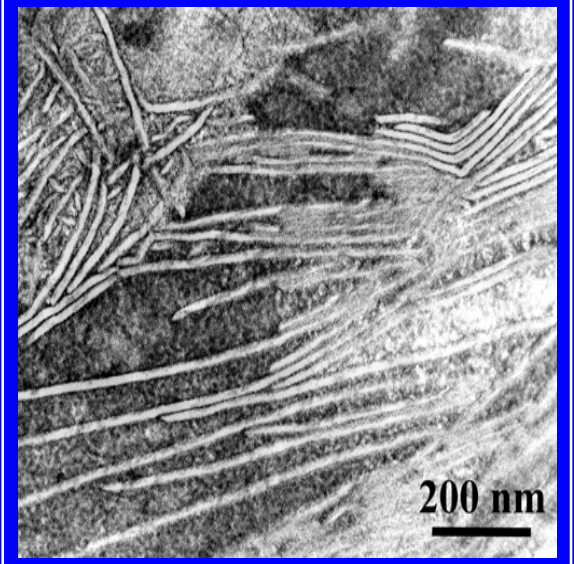
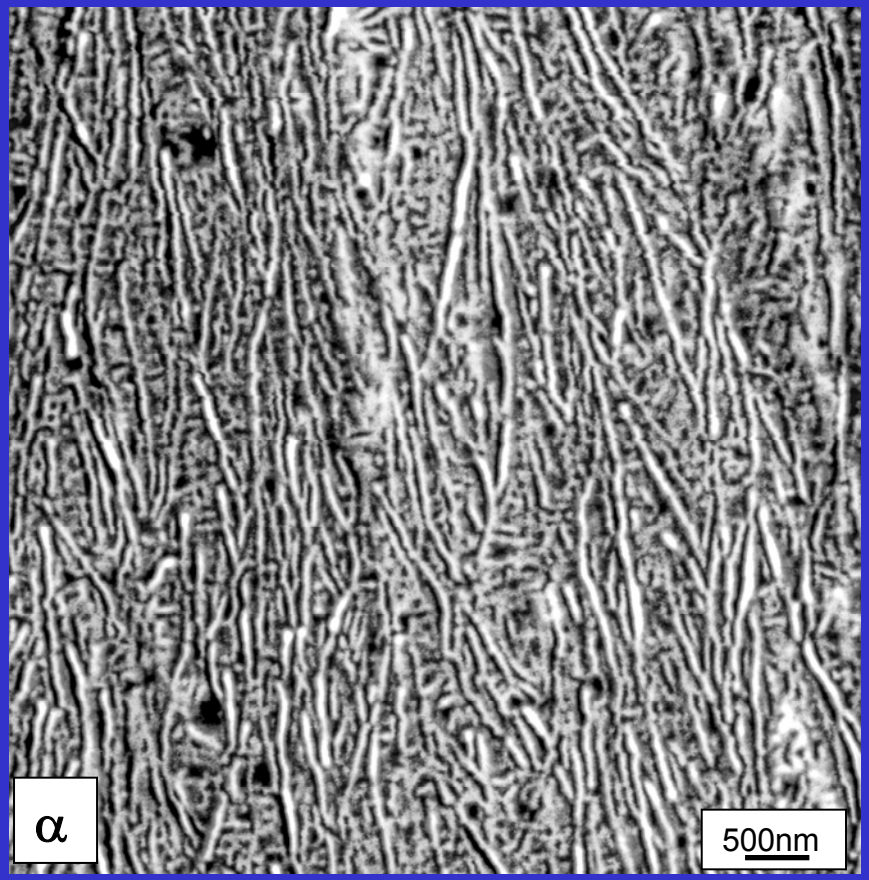
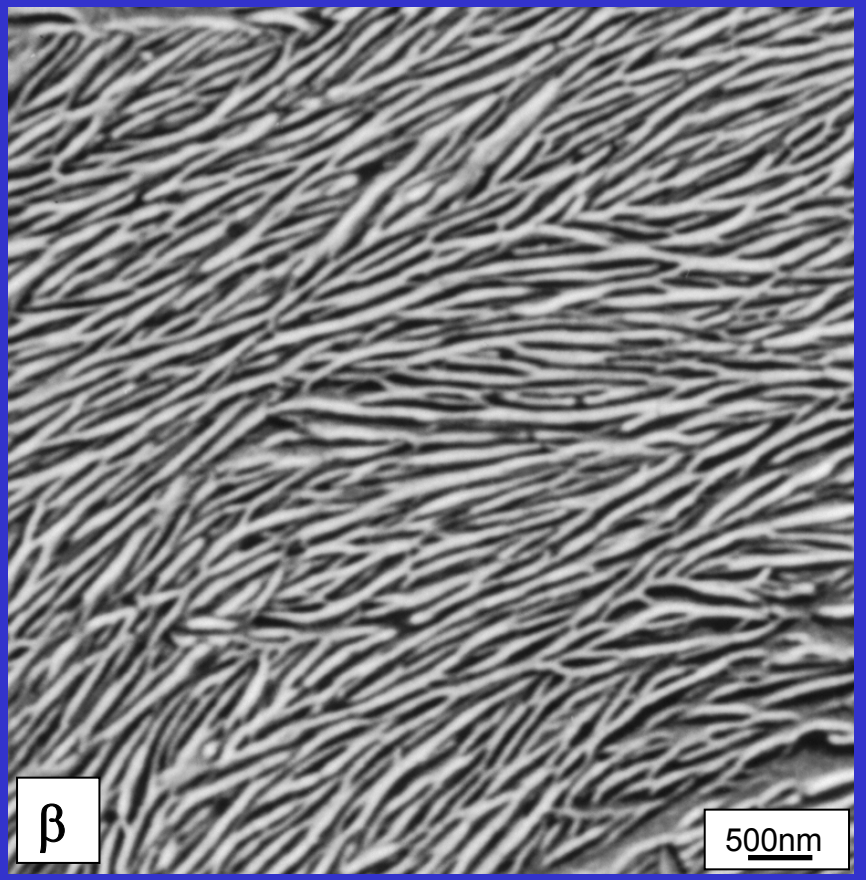
Morphological Investigations - Different Microscopic Techniques
(Semicrystalline Polymers)

Method	SEM	TEM	AFM
Typical Sample Preparation	Evaporation Surface Etching	Ultramicrotomy Selective Staining	no special, but very flat surfaces are necessary
Typical Results *HDPE/EOC blends*			

Results

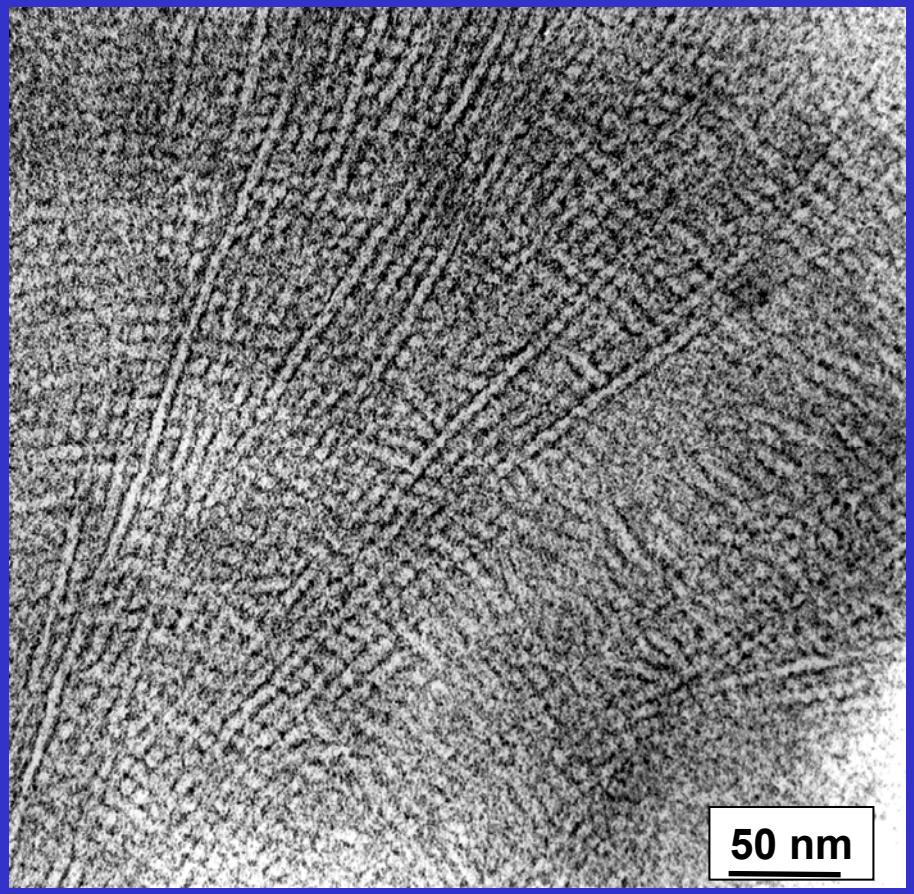
Morphology: SEM



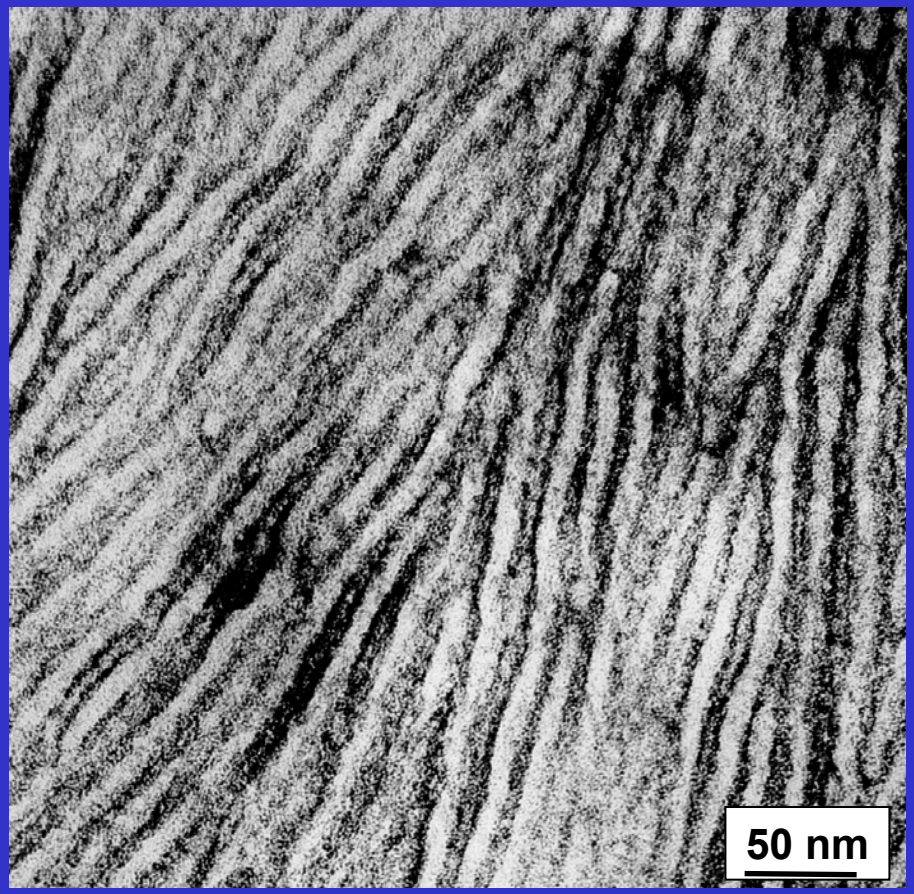


Results

Morphology: TEM



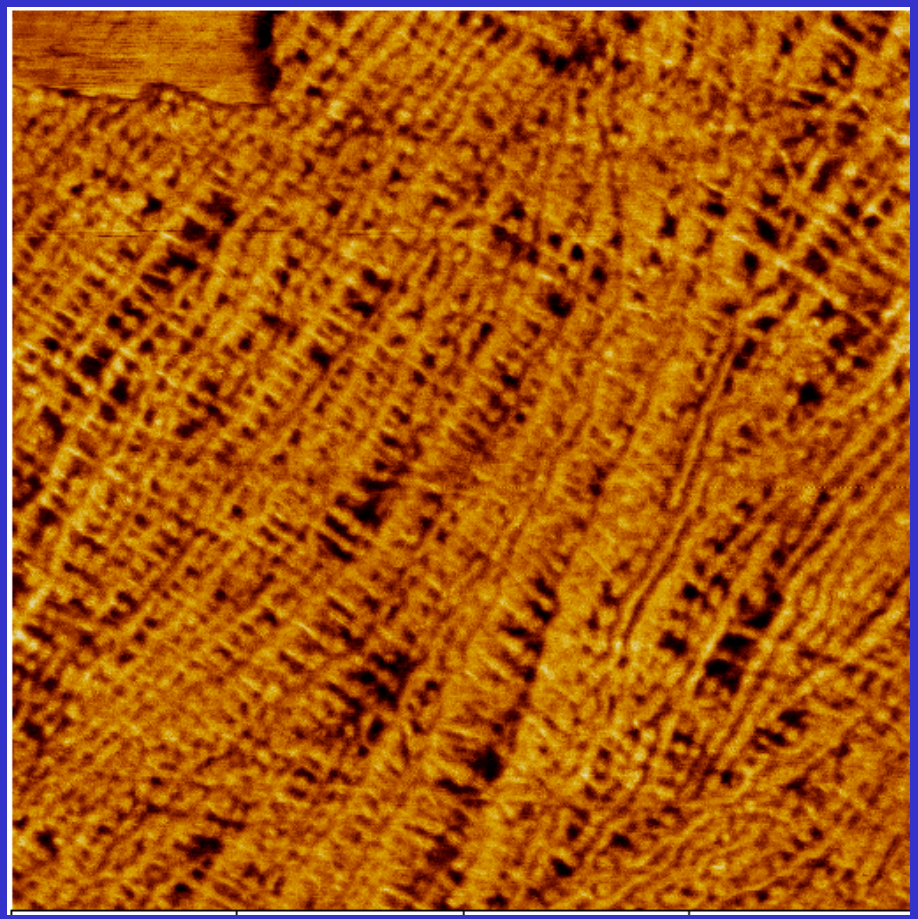
α

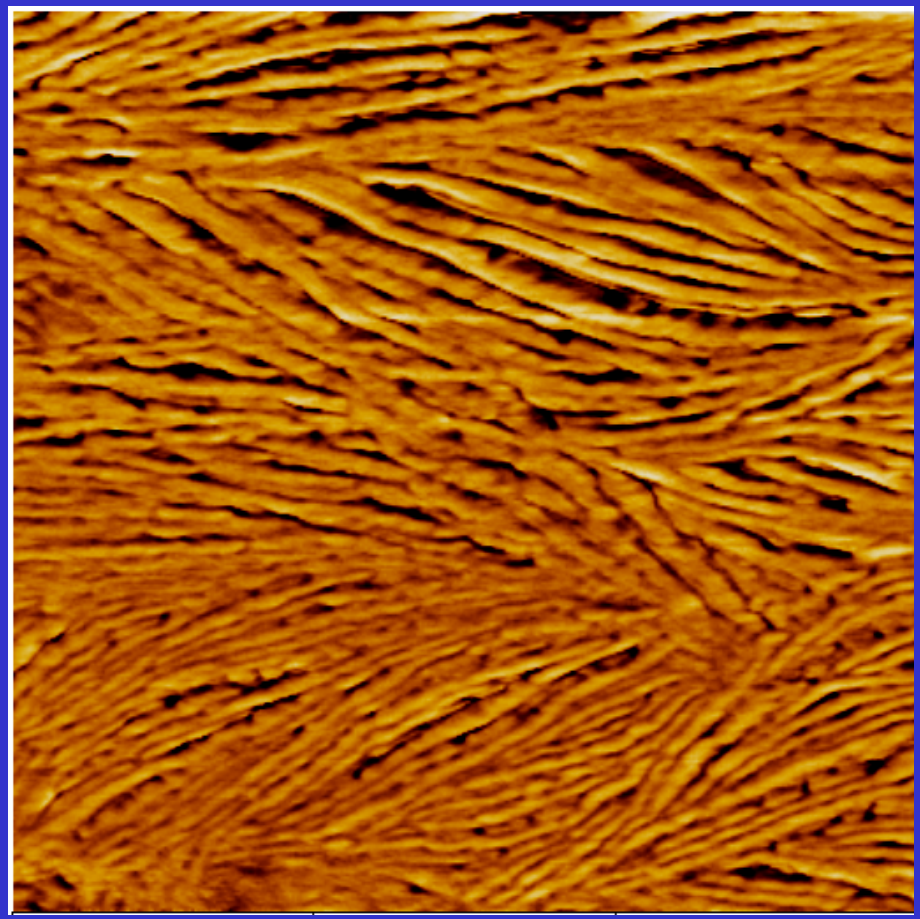


β

Results

Morphology: AFM





II. Sample Preparation

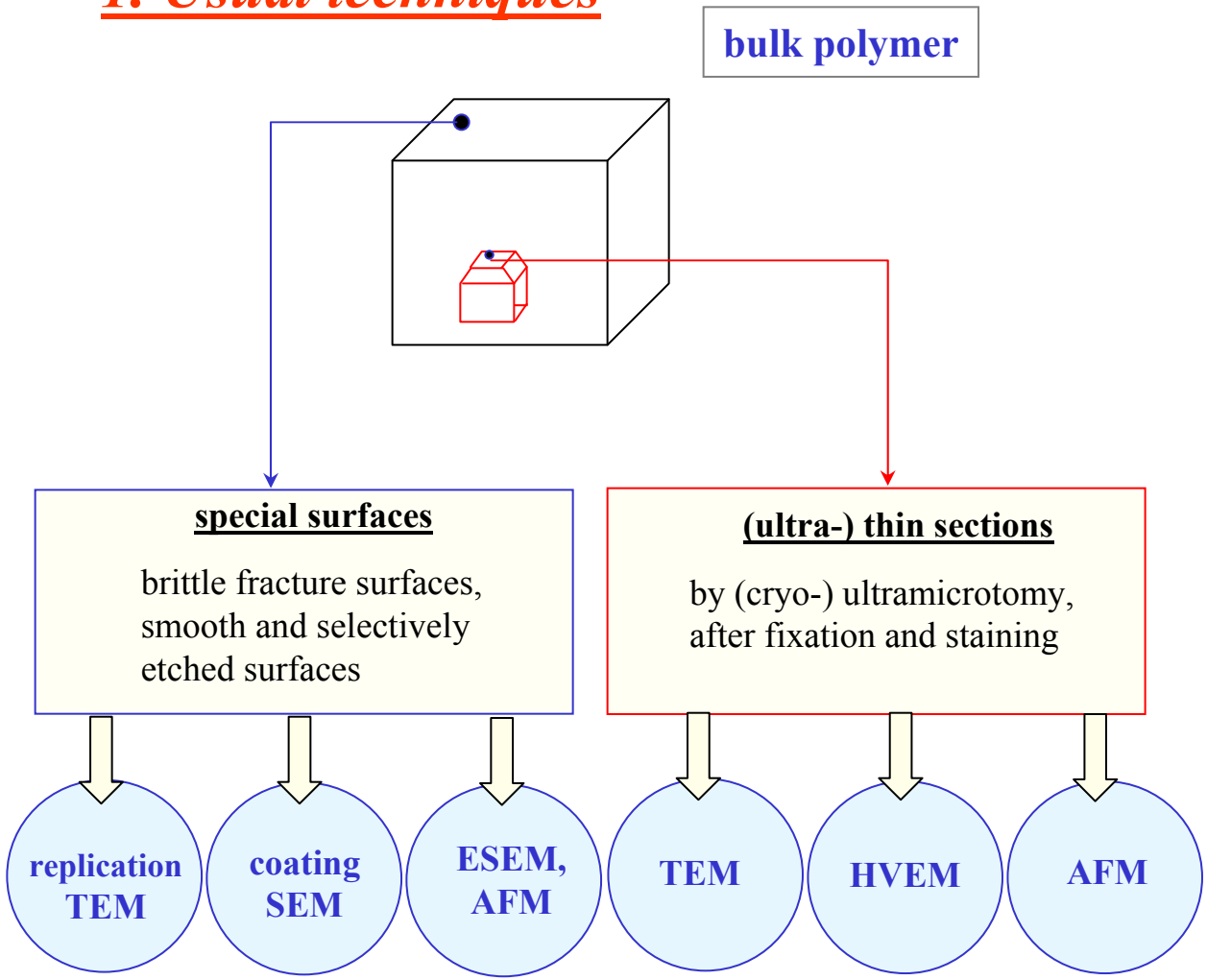
Surfaces

Cryo – Ultramicrotomy

Fixation and Staining of Polymers

EM investigation of morphology

1. Usual techniques



2. Special techniques

- **Irradiation effects**

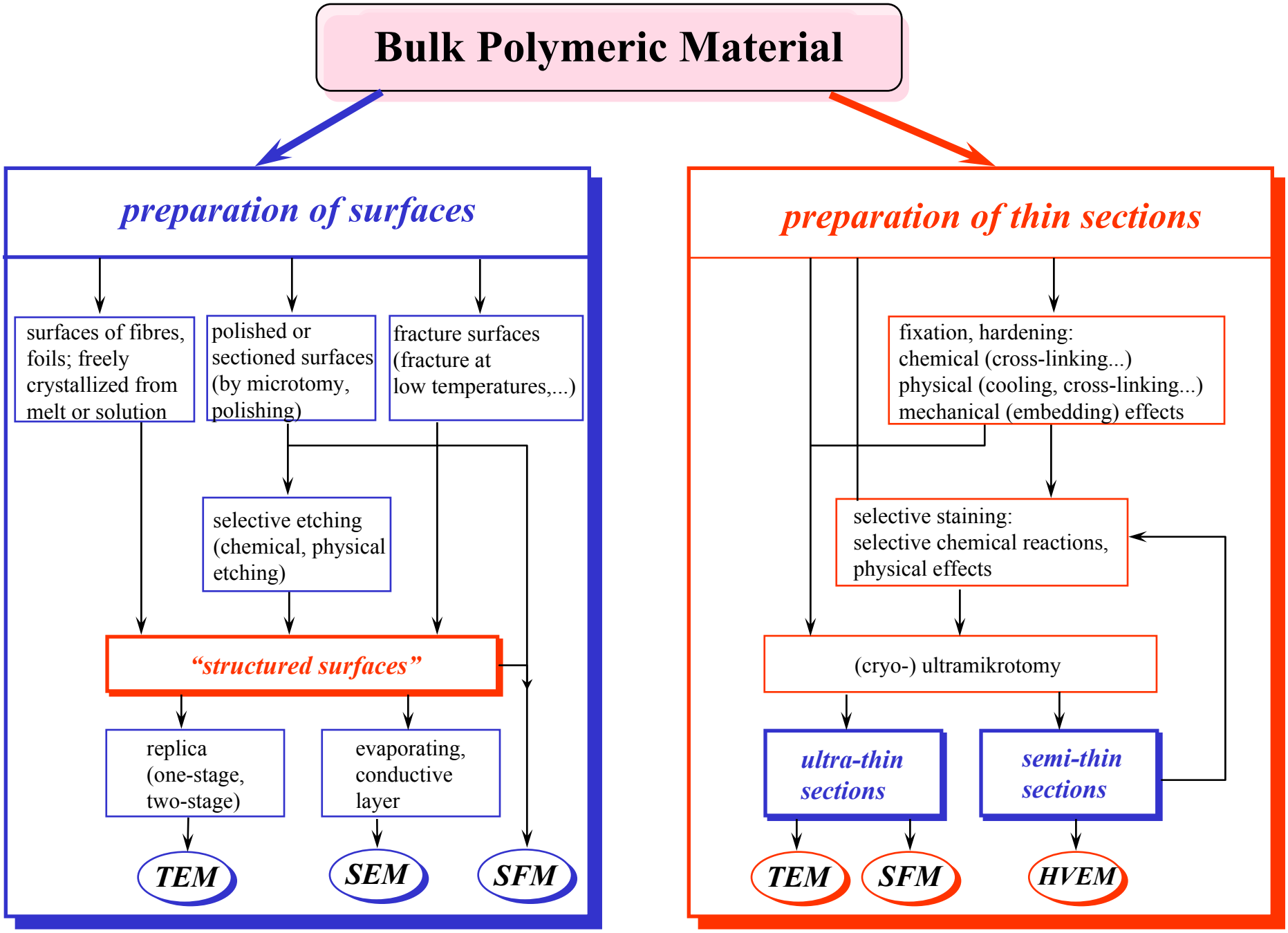
γ- or electron irradiation at $T \geq RT$

↷ fixation and contrast enhancement

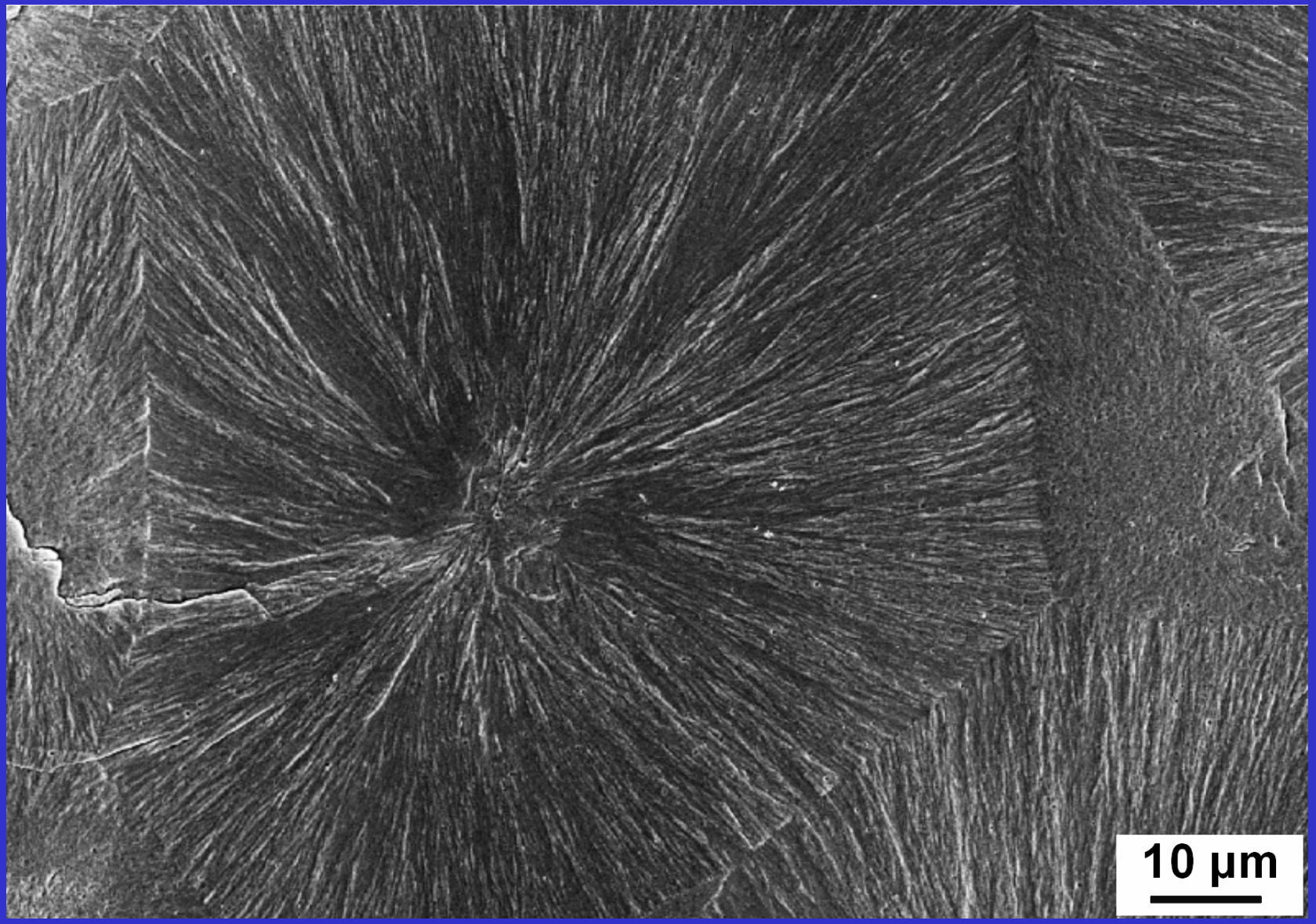
- **Straining effects**

Straining of (semi-) thin sections

↷ contrast enhancement


Bulk Polymeric Material
preparation of surfaces
surfaces of fibres, foils; freely crystallized from melt or solution
polished or sectioned surfaces (by microtomy, polishing)
fracture surfaces (fracture at low temperatures,...)
selective etching (chemical, physical etching)
"structured surfaces"
replica (one-stage, two-stage)
evaporating, conductive layer
TEM
SEM
SFM
preparation of thin sections
fixation, hardening:
chemical (cross-linking...)
physical (cooling, cross-linking...)
mechanical (embedding) effects
selective staining:
selective chemical reactions,
physical effects
(cryo-) ultramikrotomy
ultra-thin sections
semi-thin sections
TEM
SFM
HVEM

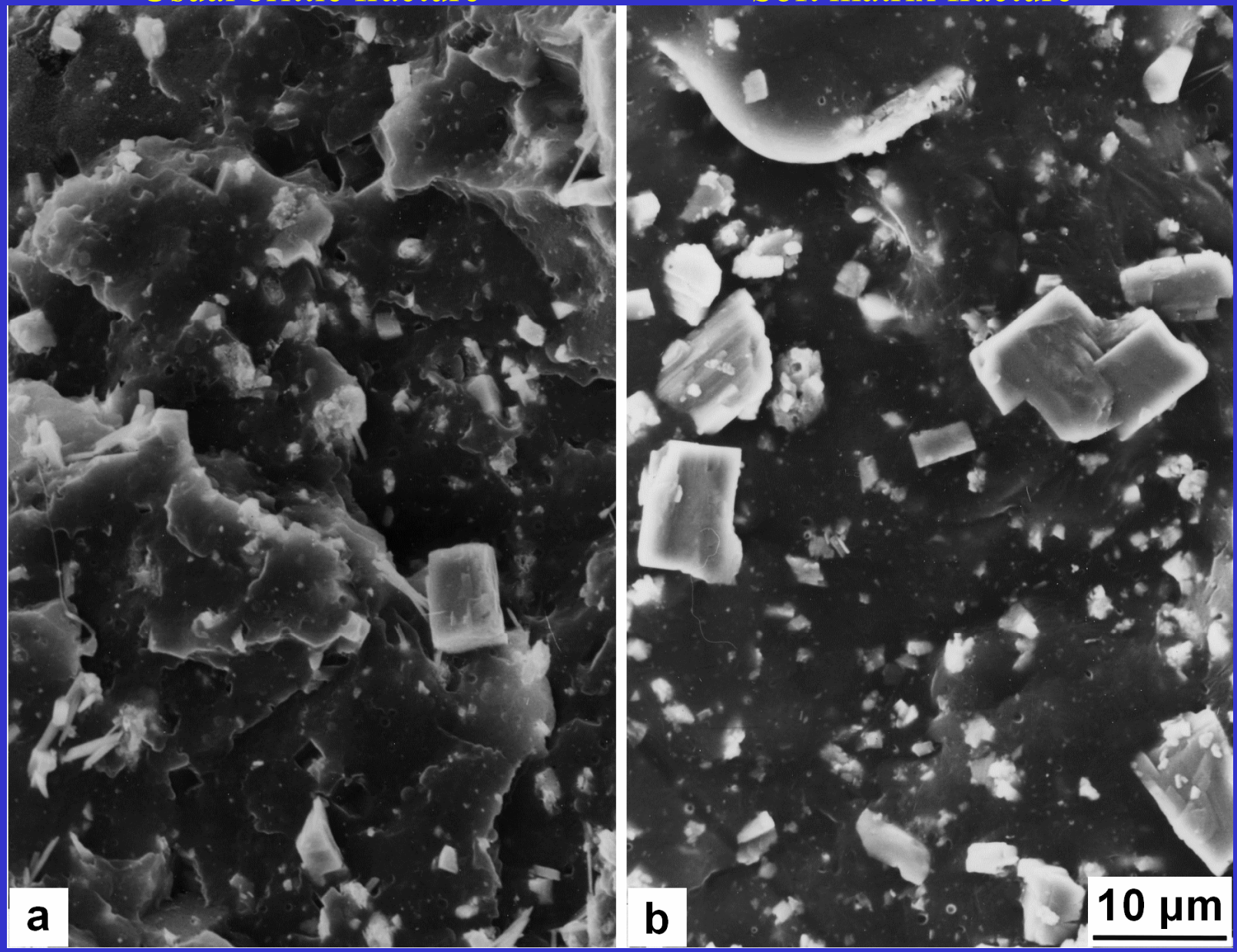
Surface of αiPP after permanganic etching, SEM



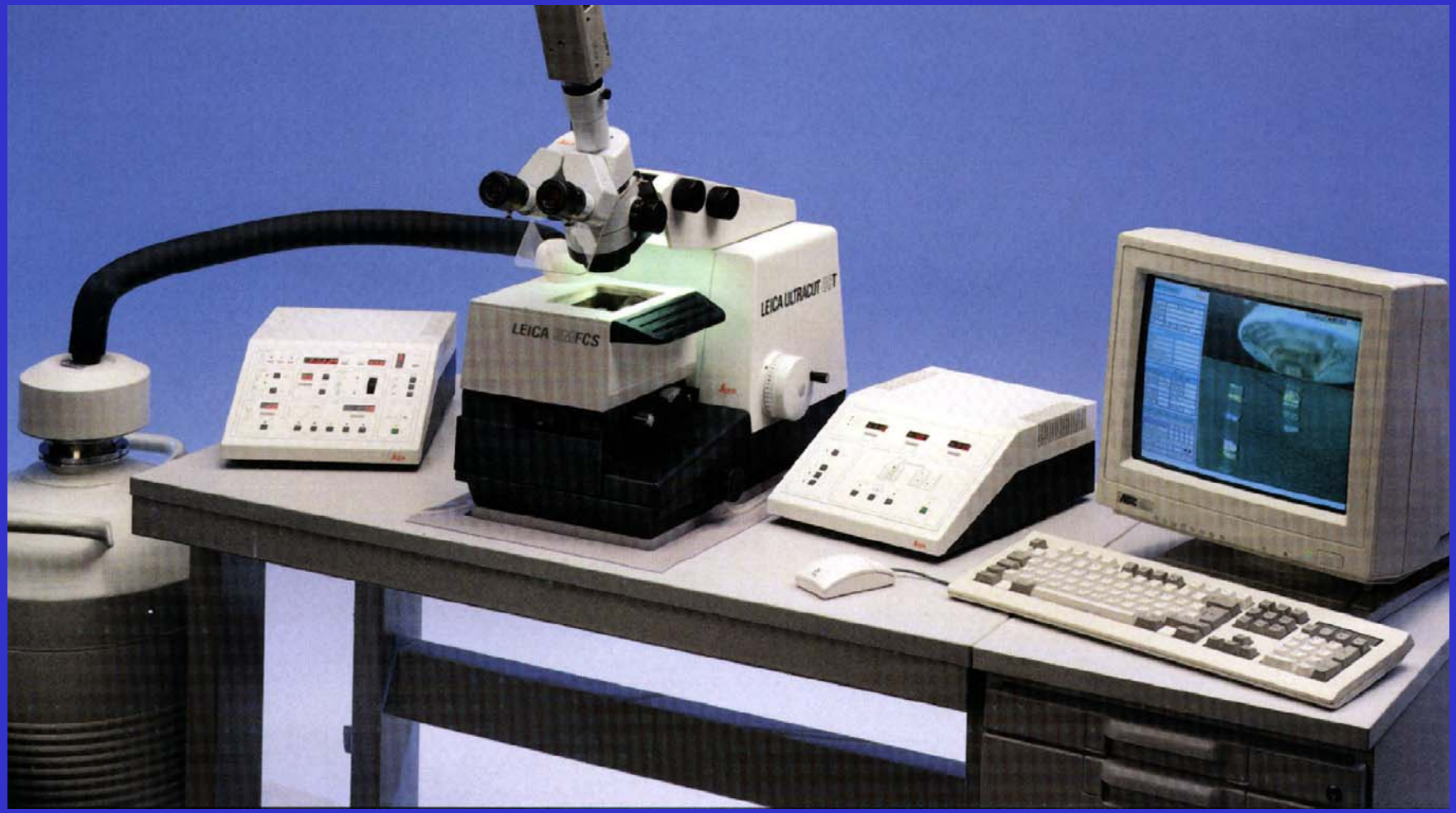
PP / $CaSO_4$ - Composite

Usual brittle fracture

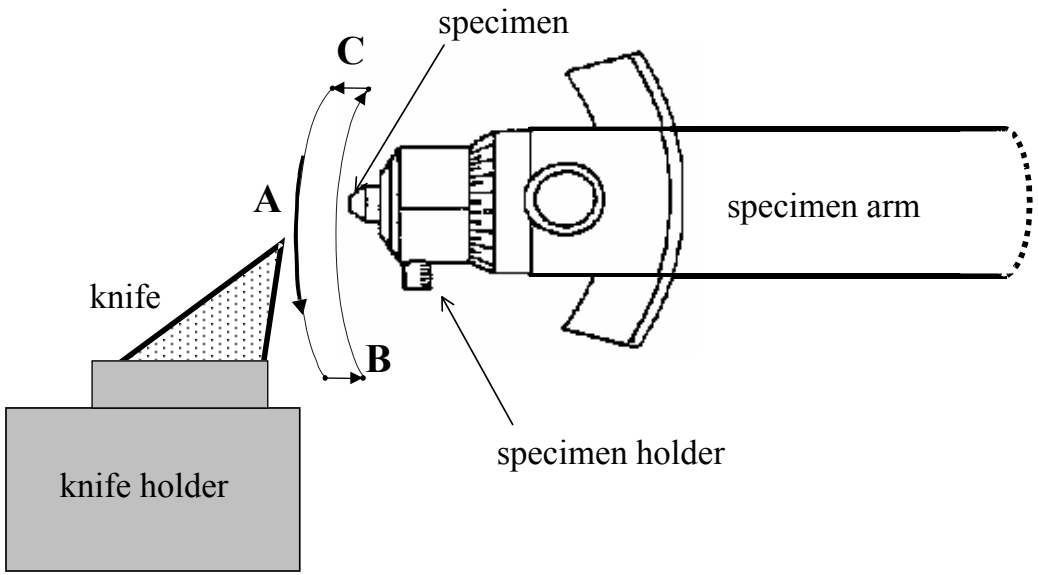
Soft matrix fracture



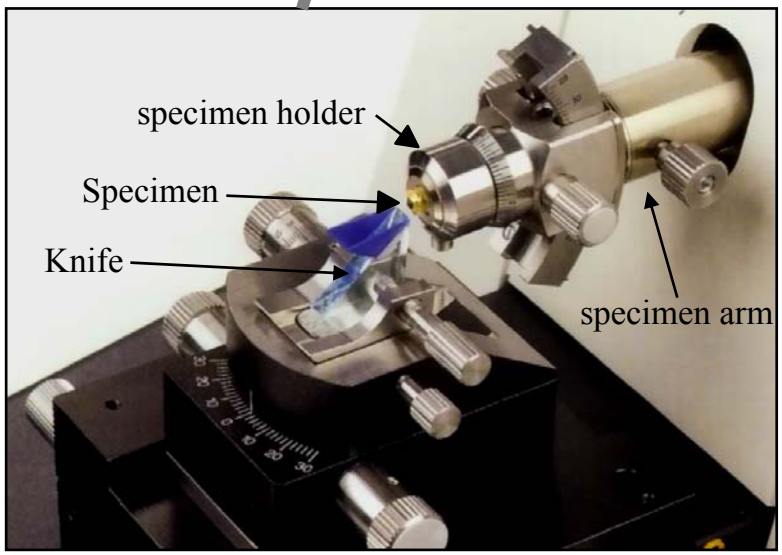
Cryo-Ultramicrotome UCT (Fa. Leica)



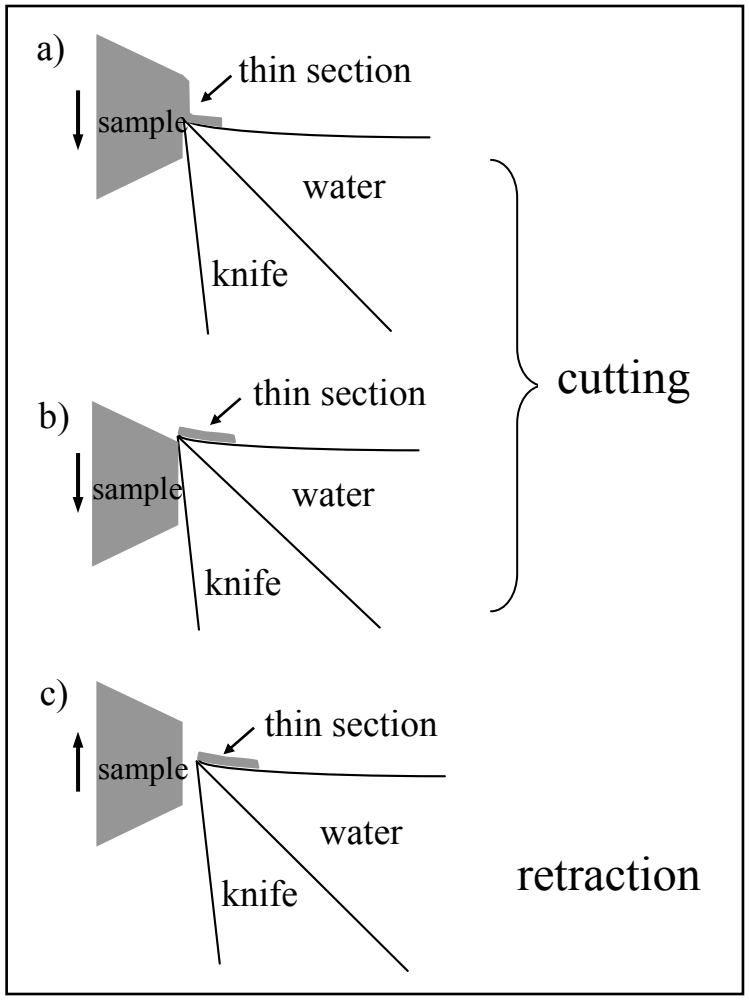
Principle

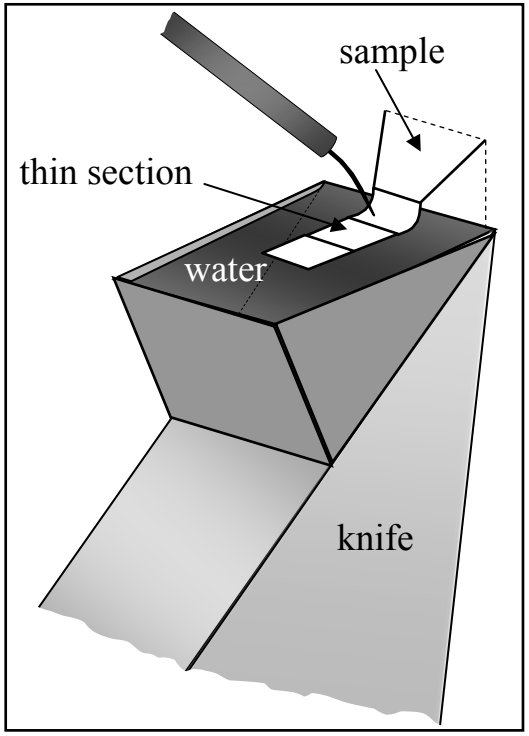


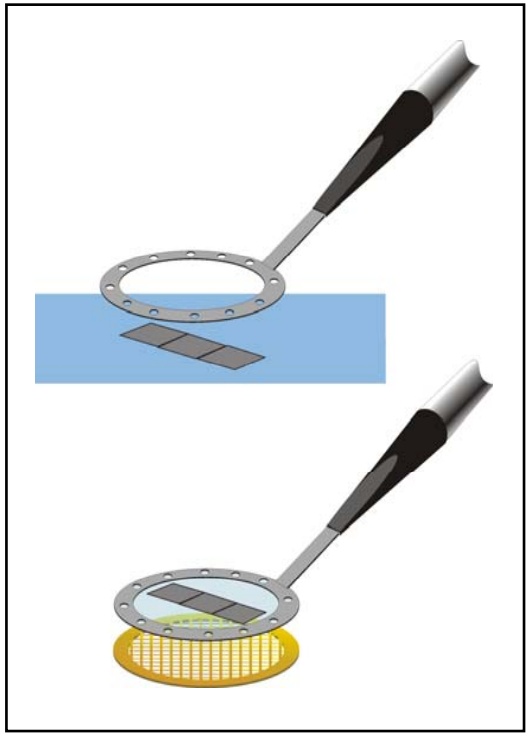
A - specimen cut with controlled speed
B - retraction
C - advance of specimen arm determines the specimen thickness



Cutting


a)
thin section
sample
water
knife
b)
thin section
sample
water
knife
cutting
c)
thin section
sample
water
knife
retraction


sample
thin section
water
knife



Important Staining Agents for Polymers

Polymer	Staining agent
Polyolefins	ClSA / OsO_4
	RuO_4
	ClSA / Uranyl acetate
Polyamide	Formalin / OsO_4
	PTA / OsO_4
	RuO_4
Polyacrylate	Hydrazine / OsO_4
	ClSA / OsO_4
	RuO_4
Polystyrol, Styrol copolymere	RuO_4
	OsO_4
Polyuretane	ClSA / OsO_4
	RuO_4
Polyvinylchlorid	ClSA / OsO_4

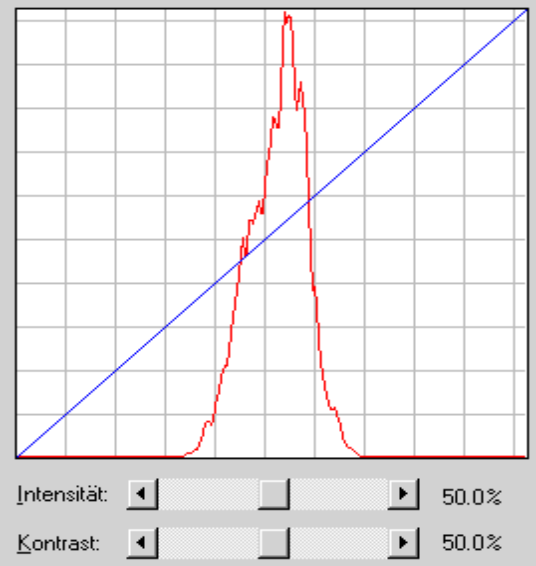
OsO_4 - Osmium tetroxide
Cl SA - Chlorosulfonic acid
RuO_4 - Ruthenium tetroxide
PTA - Phosphotungstic acid

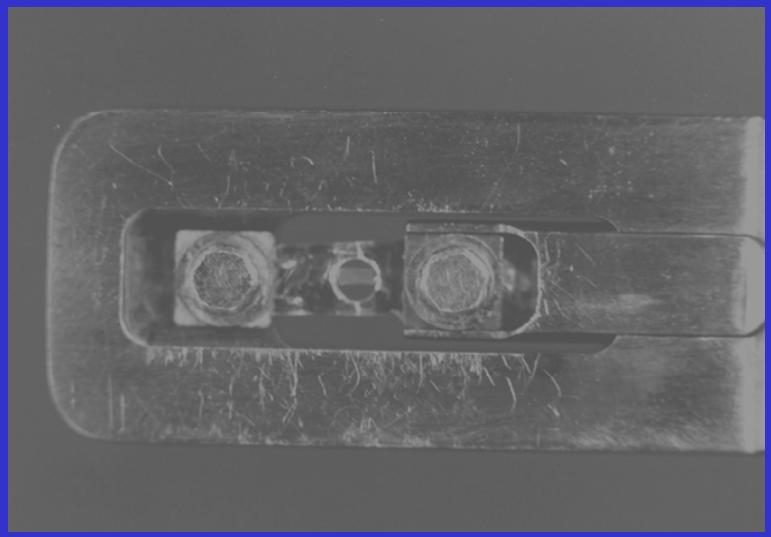
Image - Processing

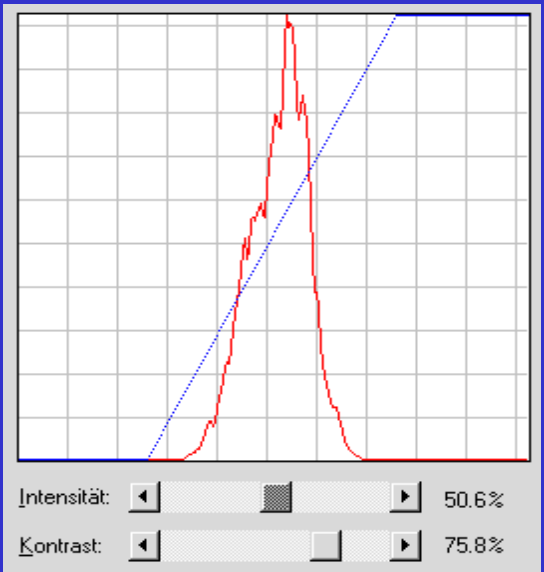
- Improvement of contrast
- Quantitative measuring of structural details

Image Processing - Optimization of gray value distribution

Lookup table







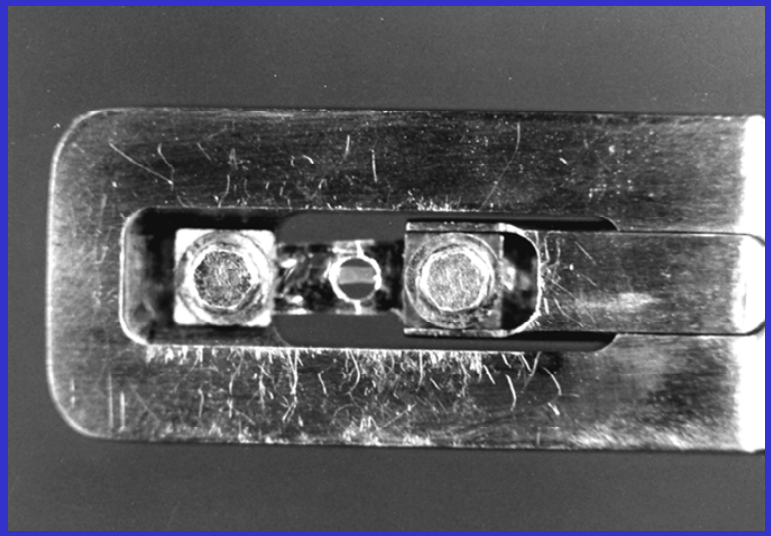
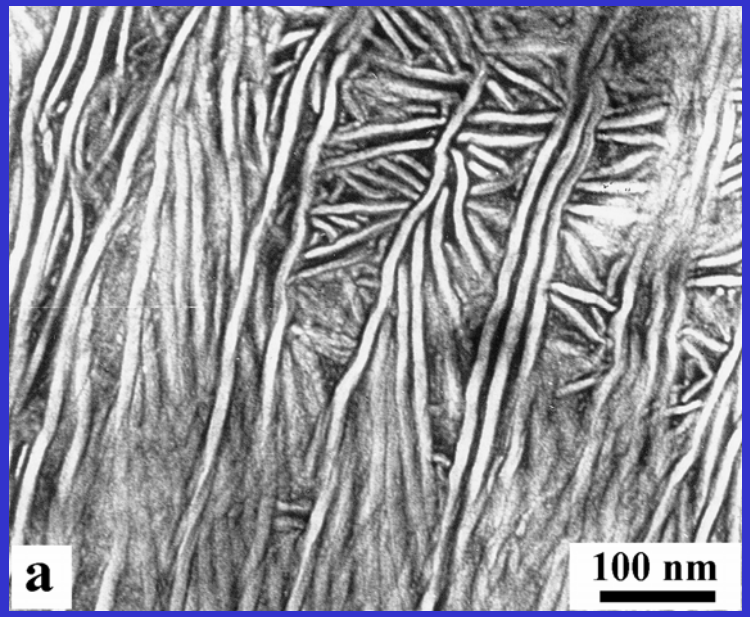
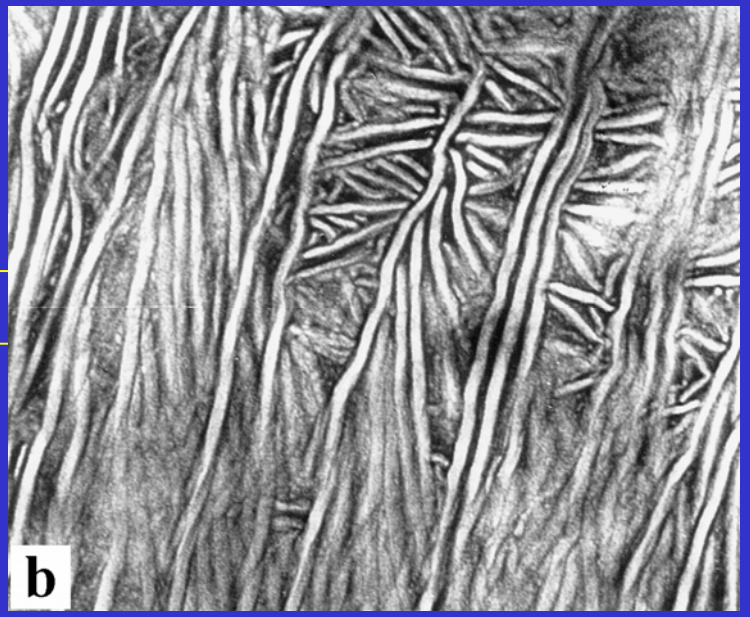


Image Processing - Filter Operation

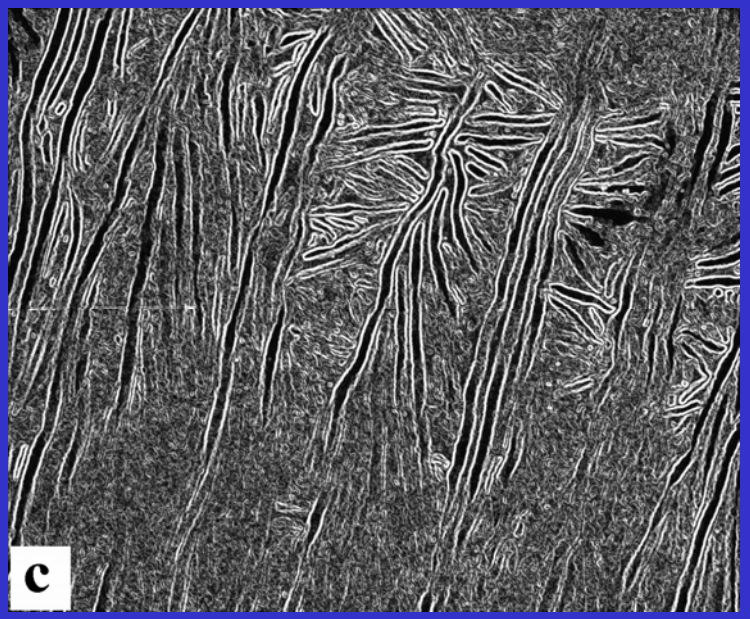
TEM micrograph of HDPE



→ Low pass



→ High pass



PE: Lamellae and laser-light diffraction pattern

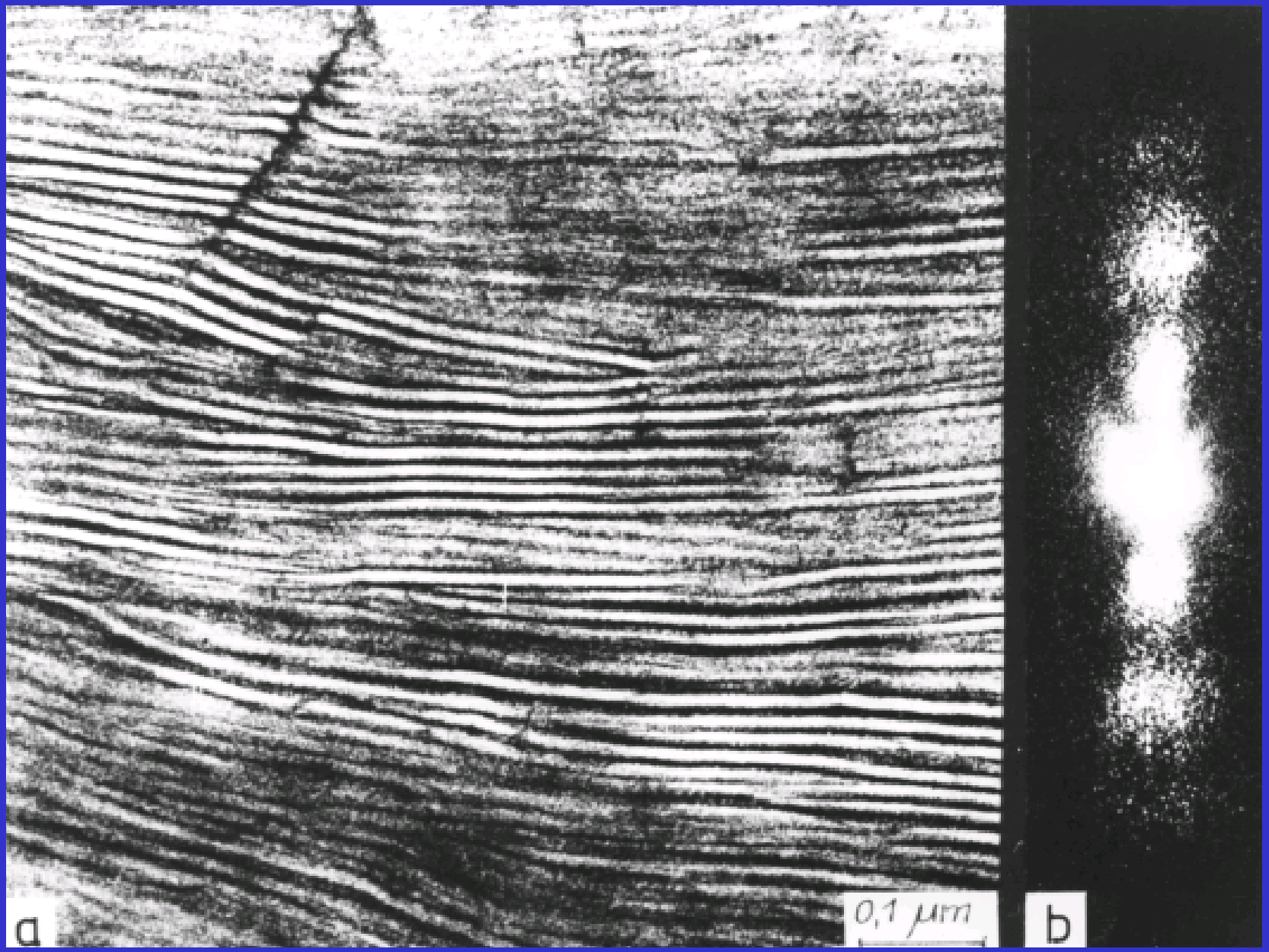
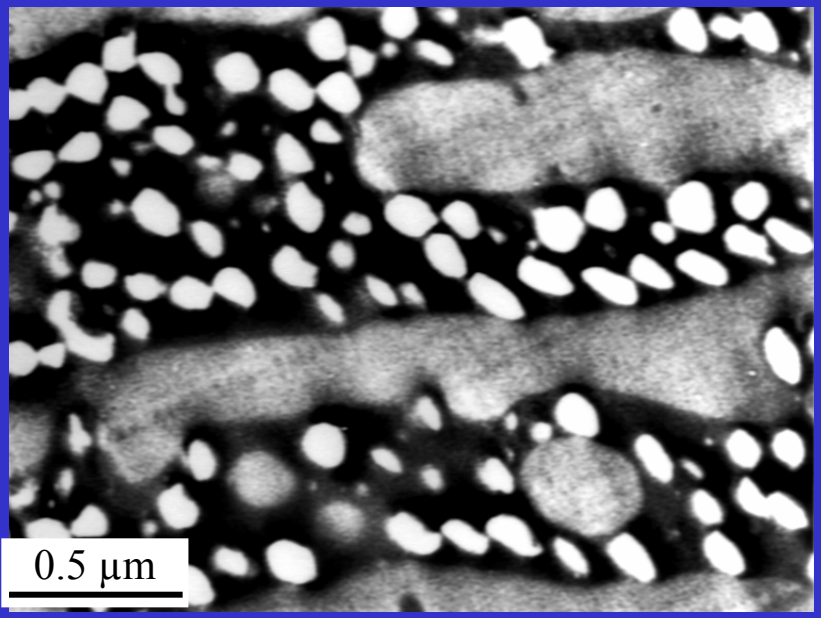
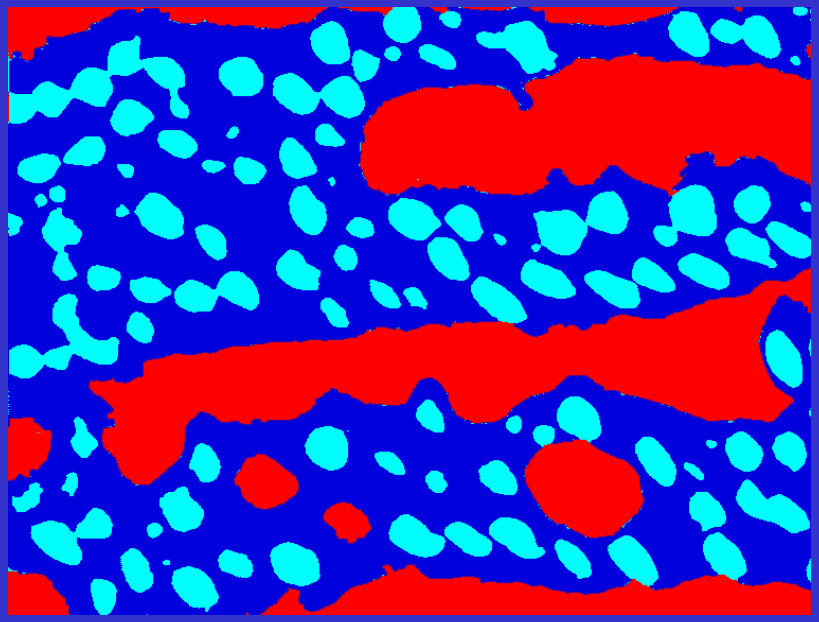
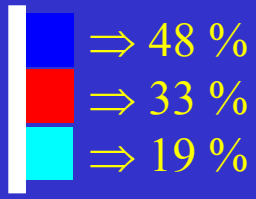


Image Processing - Phase Determination

TEM image of an ultra thin section







III. Micromechanical Testing of Polymer Properties

Micromechanical Mechanisms

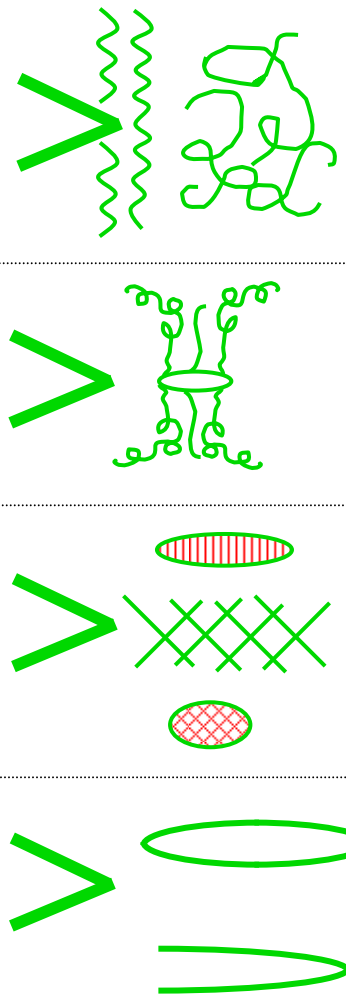
mechanical loading

Polymer

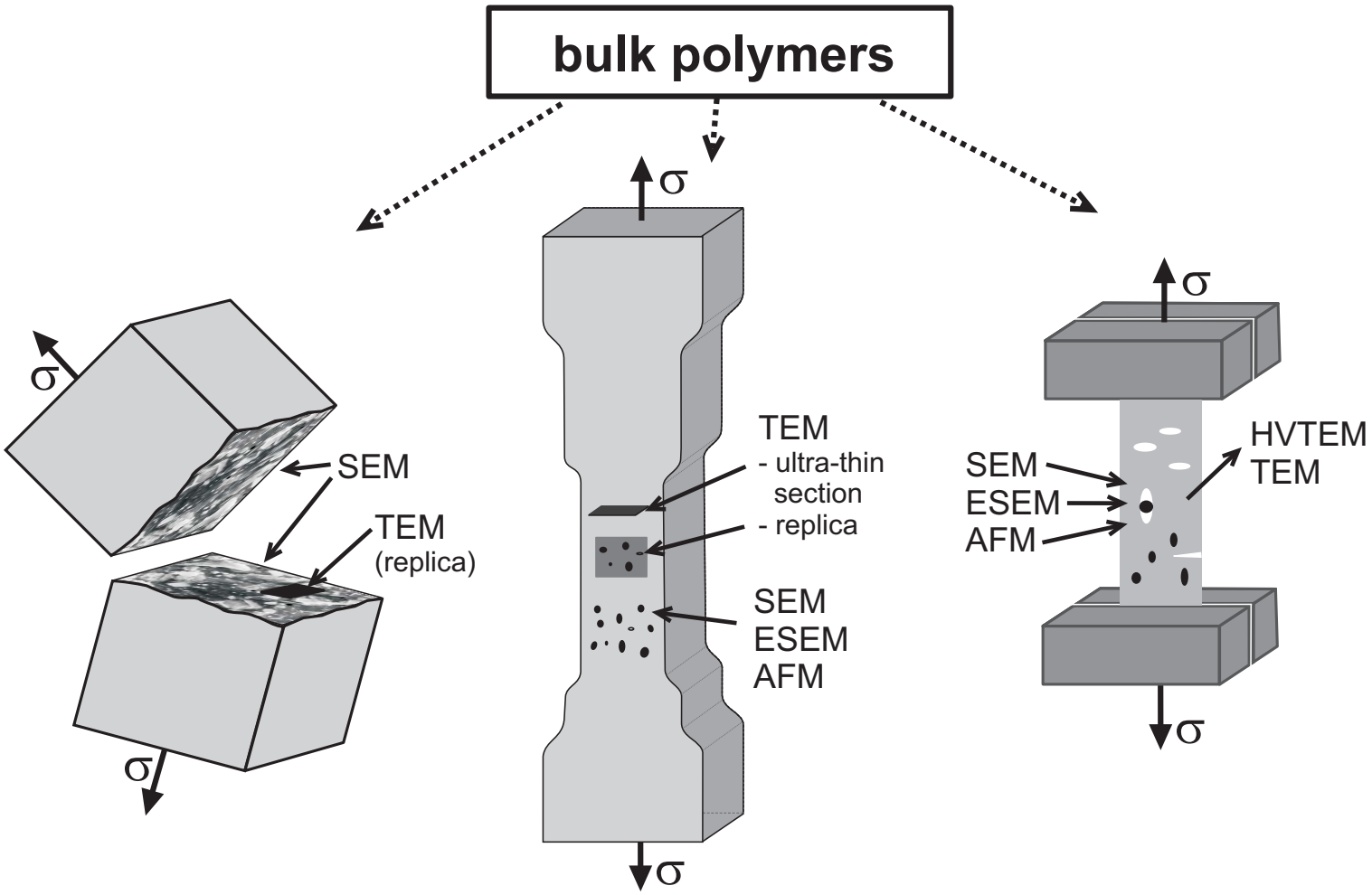
molecular structure

morphology

scale	*processes*
nm	stretching of chain segments, reptation movements, chain scission
	microvoid formation
µm	microyielding crazing shear band formation micro flow
mm	crack initation & propagation fracture



Investigation of micromechanical processes using EM



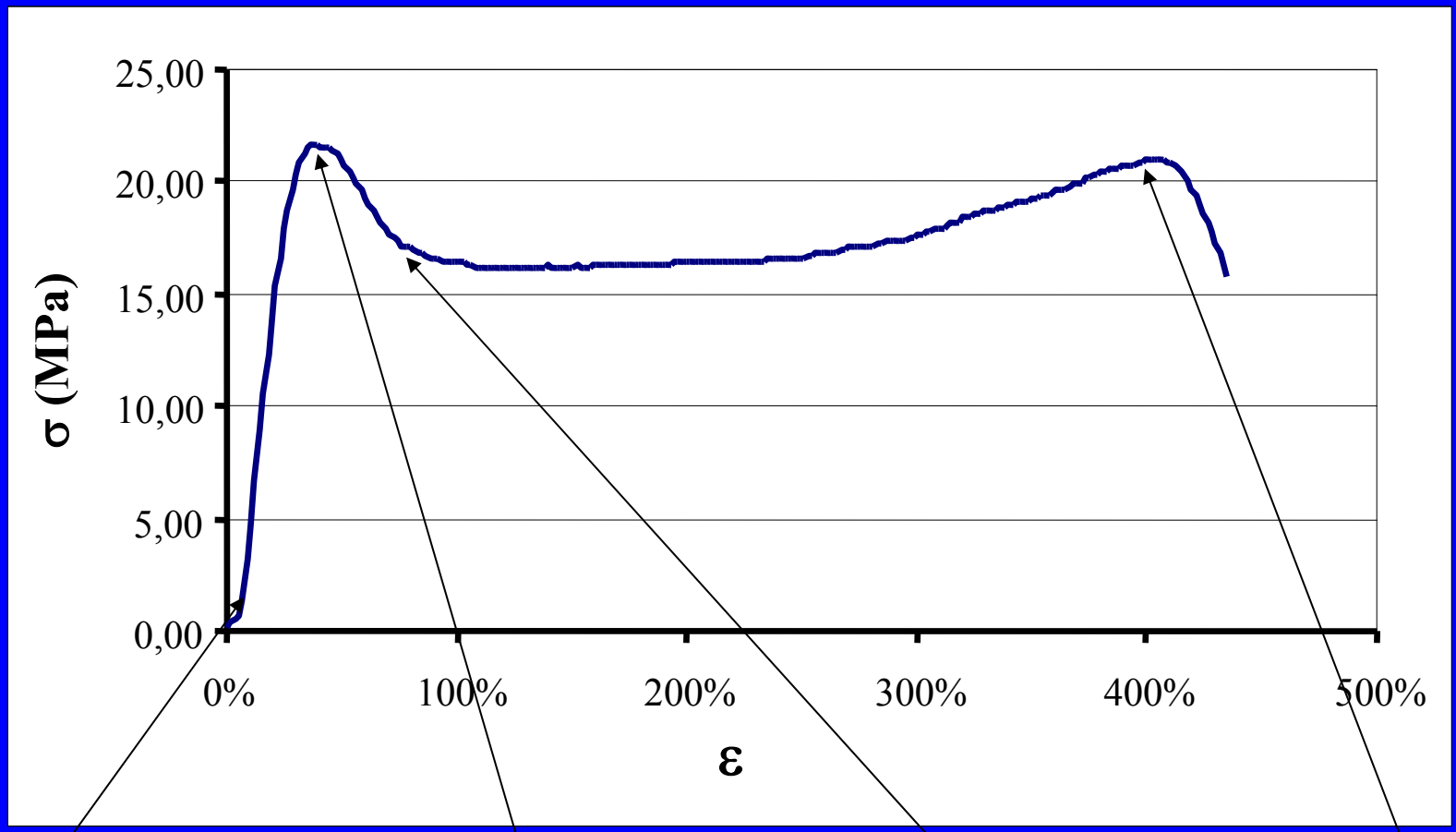
1. fracture surfaces
- tension test
- impact test
- broken pieces

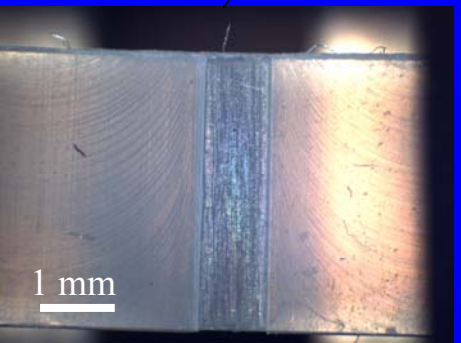
2. surfaces of deformed (loaded) bulk samples

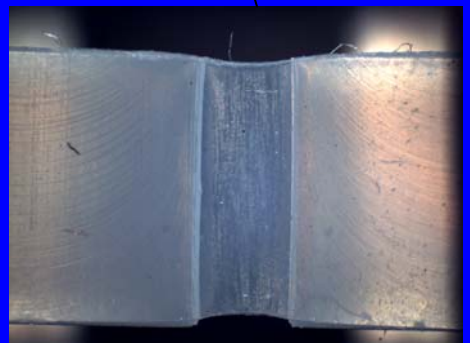
3. in situ deformation of thin samples

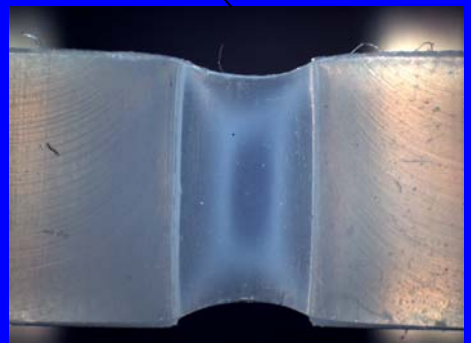
Tensile Test under Optical Microscope

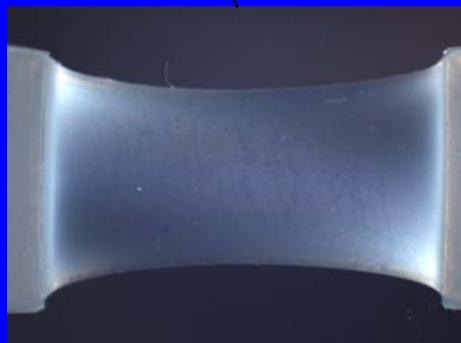
Tensile Test of HDPE using Miniaturised Specimens under Optical Microscope



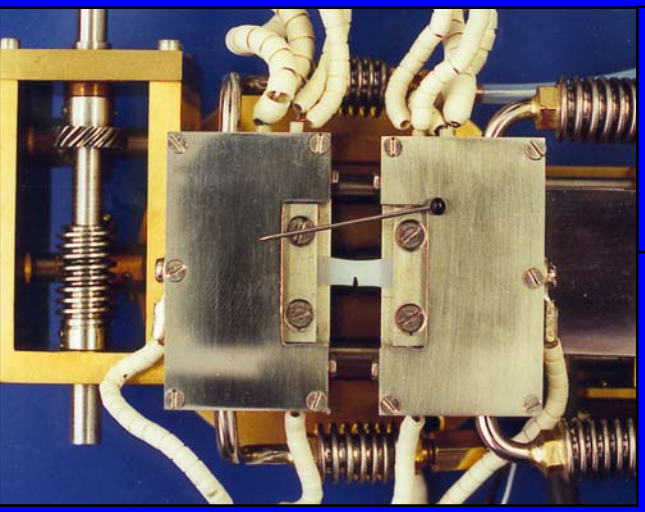




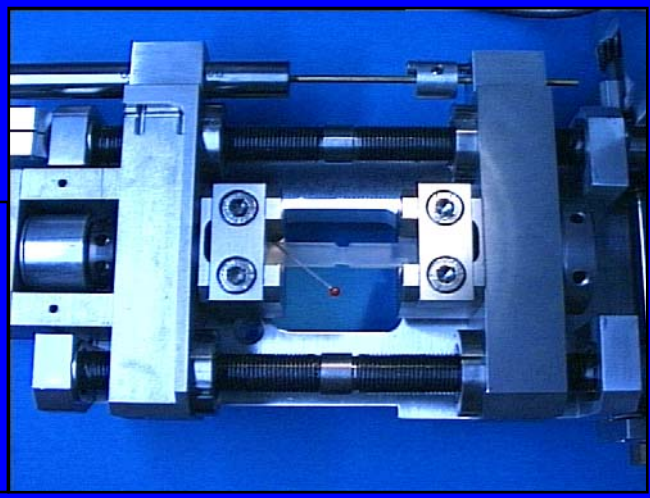




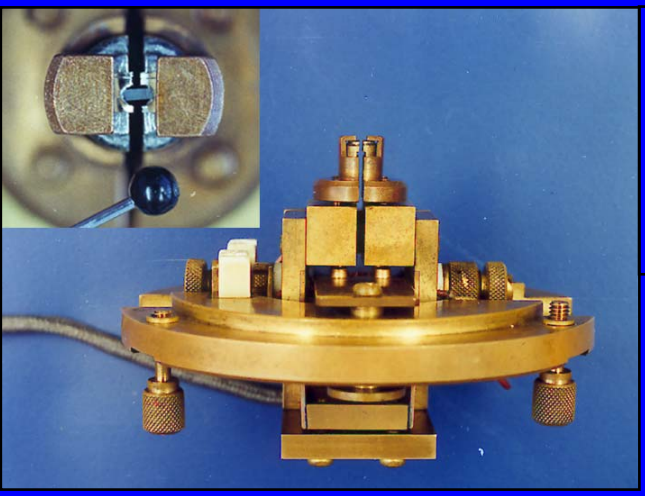
Tensile stages for micromechanical in situ investigations



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



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



High Voltage Electron Microscope

Tensile Stage (Jeol)

Temperature: Room Temperature

Thickness: 100 nm ... 5 µm

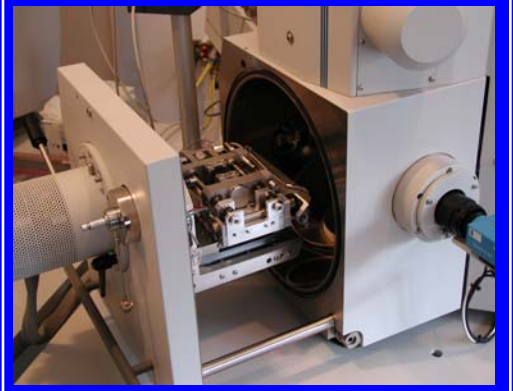
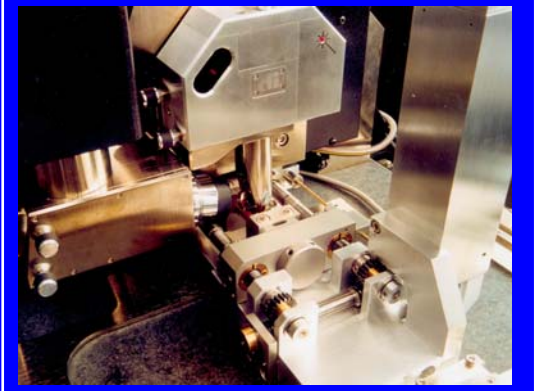
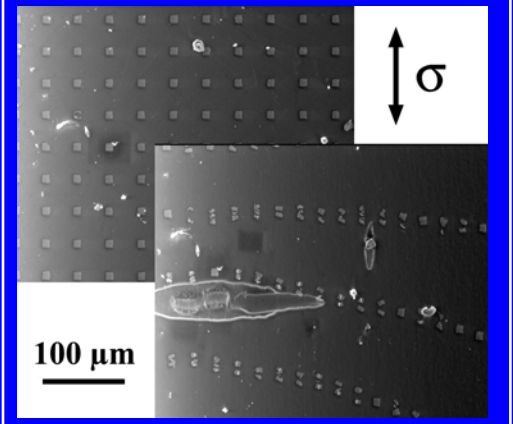
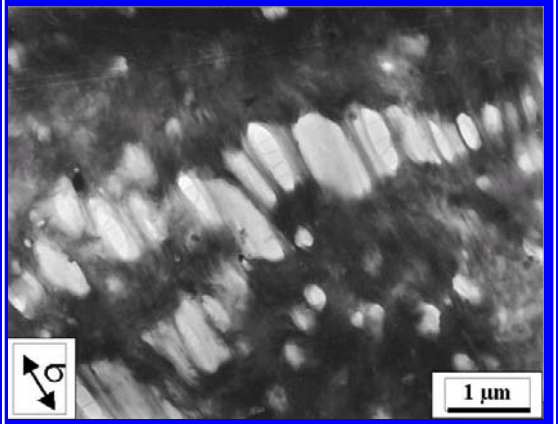
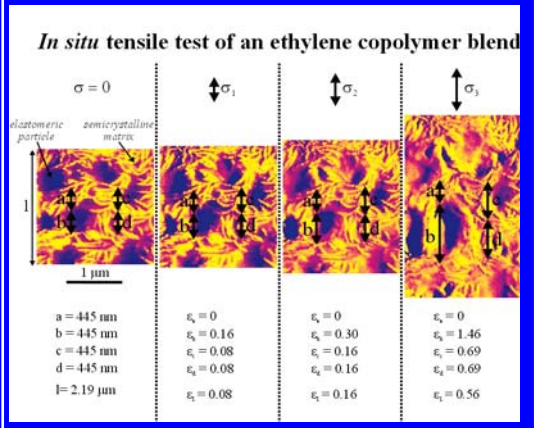
Transmission Electron Microscope

Straining Holder Model 671 (Gatan)

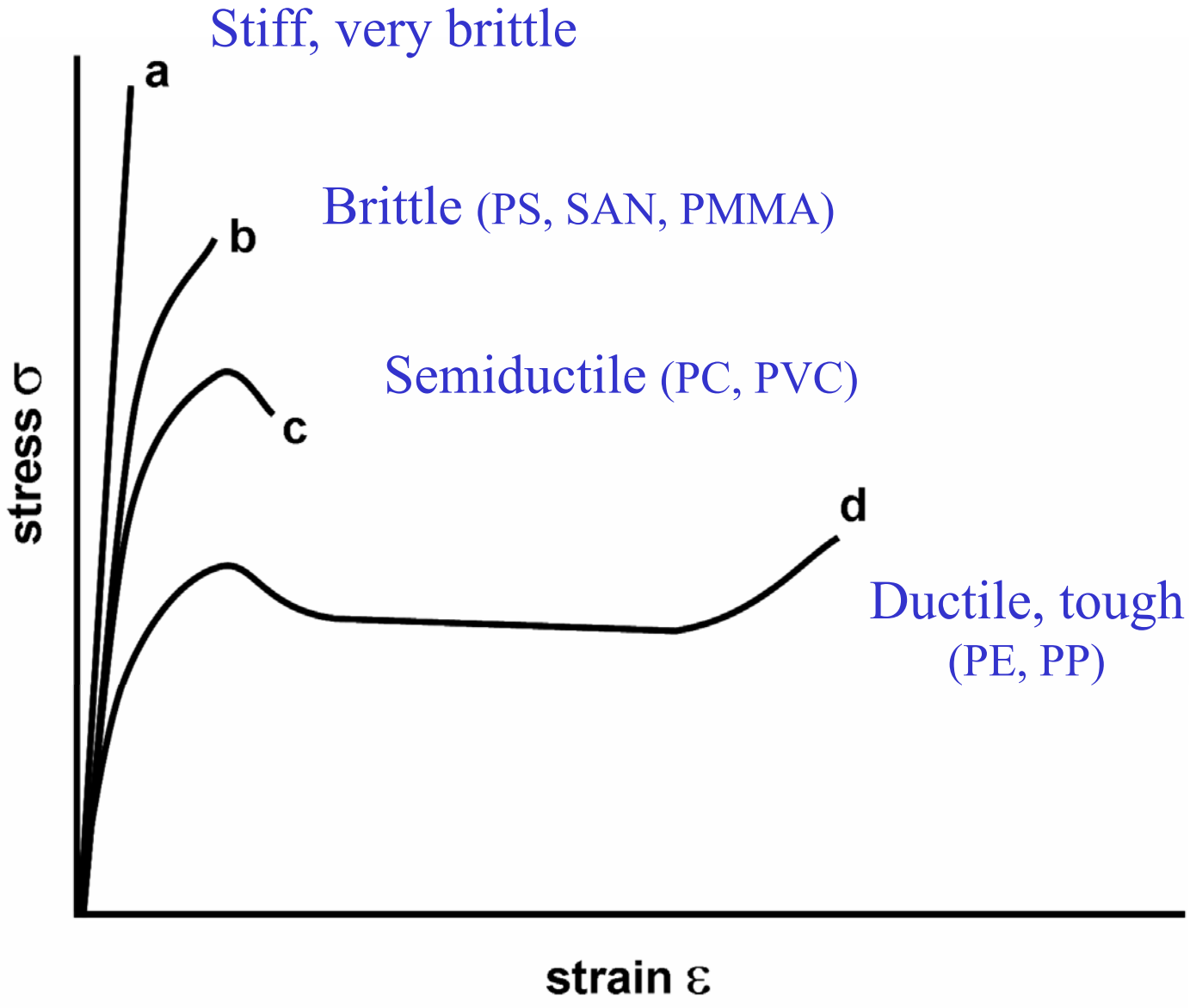
Temperature: -180 °C ... 120 °C

Thickness: 100 nm ... 0.5 µm

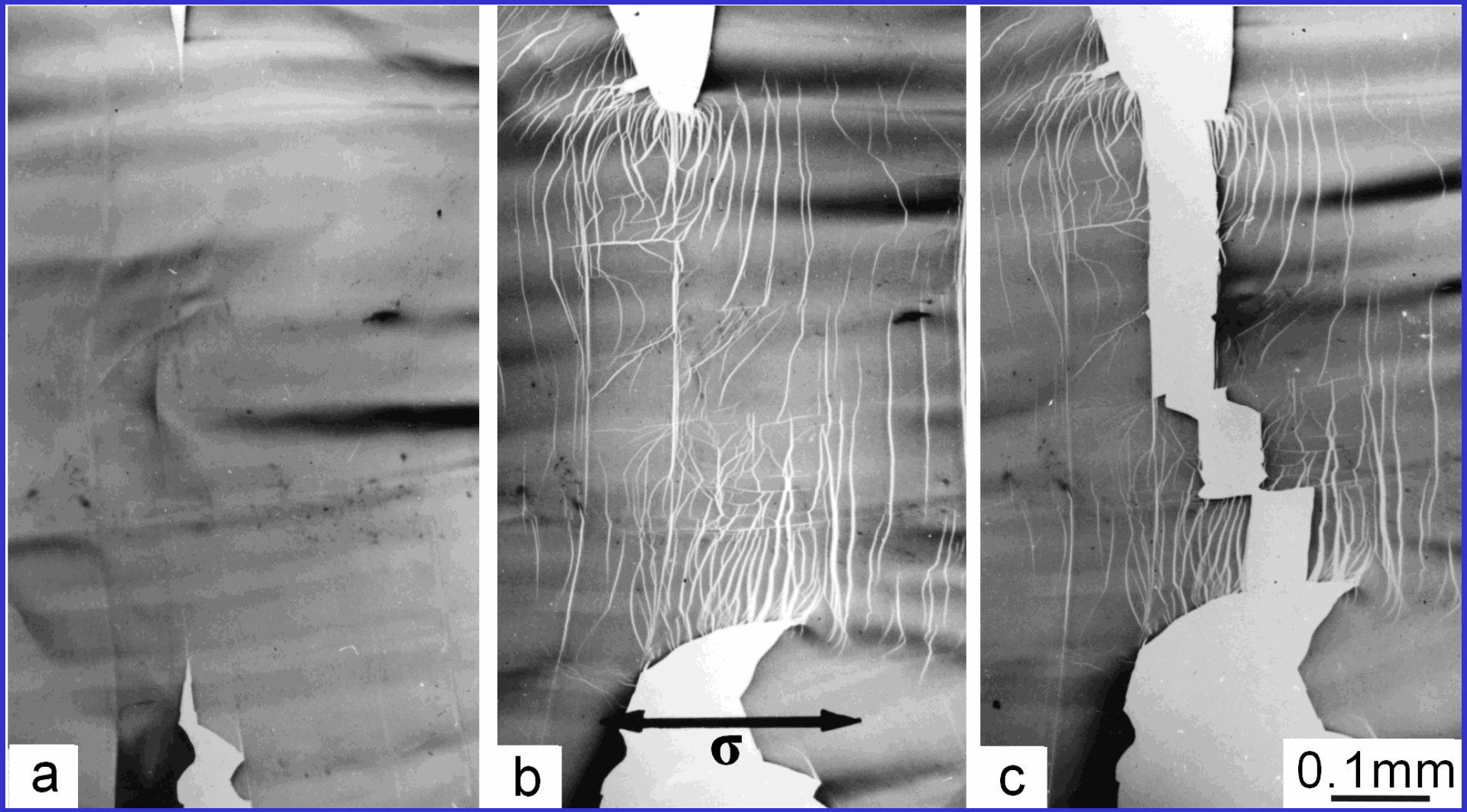
Micromechanical *in situ* Investigations
Different Microscopic Techniques (Semicrystalline Polymers)

Method	SEM	TEM	AFM
Require-ments	no evaporation, no etching	no staining	very flat surfaces
Techniques			
Typical Results HDPE/ Copolymer Blends			

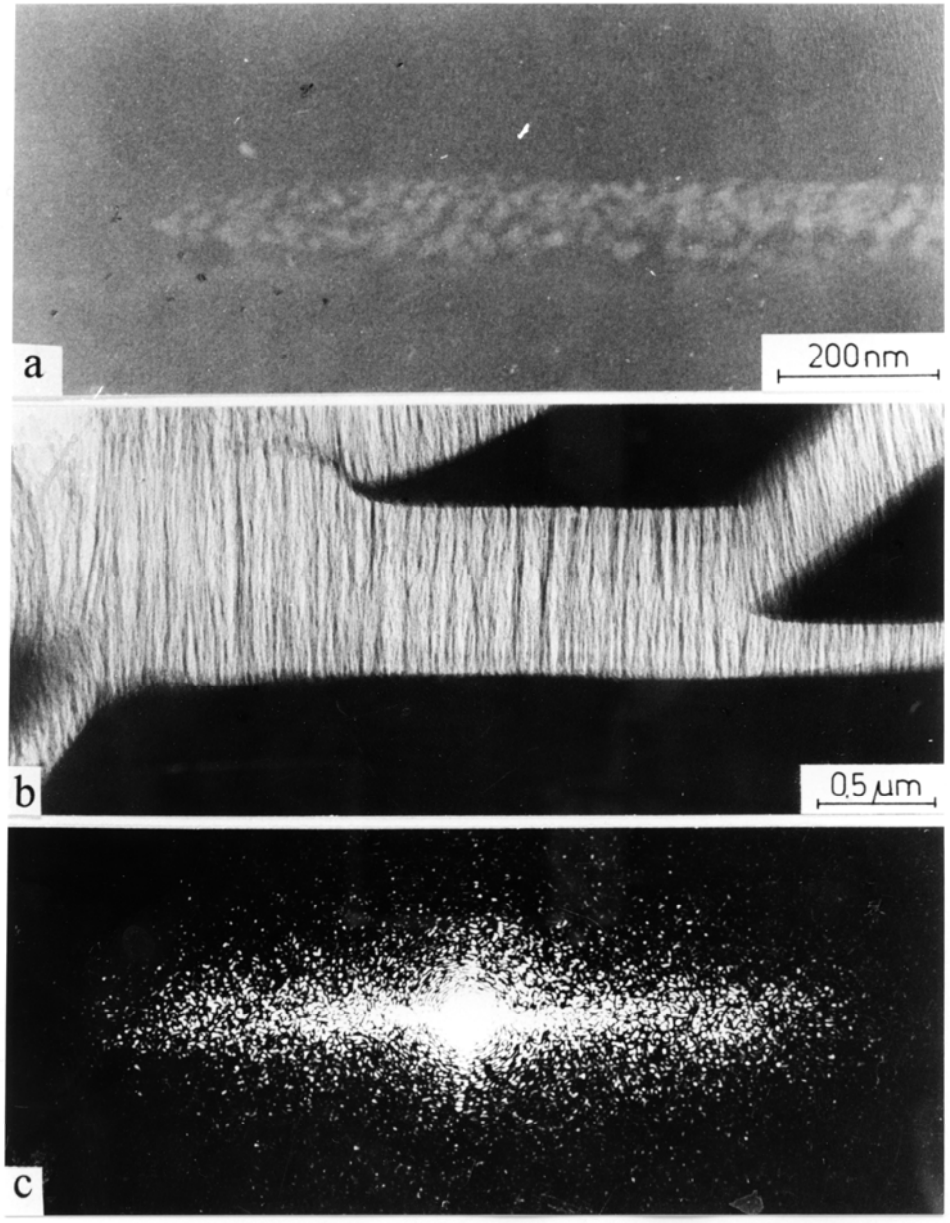
Examples


Stiff, very brittle
a
Brittle (PS, SAN, PMMA)
b
Semiductile (PC, PVC)
c
d
Ductile, tough
(PE, PP)
stress σ
strain ε

In situ deformation of PS in HVTEM



Craze in PS

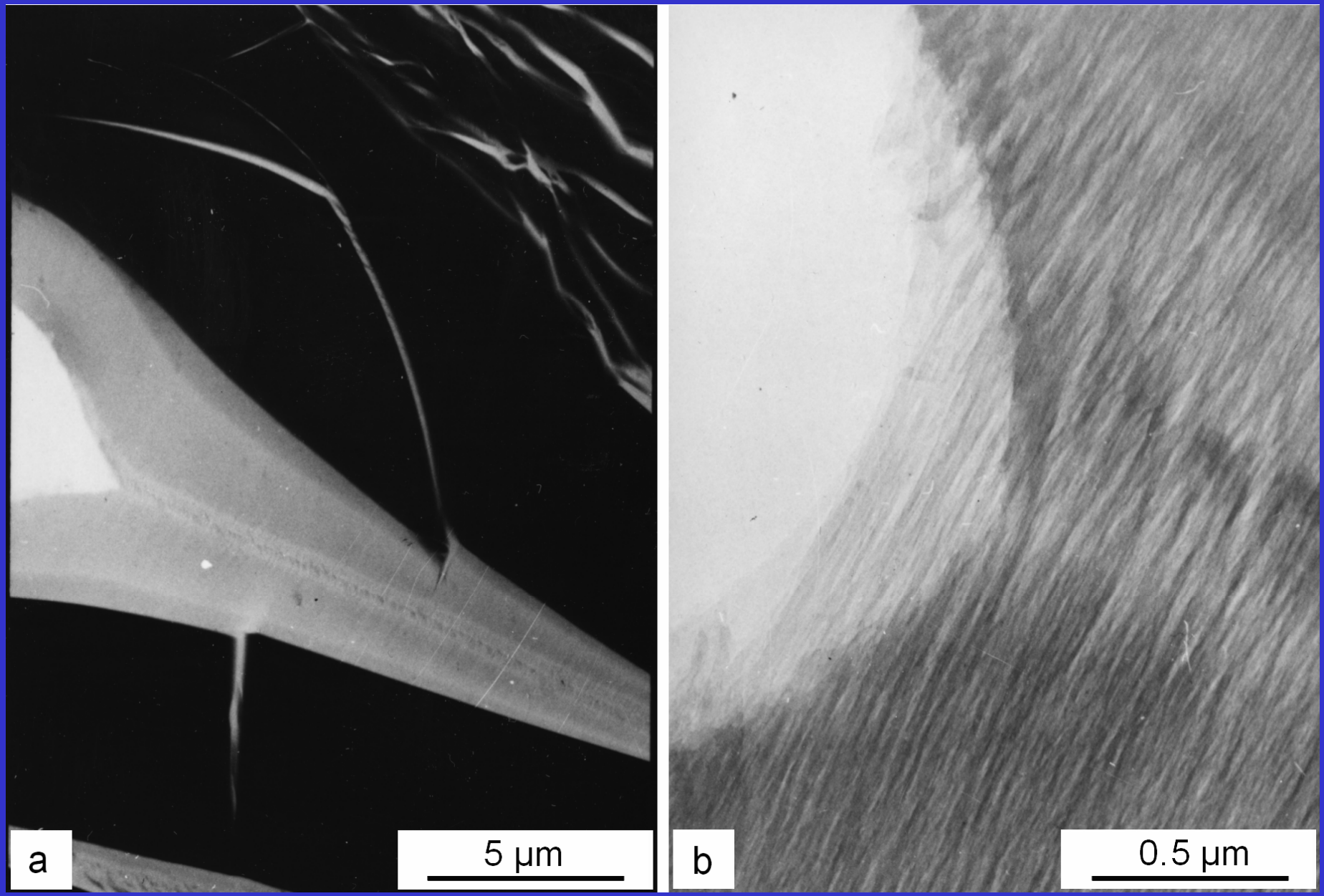


a) Pre-craze

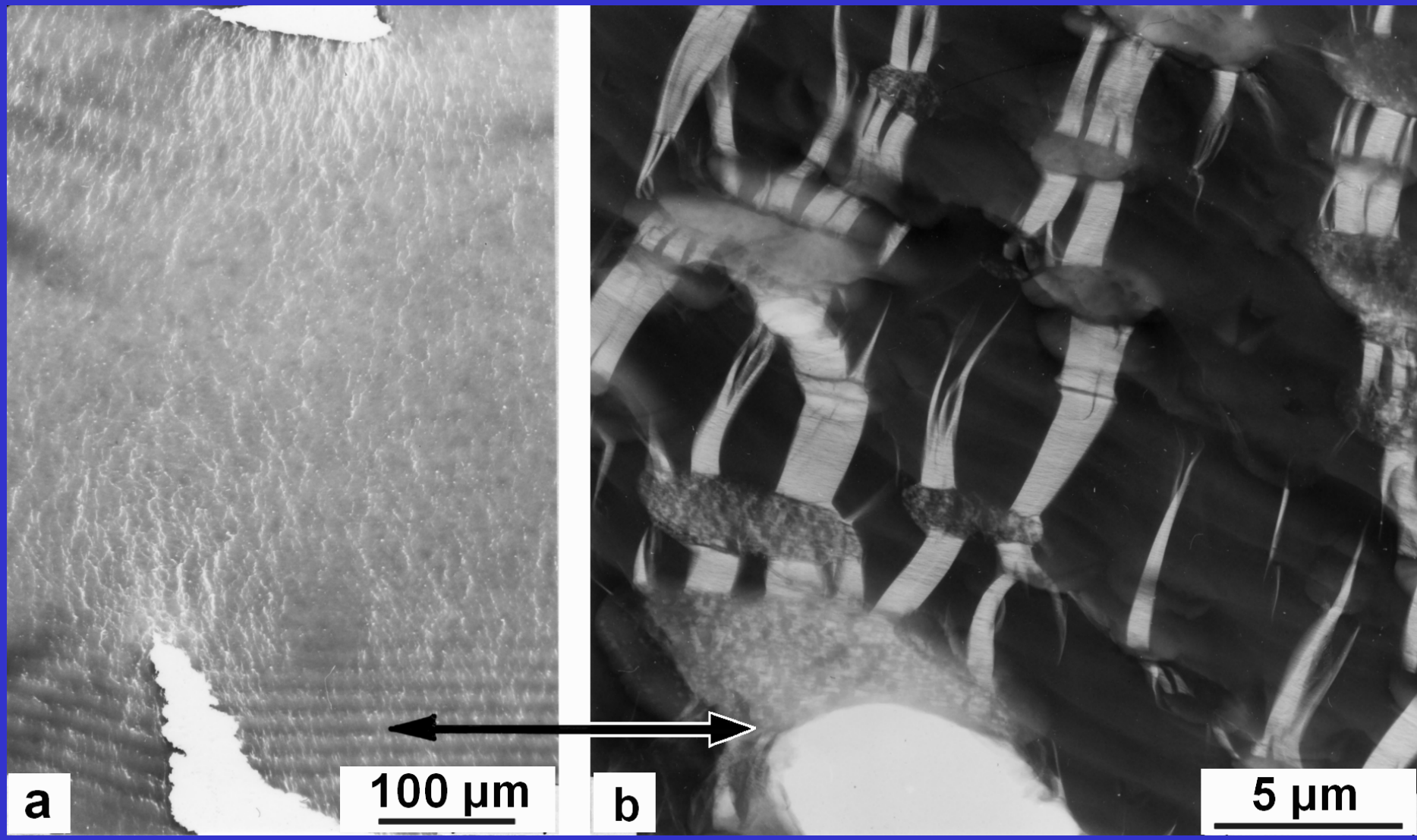
b) Fibrillated craze

c) Laser-light diffraction pattern

Craze rupture in PS (HVTEM)

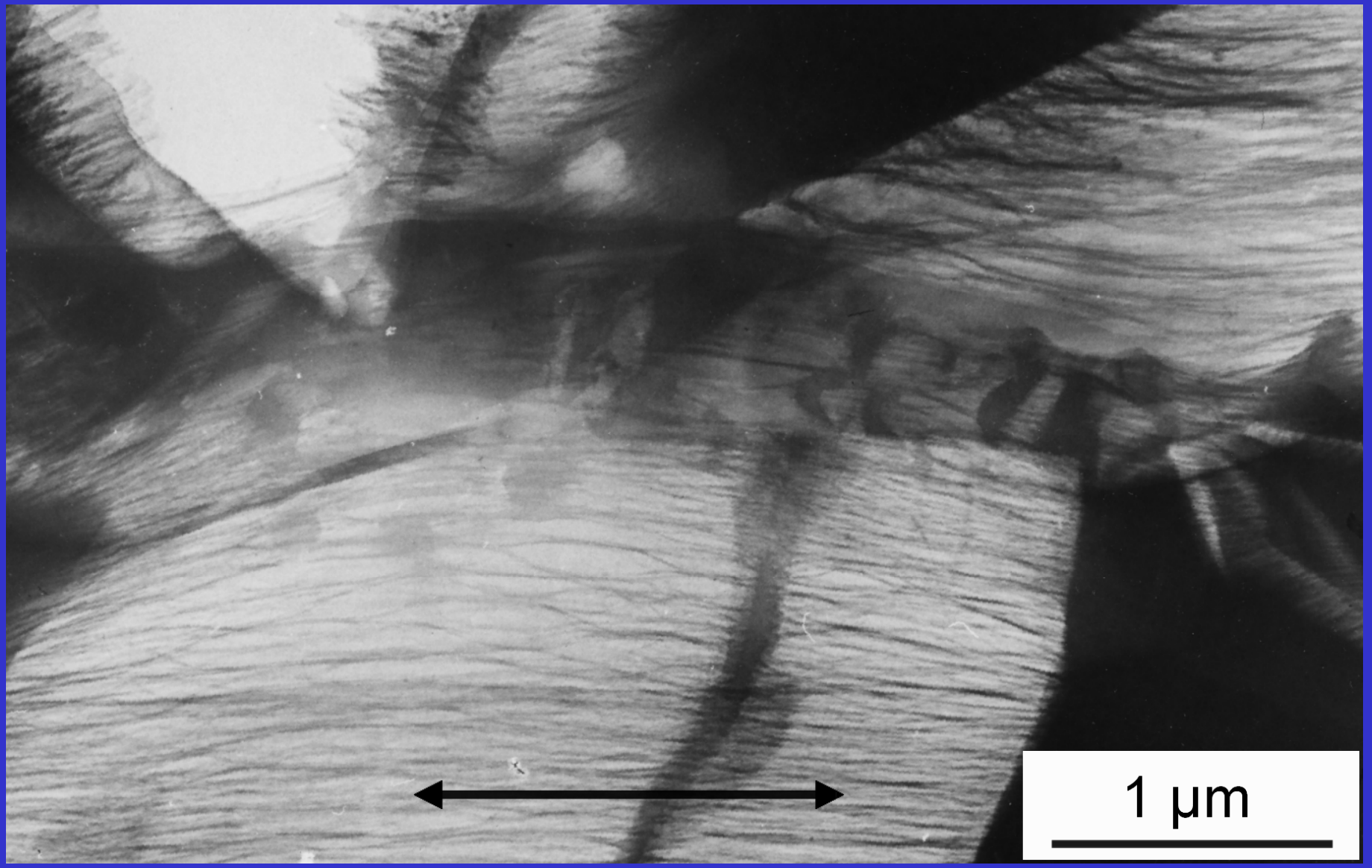


Rubber-toughened Polymer (HIPS)

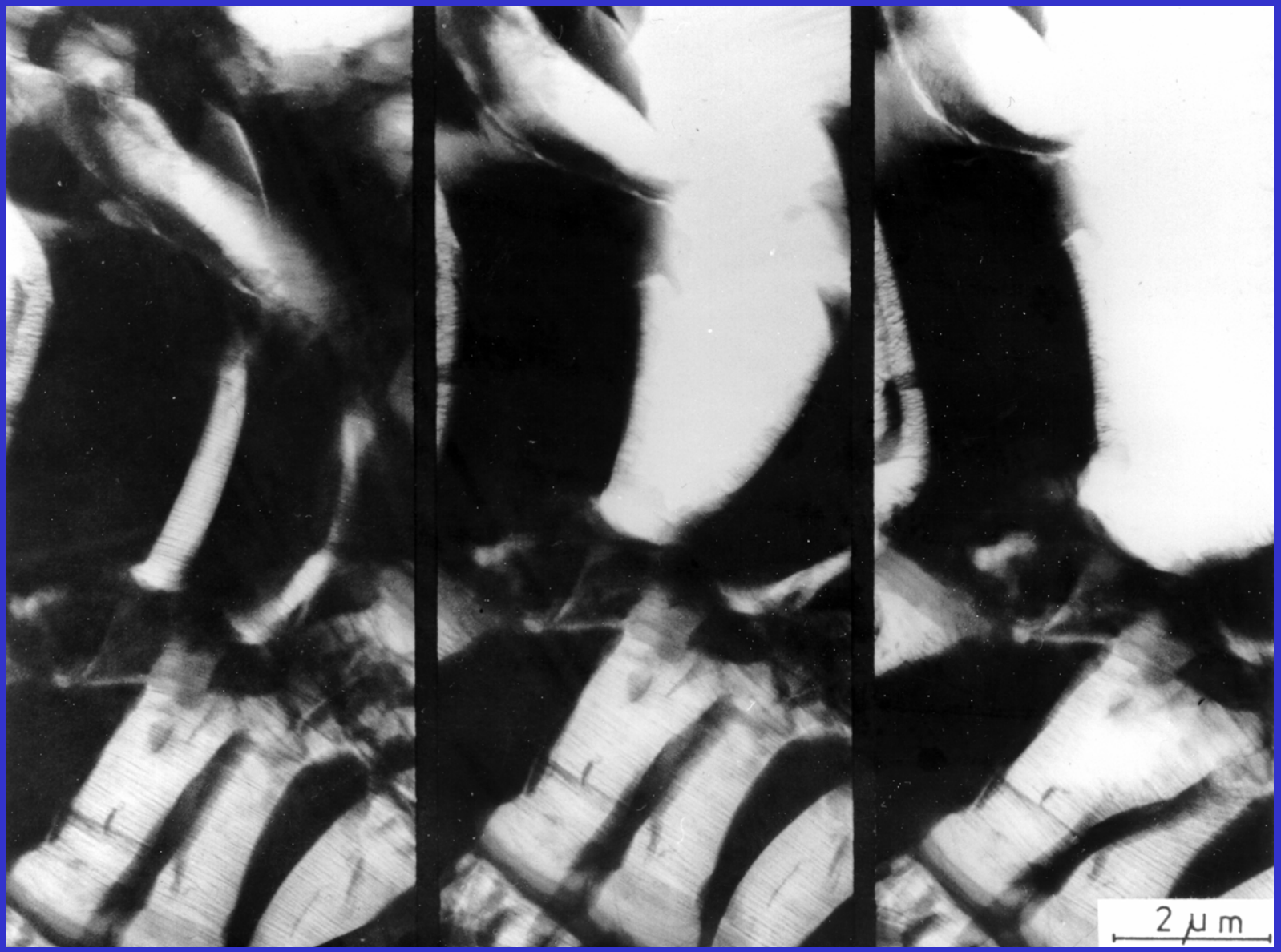


Rubber-toughened Polymer (HIPS)

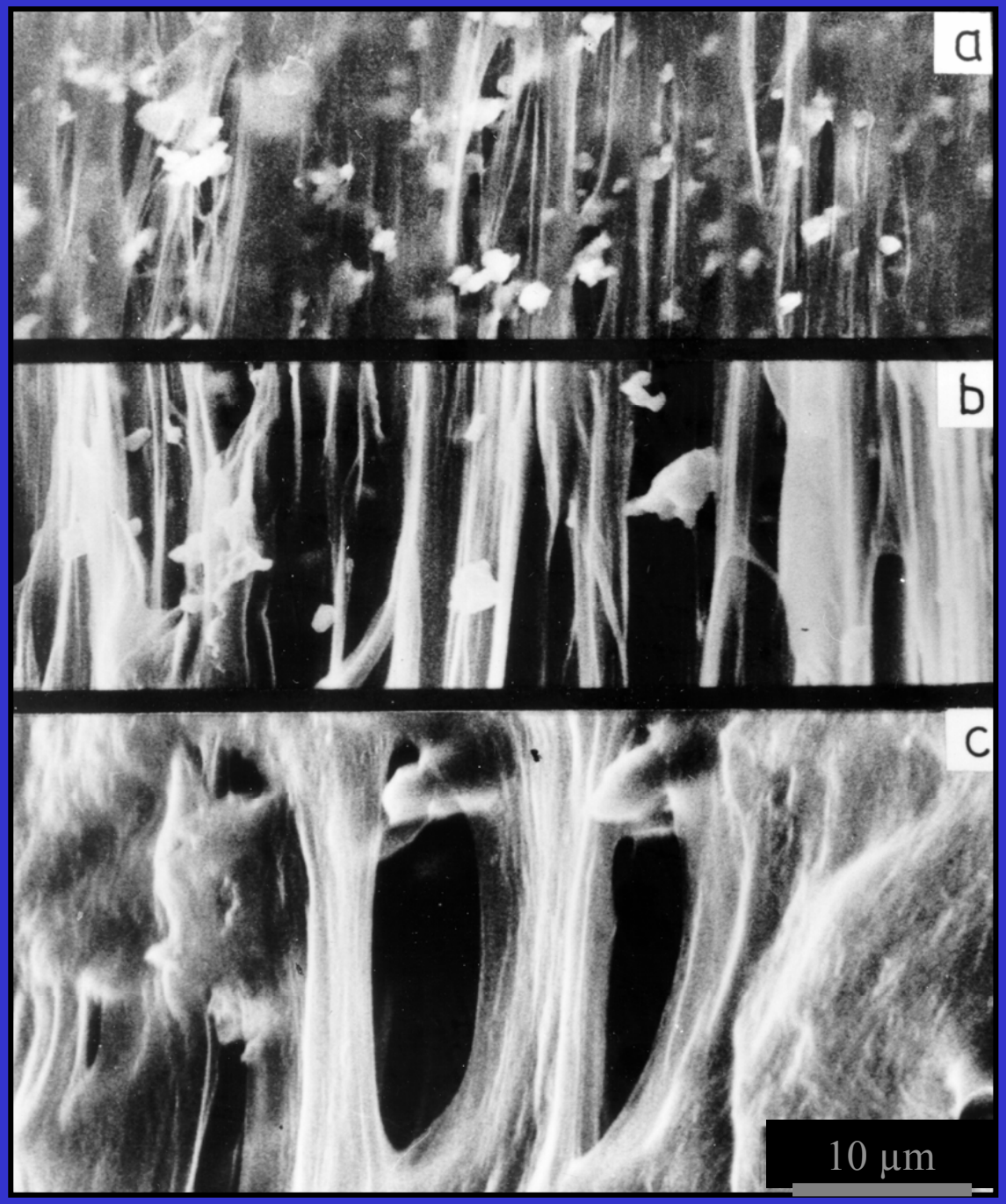
Rubber-toughened Polymer (HIPS)



Rubber-toughened Polymer (HIPS)



In-situ crack propagation in HIPS

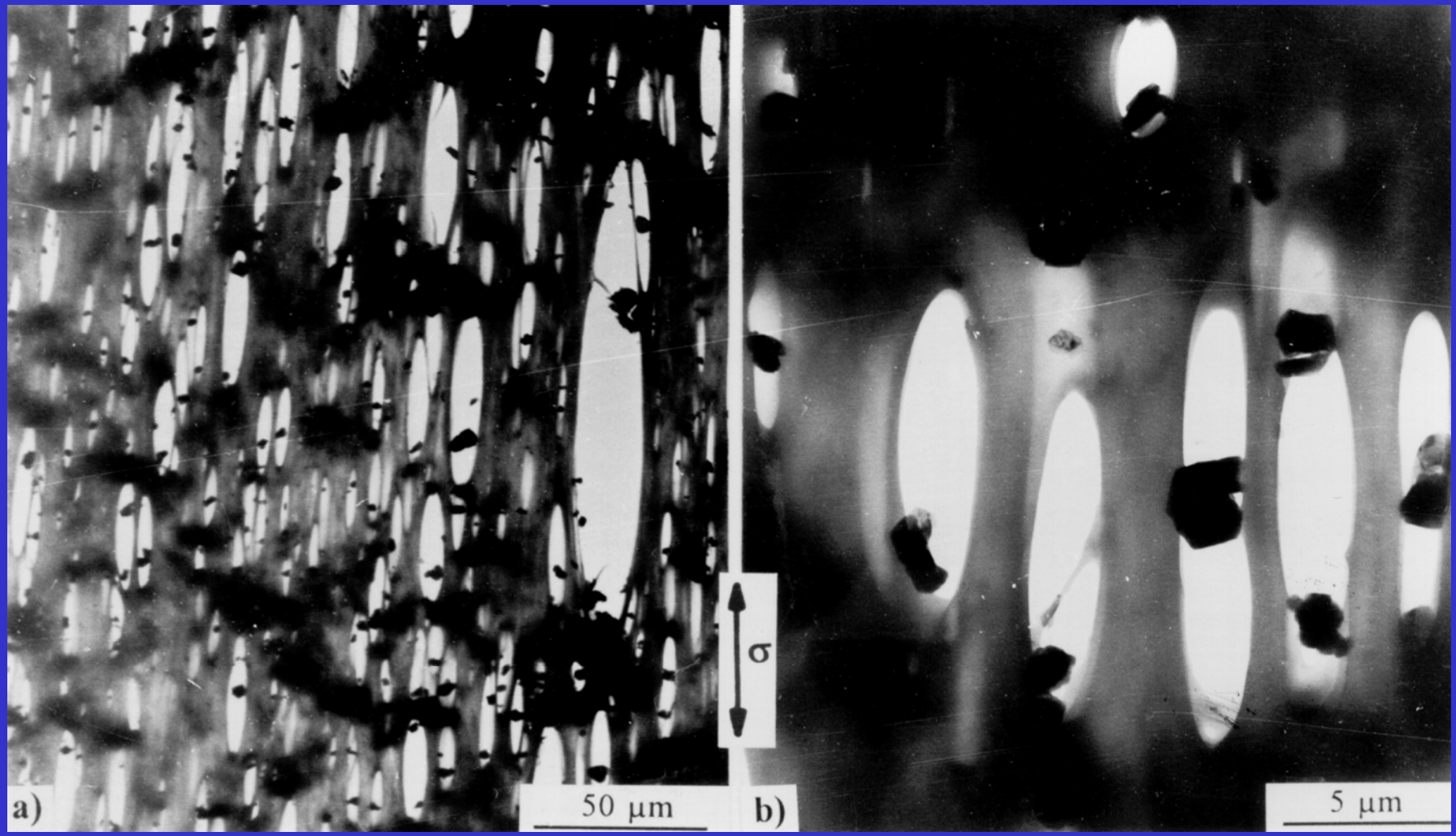


PE Composite

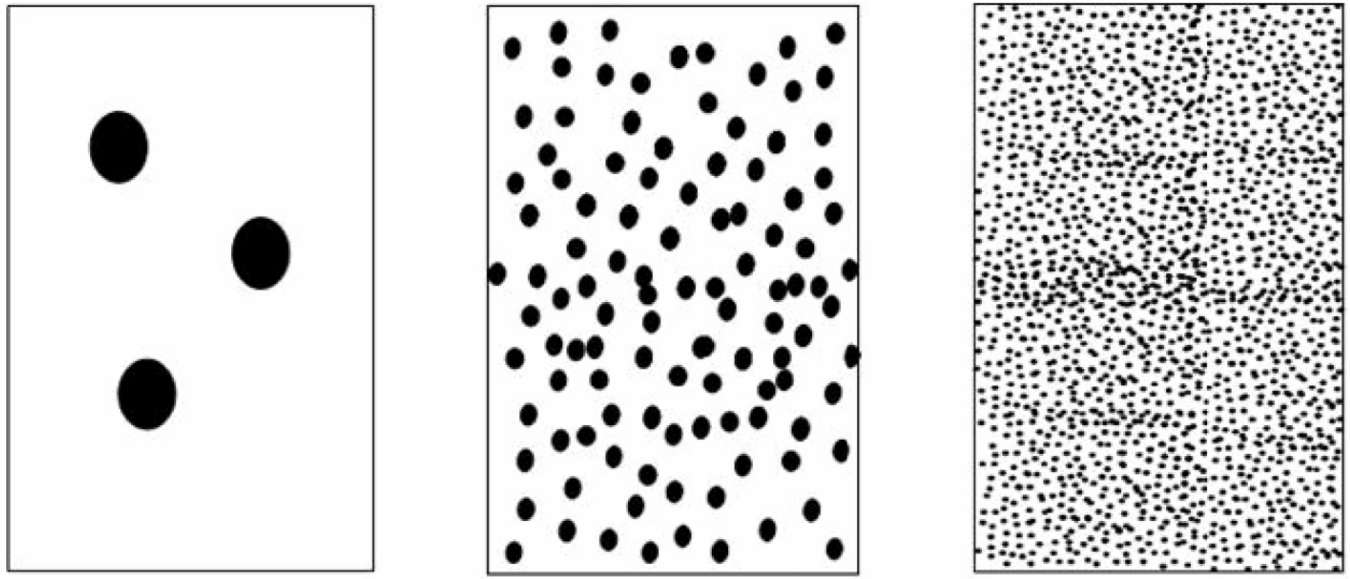
Dependence of void size and fibril thickness on particle diameter in filled HDPE:

a) 1 µm
b) 3 µm
c) 8 µm

Deformation structures of particle-filled PP (10 wt.% $Al(OH)_3$)

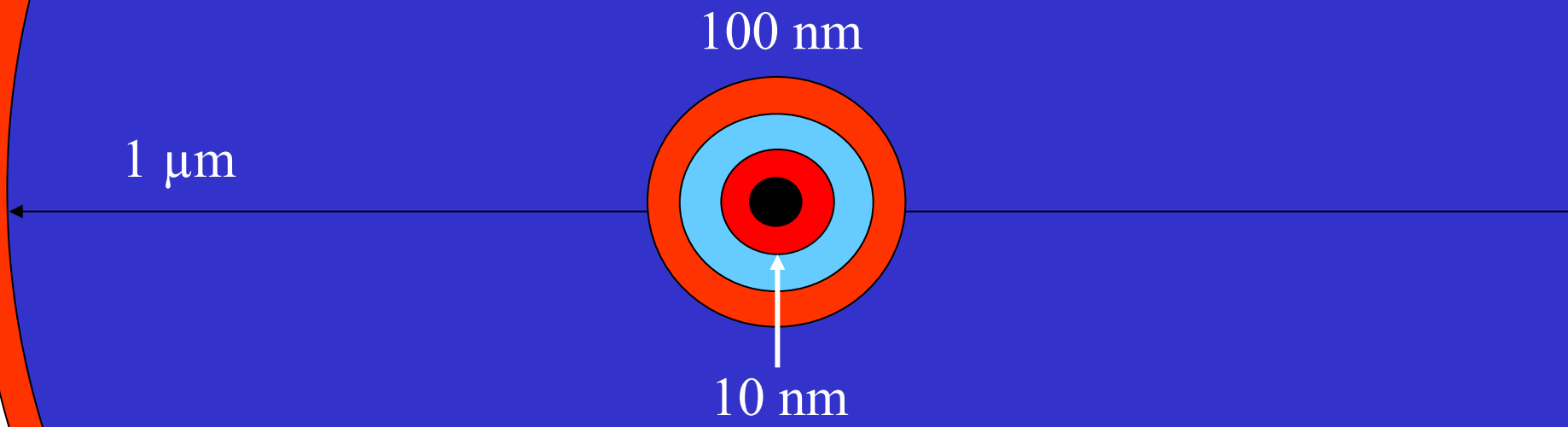


Micro- and Nanocomposites



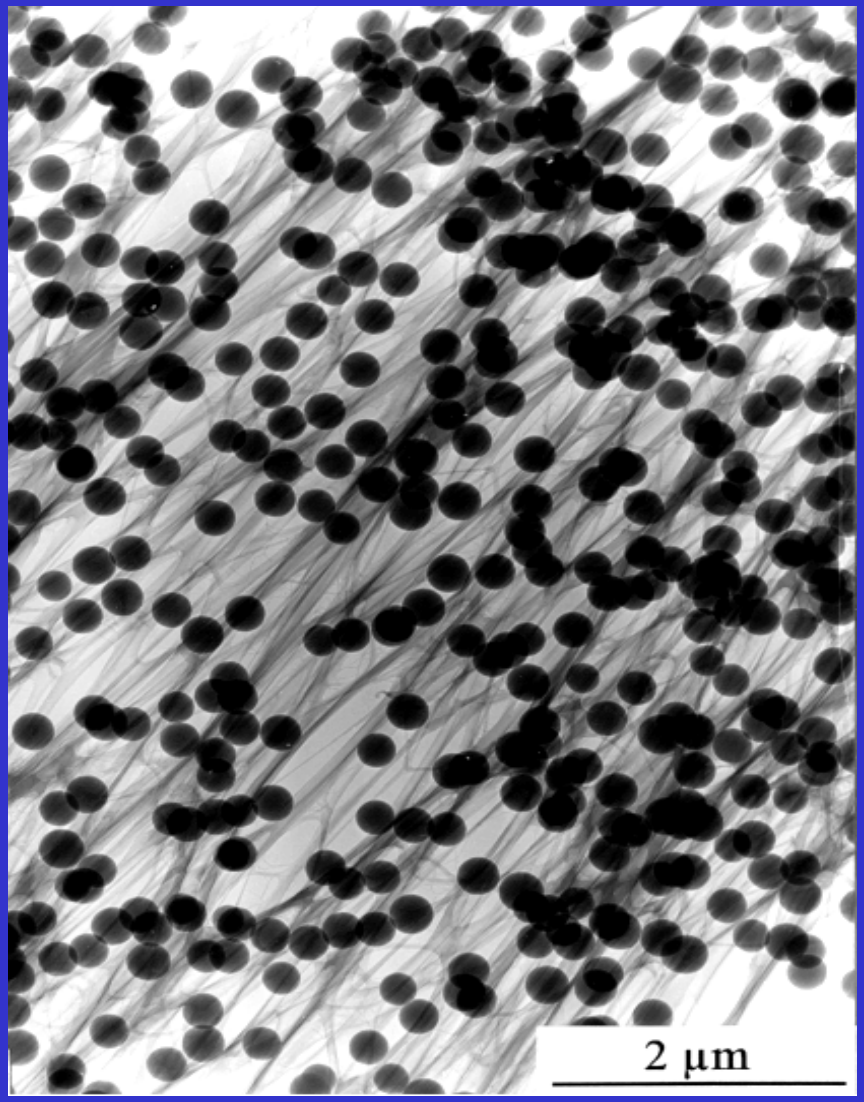
Effect of Nanoparticle

Influence of Interface

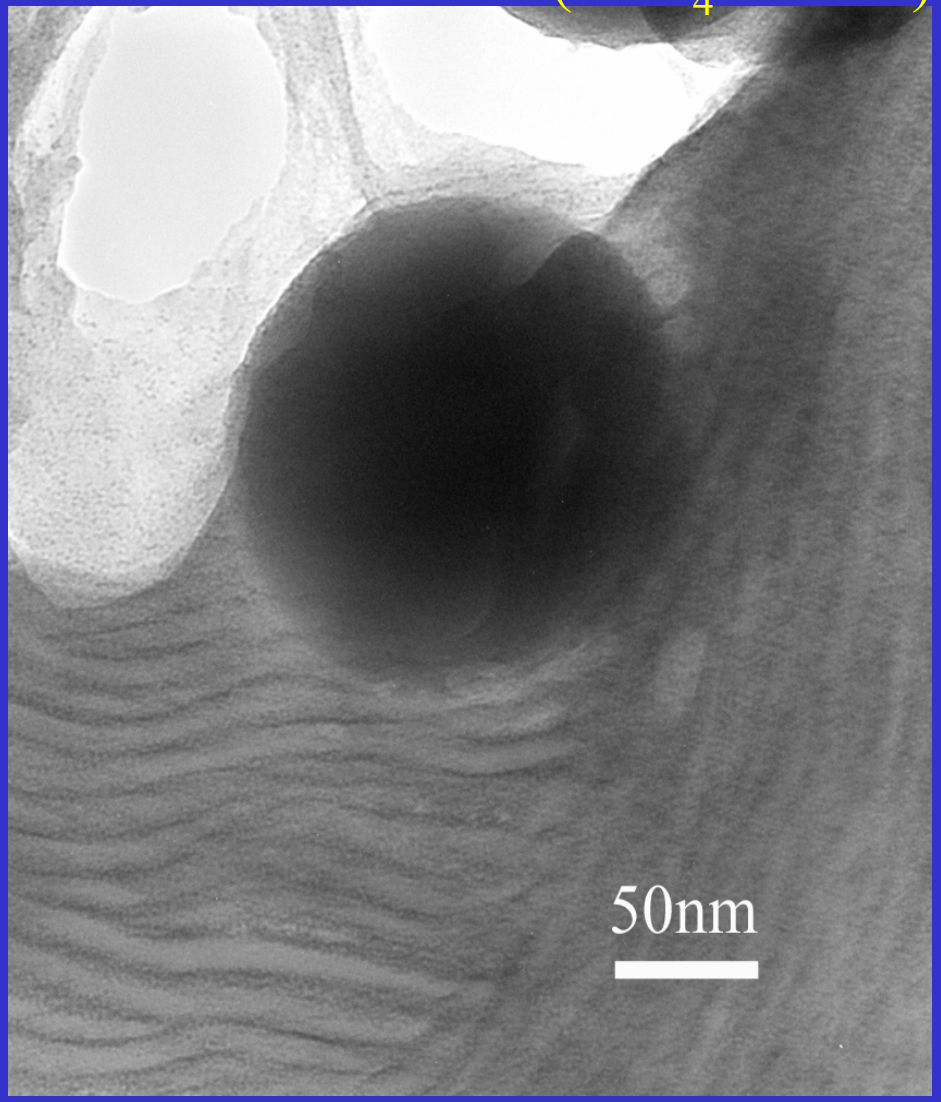


Deformation structures of particle-filled PE (10 wt.% SiO_2)

HVEM

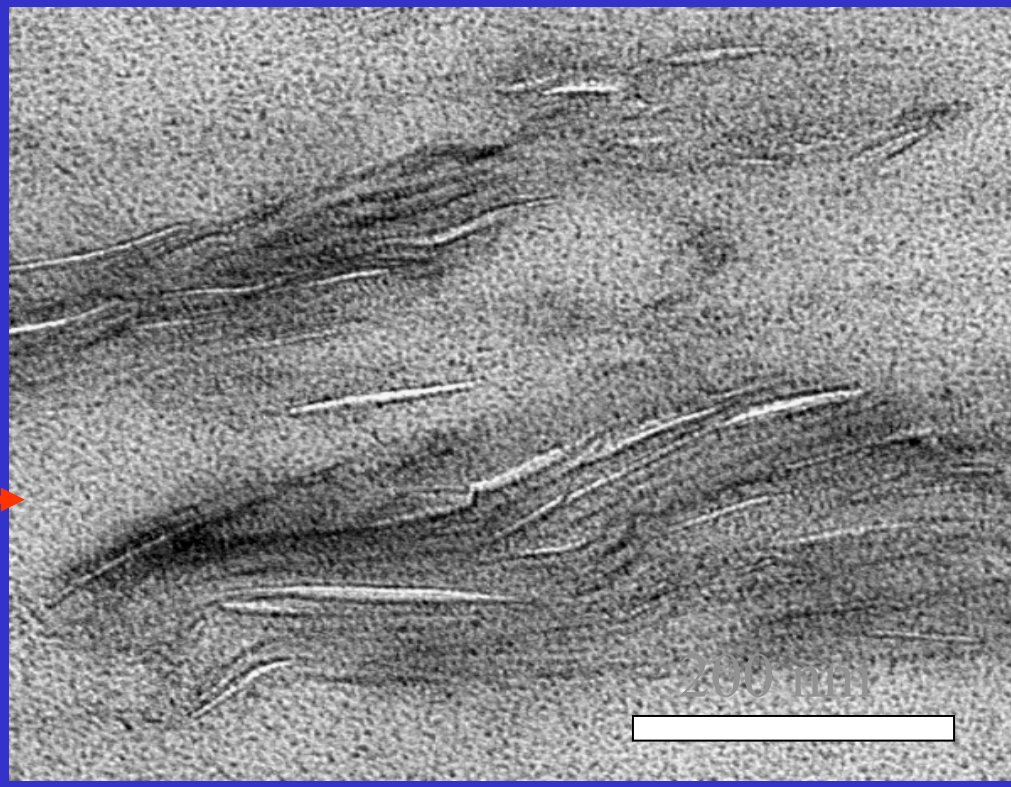


TEM (RuO_4 stained)

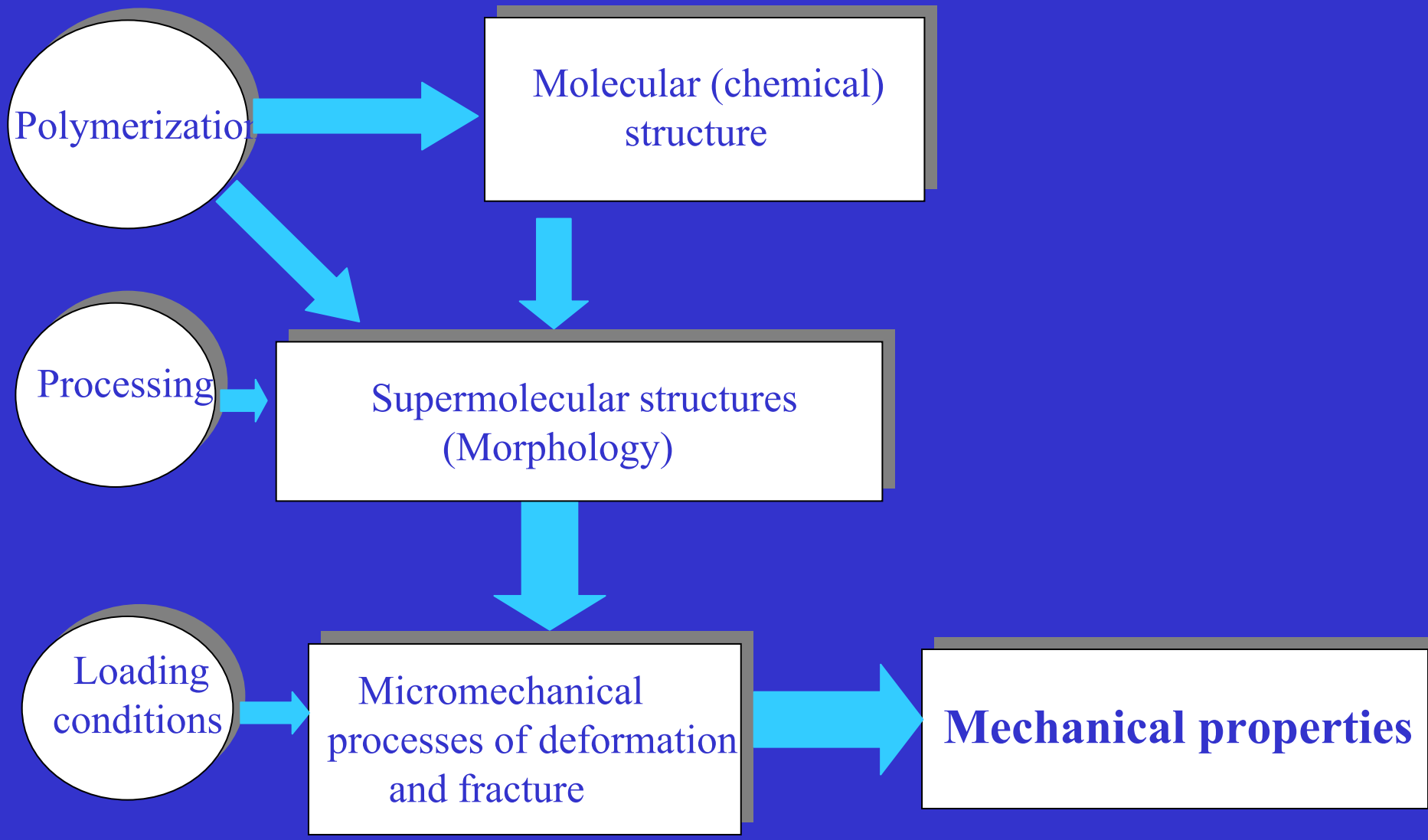


PP-Clay-Nanocomposite

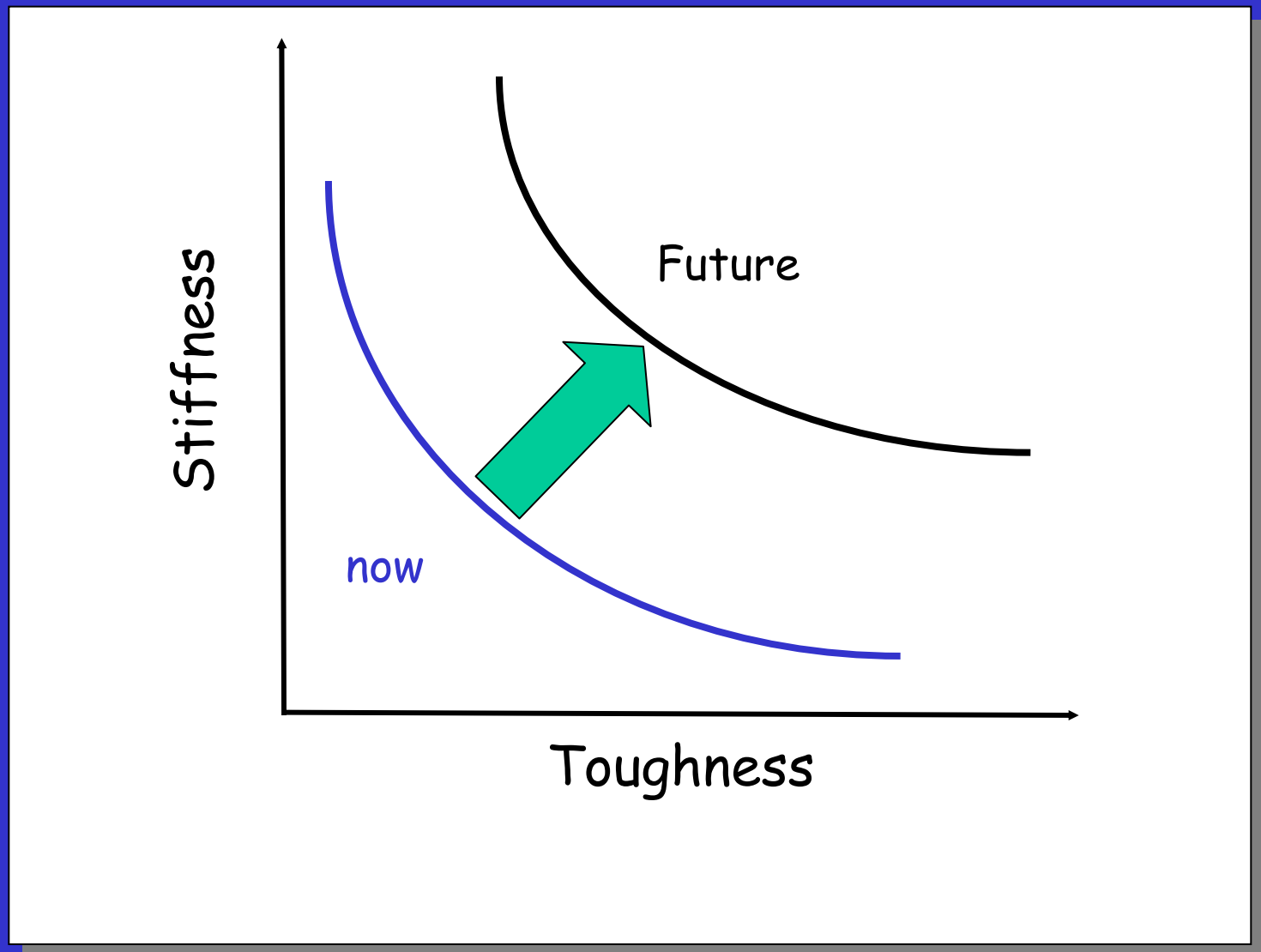
Deformation structure



RESULT of EM: *Better Correlations*



RESULT of EM: *Better Properties*



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There are many books on electron microscopy, however, the study of polymers using EM necessitates special techniques, precautions and preparation methods, including ultramicrotomy. This book discusses the general characteristics of the various techniques of EM, including scanning force microscopy (AFM). The application of these techniques to the study of morphology and properties, particularly micromechanical properties, is described in detail. Examples from all classes of polymers are presented.

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