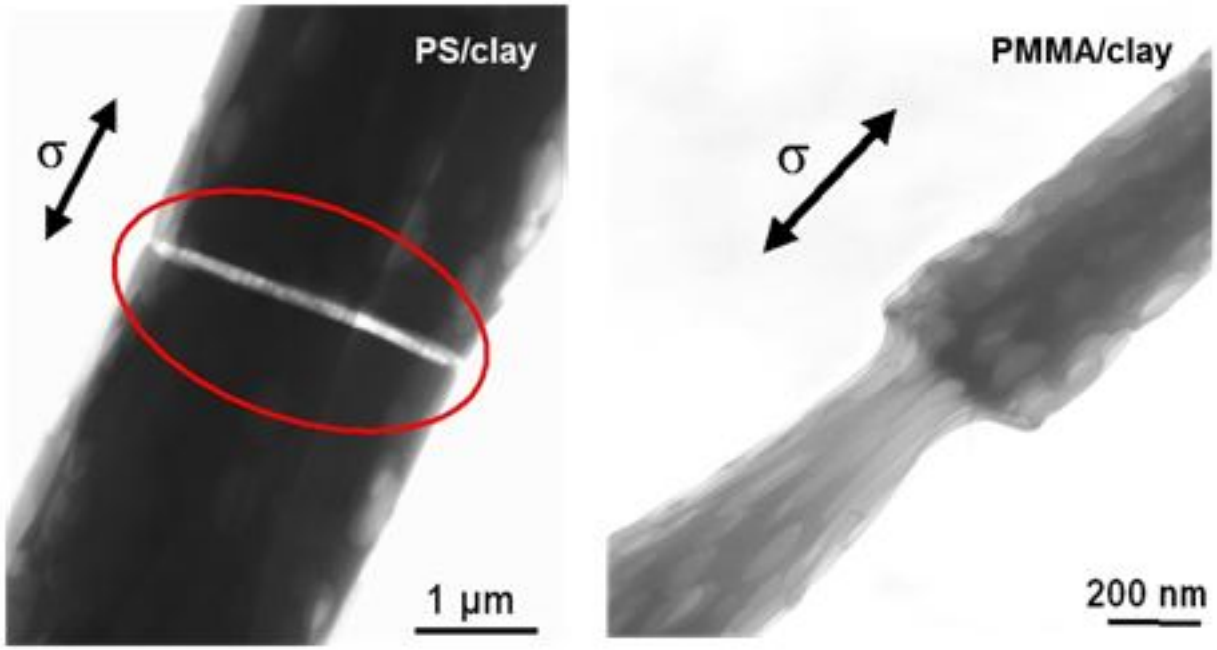
- Special effects in block copolymers, layered structures and nanofibers
  - Thin layer yielding: brittle to ductile transition in nanofibers

Matrix polymers: PS, PC, PMMA

Nanofillers: layered silicates, SiO_2, Alumina, CNT

Preparation by electrospinning

Aim: Definition of critical dimensions for the transition from crazing to yielding



Transition from crazing to thin layer yielding depending on fiber thickness

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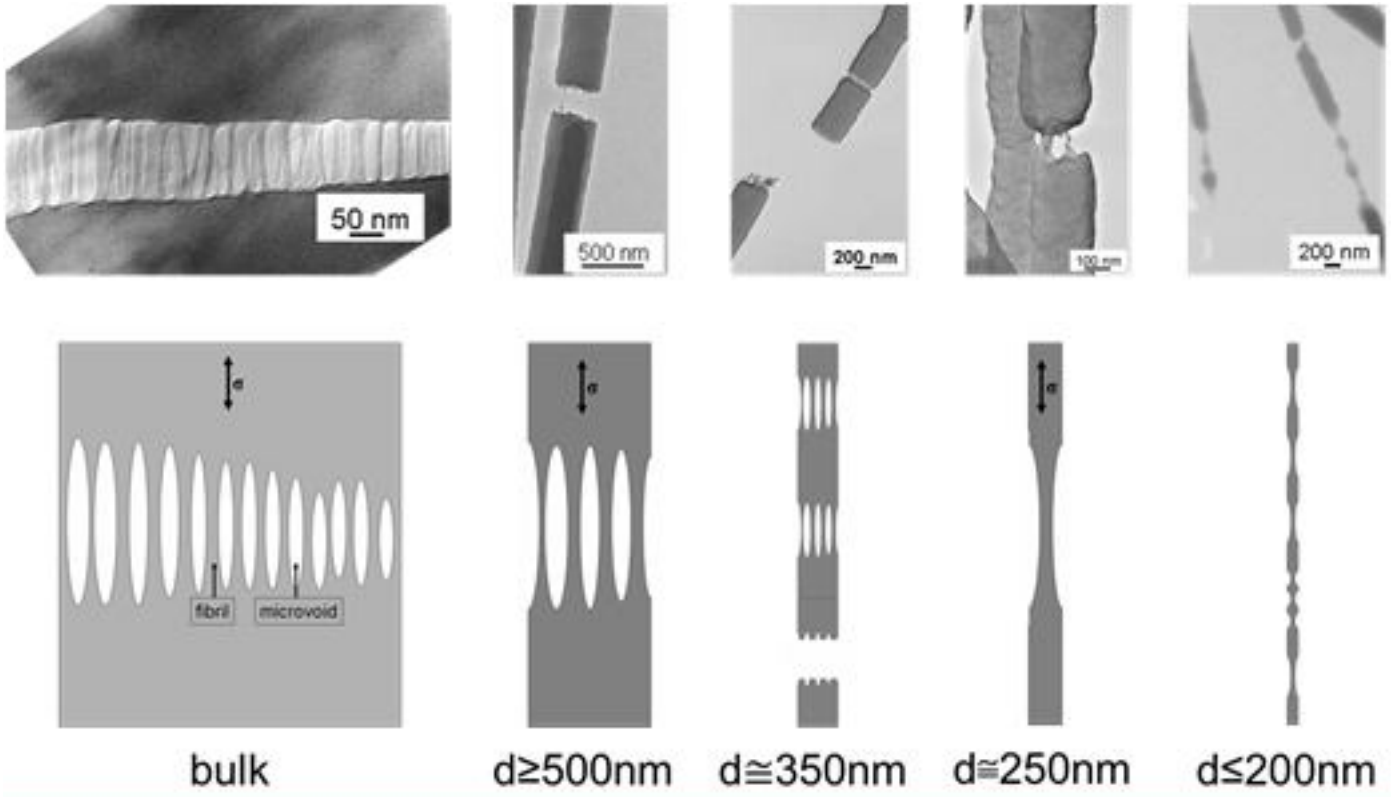
3. Examples
Thin layer yielding

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



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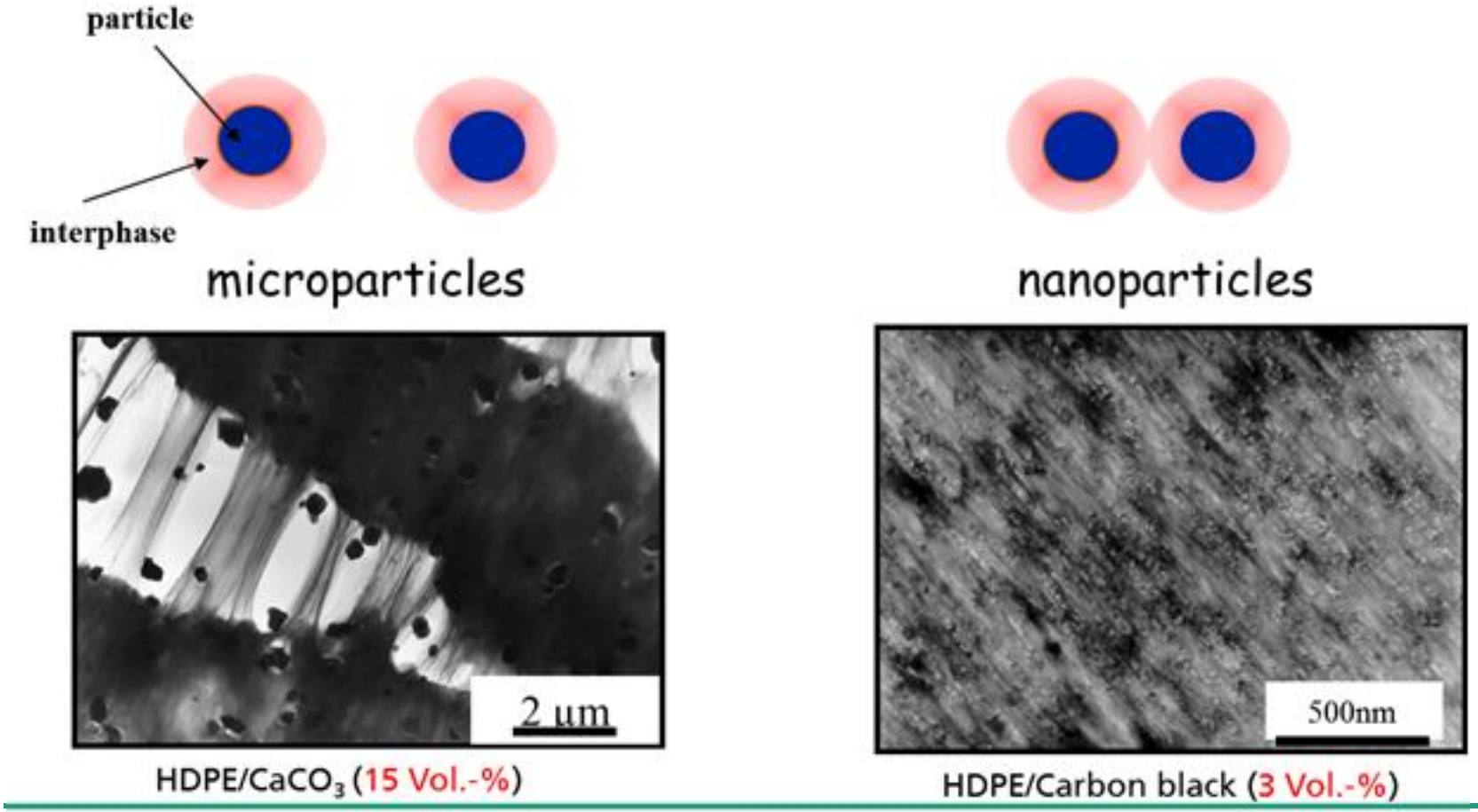
3. Examples

Nanocomposites

- Micromechanics of nanocomposites: Principles
  - Increasing influence of the interface /interphase with decreasing particle size



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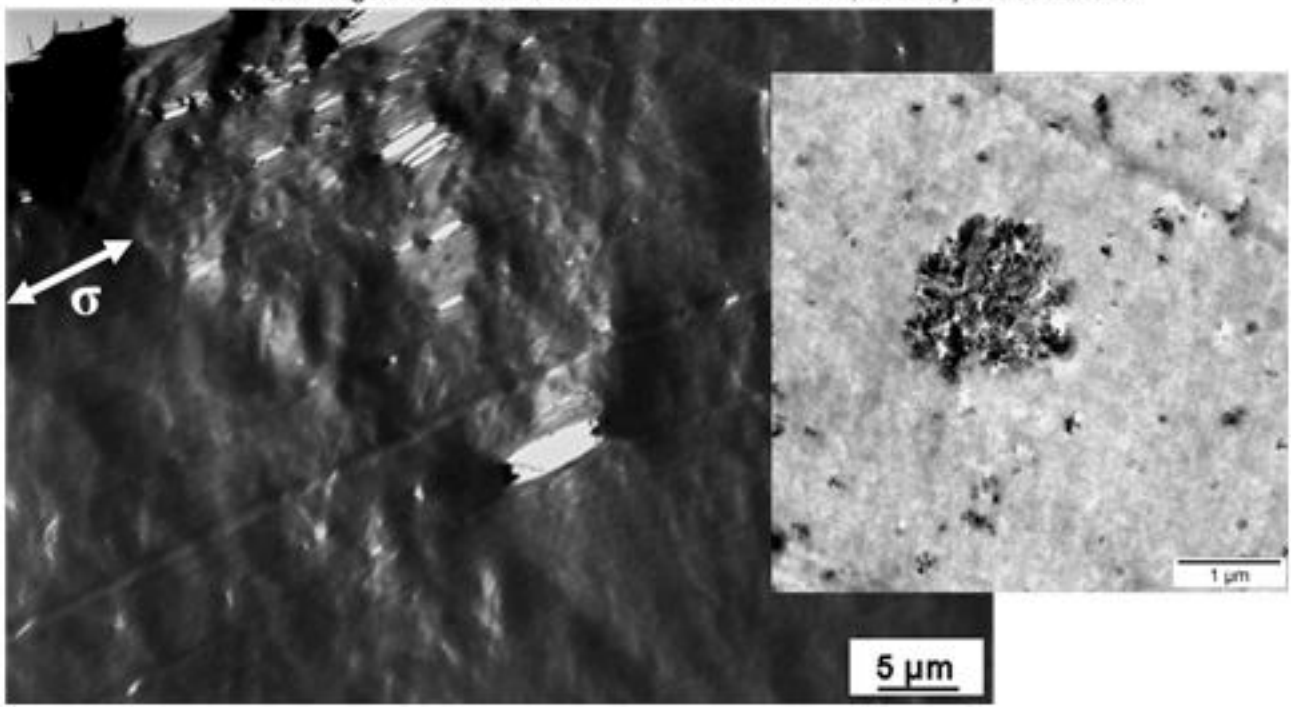
3. Examples
Nanocomposites

- 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

TEM image of deformed semithin section of PP/MMT; courtesy Dr. G.-M. Kim



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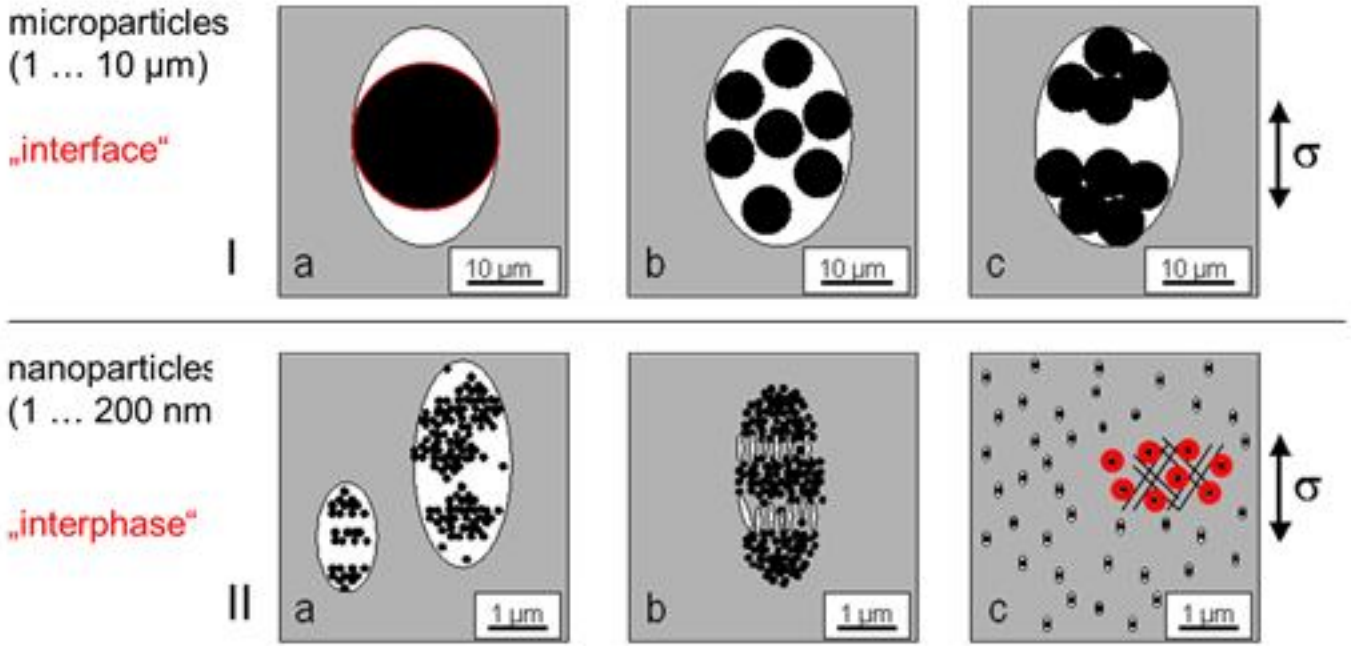
3. Examples
Nanocomposites

- Micromechanics of nanocomposites

Nanoparticles: Hard particles may induce micromechanical mechanisms that involve strong plastic deformation of the matrix polymer (IIc)
→ increased strength and toughness



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3. Examples

Nanocomposites: CB-filled rubber blends

Comfort

Noise

Feel

Price

Green Tyres
Fuel Saver Tyres
Low-Rolling Resistance Tyres

Firestone Fuel Saver | Michelin Energy | Continental Eco Contact

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).

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.

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

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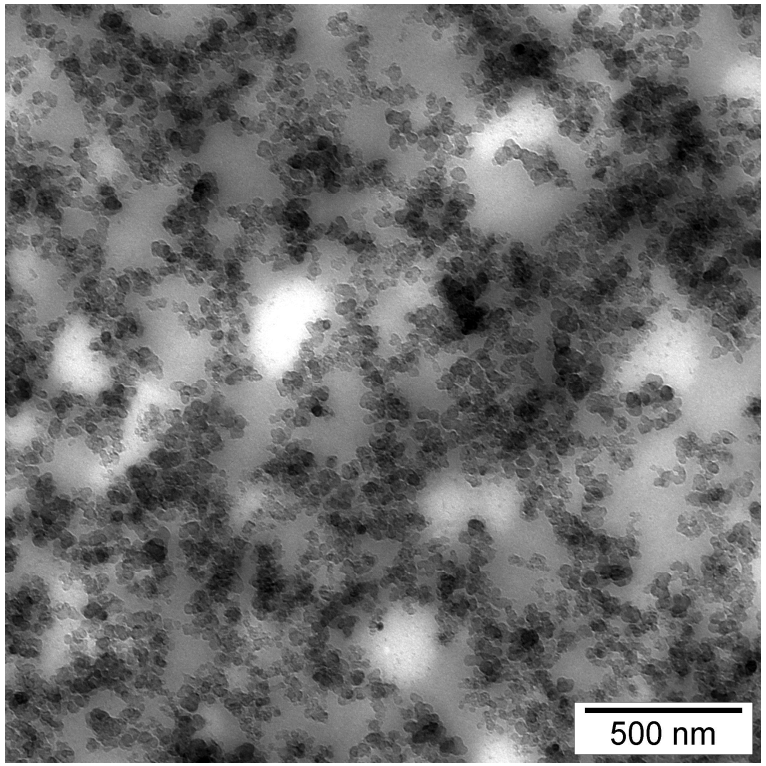
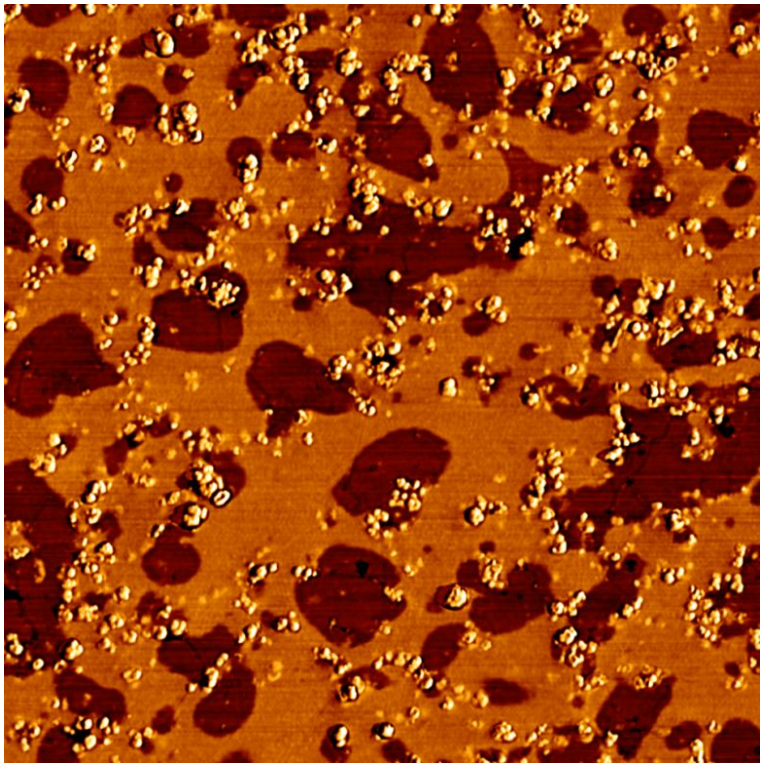
3. Examples

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)

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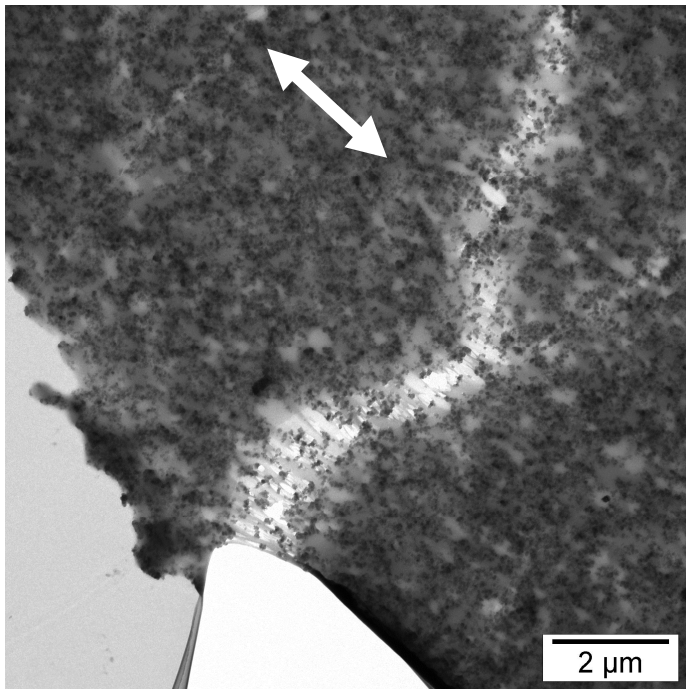
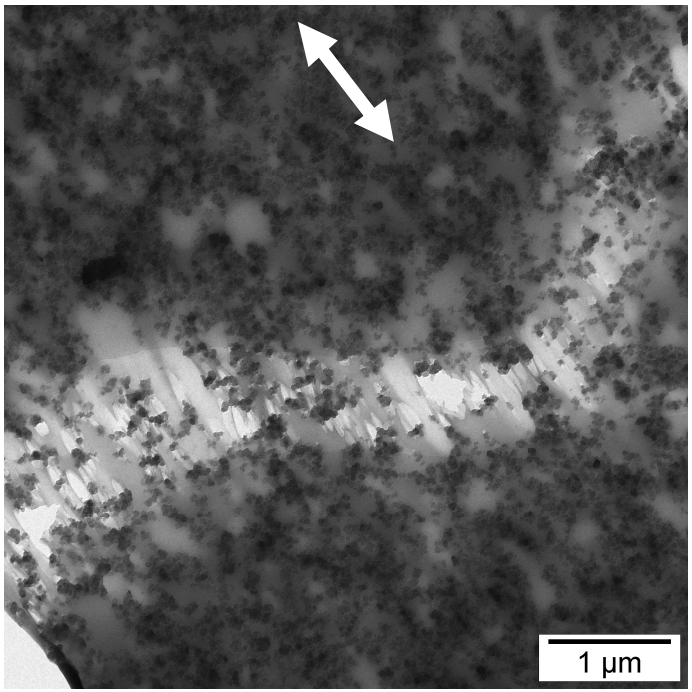
3. Examples

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





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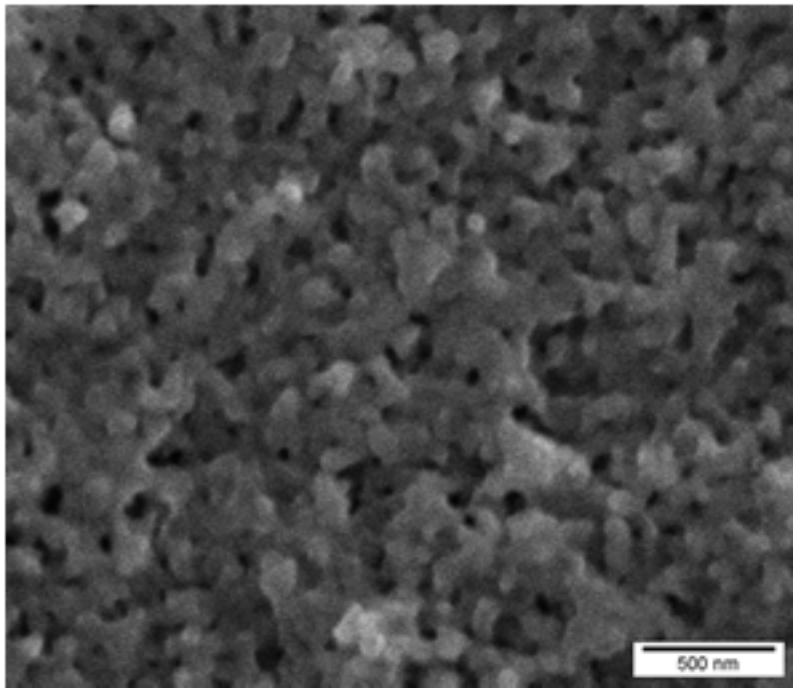
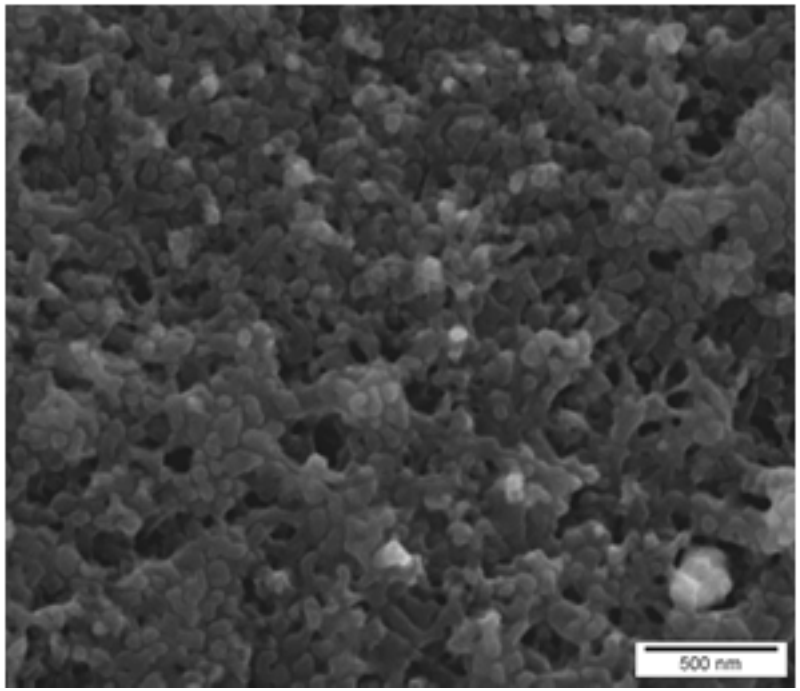
3. Examples

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

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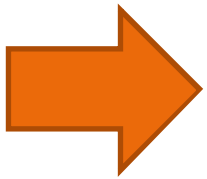
4. Summary

- 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

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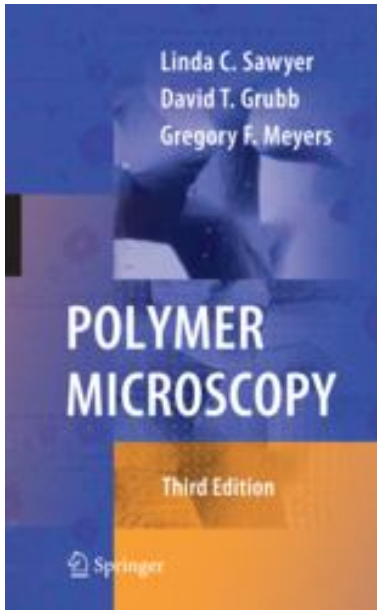
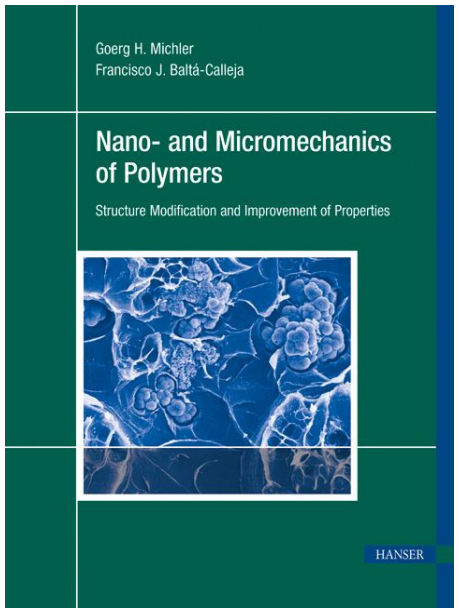
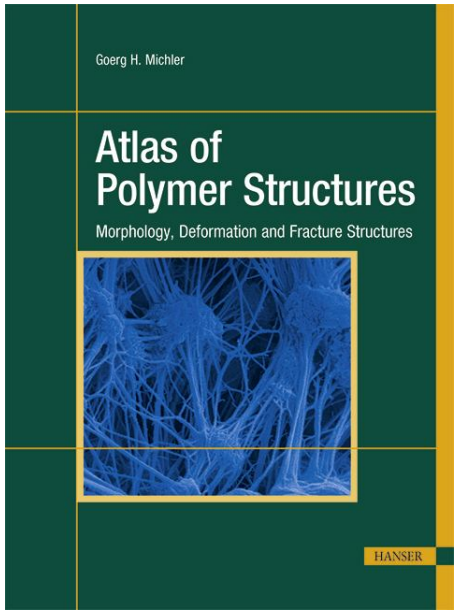
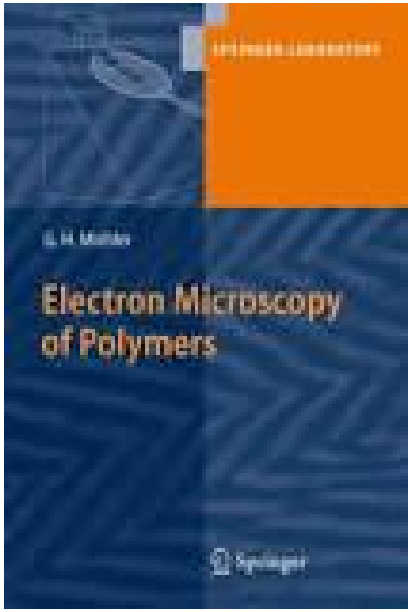
Further reading









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