Microstructure Mechanics

Polymers: Structure and Properties

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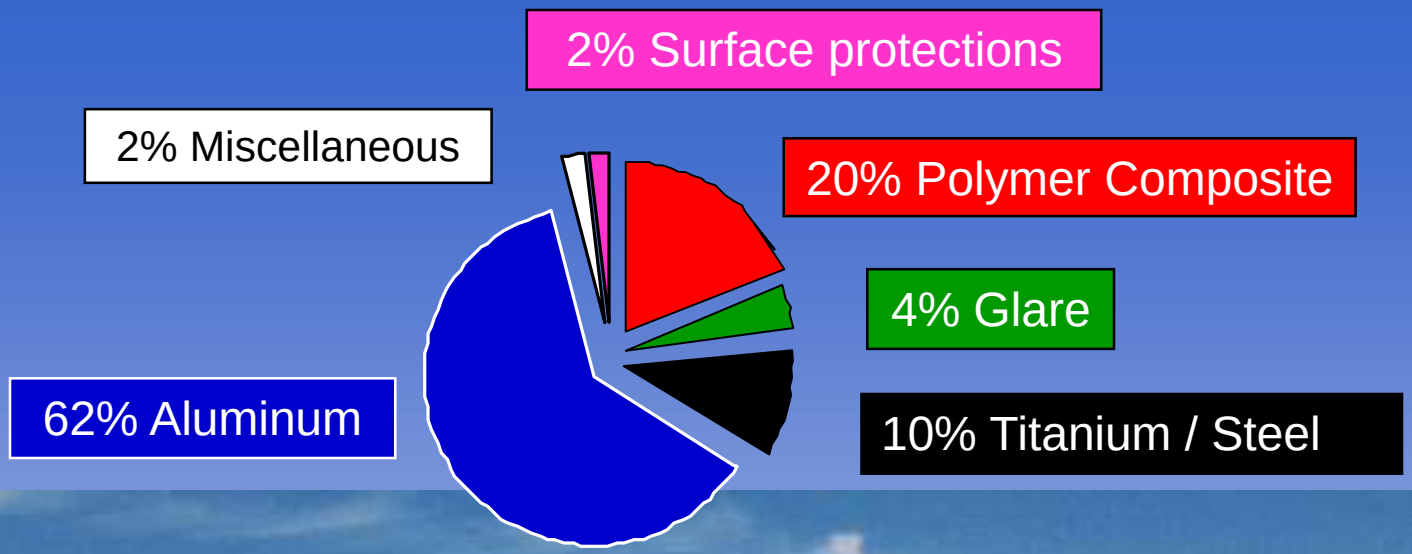
Class 2017

Technology Status A380 – Material Distribution (courtesy Airbus)

Fly



AIRBUS

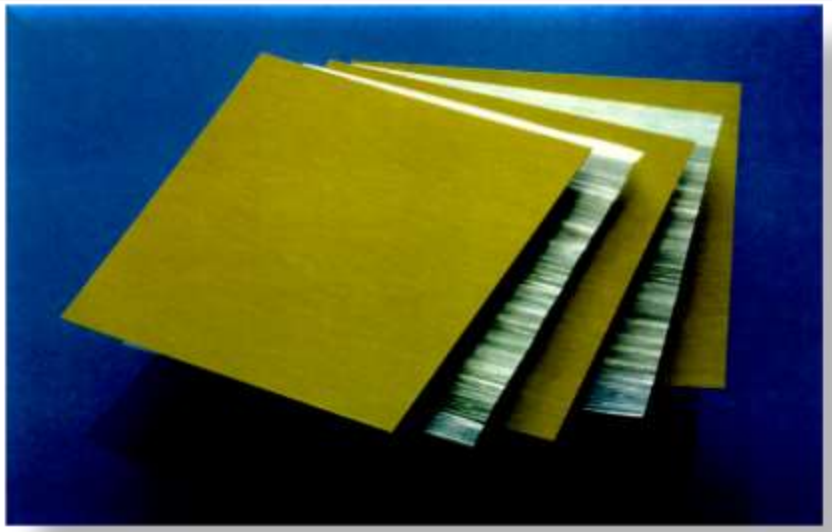
Technology Status A380 – Material Distribution (courtesy Airbus)

GLARE: "Glass Laminate Aluminium Reinforced Epoxy“

several thin layers of metal (usually aluminium) interspersed with layers of glass-fibre "pre-preg", bonded together with a matrix such as epoxy.

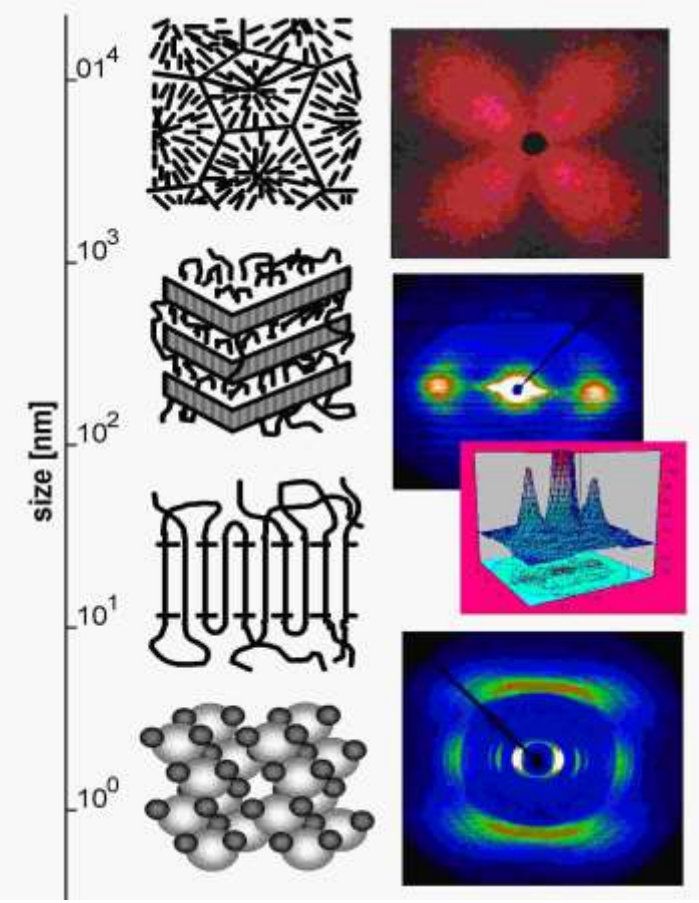
Uni-directional pre-preg layers may be aligned in different directions to suit the predicted stress conditions.

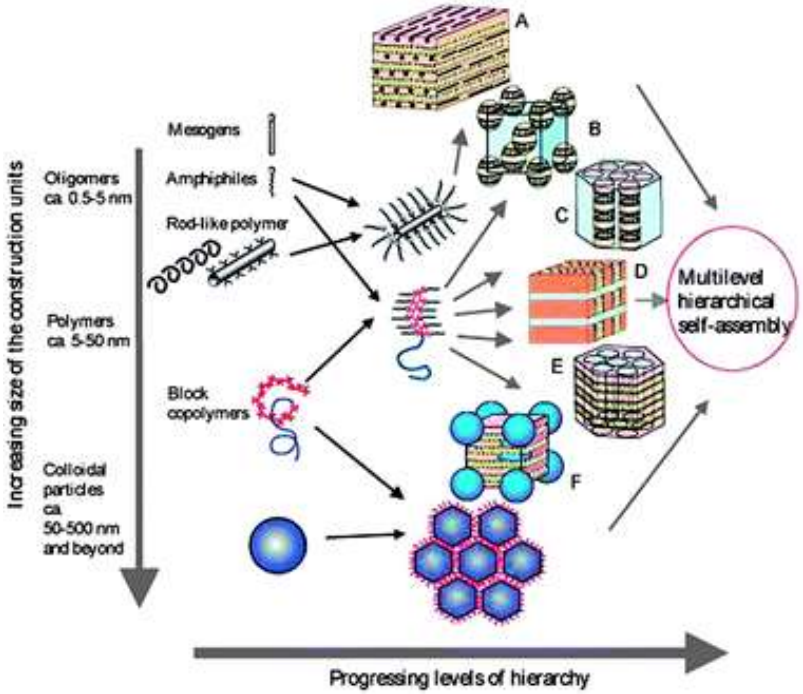
Next generation: CFK



- Improved Stiffness
- Improved hot-wet shear
- Material Optimised Hybrid
- Cost reduction
- Design rules
  - *Fiber dominated*
  - *Bonded Metal laminate*

Hierarchy of polymers





Polymers: Introduction

- **Polymers** – materials consisting of *polymer molecules* that consist of repeated chemical units (`mers') joined together, like beads on a string. Some polymer molecules contain hundreds or thousands of monomers and are often called *macromolecules*.

- Polymers may be **natural**, such as leather, rubber, cellulose or DNA, or **synthetic**, such as nylon or polyethylene.

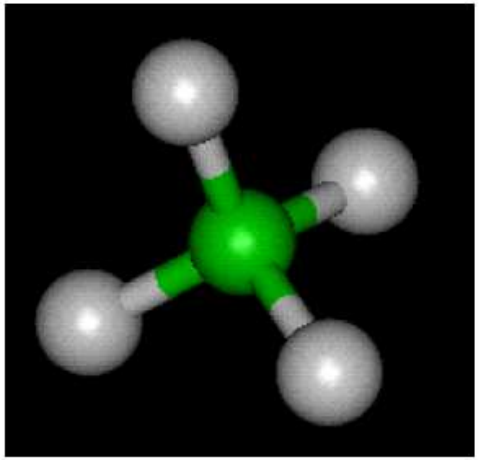
Structure of polymers

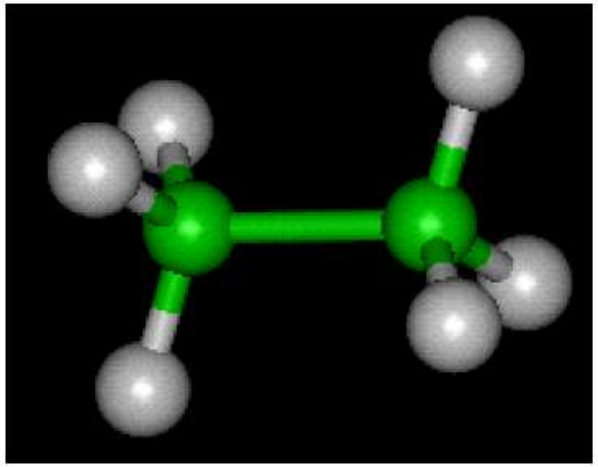
- Macromolecules are formed by linking of repeating units through covalent bonds in the main backbone

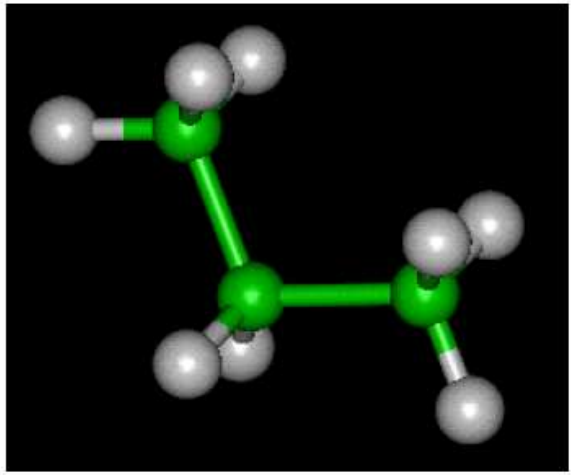
- Properties of macromolecules are determined by
  - molecular weight
  - length
  - backbone structure
  - side chains
  - crystallinity

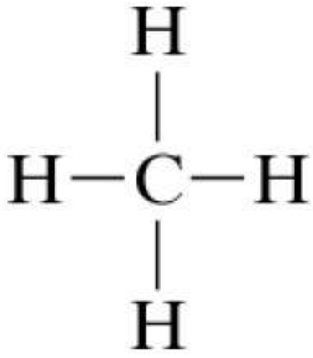
- Resulting macromolecules have huge molecular weights

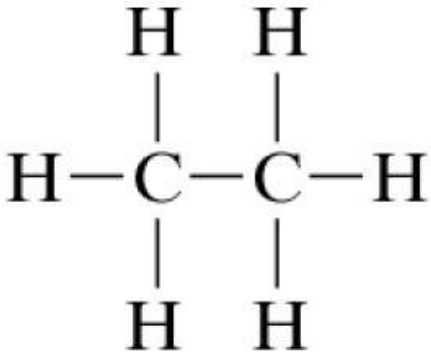
Types of polymers

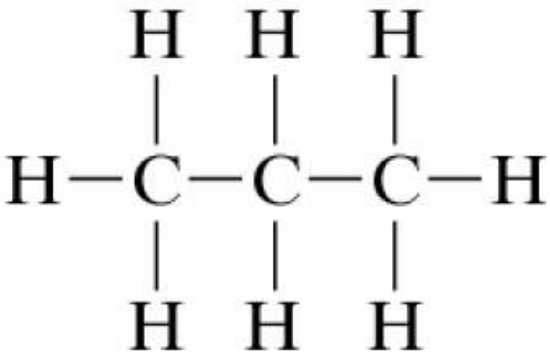








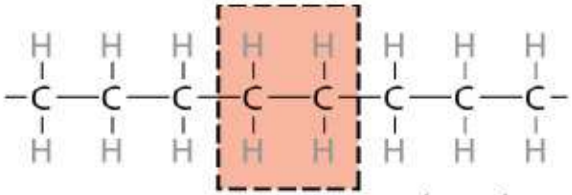




Methane, CH_4 **Ethane, C_2H_6** **Propane, C_3H_8**

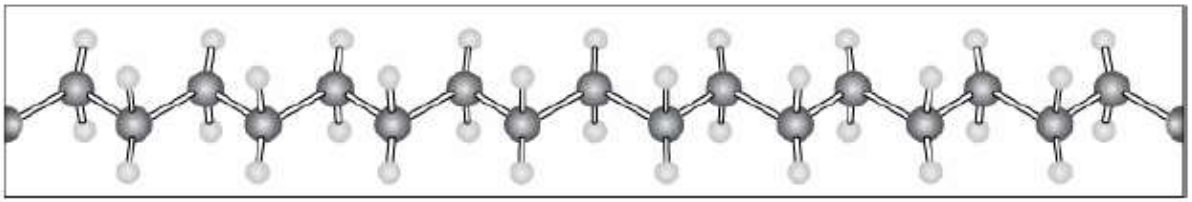
Types of polymers

- Polymer molecules can be very large (macromolecules)
- Most polymers consist of long and flexible chains with a string of C atoms as a backbone
- Side-bonding of C atoms to H atoms or radicals
- Double bonds are possible in both chain and side bonds
- Repeat unit in a polymer chain ("unit cell") is a **mer**
- Small molecules from which polymer is synthesized is **monomer**. A single mer is sometimes also called a monomer.



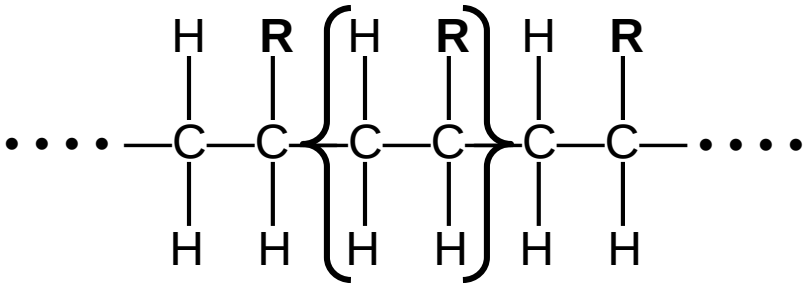
Repeat unit (mer)

polyethylene (e.g. paraffin wax for candles)



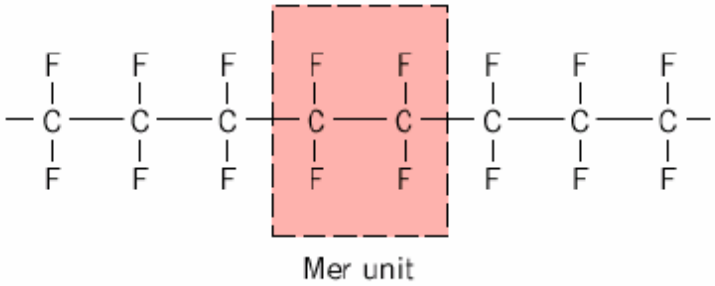
C H

Types of polymers



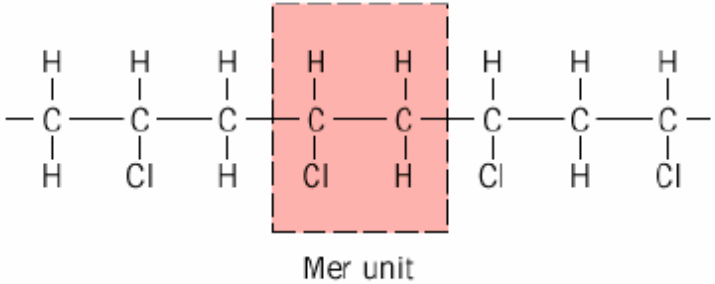
Structure	Source-Based Name	Application
R = -H	Polyethylene	Plastic
R = $-CH_3$	Polypropylene	Rope
R = -Cl	Poly(vinyl chloride)	"Vinyl"
X = -H, R = $-C_2H_5$	Poly(ethyl acrylate)	Latex paints
X = $-CH_3$, R = $-CH_3$	Poly(methyl methacrylate)	Plastic
R = -H	Polybutadiene	Tires
R = $-CH_3$	Polyisoprene	Tires
X = -F, R = -F	Polytetrafluoroethylene	Teflon®

Types of polymers



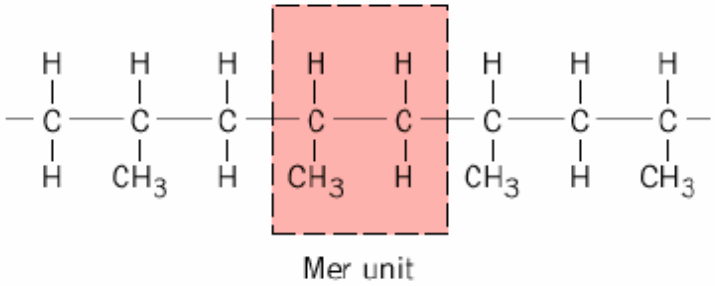
(a)

hydrogen atoms in polyethylene are replaced by fluorine: polytetraflouroethylene PTFE – Teflon



(b)

every fourth hydrogen atom in polyethylene is replaced with chlorine: poly(vinyl chloride) PVC

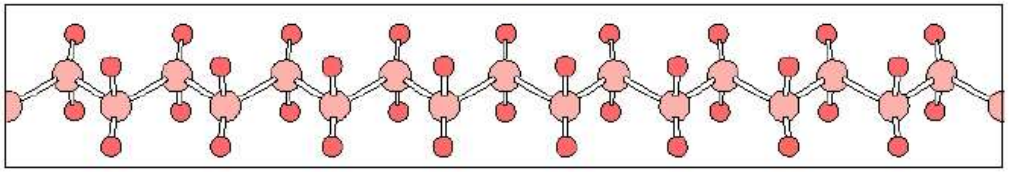


(c)

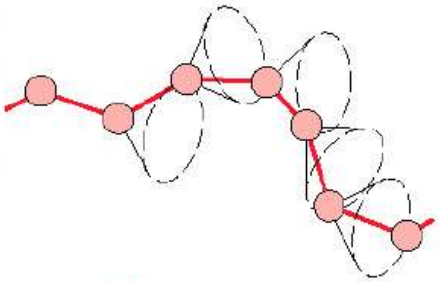
every fourth hydrogen atom in polyethylene is replaced with methyl group (CH_3): polyproplylene PP

Polymer structure: large variety in conformation

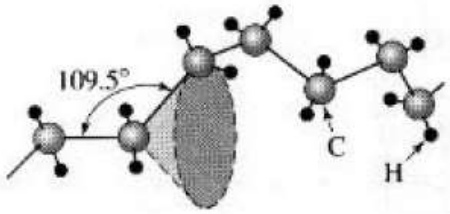
Molecular shape (conformation)

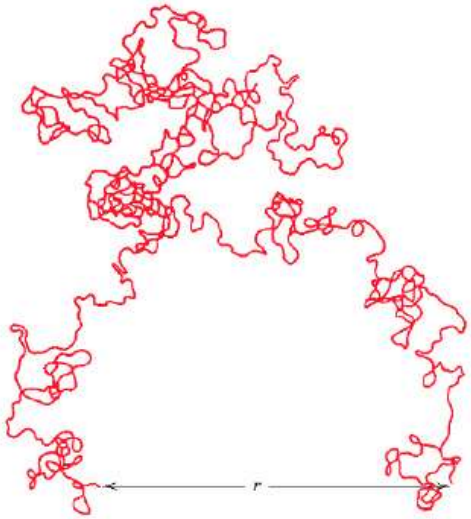


- The angle between the singly bonded carbon atoms is ~109° – carbon atoms form a zigzag pattern in a polymer molecule.
- Moreover, while maintaining the 109° angle between bonds polymer chains can rotate around single C-C bonds (double and triple bonds are very rigid).



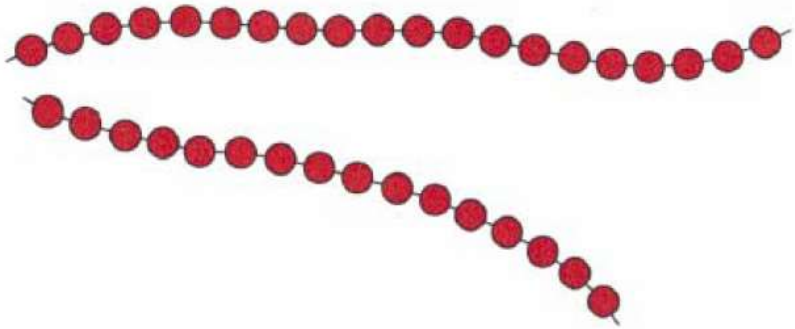
- Random kinks and coils lead to entanglement, like in the spaghetti structure:





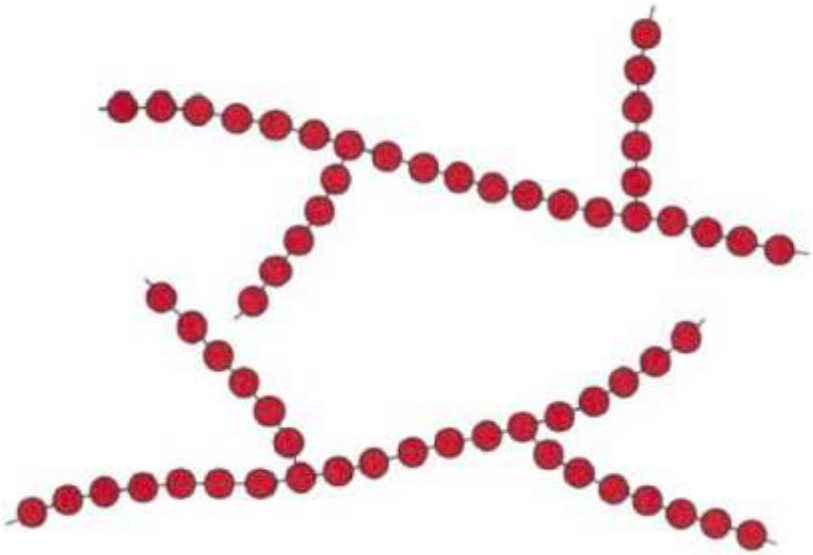
Polymer structure

1 **Linear polymers**: Van der Waals bonding between chains. Examples: polyethylene, nylon.

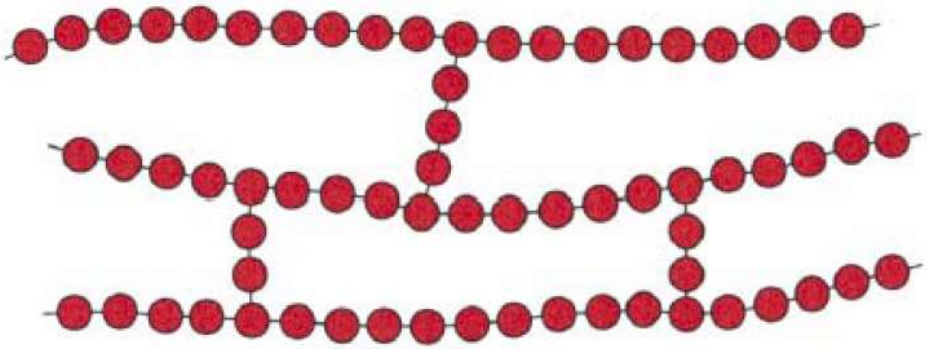


Polymer structure

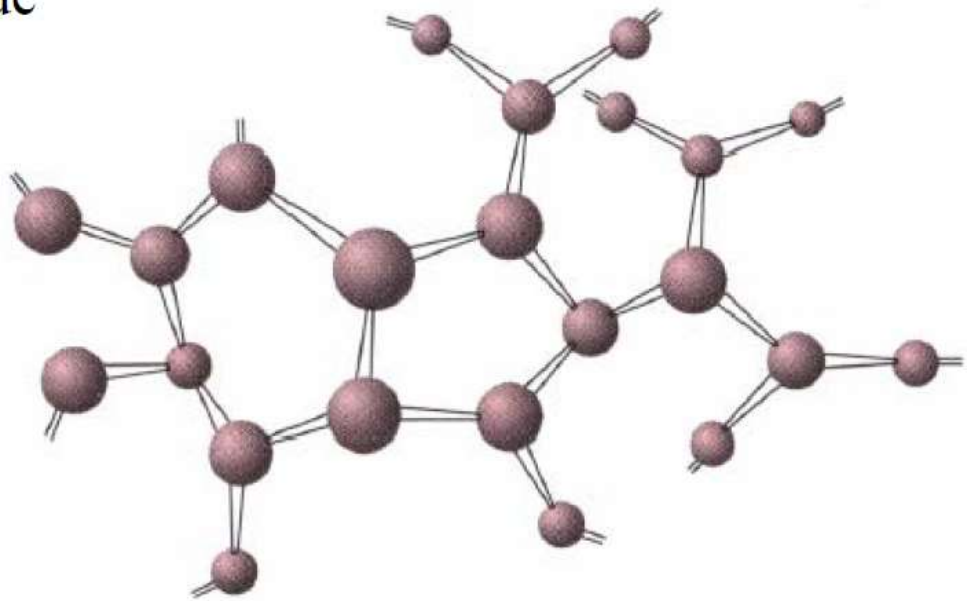
2 **Branched polymers**: Chain packing efficiency is reduced compared to linear polymers - lower density



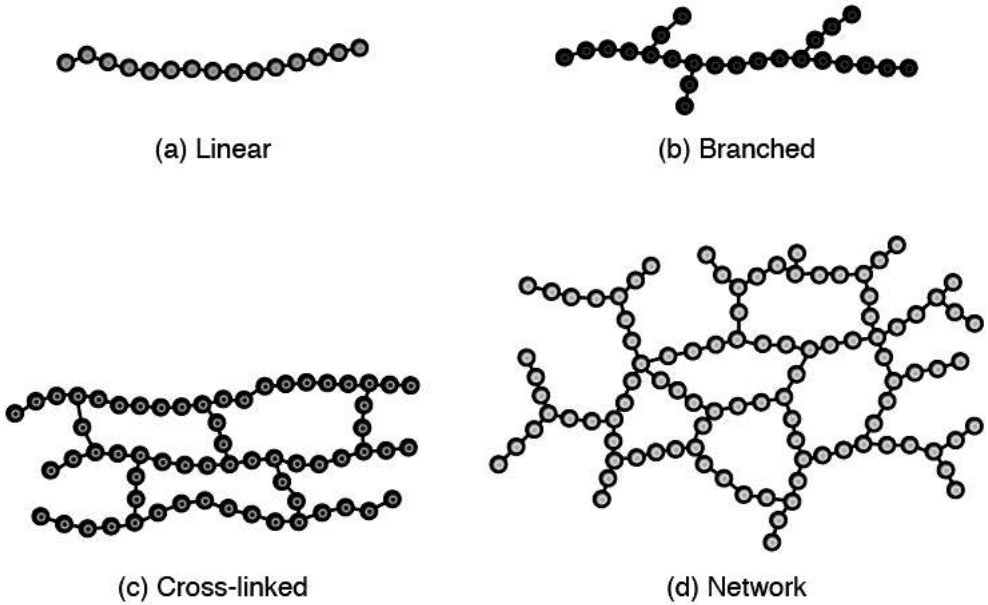
3 **Cross-linked polymers**: Chains are connected by covalent bonds. Often achieved by adding atoms or molecules that form covalent links between chains. Many rubbers have this structure.



4 **Network polymers**: 3D networks made from trifunctional mers. Examples: epoxies, phenol-formaldehyde



Polymer structure: overview

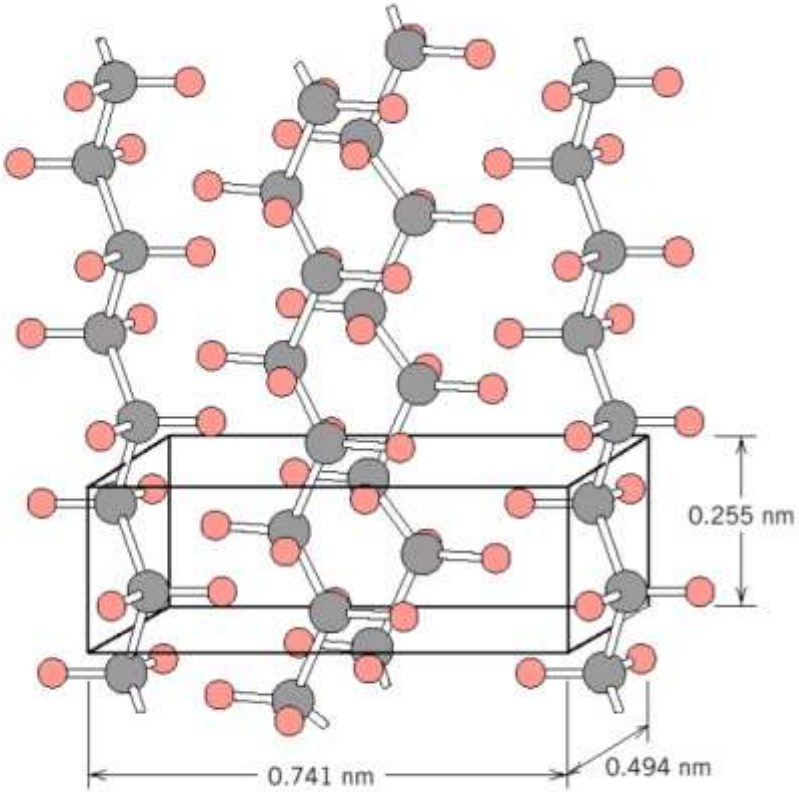


Schematic illustration of polymer chains.

(a) Linear structure; thermoplastics such as acrylics, nylons, polyethylene, and polyvinyl chloride have linear structures.
(b) Branched structure, such as polyethylene.
(c) Crosslinked structure; many rubbers and elastomers have this structure. Vulcanization of rubber produces this structure.
(d) Network structure, which is basically highly cross-linked; examples include thermosetting plastics such as epoxies and phenolics.

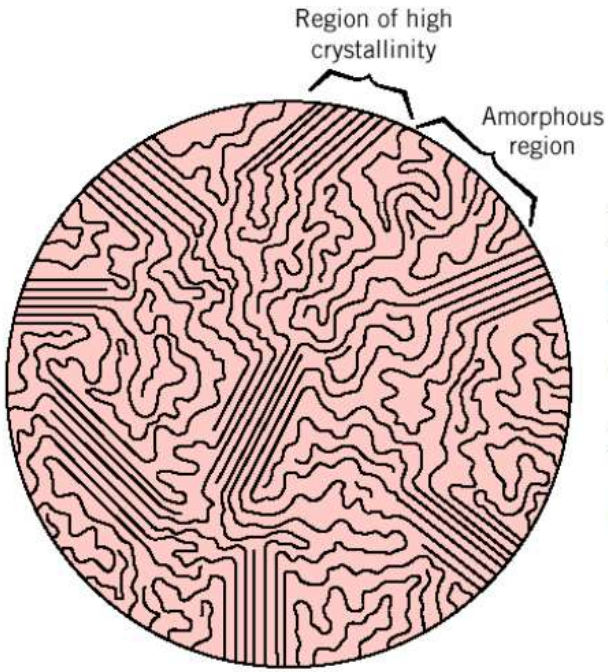
Polymer structure, crystals

Atomic arrangement in polymer crystals is more complex than in metals or ceramics (unit cells are typically large and complex).



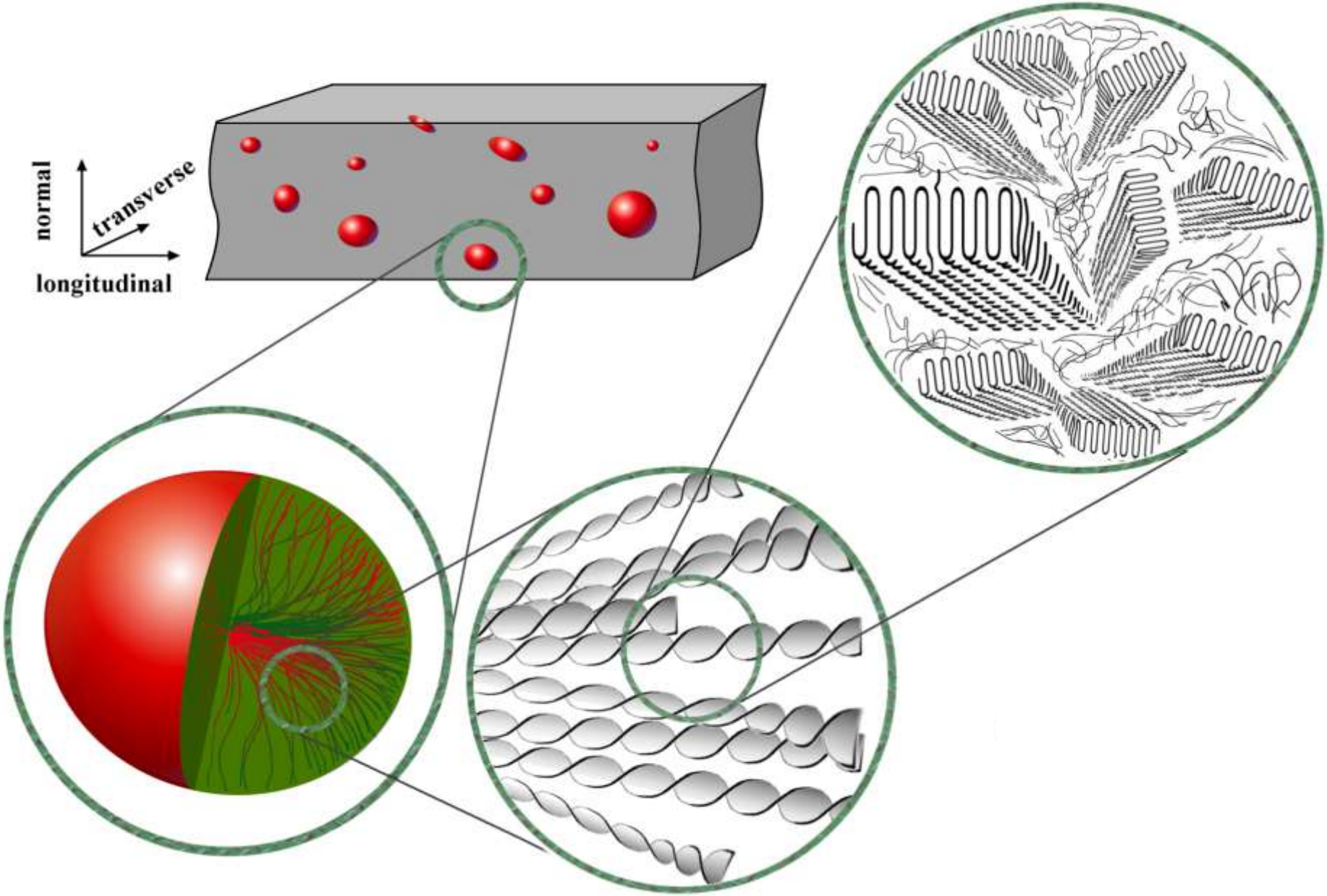
Polyethylene

Polymer structure, crystals and amorphous structure

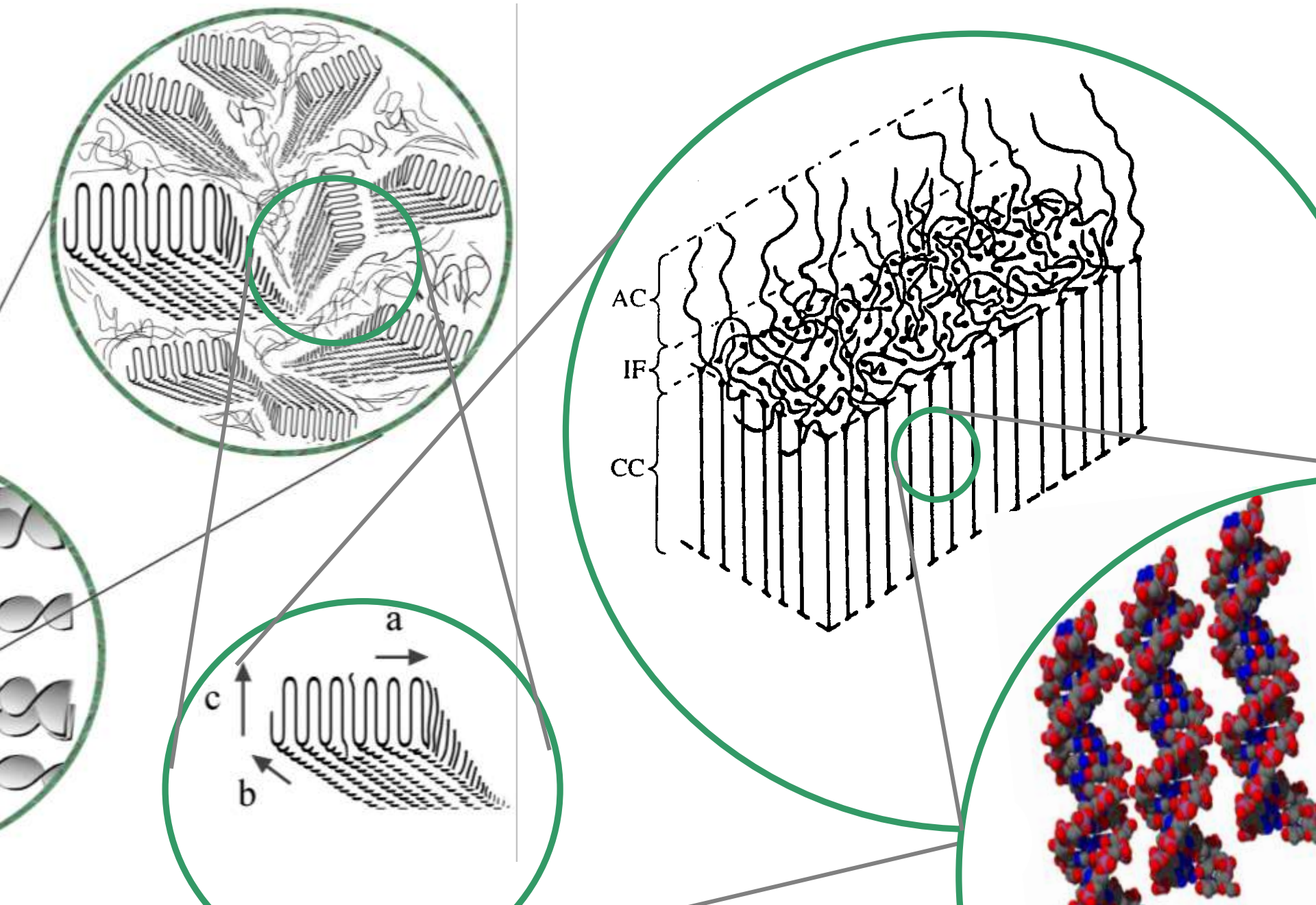


Polymer molecules are often partially crystalline (semi-crystalline), with crystalline regions dispersed within amorphous material.

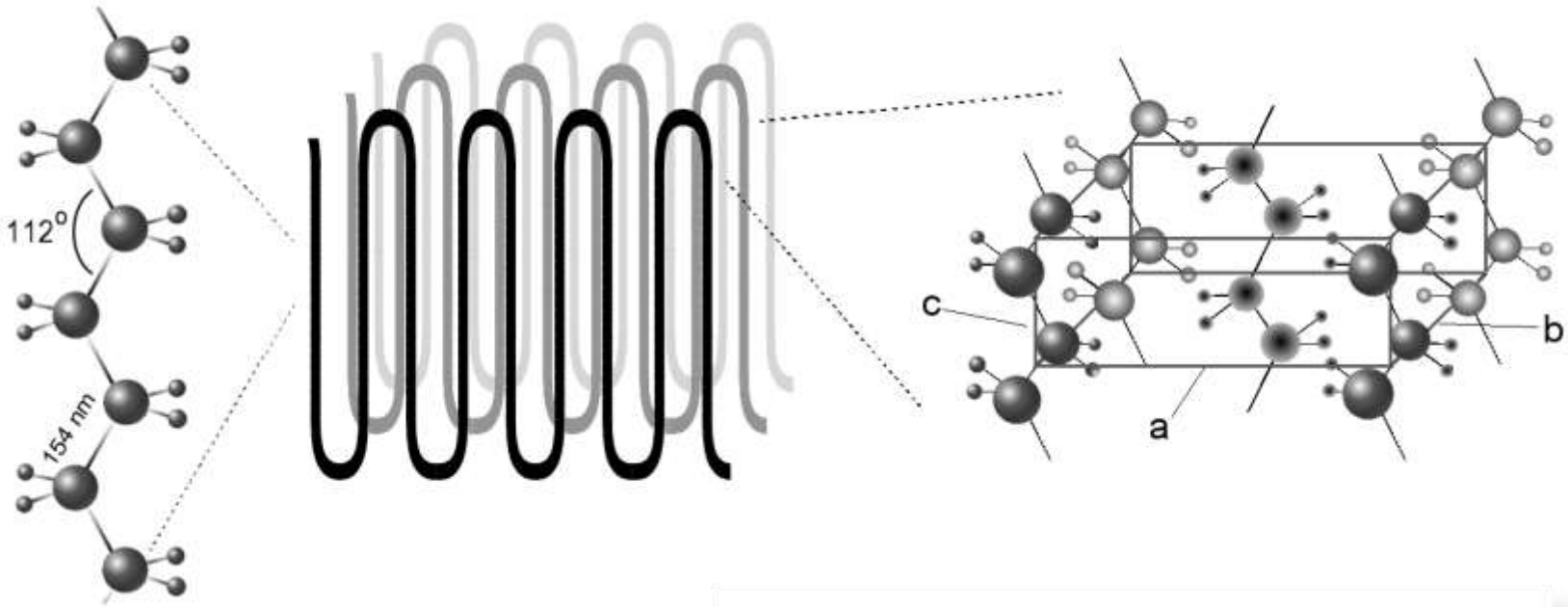
Structure, scales, partially crystalline polymers



Structure, scales, partially crystalline polymers

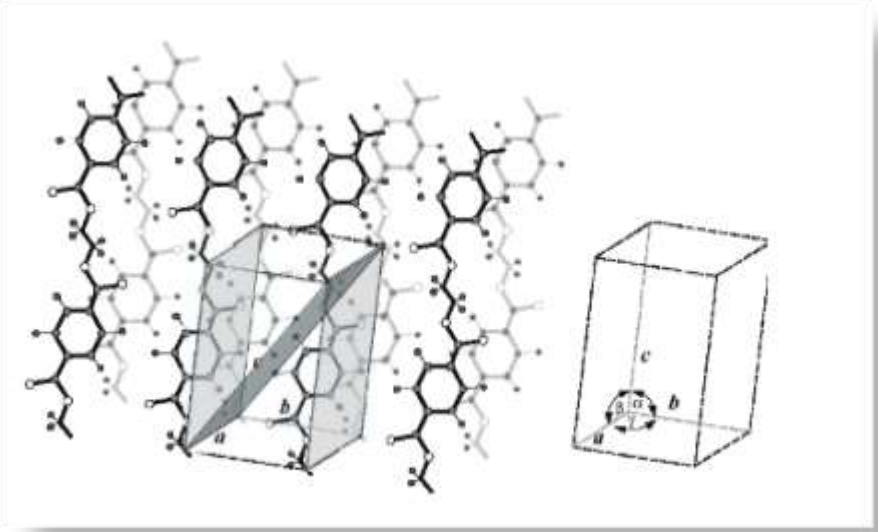


Structure, scales, partially crystalline polymers

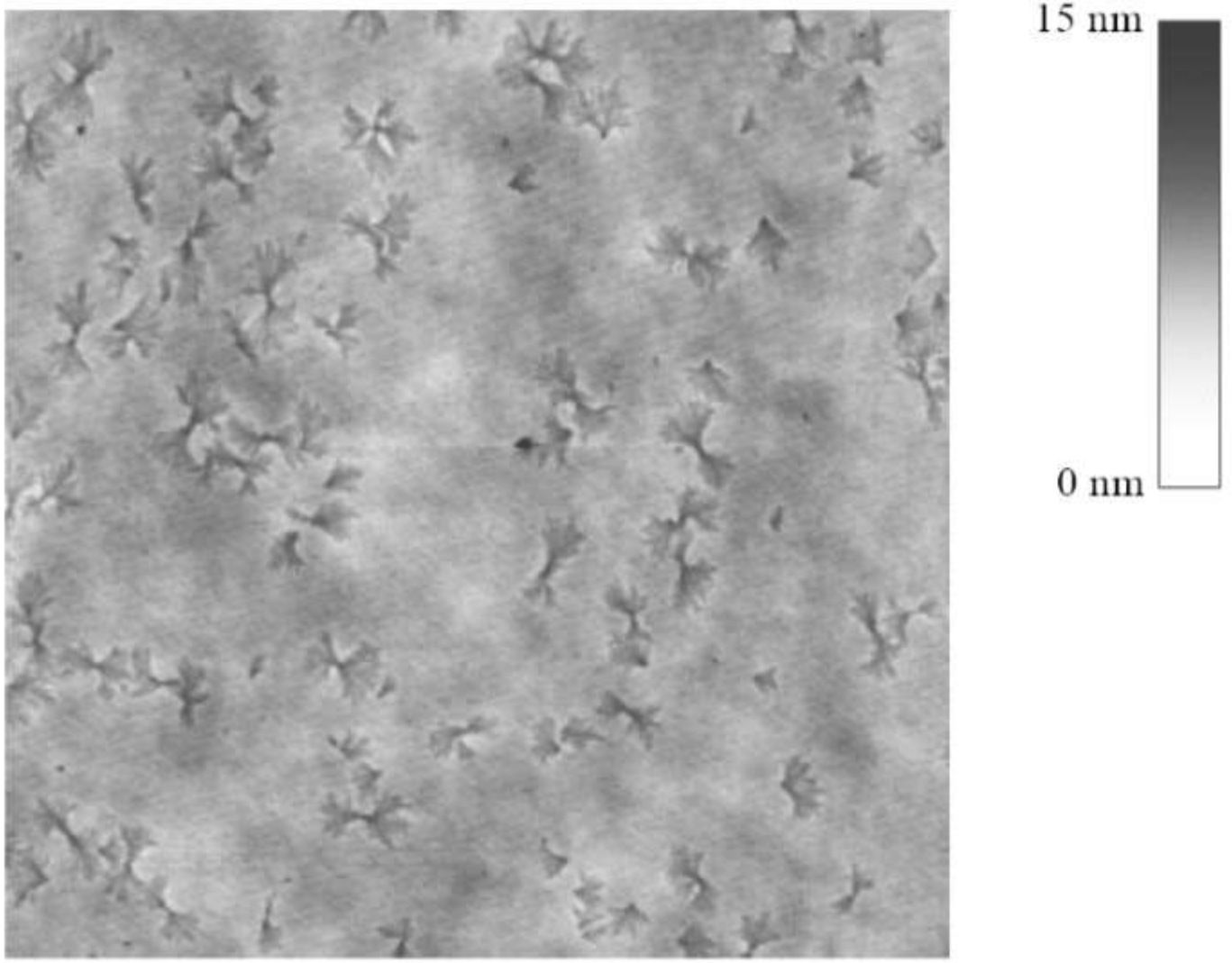


The crystalline unit cell for PET (a = 4.56 Å, b = 5.94 Å, c = 10.75 Å; α = 98.5°, β = 118°, γ = 112°),

M Durell (2002)



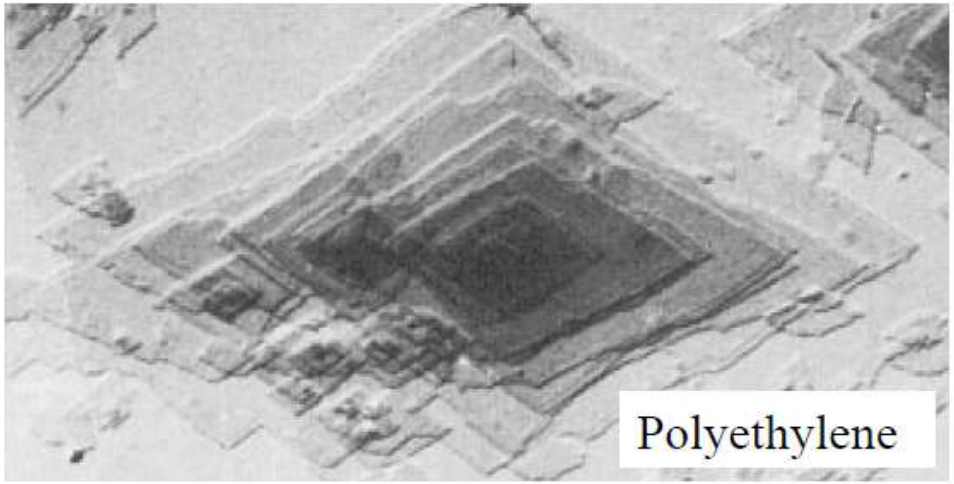
Polymer structure: spherulite growth



PET / AFM: M Durell, J E Macdonald, D Trolley, Europhysics Letters (2002)

Polymer structure: spherulite growth

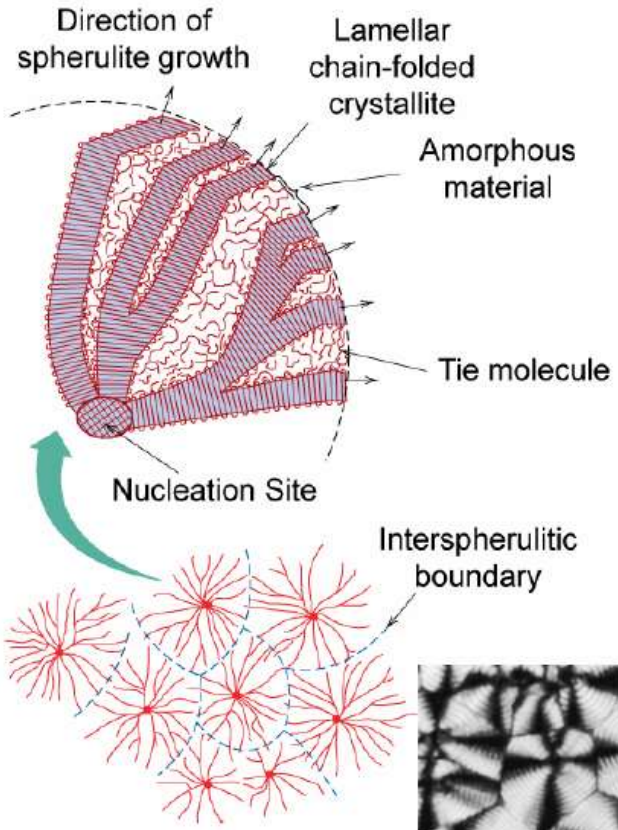
Thin crystalline platelets grown from solution - chains fold back and forth: chain-folded model



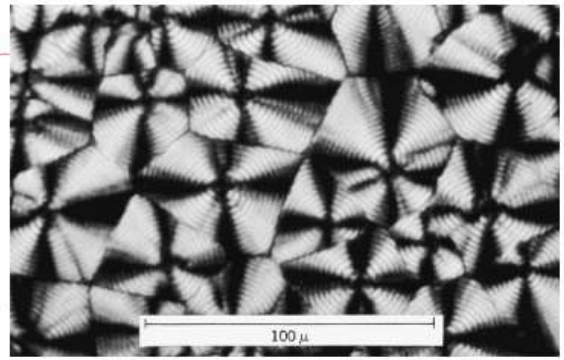
The average chain length can be much greater than the thickness of the crystallite

Polymer structure: spherulite growth

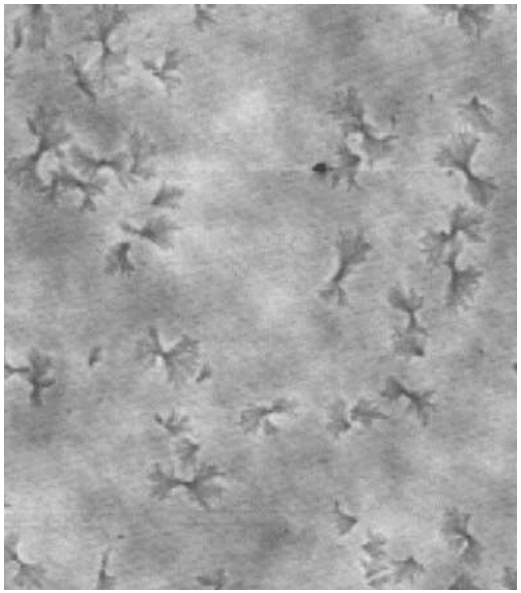
Spherulites: Aggregates of lamellar crystallites ~ 10 nm thick, separated by amorphous material. Aggregates are formed upon solidification from a melted state and are approximately spherical in shape.

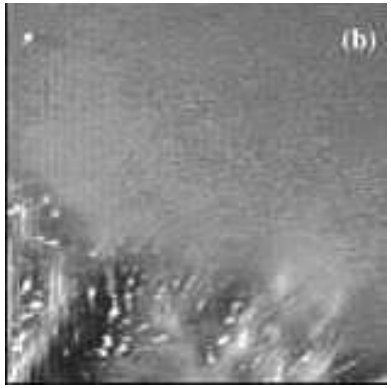


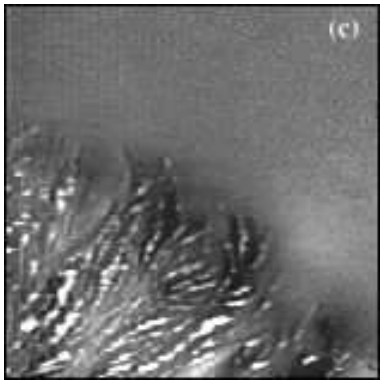
Photomicrograph of spherulite structure of polyethylene



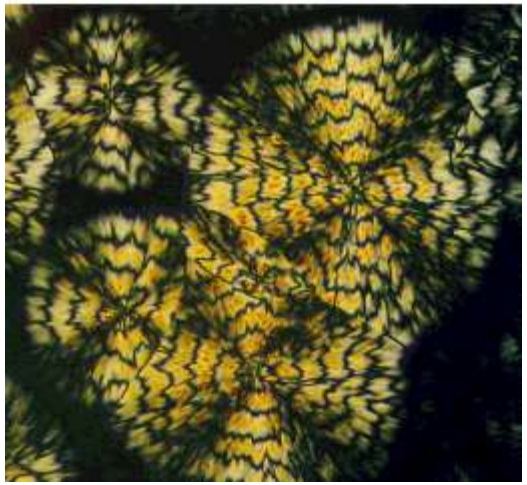
Polymer structure: spherulite growth







1 micron square, AFM



1 millimeter square, OM

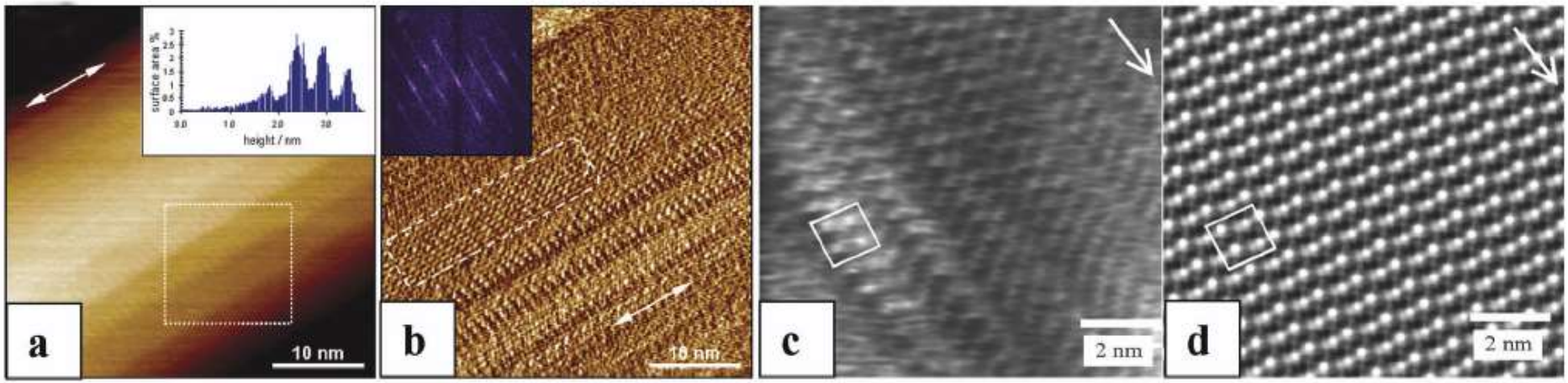
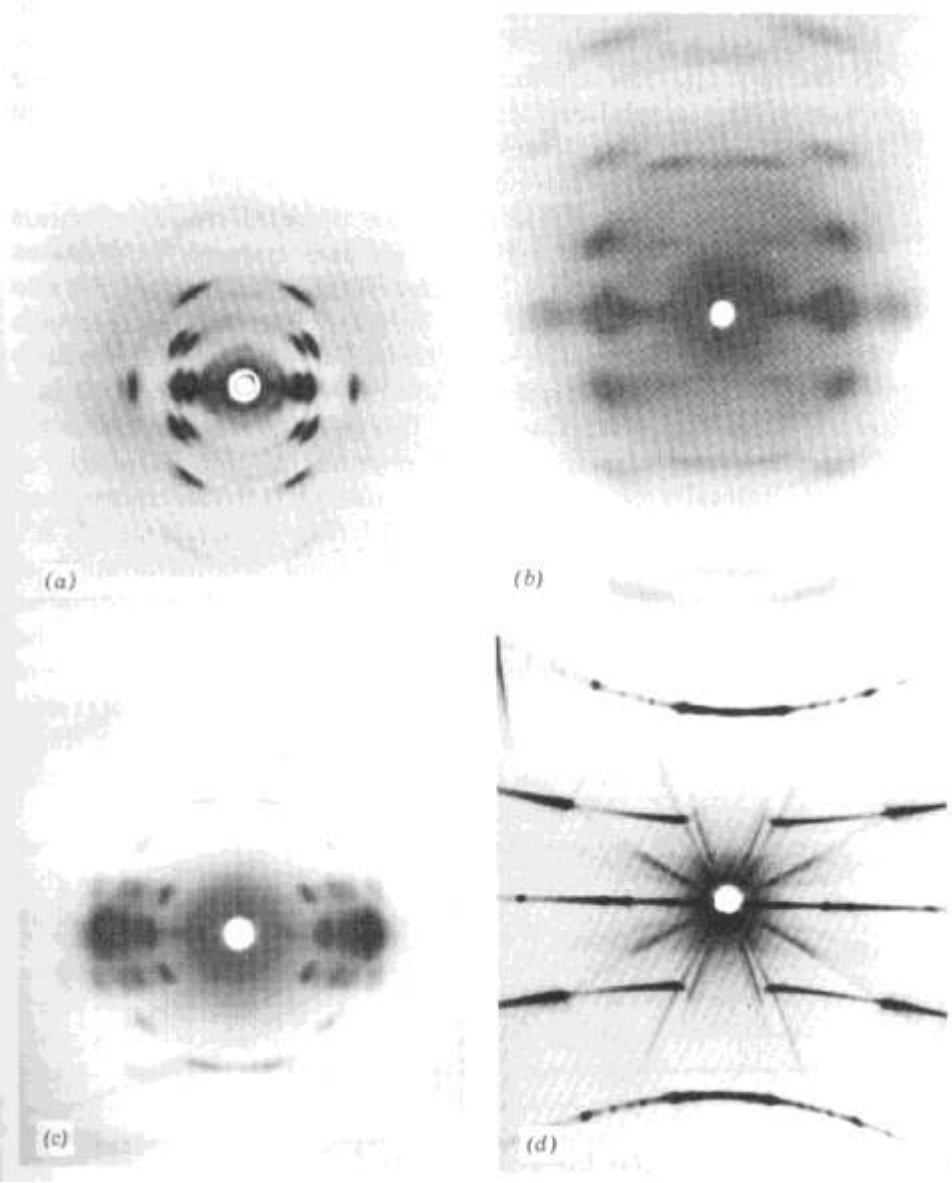
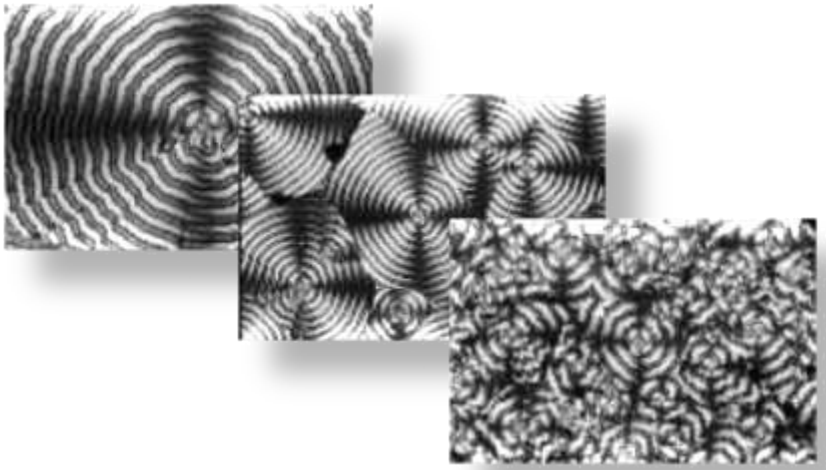


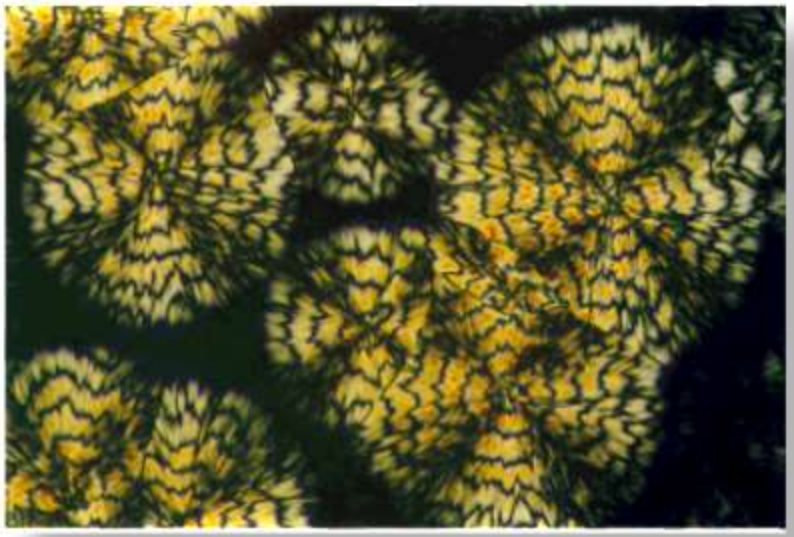
Fig. 2 AFM contact mode images. Cellulose molecules in micro-fibril crystal: (a) topographic image; and (b) error-signal image. Polybutene-1 molecules: (c) topographic image; and (d) simulated AFM image based on crystallographic data.

M. Miles, M. Antognozzi, H. Haschke, J. Hobbs, A. Humphris, T. McMaster
H.H. Wills Physics Laboratory, University of Bristol, Materials Today, Feb. 2003

Polymer structure: spherulite growth



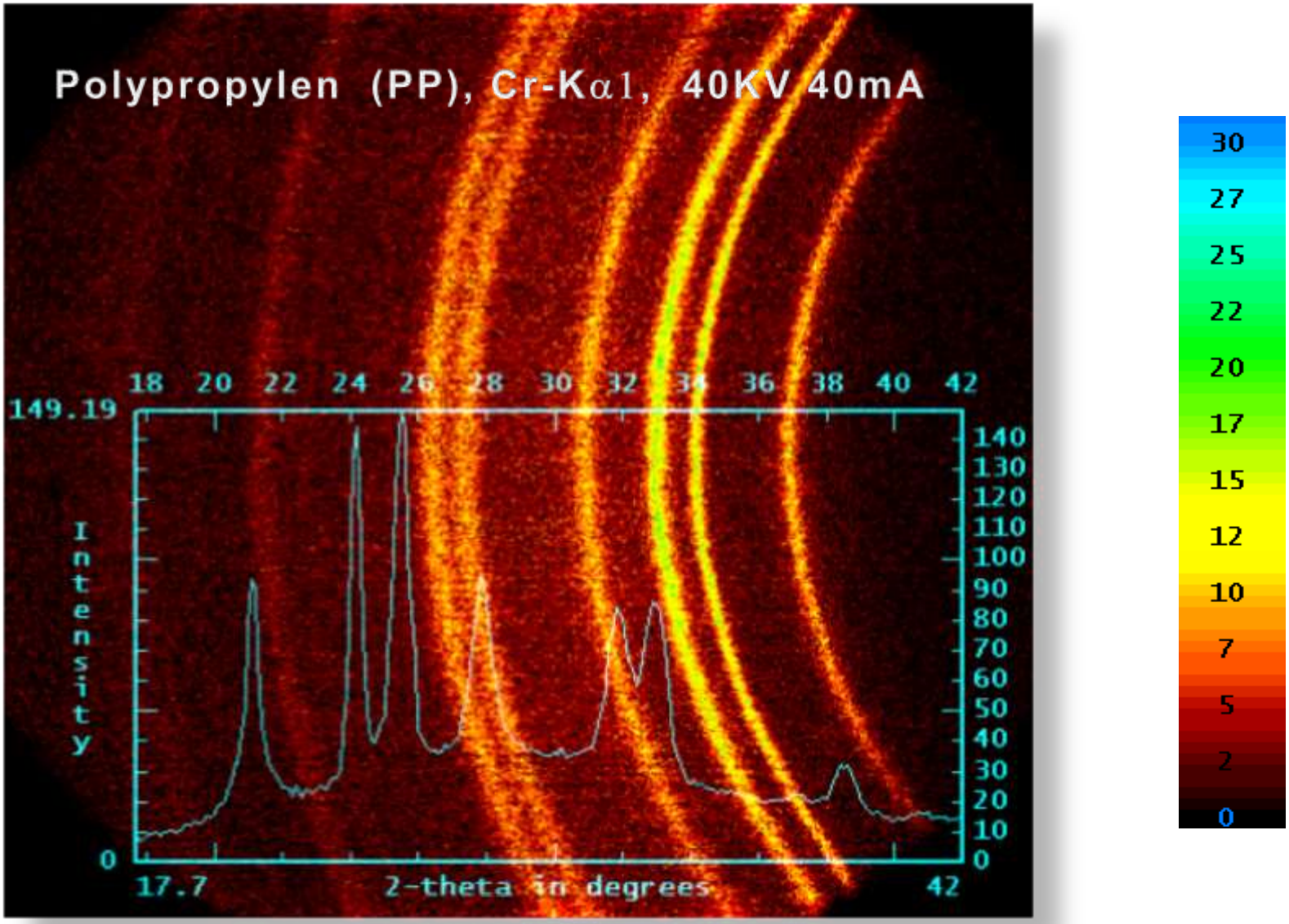




1 millimeter square, OM

Bamford, Nature 173 (1954) p. 27; Astbury, Endeavor 1(1942) p. 70

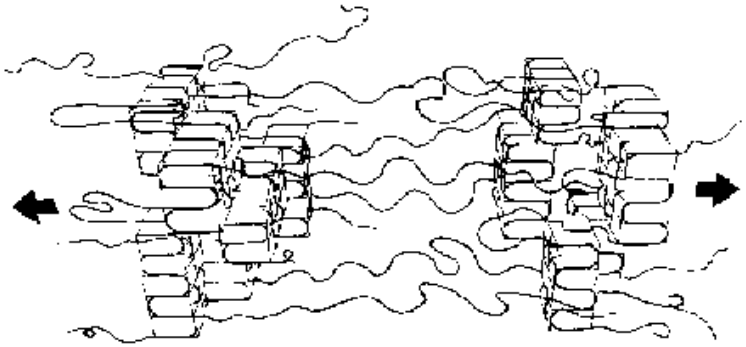
Polymer structure: PP: XRD



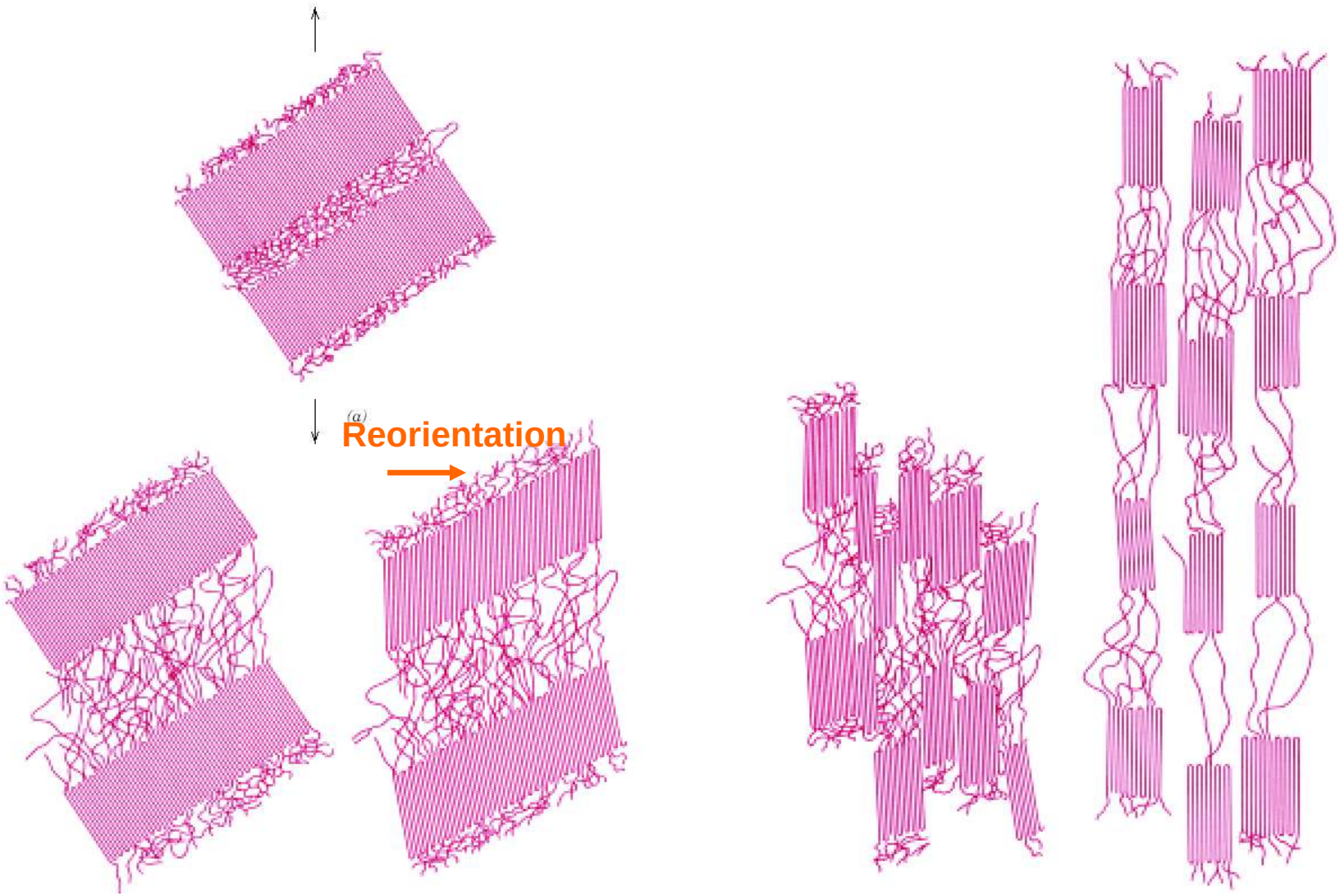
Polymer structure: deformation of semi-crystalline polymers

Structure of semicrystalline polymers on a molecular scale can be approximated as consisting of two phases:
(a) crystalline regions
(b) disordered quasi-amorphous interlamellar (IL) regions.

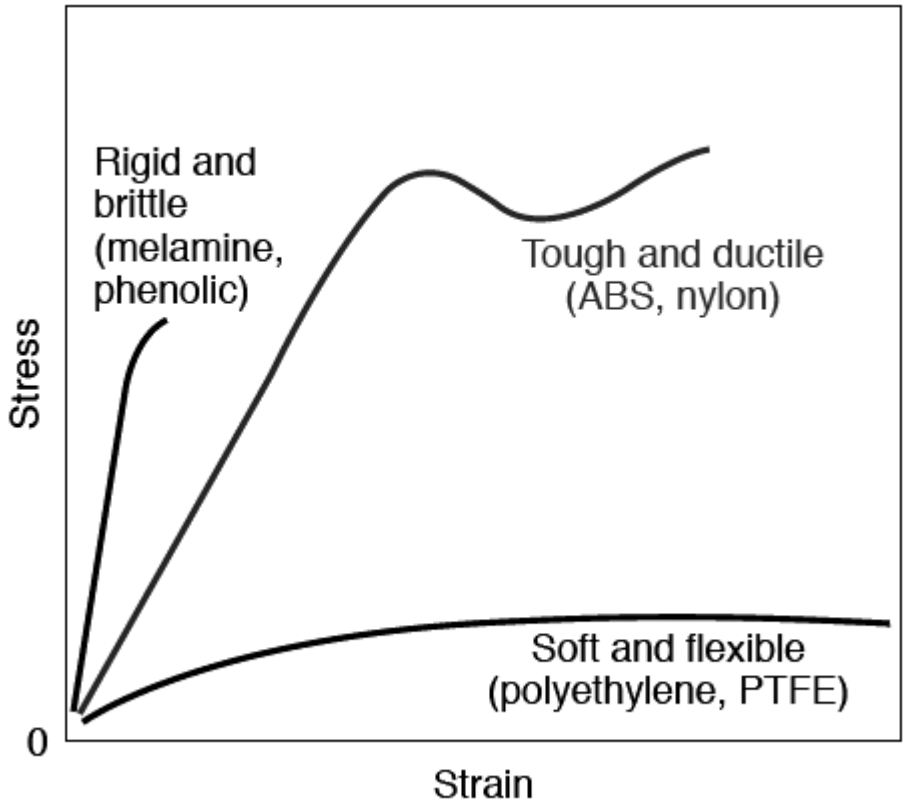
Crystal regions typically consist of crystal lamellae by regular folding chains.
Within the IL regions four types of molecules are present
(a)- tails with one free end;
(b)- loops, which start and end in the same lamellae;
(c)- bridges (**tie molecules**) which join up two lamellae
(d)- floating molecules which are unattached to any lamella



Polymer structure: deformation of semi-crystalline polymers

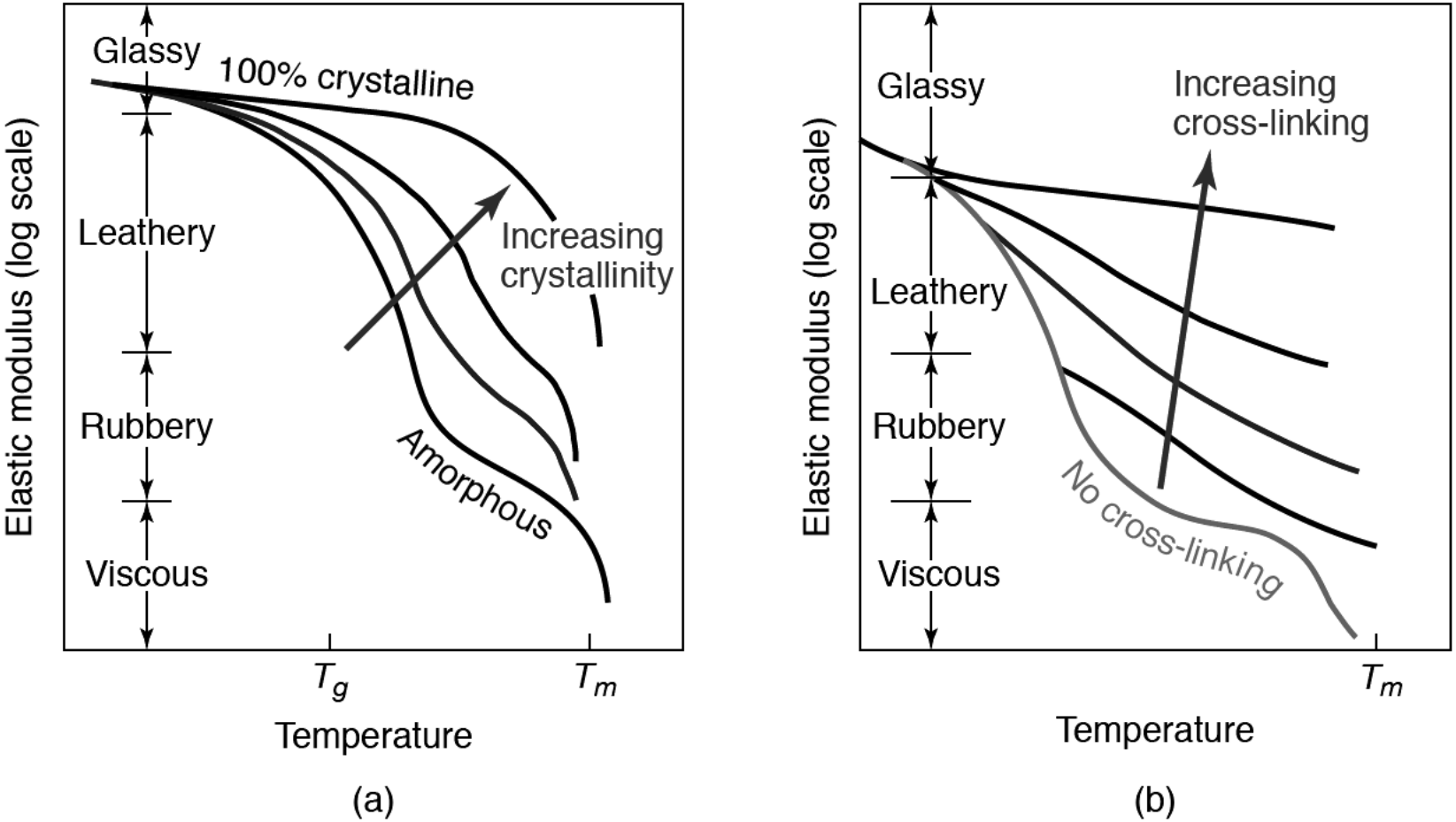


Polymers: mechanical properties – trends



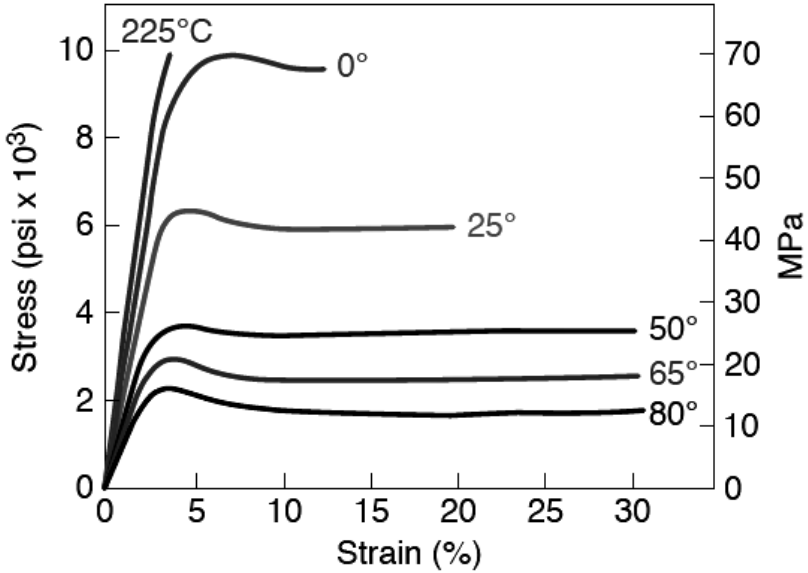
General terminology describing the behavior of three types of plastics. PTFE is polytetrafluoroethylene (Teflon, a trade name).
Source: After R.L.E. Brown.

Polymers: mechanical properties – the influence of temperature



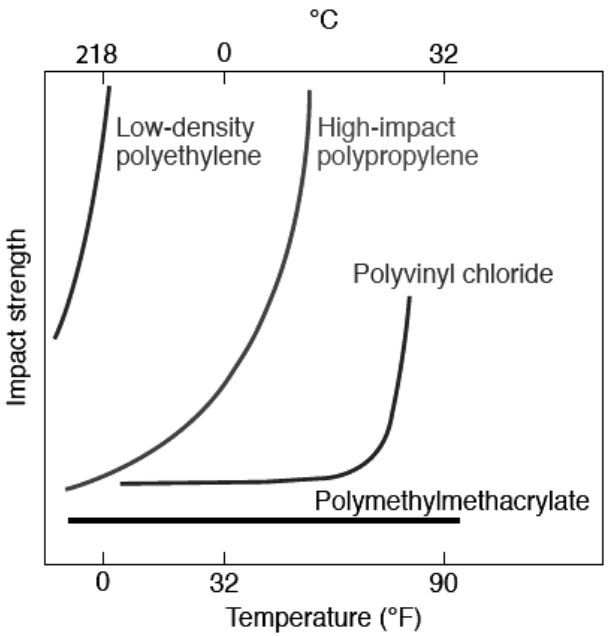
Behavior of polymers as a function of temperature and (a) degree of crystallinity and (b) crosslinking. The combined elastic and viscous behavior of polymers is known as viscoelasticity.

Polymers: mechanical properties – the influence of temperature



Effect of temperature on the stress-strain curve for cellulose acetate, a thermoplastic. Note the large drop in strength and increase in ductility with a relatively small increase in temperature.

Source: After T.S. Carswell and H.K. Nason.



Effect of temperature on the impact strength of various plastics. Note that small changes in temperature can have a significant effect on impact strength.

Source: P.C. Powell.

Durability of polymer composites

Polymer composites change with time and most significant factors are

- Elevated temperatures
- Fire
- Moisture
- Adverse chemical environments
- Natural weathering when exposed to sun's ultra-violet radiation

Polymer composites: mechanical properties

MATERİAL	Relative density	Diameter thickness ratio (microns)	Length (mm)	E (GPa)	Tens. Str. (MPa)	Failure strain (%)	Volume in composite (%)
Mortar matrix	1.8-2.0	300-5000	-	10-30	1-10	0.01-0.05	85-97
Concrete matrix	1.8-2.4	10000-20000	-	20-40	1-4	0.01-0.02	97-99.5
Asbestos	2.55	0.02-30	5-40	164	200-1800	2-3	5-15
Carbon	1.16-1.95	7-18	3-cont.	30-390	600-2700	0.5-2.4	3-5
Glass	2.7	12.5	10-50	70	600-2500	3.6	3-7
Polyethylene							
HDPE filament	0.96	900	3-5	5	200	-	2-4
High modulus	0.96	20-50	Cont.	10-30	> 400	> 4	5-10
Polypropylene (Monofilament)	0.91	20-100	5-20	4	-	-	0.1-0.2
Polyvinyl alcohol (PVA)	1-3	3-8	2-6	12-40	700-1500	-	2-3
Steel	7.86	100-600	10-60	200	700-2000	3-5	0.3-2.0

Performance is controlled by

- **vol. fraction of fibers**
- **properties of fibers and matrix**
- **bond between the two**

Polymer composites: mechanical properties

Material	UTS (MPa)	E (GPa)	Elongation in 50 mm (%)	Poisson's ratio (ν)
ABS	28–55	1.4–2.8	75–5	–
ABS (reinforced)	100	7.5	–	0.35
Acetals	55–70	1.4–3.5	75–25	–
Acetals (reinforced)	135	10	–	0.35–0.40
Acrylics	40–75	1.4–3.5	50–5	–
Cellulosics	10–48	0.4–1.4	100–5	–
Epoxies	35–140	3.5–17	10–1	–
Epoxies (reinforced)	70–1400	21–52	4–2	–
Fluorocarbons	7–48	0.7–2	300–100	0.46–0.48
Nylon	55–83	1.4–2.8	200–60	0.32–0.40
Nylon (reinforced)	70–210	2–10	10–1	–
Phenolics	28–70	2.8–21	2–0	–
Polycarbonates	55–70	2.5–3	125–10	0.38
Polycarbonates (reinforced)	110	6	6–4	–
Polyesters	55	2	300–5	0.38
Polyesters (reinforced)	110–160	8.3–12	3–1	–
Polyethylenes	7–40	0.1–0.14	1000–15	0.46
Polypropylenes	20–35	0.7–1.2	500–10	–
Polypropylenes (reinforced)	40–100	3.6–6	4–2	–
Polystyrenes	14–83	1.4–4	60–1	0.35
Polyvinyl chloride	7–55	0.014–4	450–40	–

Approximate range of mechanical properties for various engineering plastics at room temperature.

Polymer structure: deformation of polymers-based composites

Type	Tensile Strength (MPa)	Elastic Modulus (GPa)	Density (kg/m^3)	Relative Cost
Boron	3500	380	2600	Highest
Carbon				
High strength	3000	275	1900	Low
High modulus	2000	415	1900	Low
Glass				
E type	3500	73	2480	Lowest
S type	4600	85	2540	Lowest
Kevlar				
29	2800	62	1440	High
49	2800	117	1440	High
129	3200	85	1440	High
Nextel				
312	1630	135	2700	High
610	2770	328	3960	High
Spectra				
900	2270	64	970	High
1000	2670	90	970	High

Note: These properties vary significantly, depending on the material and method of preparation. Strain to failure for these fibers is typically in the range of 1.5% to 5.5%.

Typical properties of reinforcing fibers

Microstructure Mechanics

Biological (Natural) Materials

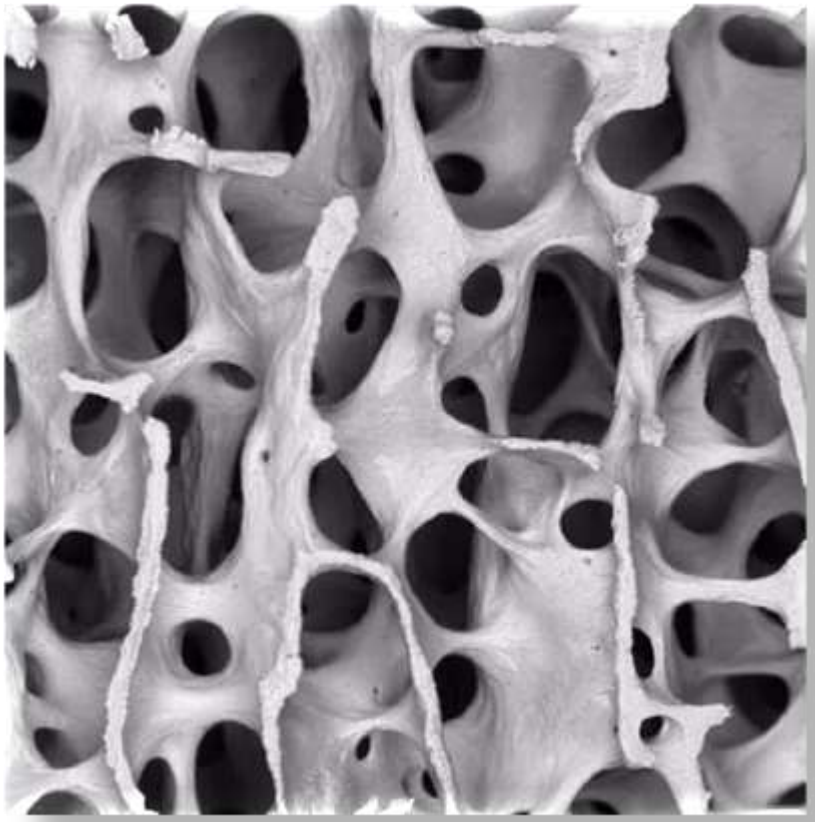
Dierk Raabe

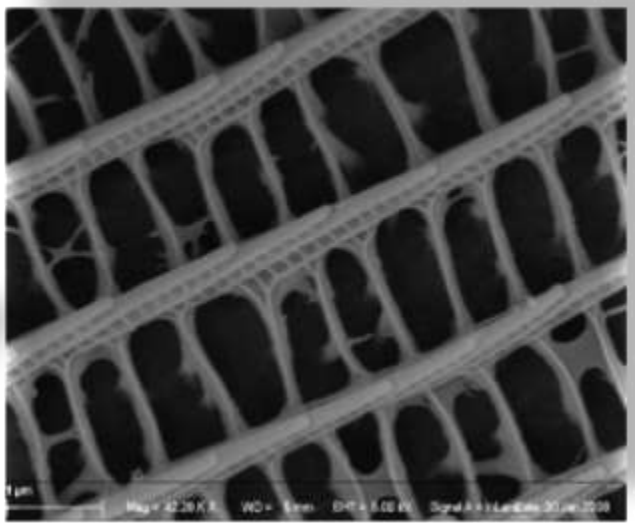
Max-Planck-Institut
für Eisenforschung GmbH
Düsseldorf, Germany

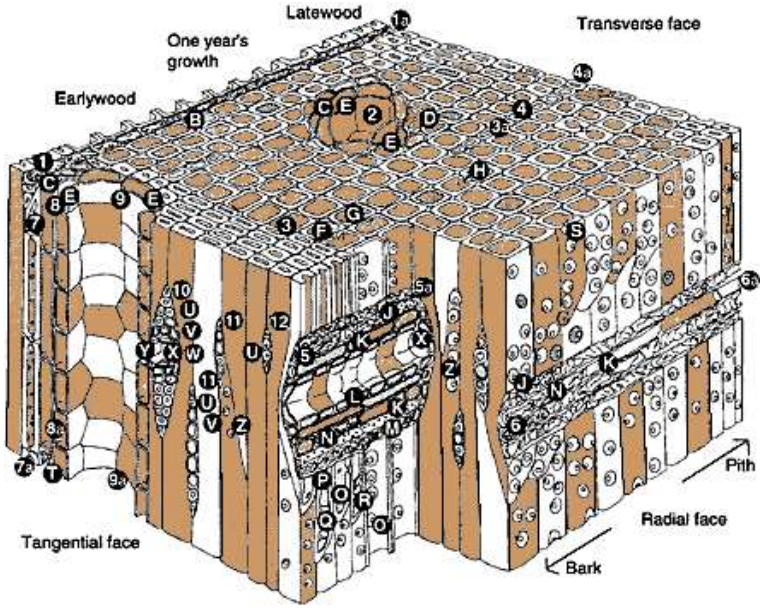
WWW.MPIE.DE
d.raabe@mpie.de

Class 2017

Natural materials





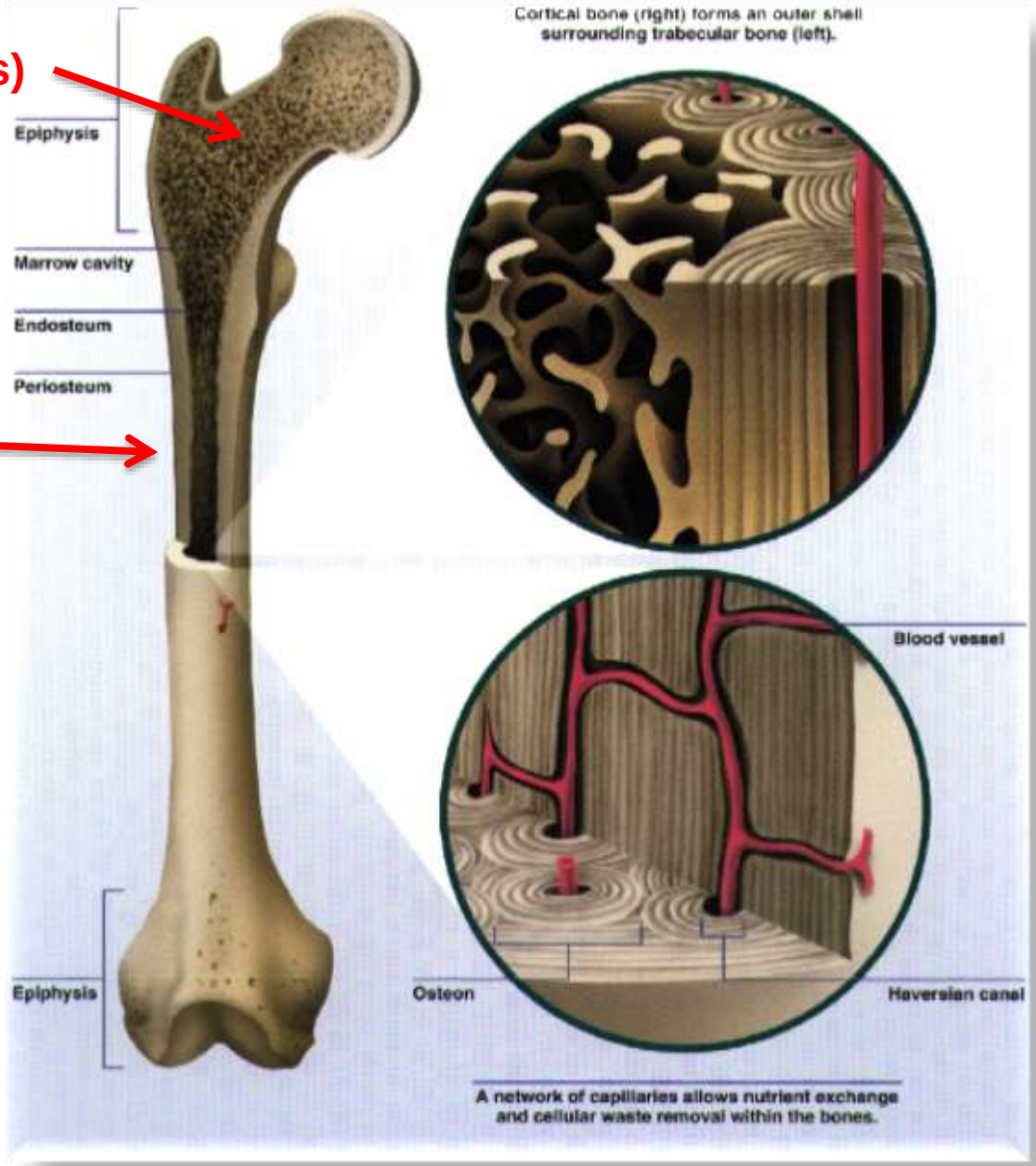


- complex structure
- hierarchical structure
- soft matter plus ceramics

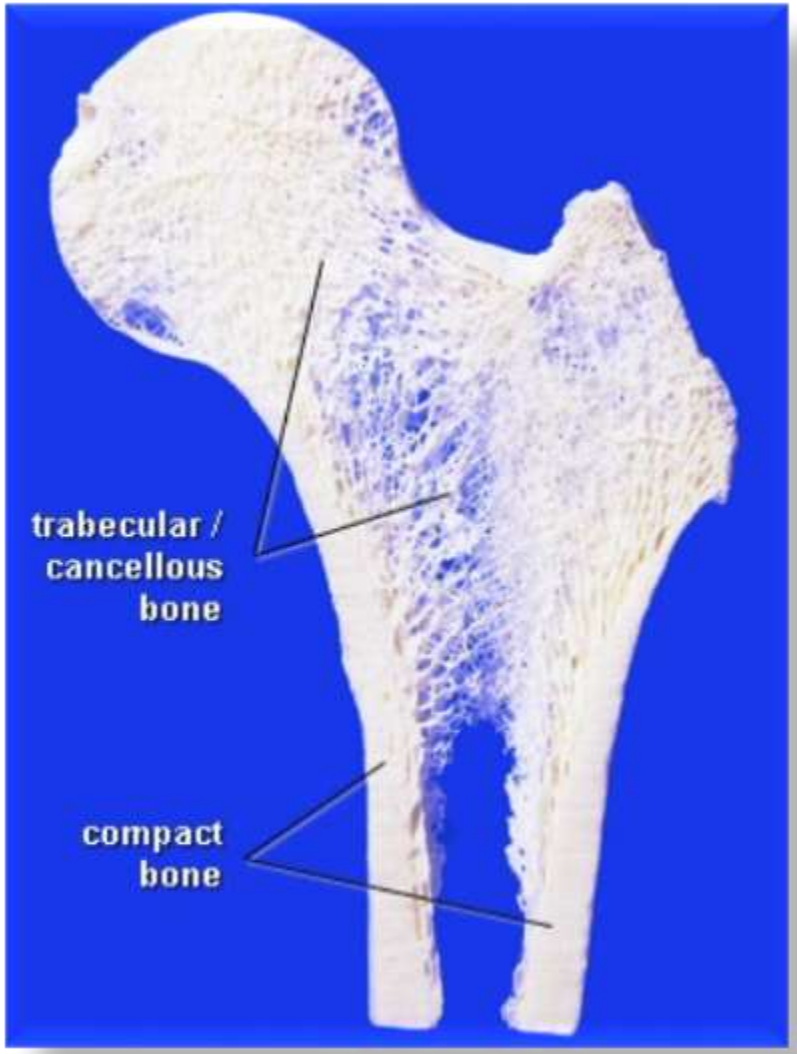
Bone

trabecular (cancellous) bone

cortical (compact) bone



Bone



Compact bone: mesoscopic structure

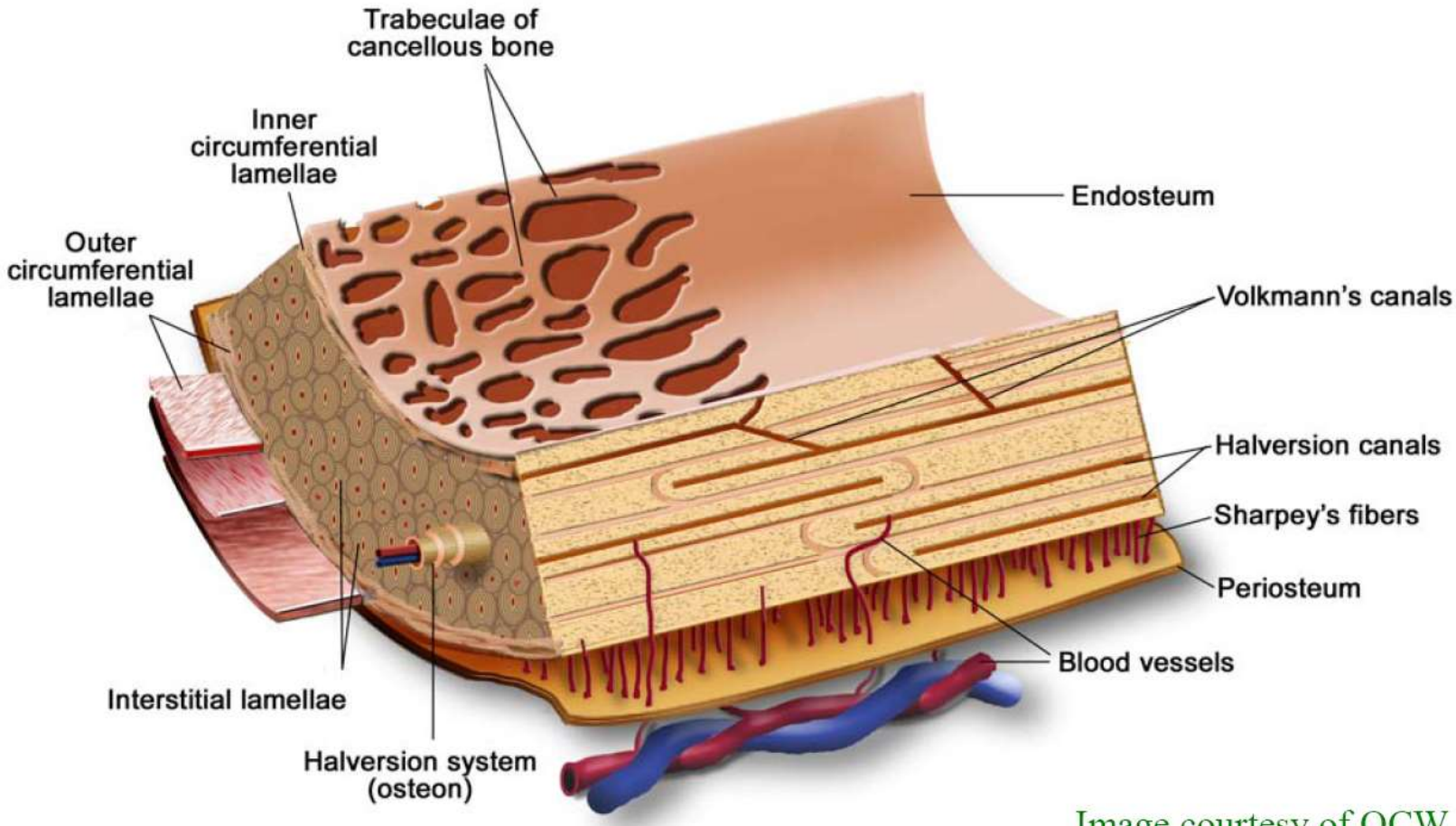
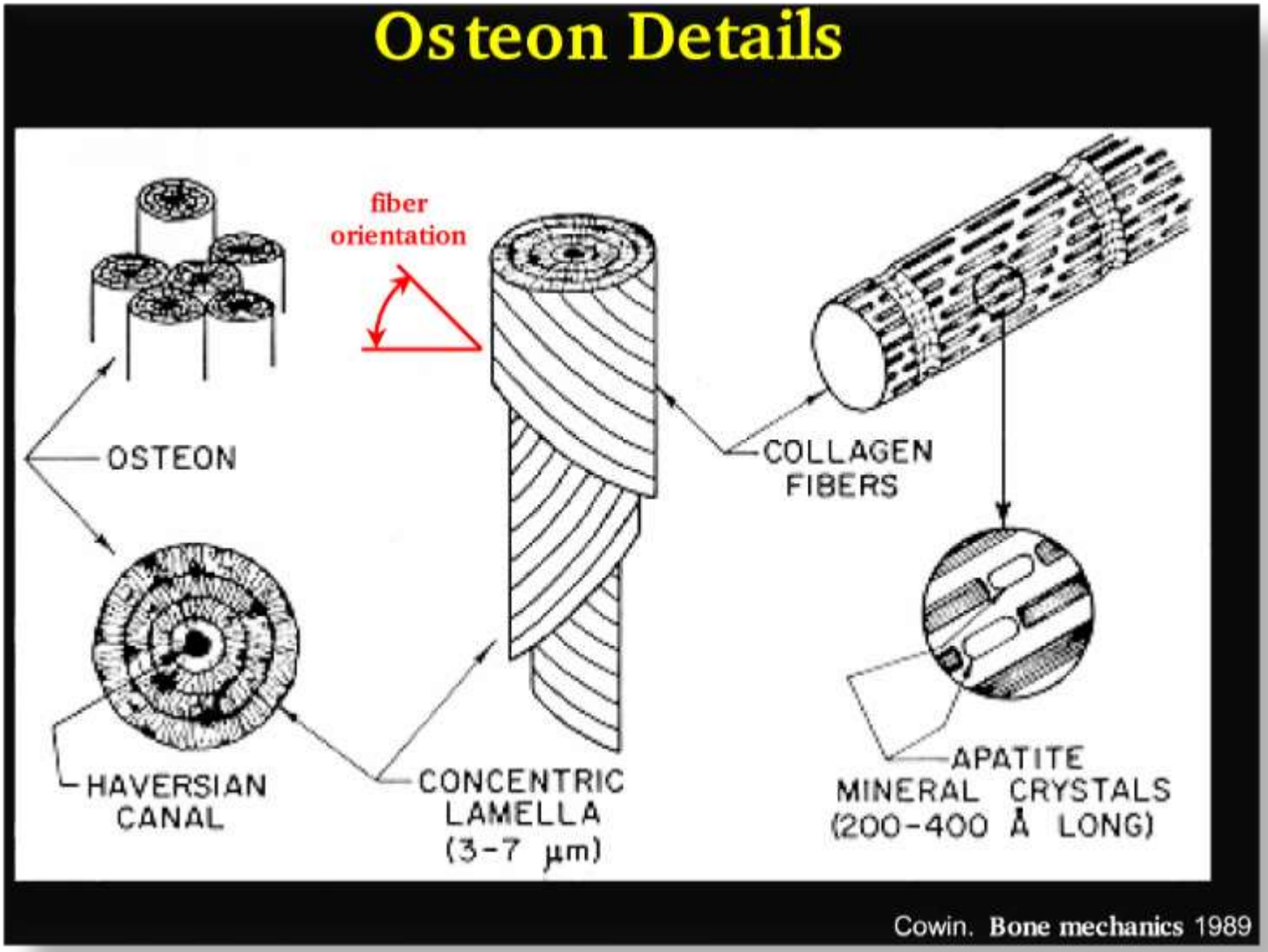
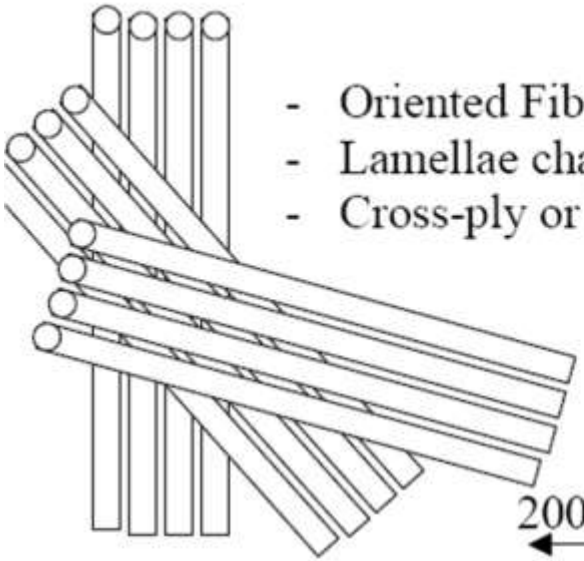


Image courtesy of OCW.
Adapted from figure in Martin, R.B. et al. *Skeletal Tissue Mechanics*. New York: Springer-Verlag, 1998

Bone: details of osteon structure



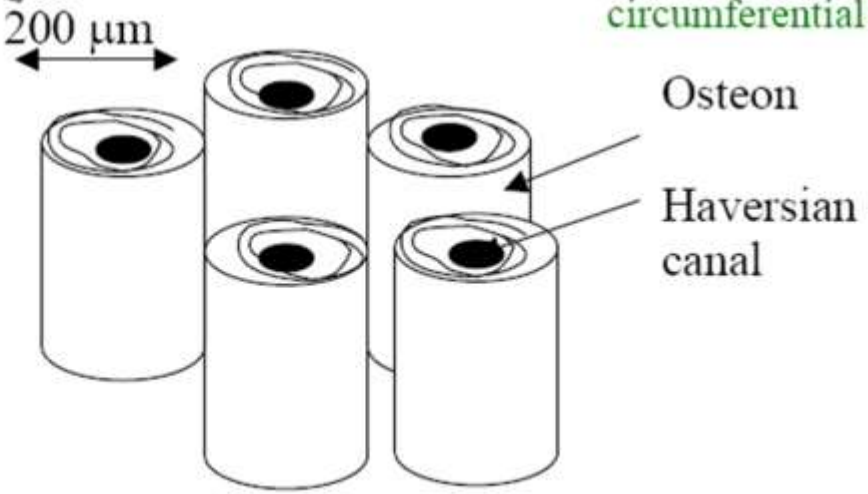
Bone: details of osteon structure



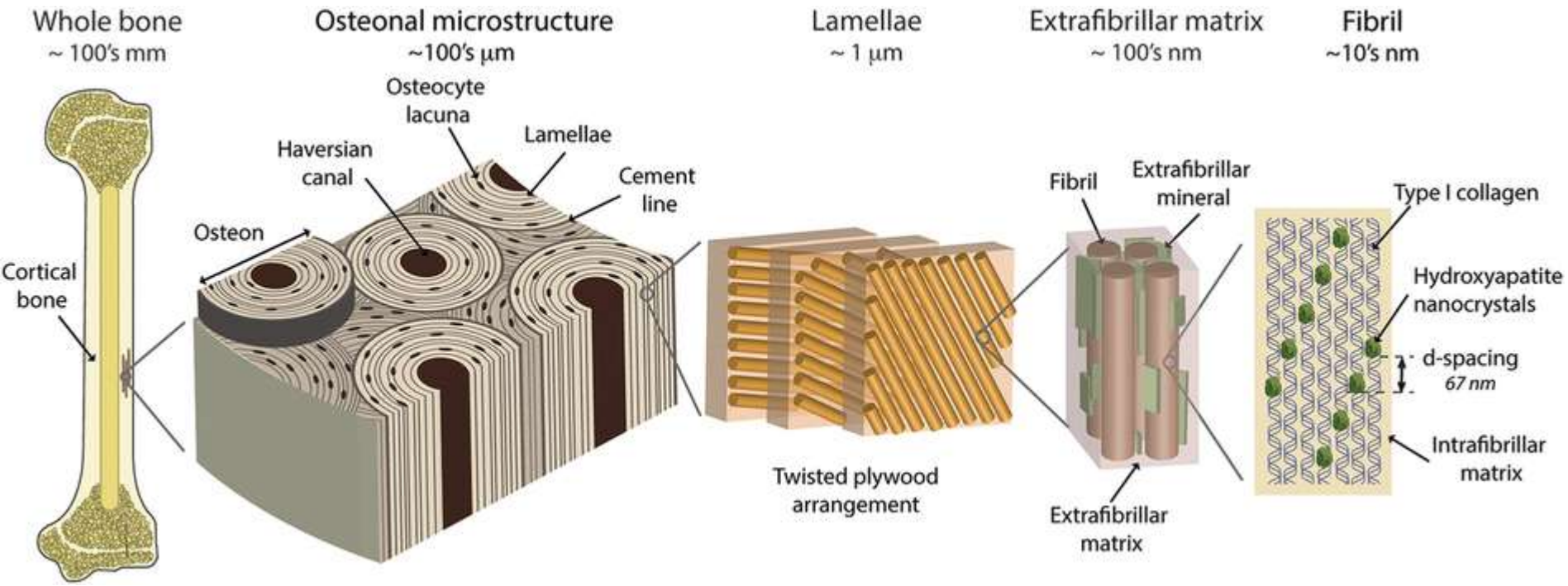
- Oriented Fibers form Lamellae
- Lamellae change orientation concentrically
- Cross-ply or Helicoid structures

In children:
- circumferential lamellae
-osteons around vessels

In adults:
-secondary osteons replace circumferential bone

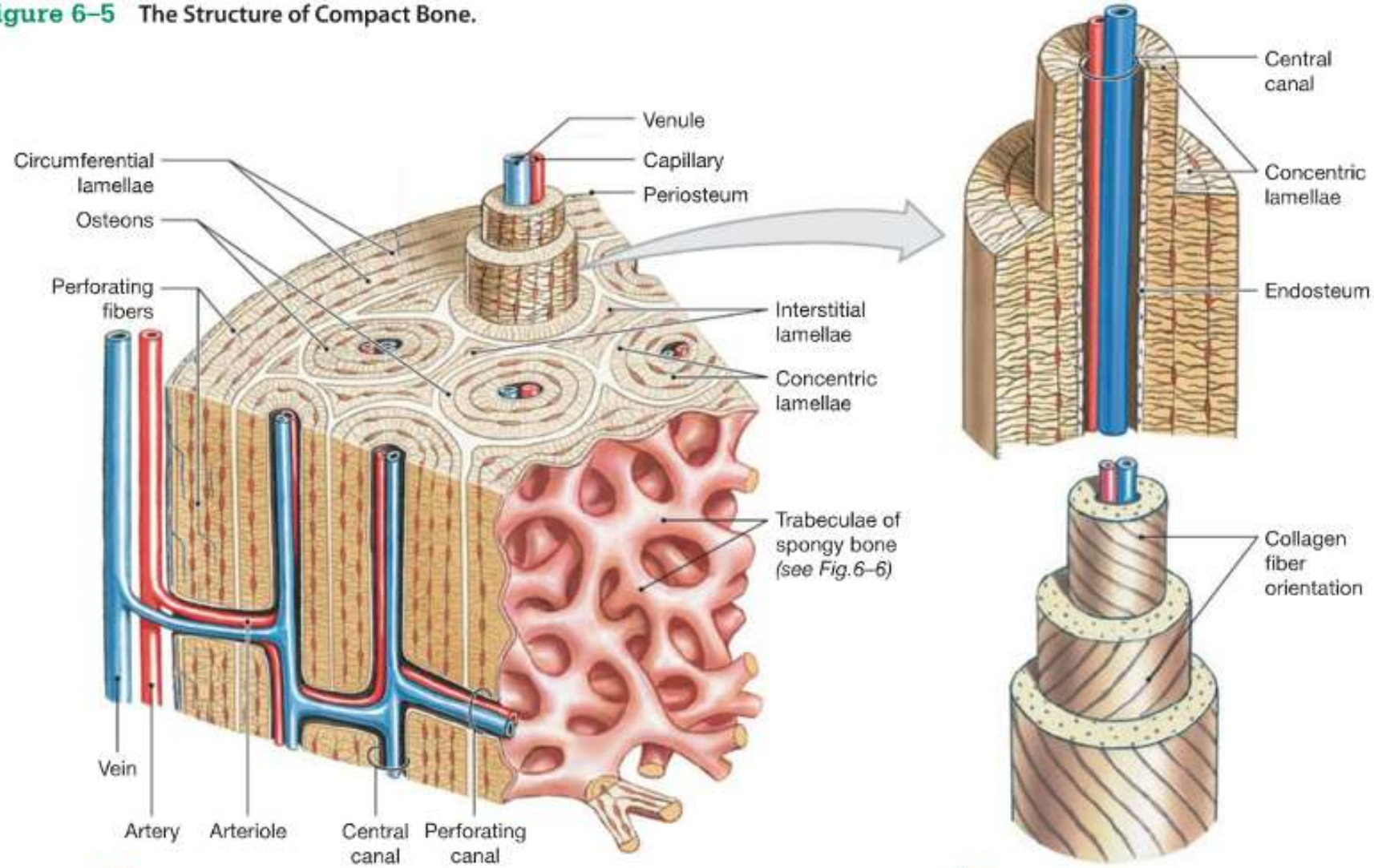


Bone: details of osteon structure: Overview



Bone: details of osteon structure: Overview

Figure 6–5 The Structure of Compact Bone.



a The organization of osteons and lamellae in compact bone

b The orientation of collagen fibers in adjacent lamellae

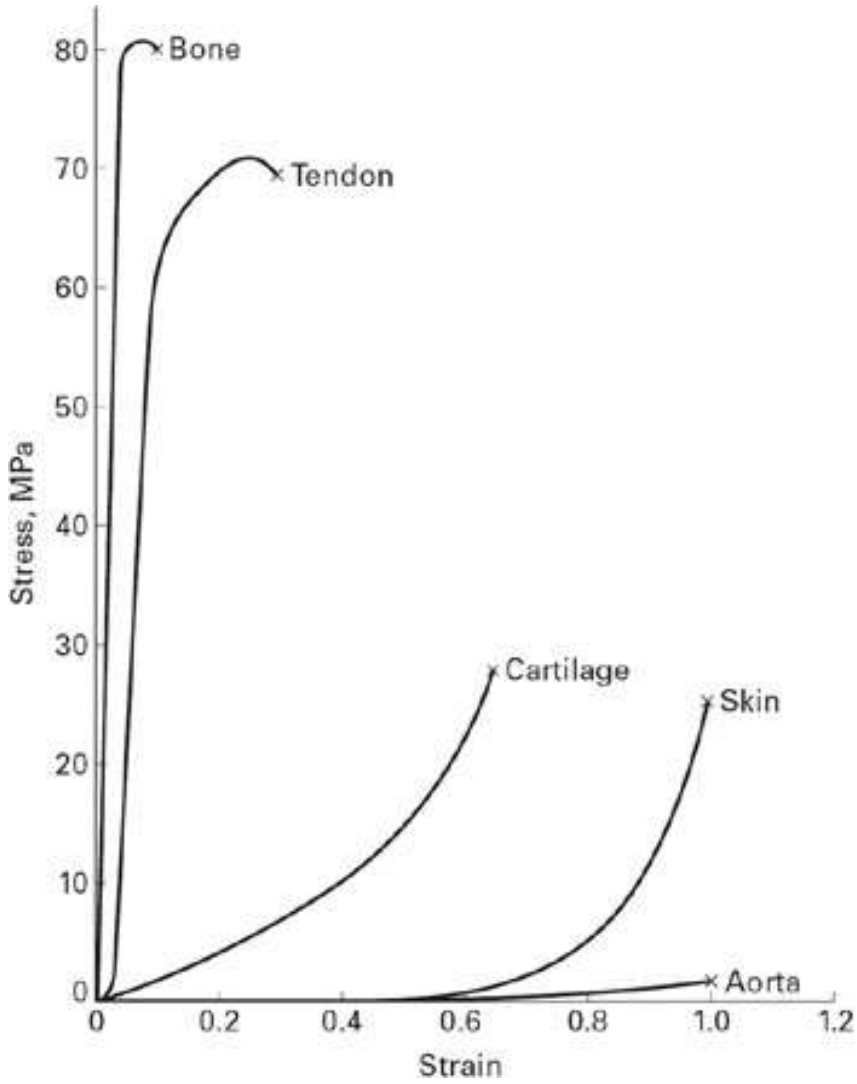
Bone: macroscopic mechanical properties: human materials

Very high variety by structure modifcation, particularly mineral content modifcation

Self-repair

Stiffness scaling by mineral content

	Ultimate Comp. Str. (MPa)	Modulus of Elasticity (GPa)
Cortical Bone	140 - 200	14 - 20
Cancellous Bone	5 - 60	0.7 - 1.5
Synthetic HA	200 - 900	34 - 100
Bone Mineral	25 (anorganic bone)	6



chitin: 3 examples

- Homarus americanus

- Carabus auronitens

- Chrysophanes virgaurea

Introduction - Arthropod cuticle

Main exoskeleton component of more than 90% of all animal species …

adaptive material → candidate for bio-inspired material

Crustacean cuticle (subgroup of arthropods)

- cuticle surrounds the whole animal
- forms different skeletal elements
- cover a vast variety of physical properties
- adapted to:
  - the specific function of the skeletal element
  - ecophysiological strains of the animal

Birgus latro

Porcellio scaber

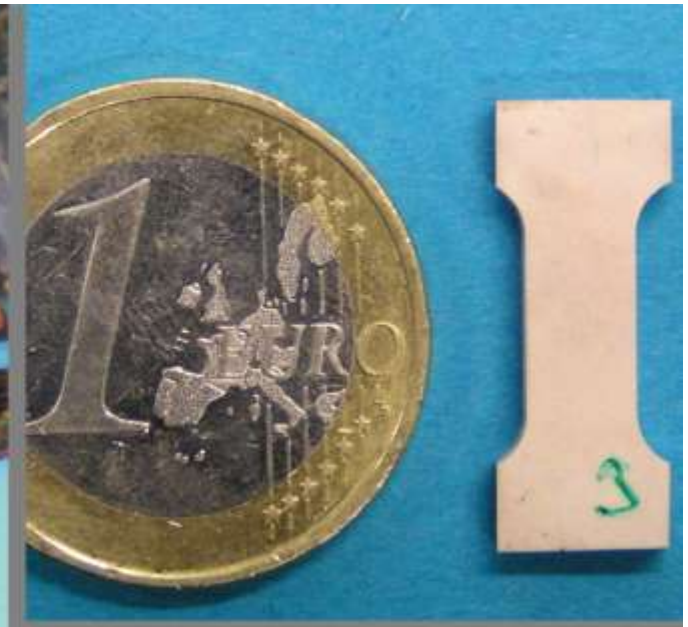
Armadillidium vulgare

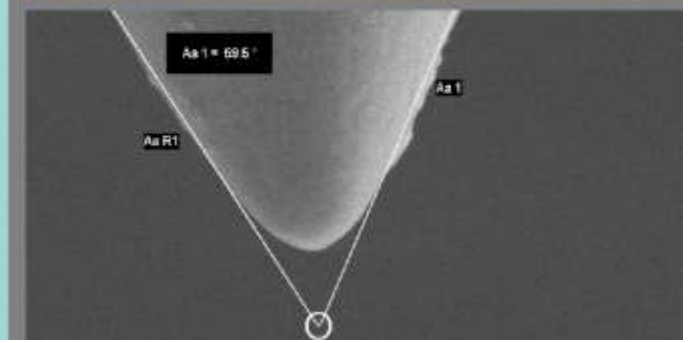
Horseshoe crab

Homarus americanus

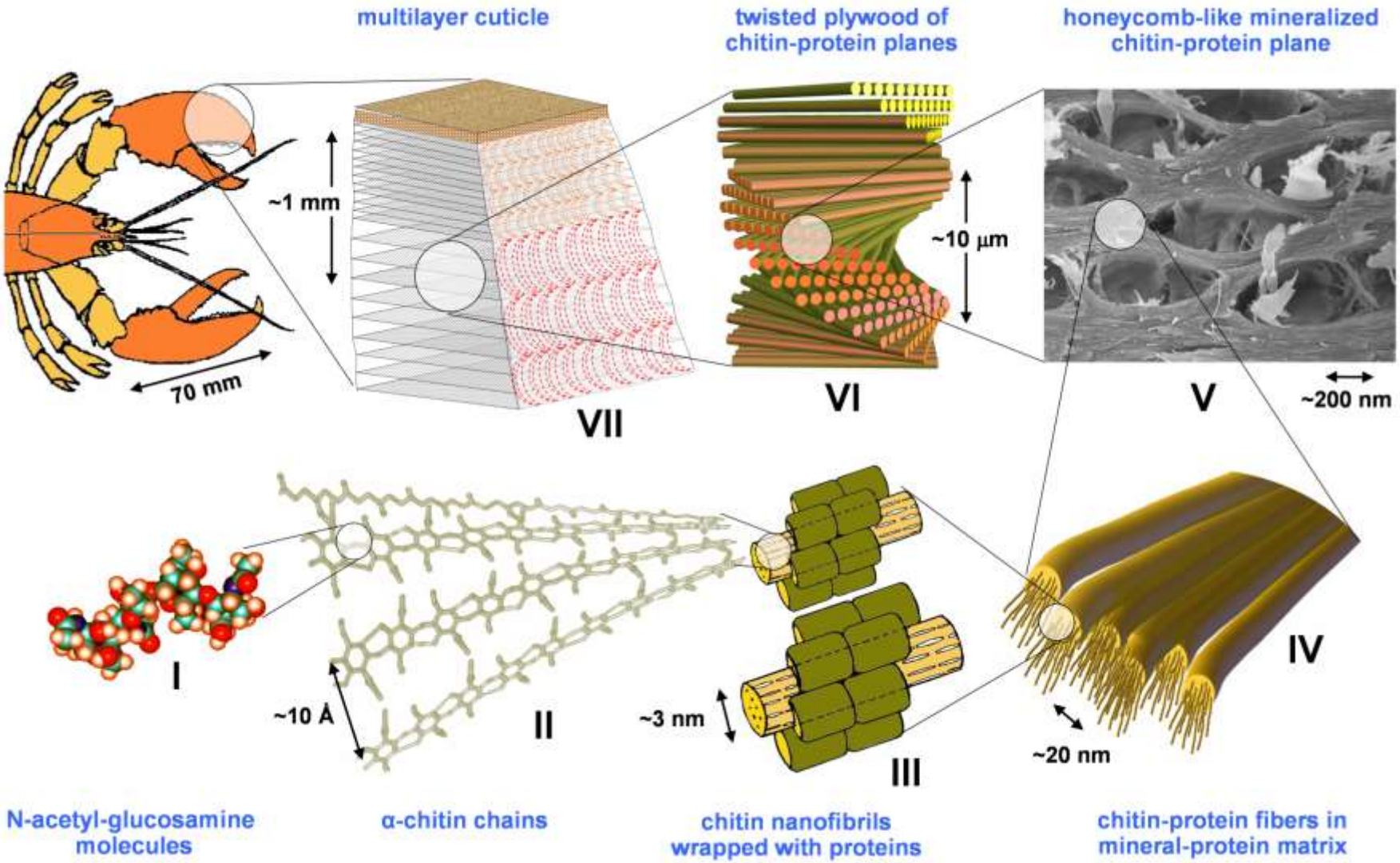
- hierarchical structure follows the same principle regardless of the specific properties of the cuticle

The materials science of the arthropods

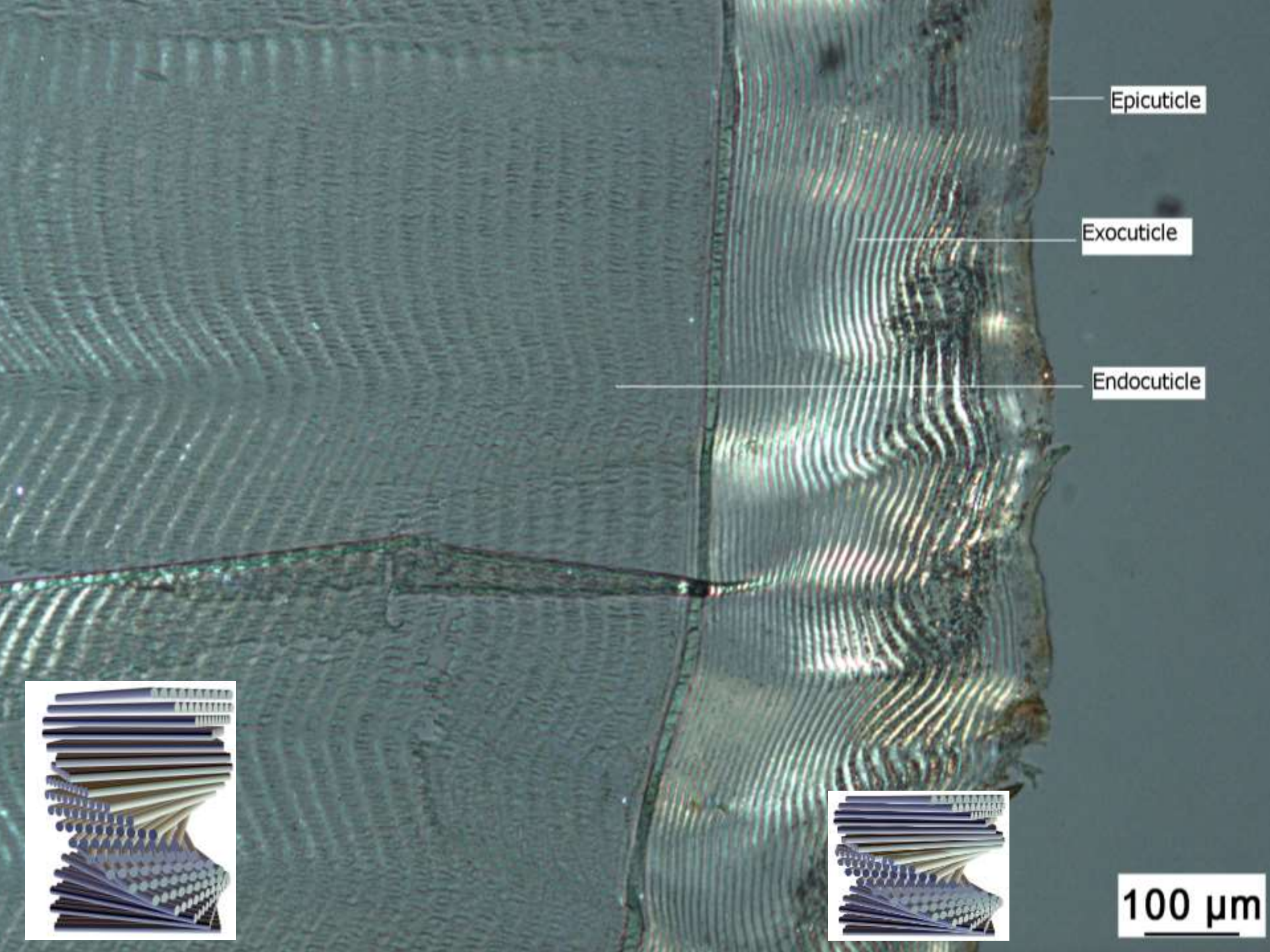


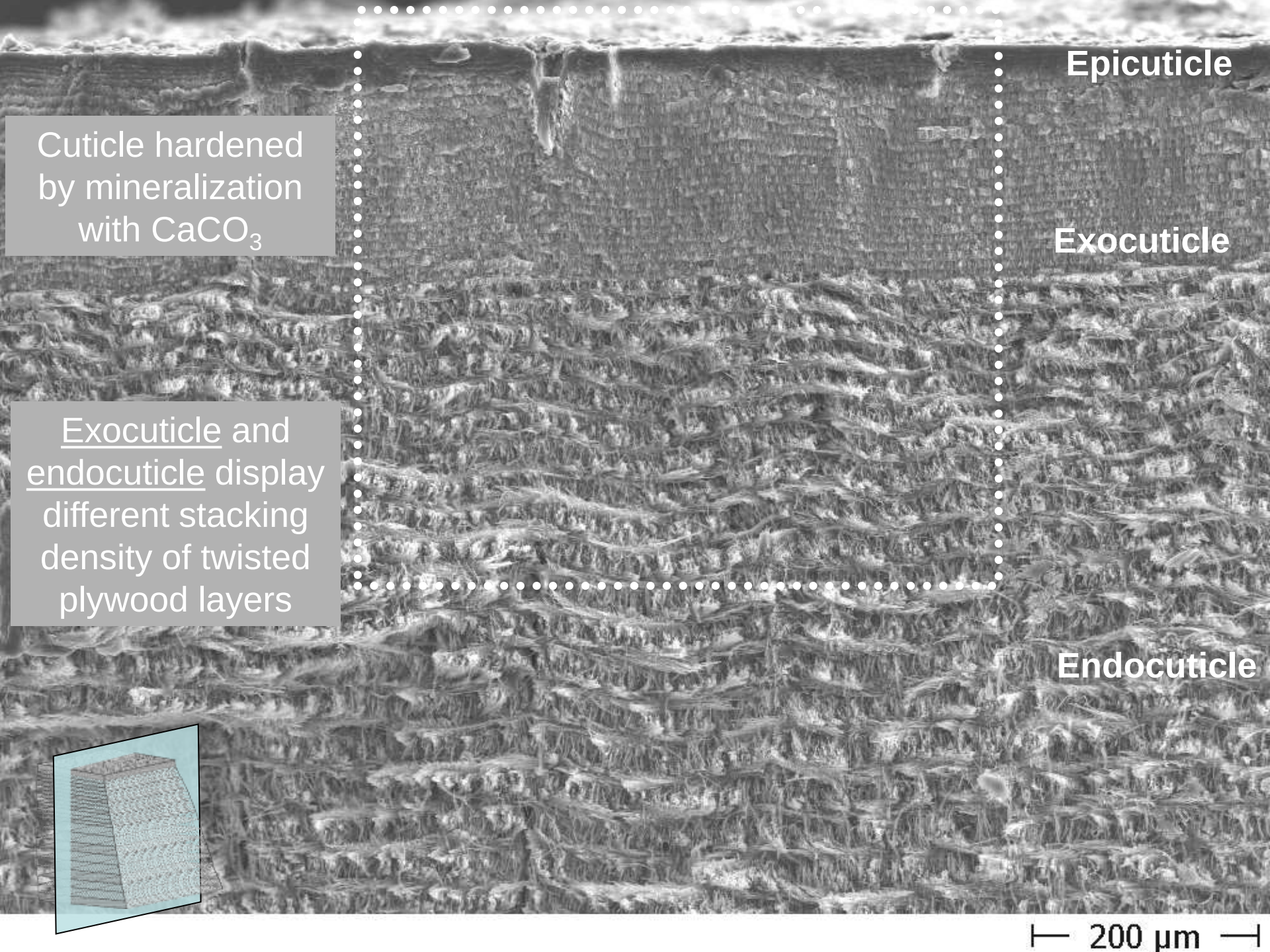


Structure hierarchy of arthropods



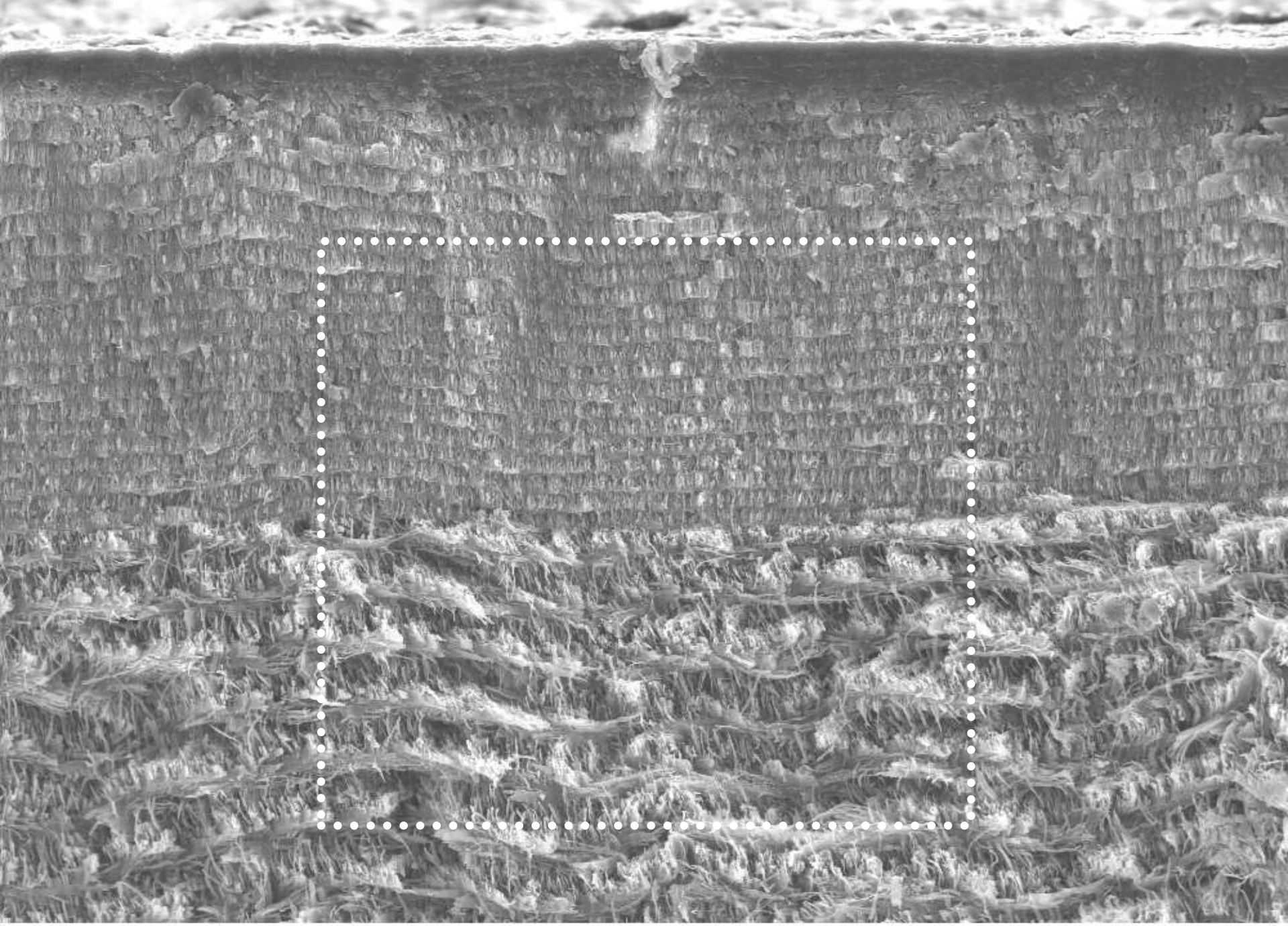
Al-Sawalmih, C. Li, S. Siegel, H. Fabritius, S.B. Yi, D. Raabe, P. Fratzl, O. Paris: Advanced functional materials 18 (2008) 3307
H. Fabritius, C. Sachs, S. Nikolov, and D. Raabe, Advanced materials

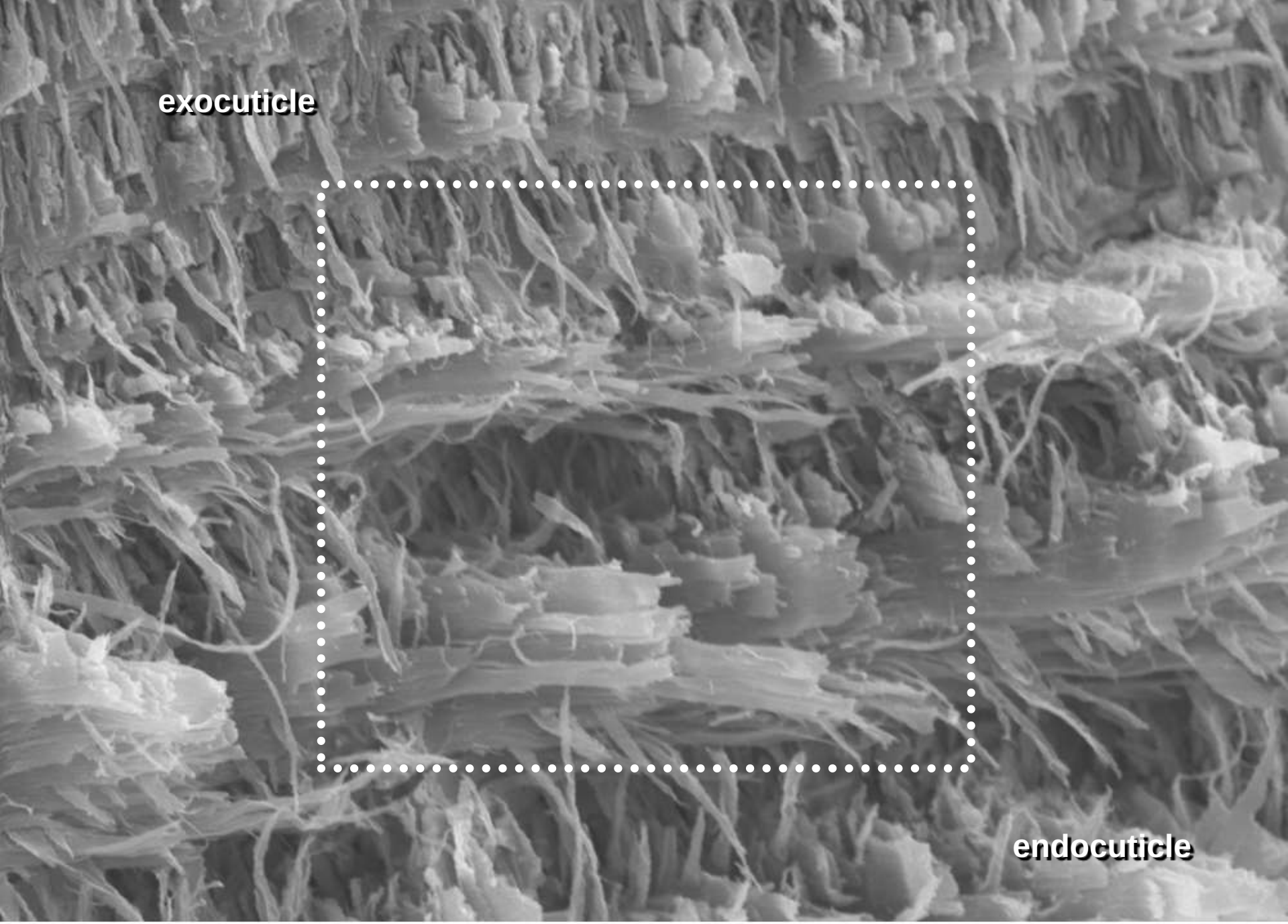

Epicuticle
Exocuticle
Endocuticle
100 µm

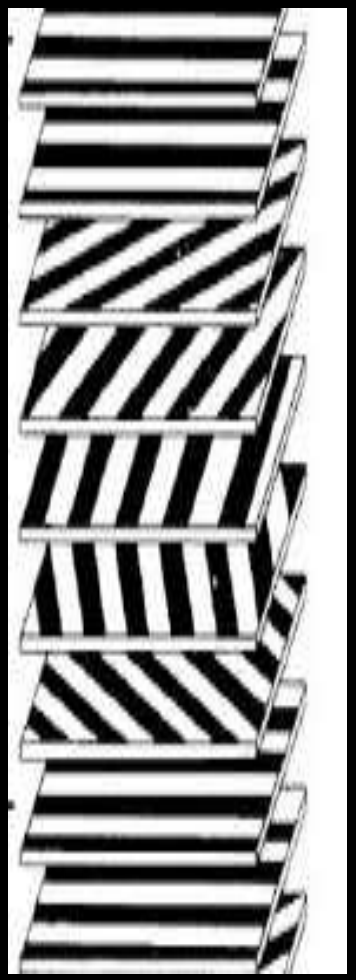


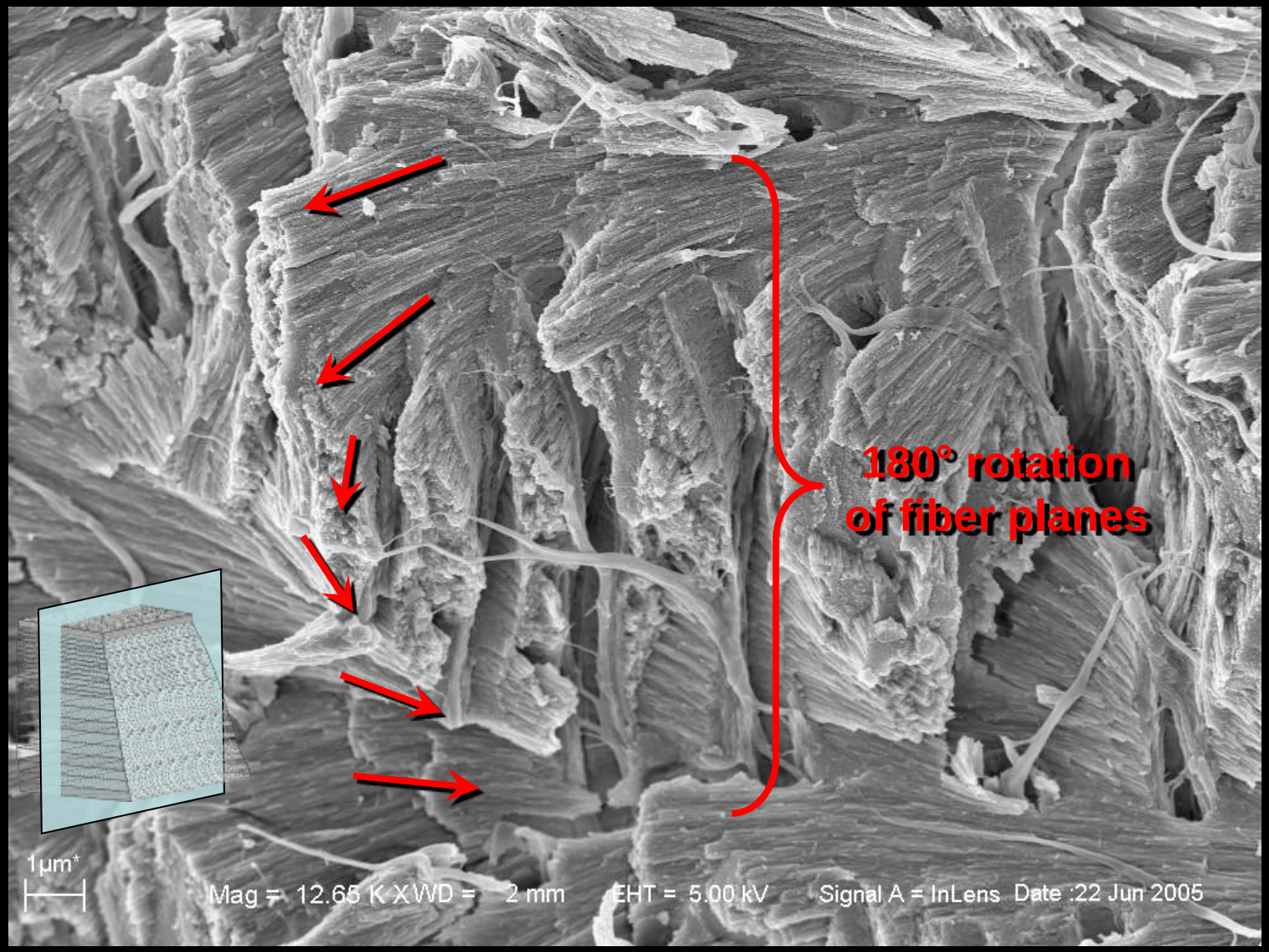
Cuticle hardened by mineralization with $CaCO_3$

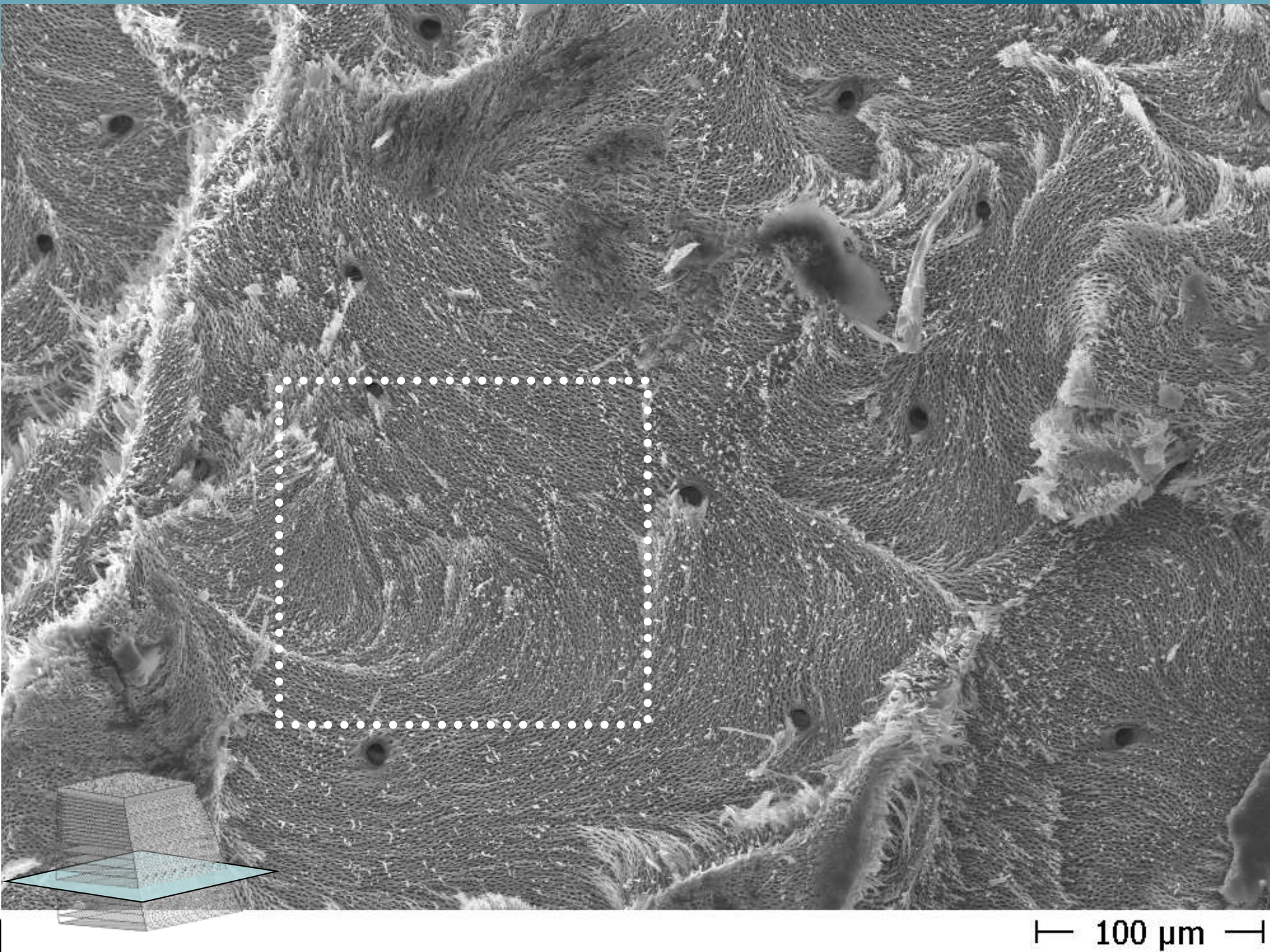
Exocuticle and endocuticle display different stacking density of twisted plywood layers

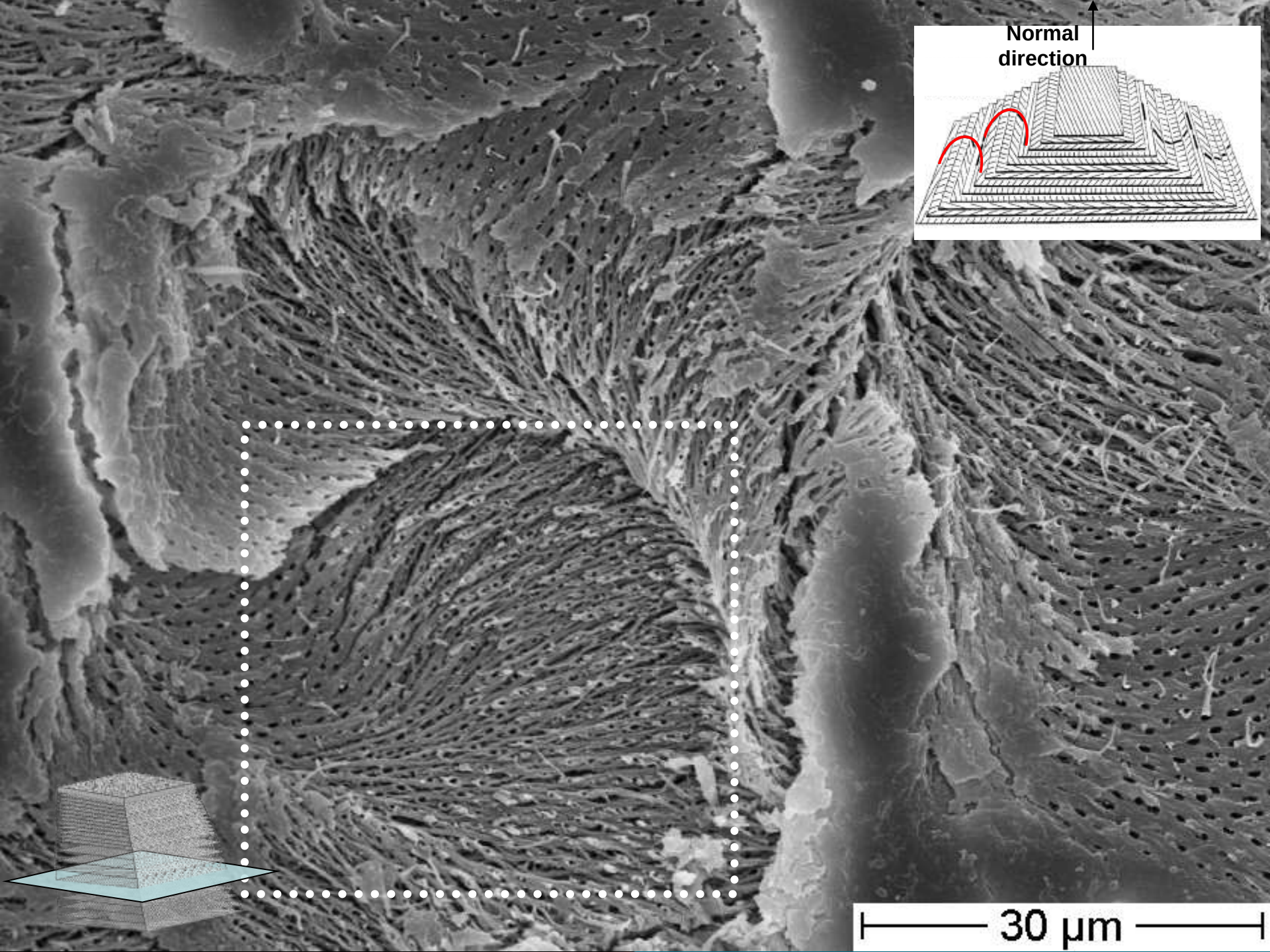

100 µm

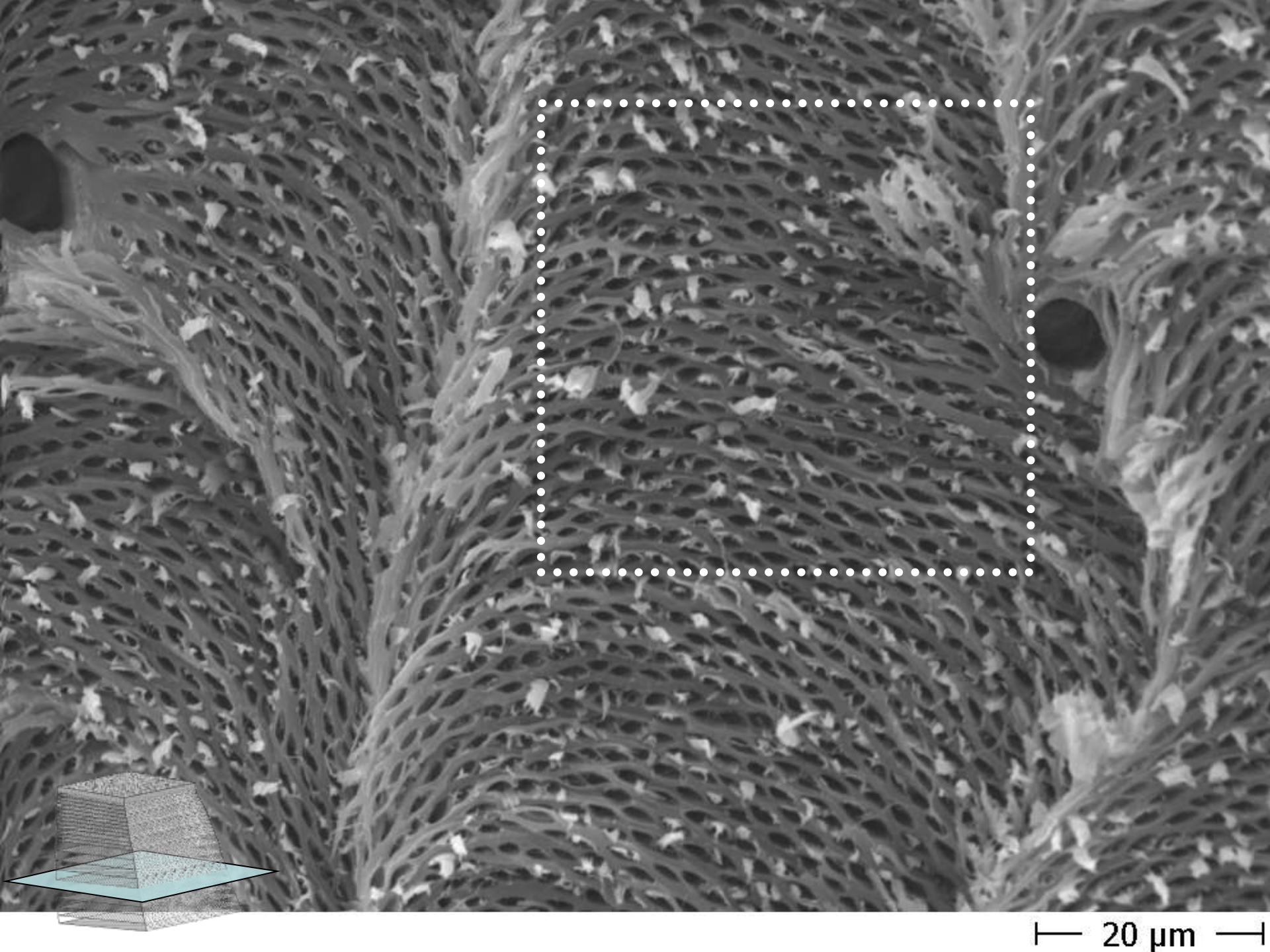

exocuticle
endocuticle
10 µm

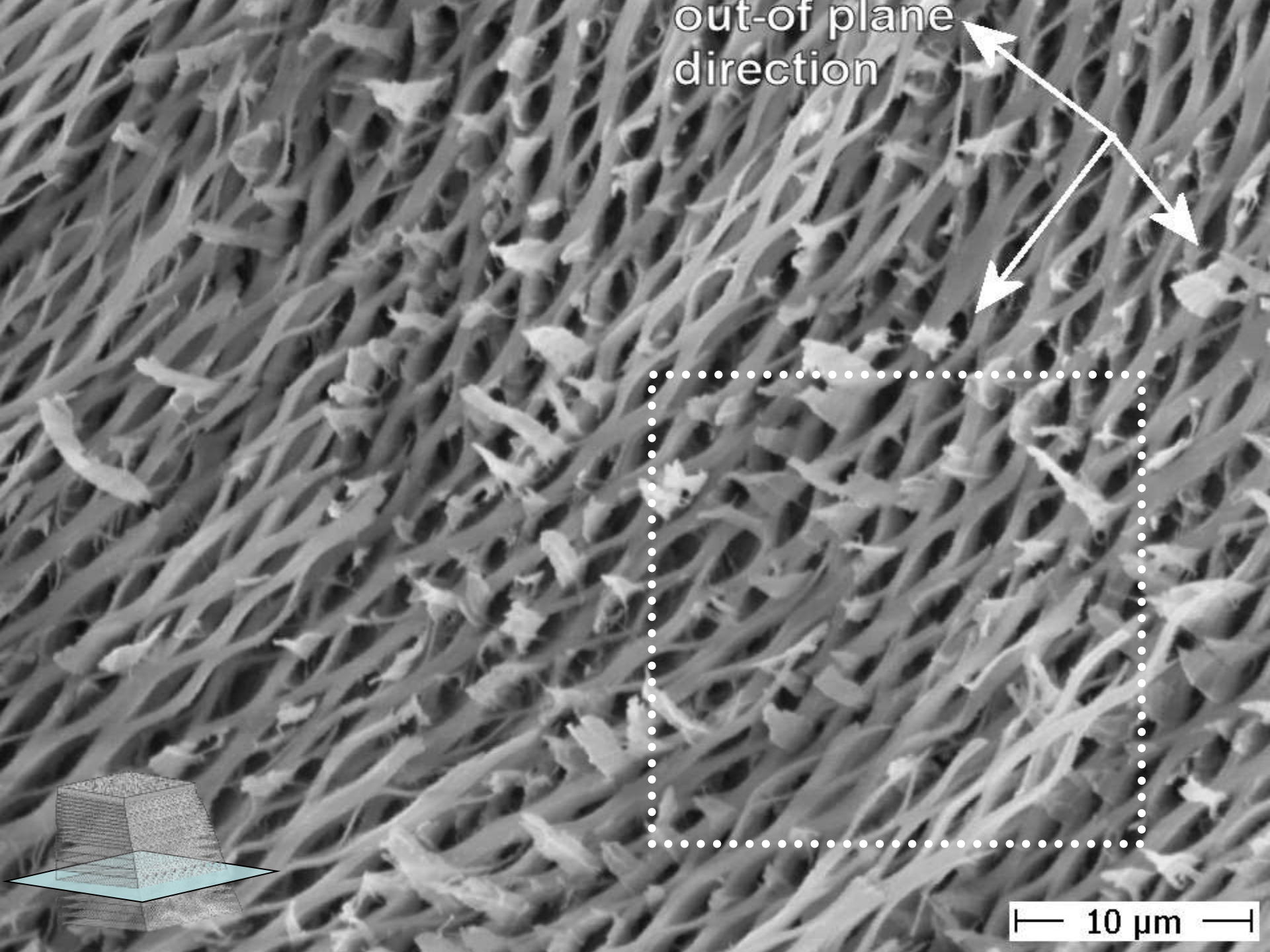


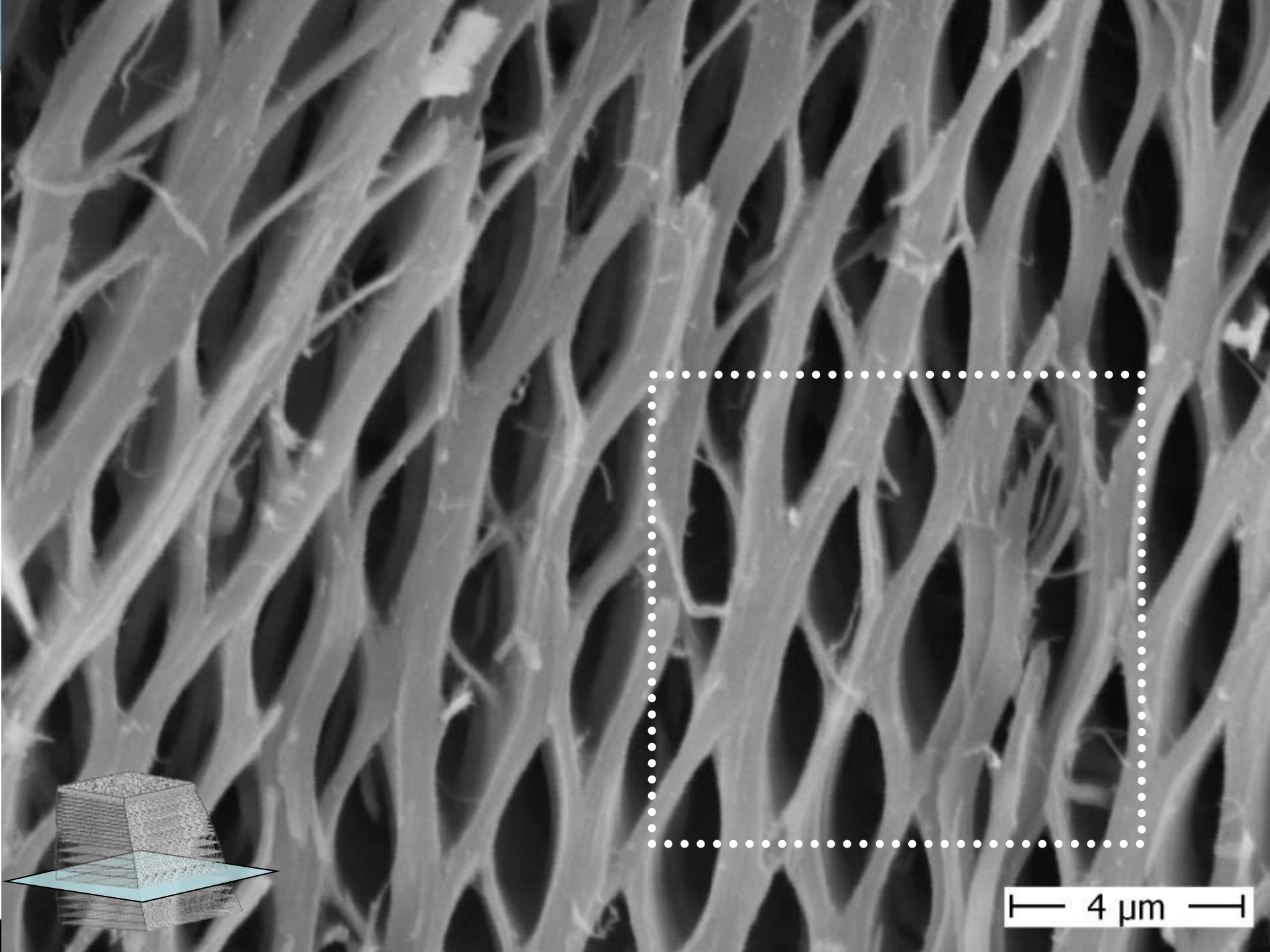

180° rotation
of fiber planes
1µm*
Mag = 12.66 K X WD = 2 mm
EHT = 5.00 kV
Signal A = InLens Date :22 Jun 2005

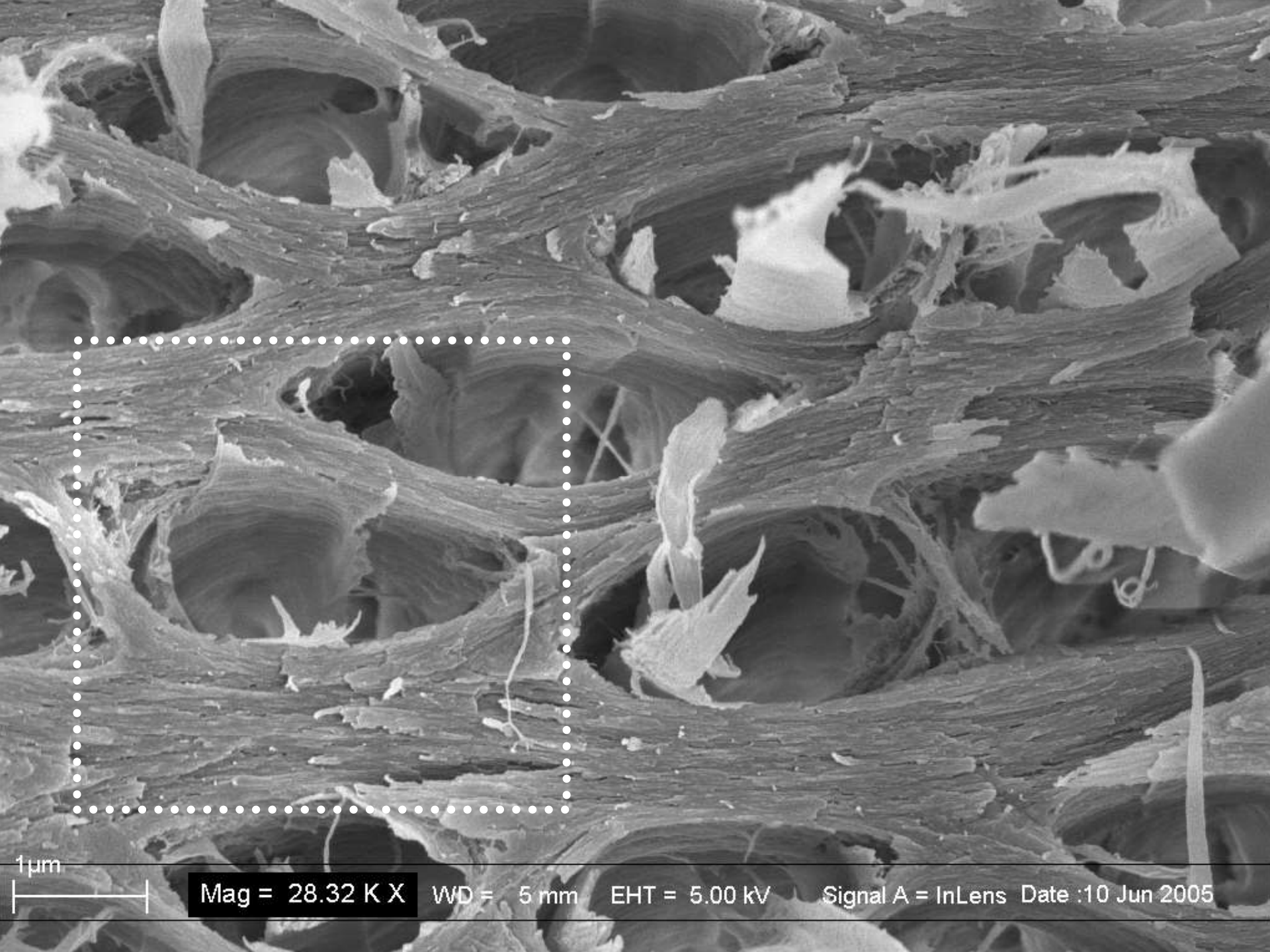

100 µm

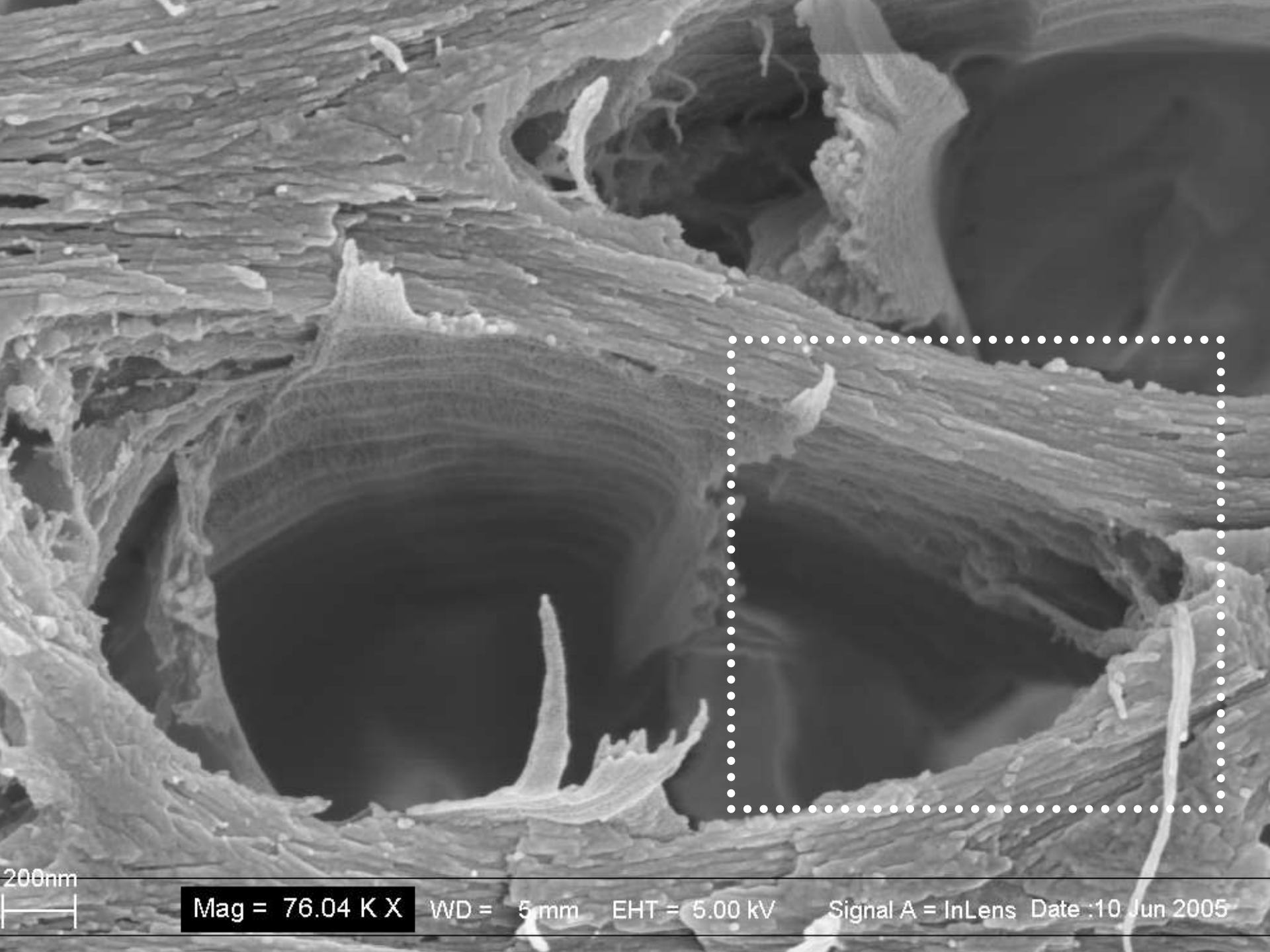

Normal
direction
30 µm


20 µm

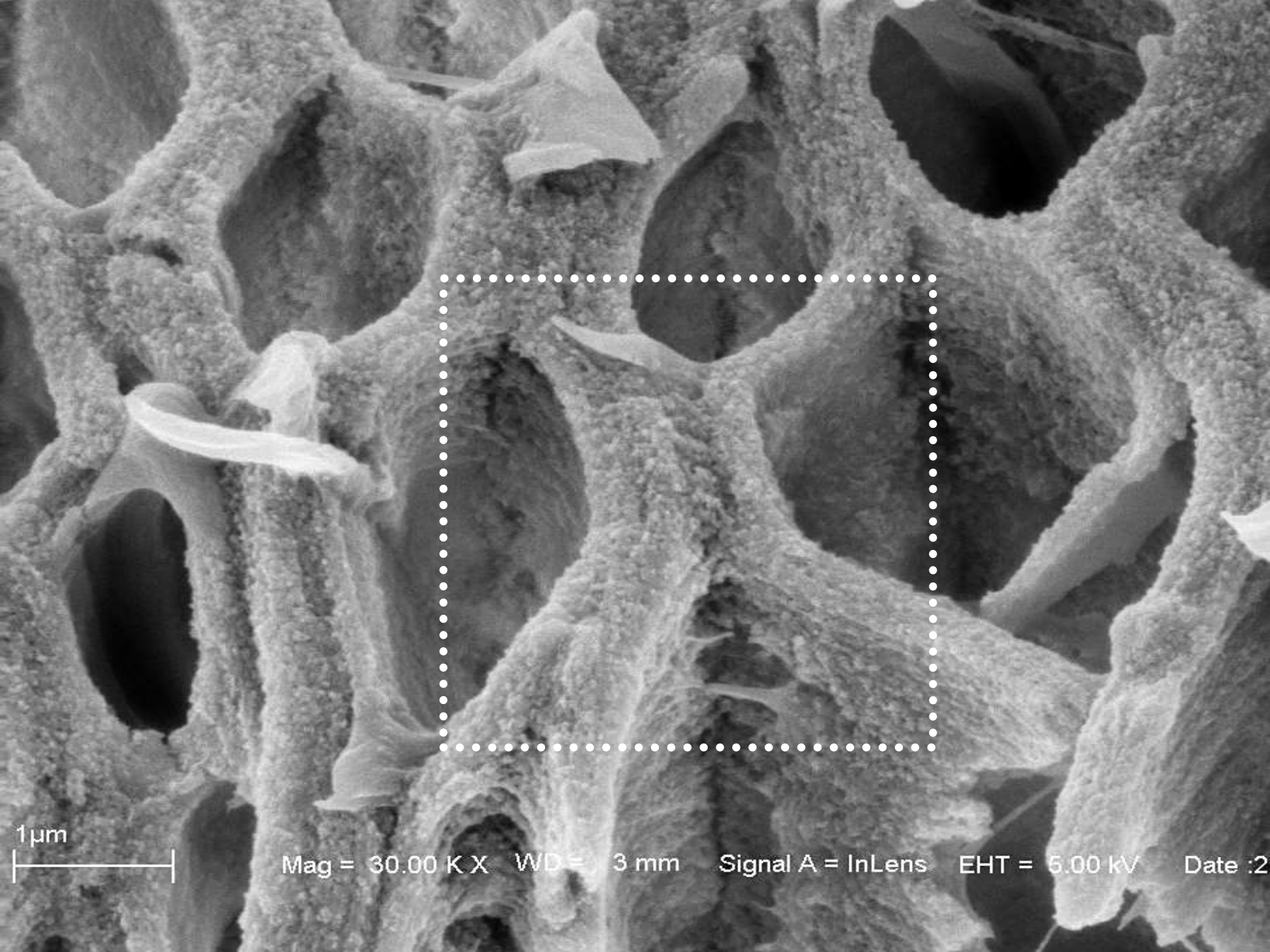

out-of plane
direction
10 µm


4 µm


1µm
Mag = 28.32 K X
WD = 5 mm
EHT = 5.00 kV
Signal A = InLens
Date :10 Jun 2005

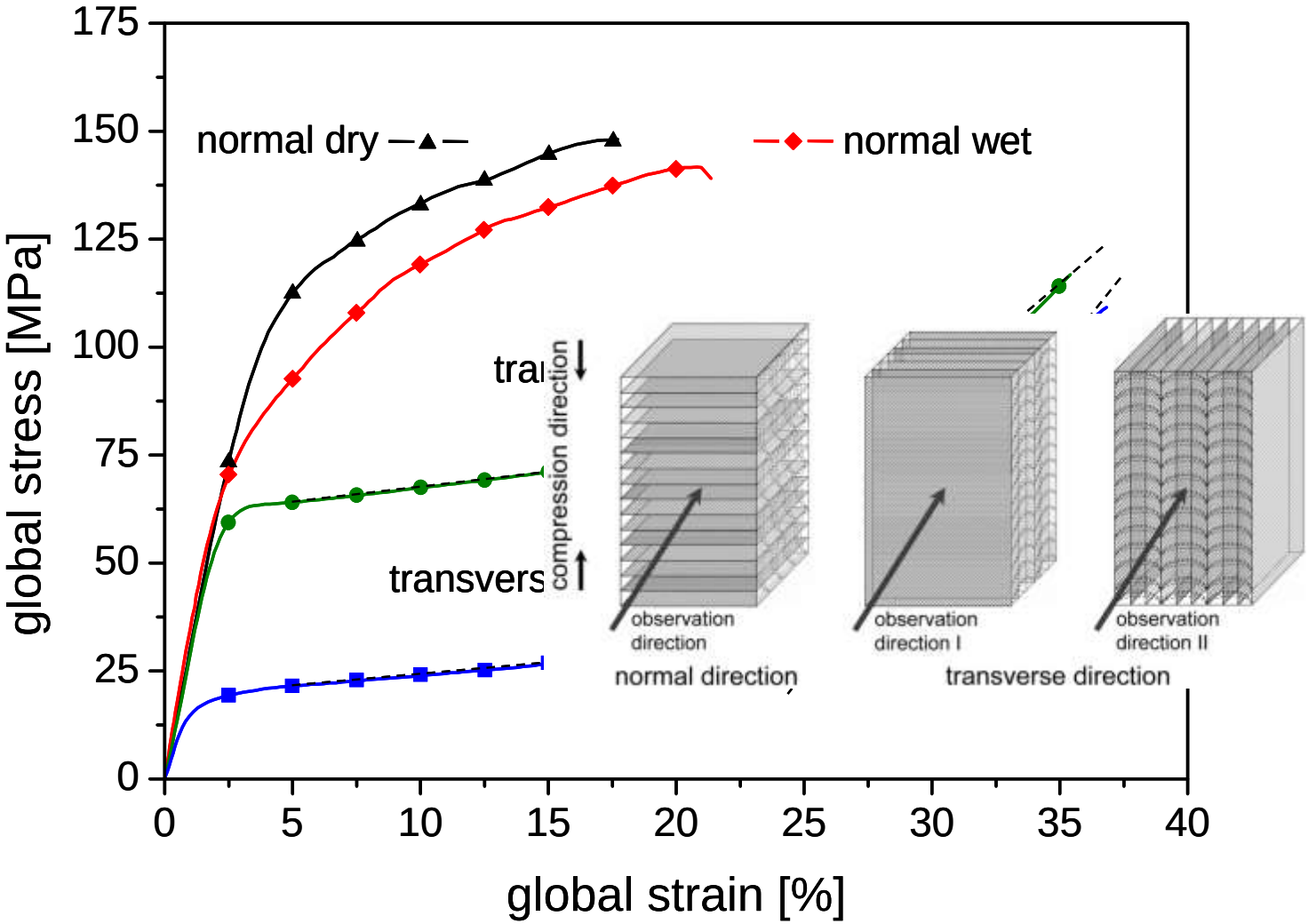

200nm
Mag = 76.04 K X
WD = 5 mm
EHT = 5.00 kV
Signal A = InLens
Date :10 Jun 2005

100nm
Mag = 133.31 K X
WD = 5 mm
EHT = 5.00 kV
Signal A = InLens Date :9 Jun 2005

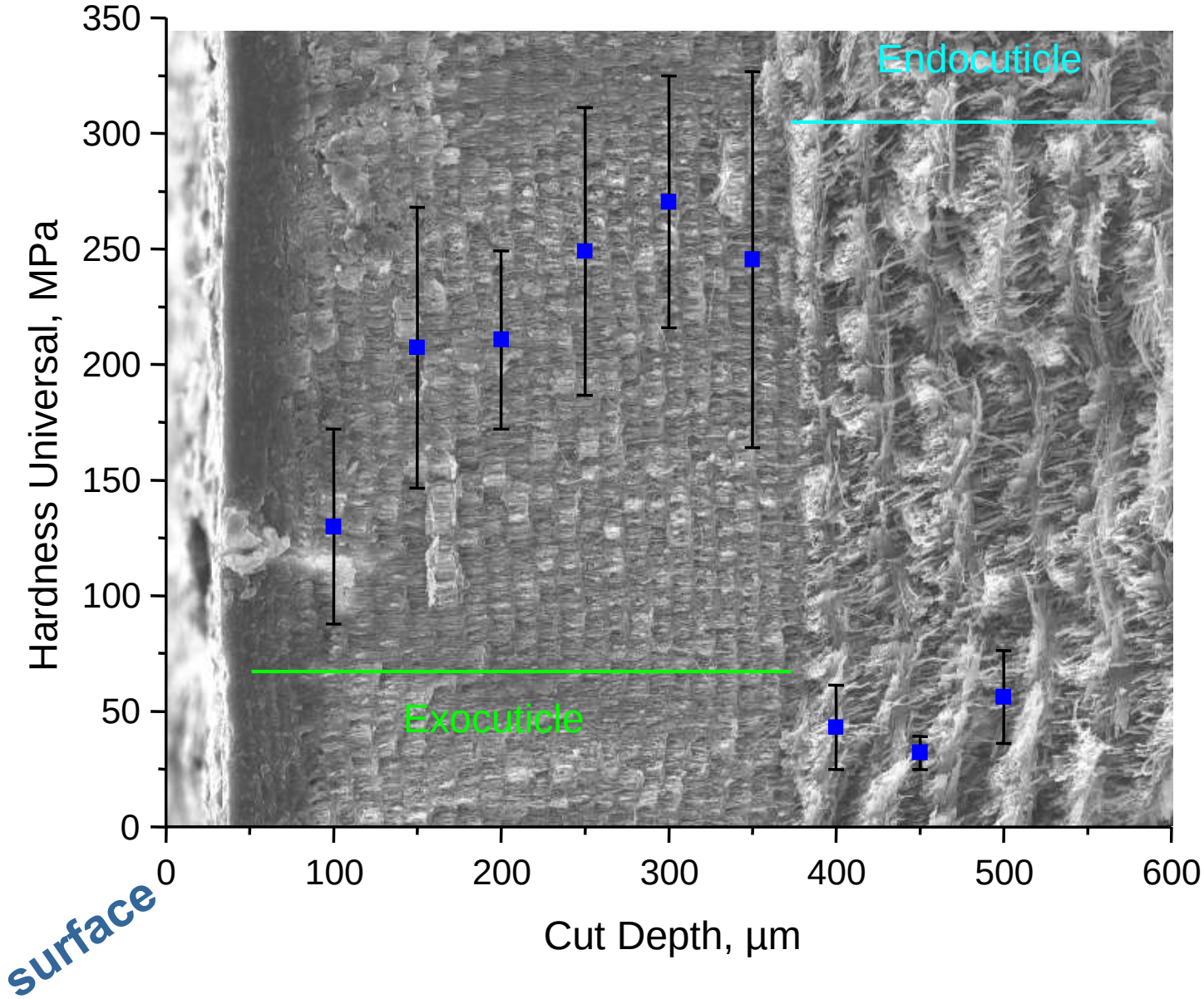

1µm
Mag = 30.00 K X
WD = 3 mm
Signal A = InLens
EHT = 5.00 kV
Date :2

200nm
Mag = 100.00 K X WD = 3 mm Signal A = InLens EHT = 5.00 kV Date :20 Ja

Compression tests (macroscopic), lobster

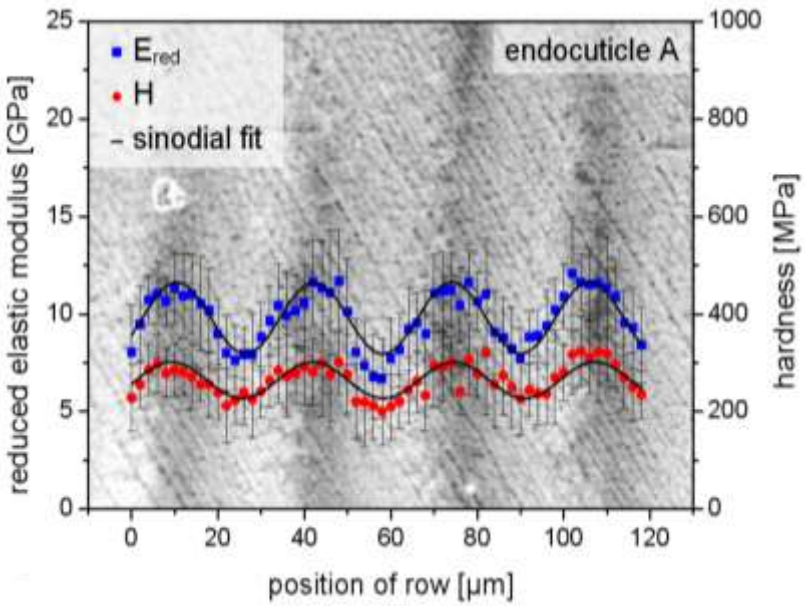


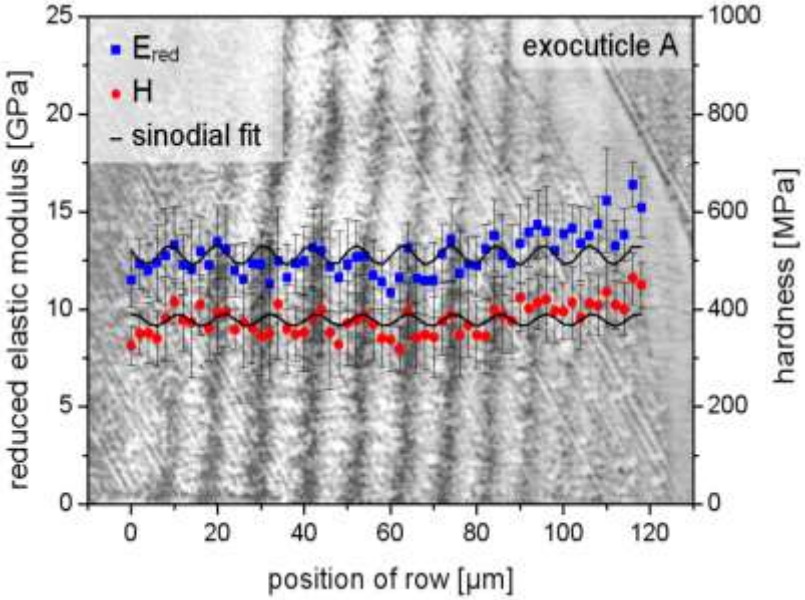
Hardness (mesoscopic)



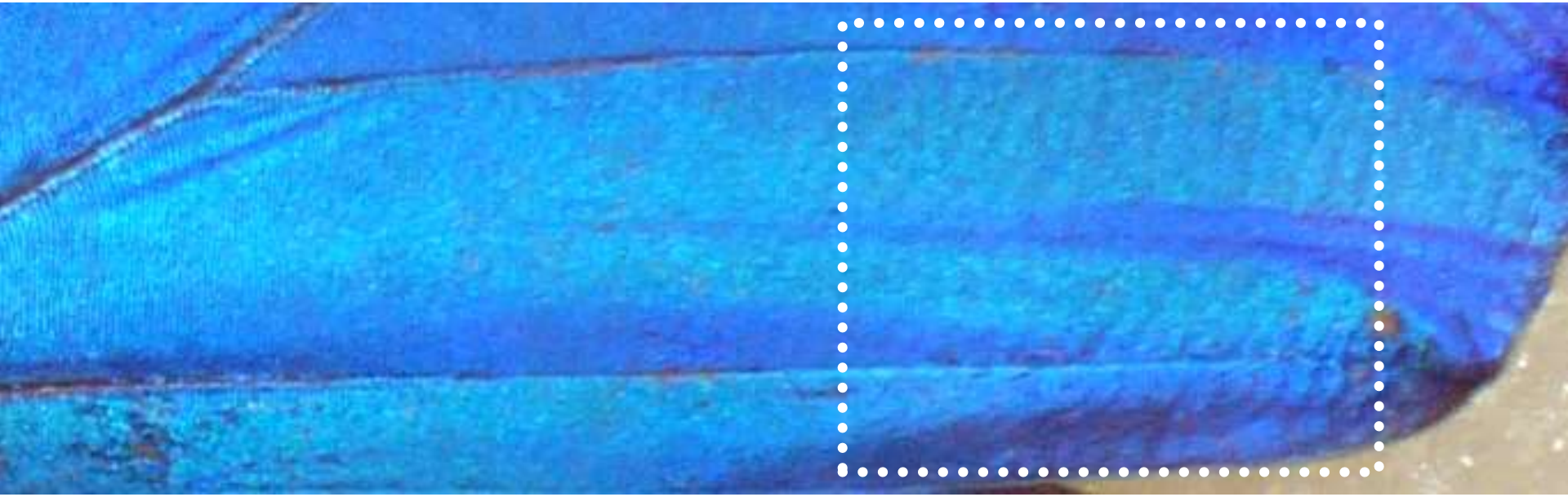
Mechanical properties (microscopic)

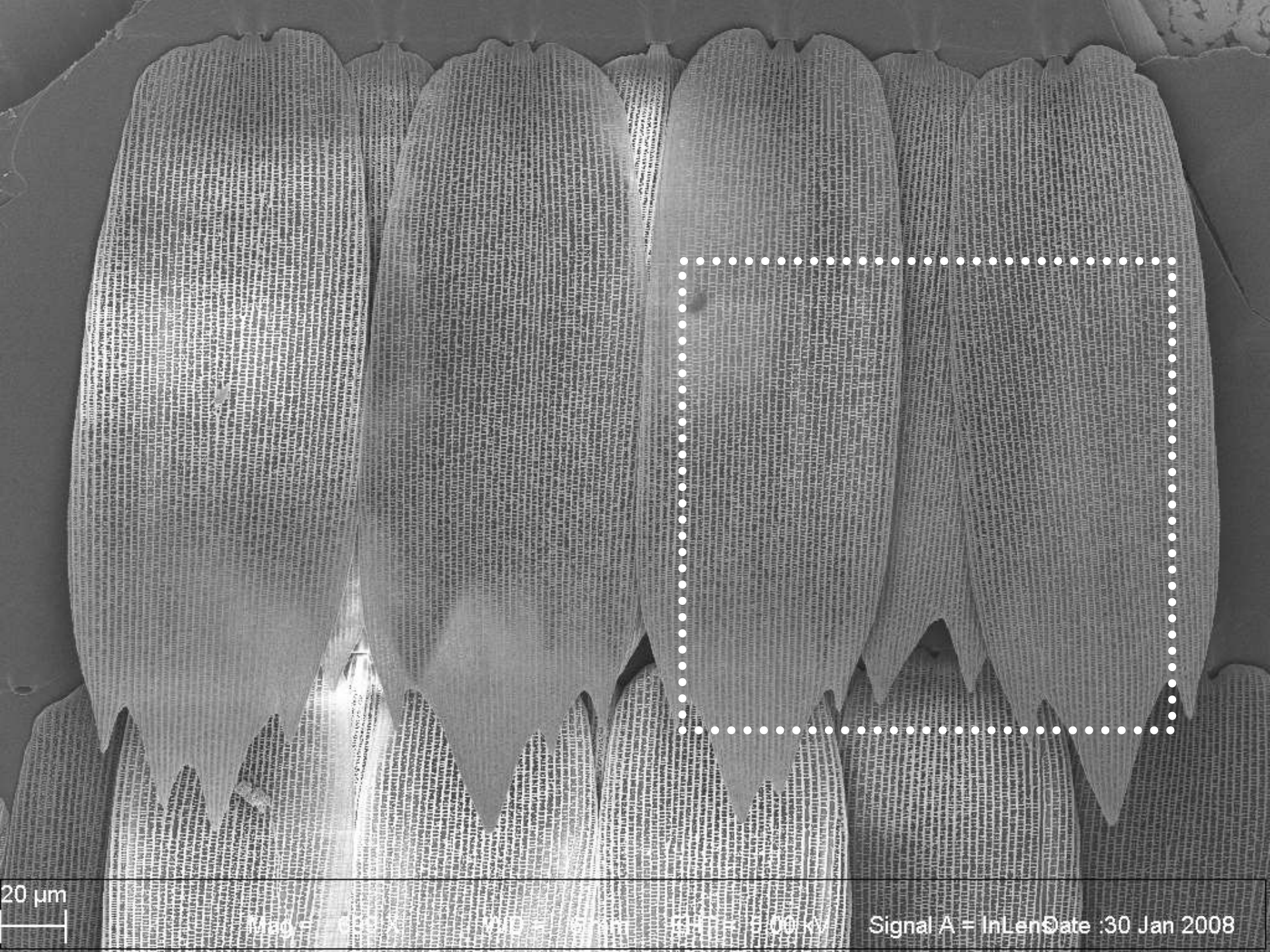
nanoindentation

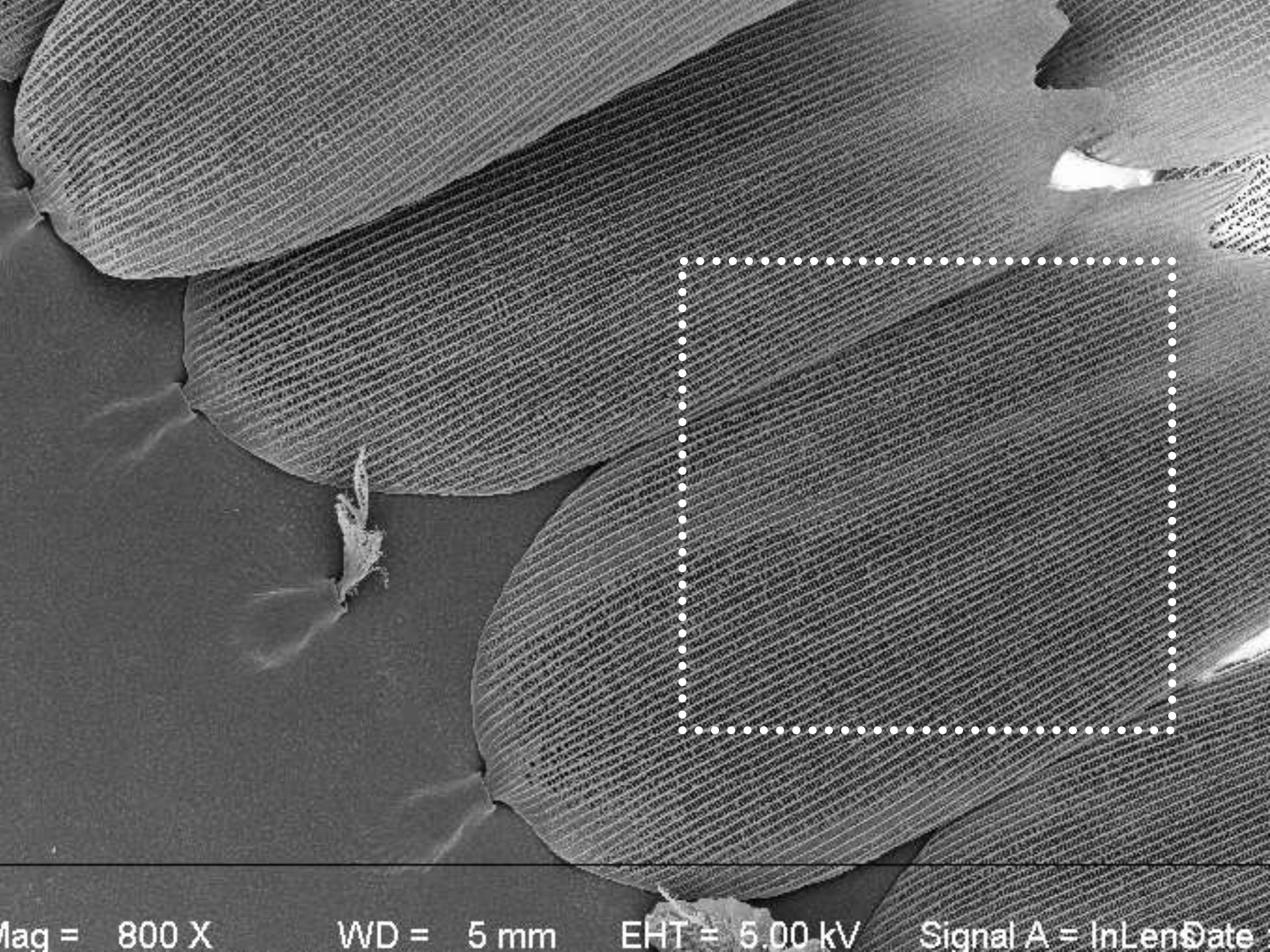


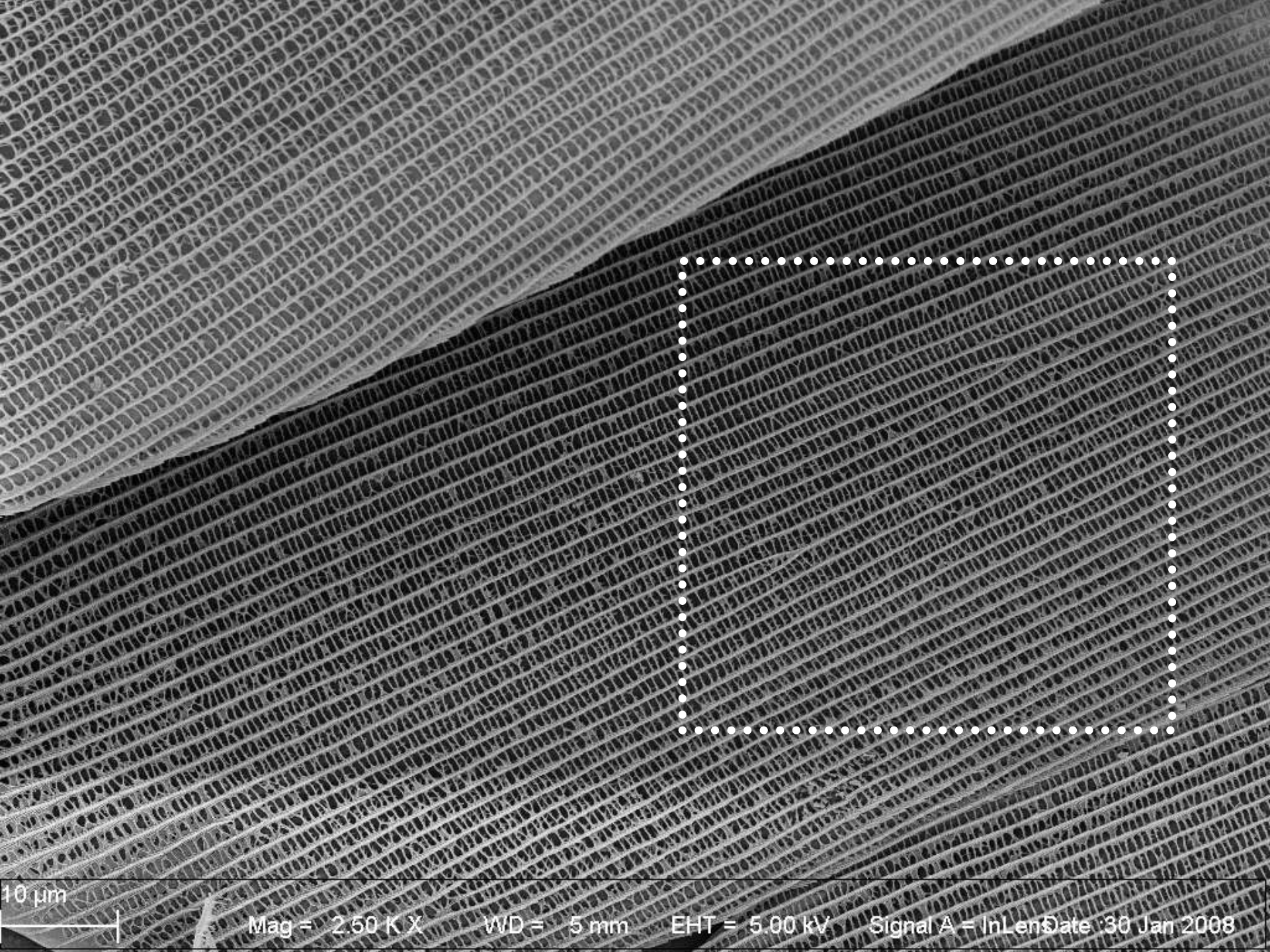


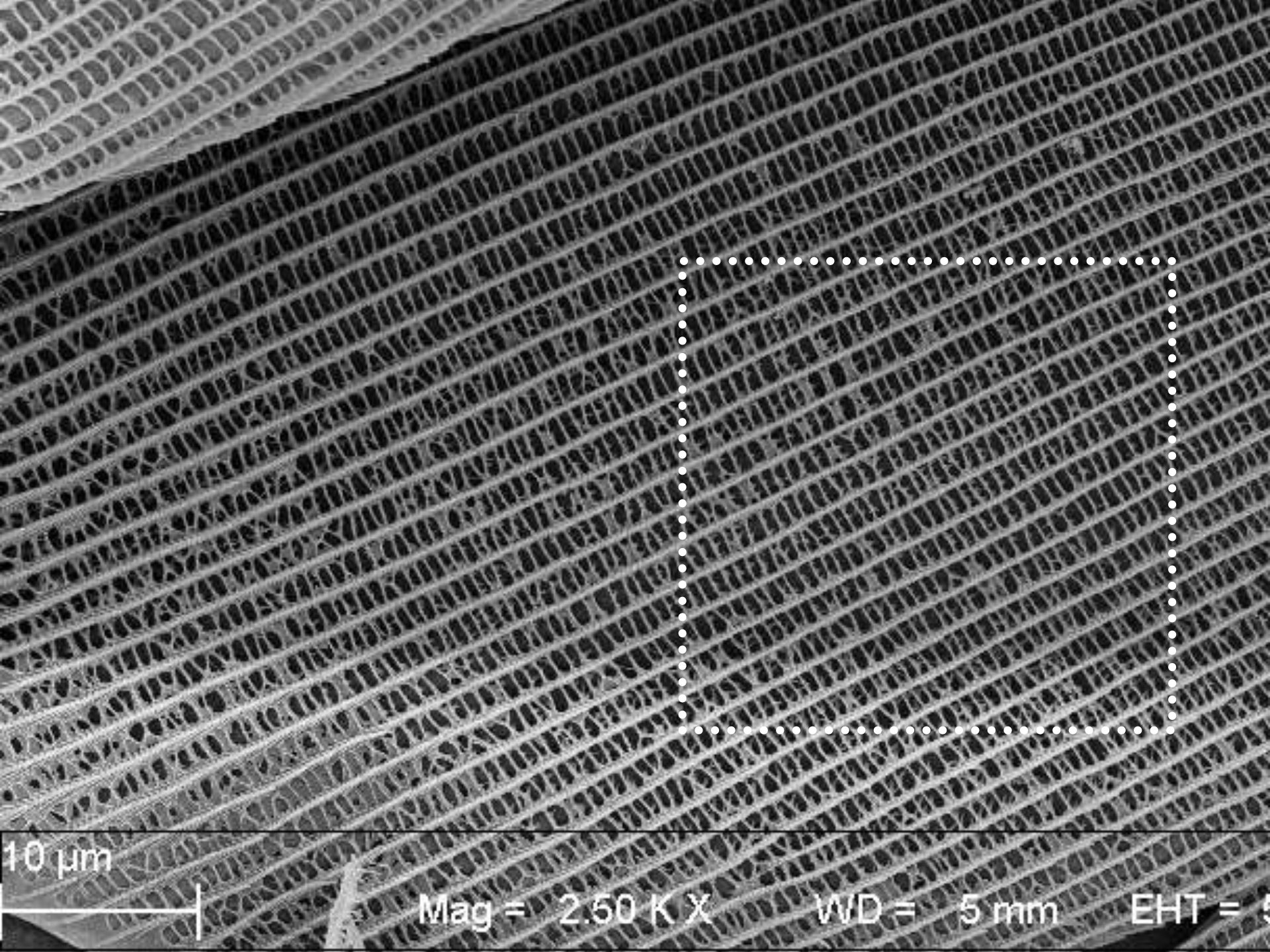
Variations in mechanical properties are the result of structural and chemical variations within the hierarchical level rather than by changes in the overal structural organisation

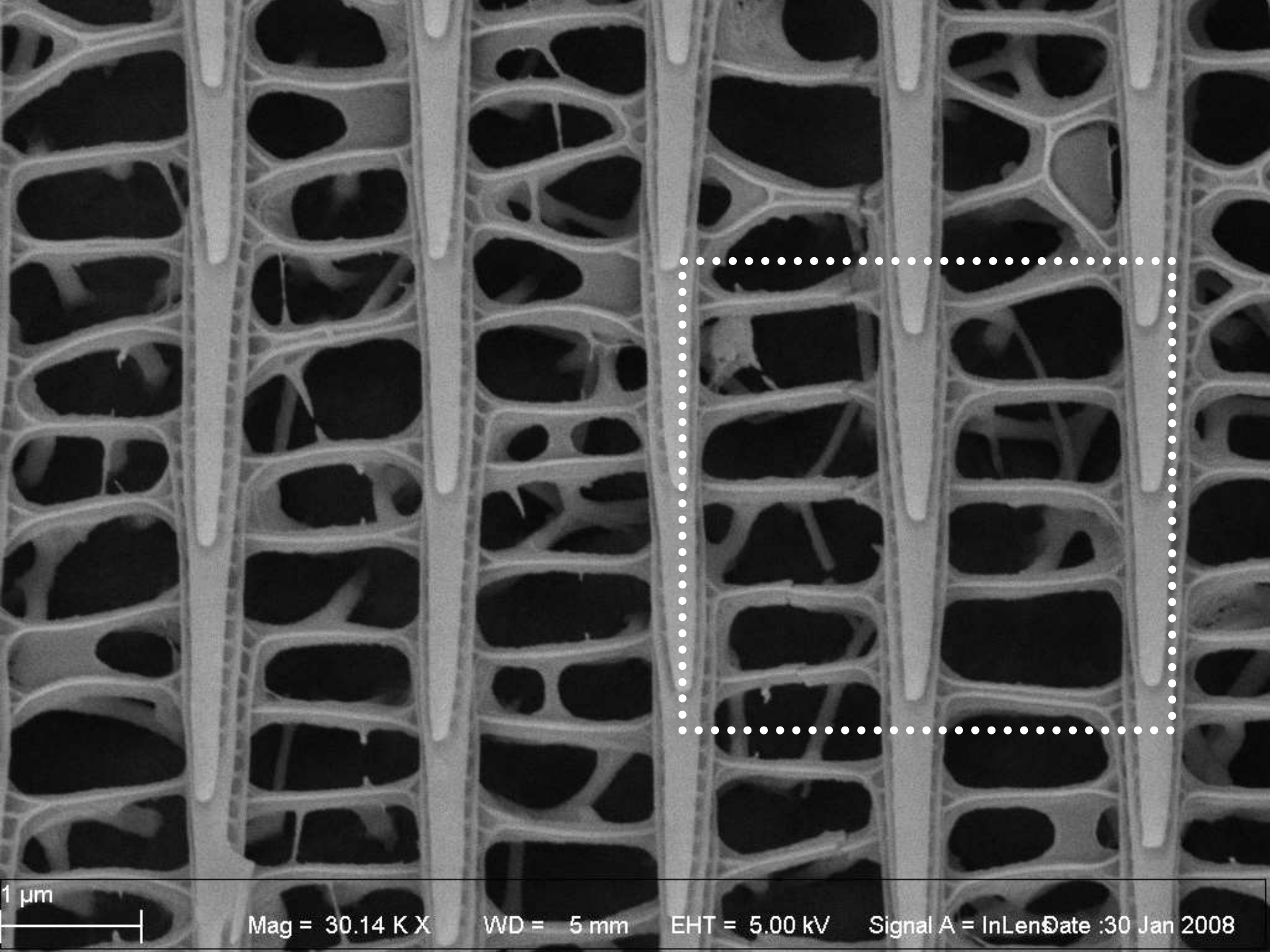


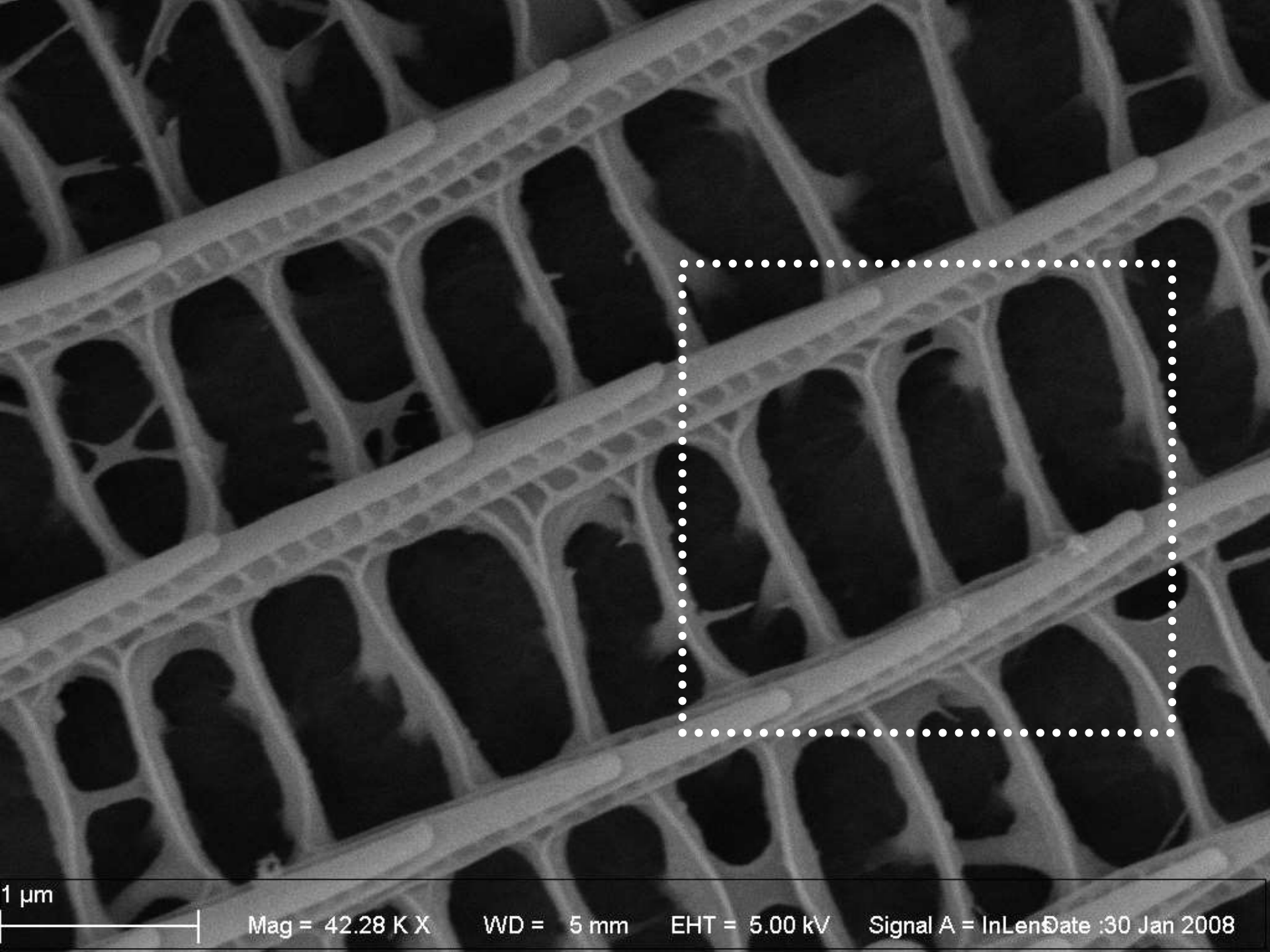

20 µm
Signal A = InLens
Date :30 Jan 2008

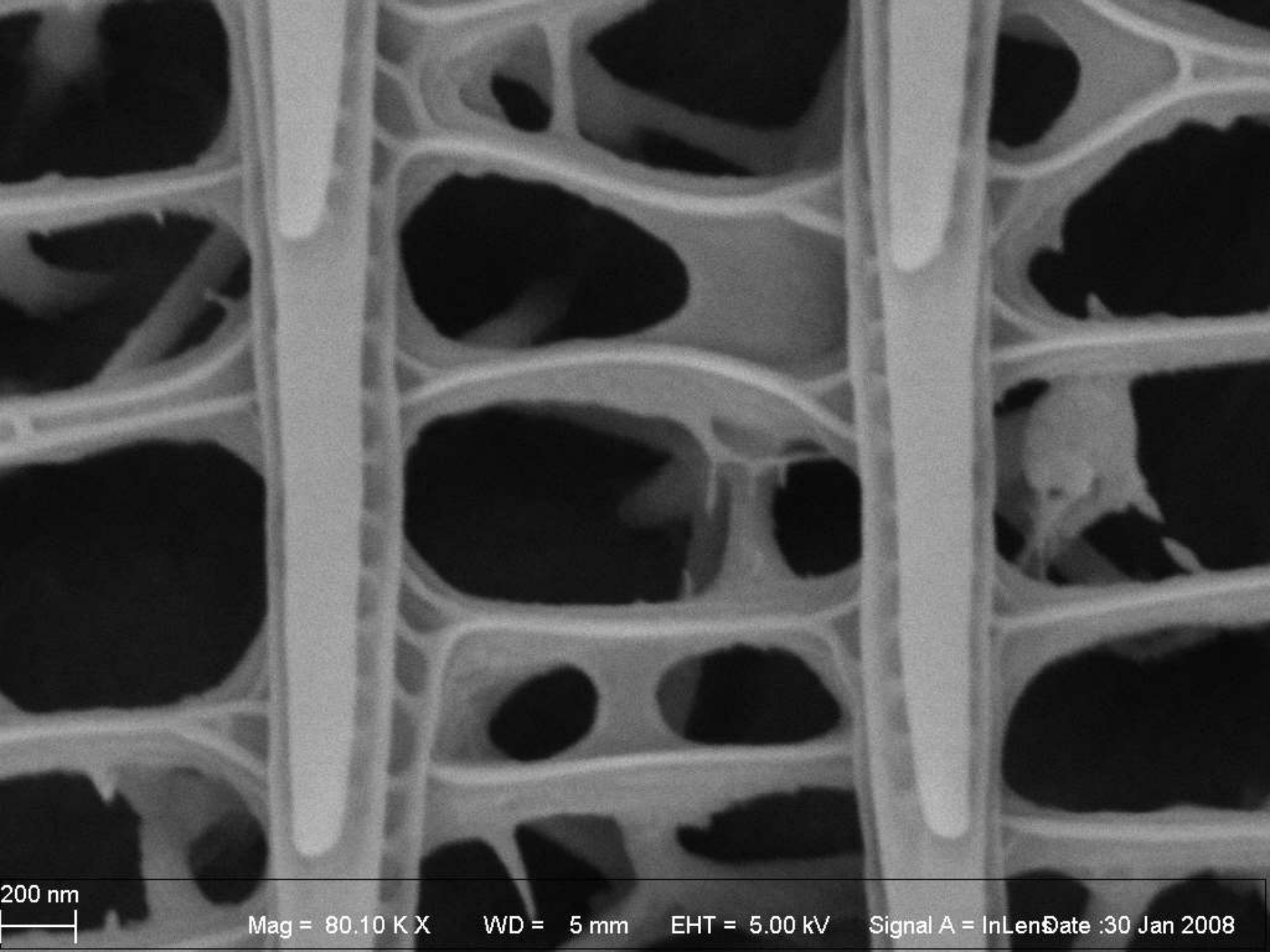

Mag = 800 X
WD = 5 mm
EHT = 5.00 kV
Signal A = InLens
Date


10 µm
Mag = 2.50 K X
WD = 5 mm
EHT = 5.00 kV
Signal A = InLens
Date :30 Jan 2008


10 µm
Mag = 2.50 K X
WD = 5 mm
EHT =

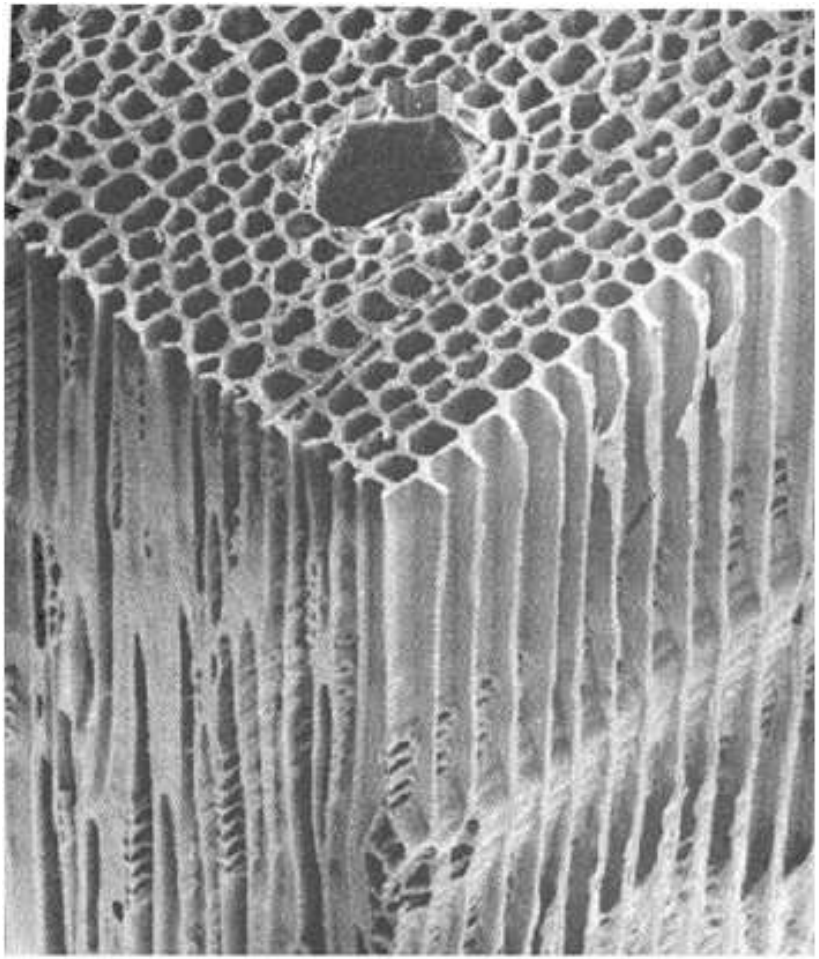

1 µm
Mag = 30.14 K X
WD = 5 mm
EHT = 5.00 kV
Signal A = InLens
Date :30 Jan 2008


1 µm
Mag = 42.28 K X
WD = 5 mm
EHT = 5.00 kV
Signal A = InLens
Date :30 Jan 2008

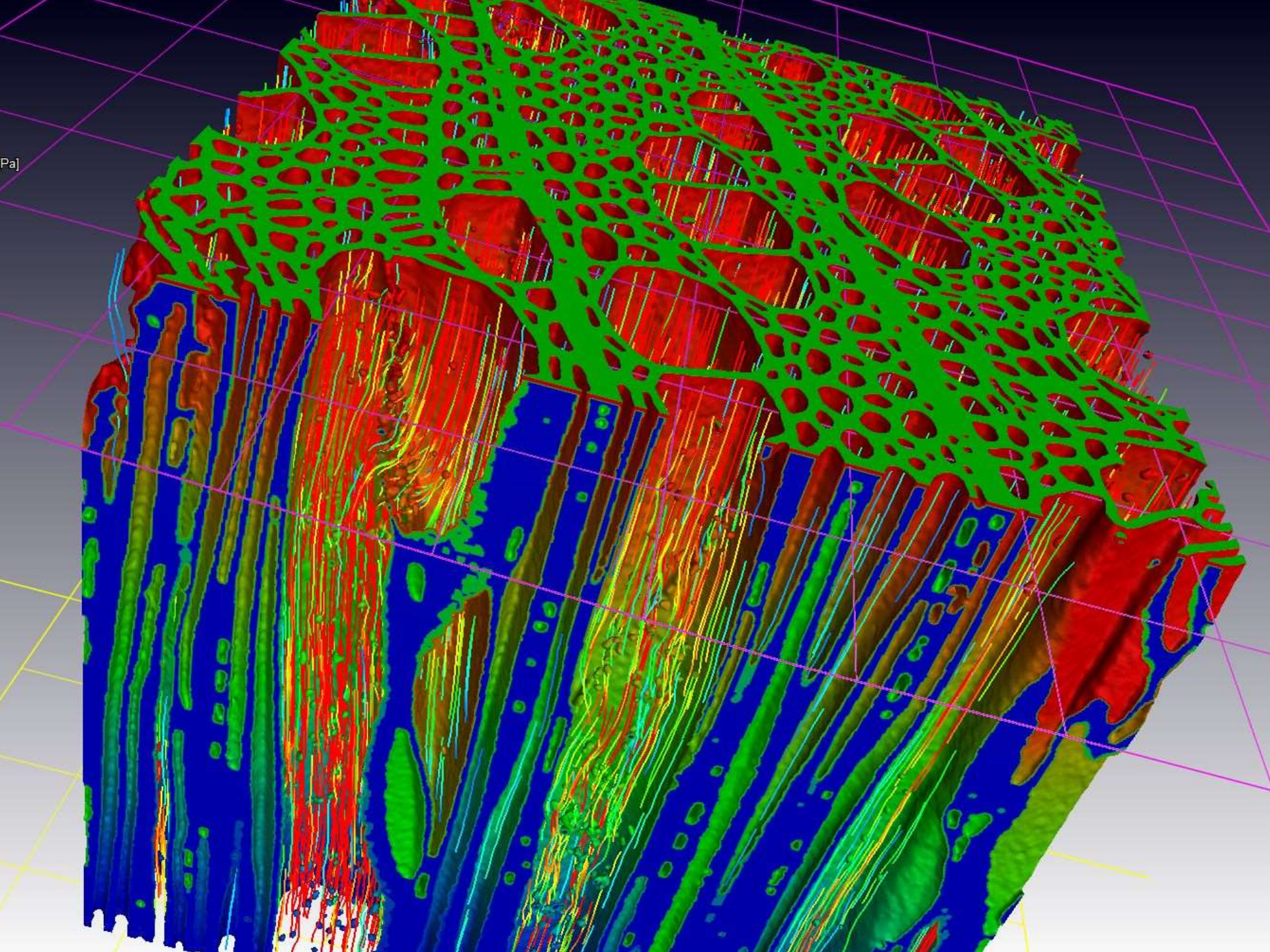

200 nm
Mag = 80.10 K X
WD = 5 mm
EHT = 5.00 kV
Signal A = InLens
Date :30 Jan 2008

Wood

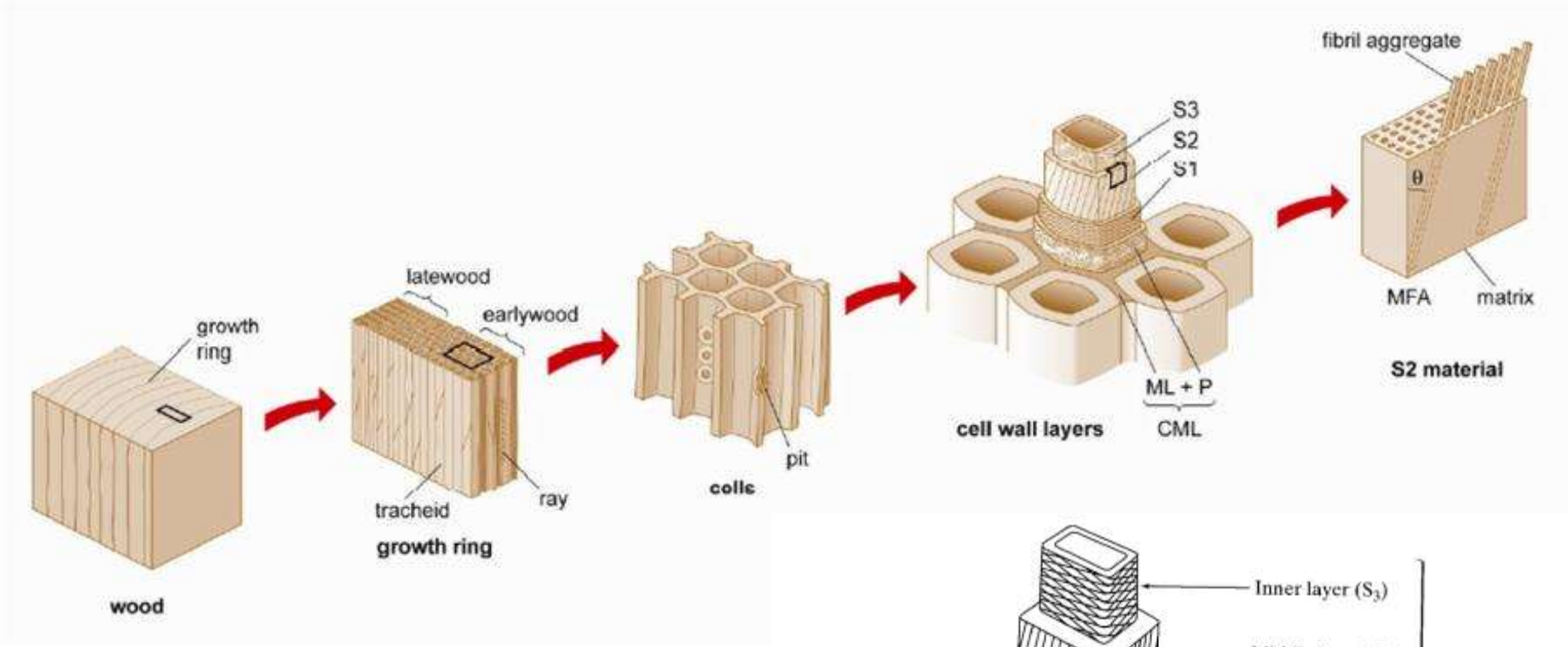
multicomponent	inelastic
hygroscopic	fibrous
anisotropic	porous
inhomogeneous	biodegradable
discontinuous	renewable

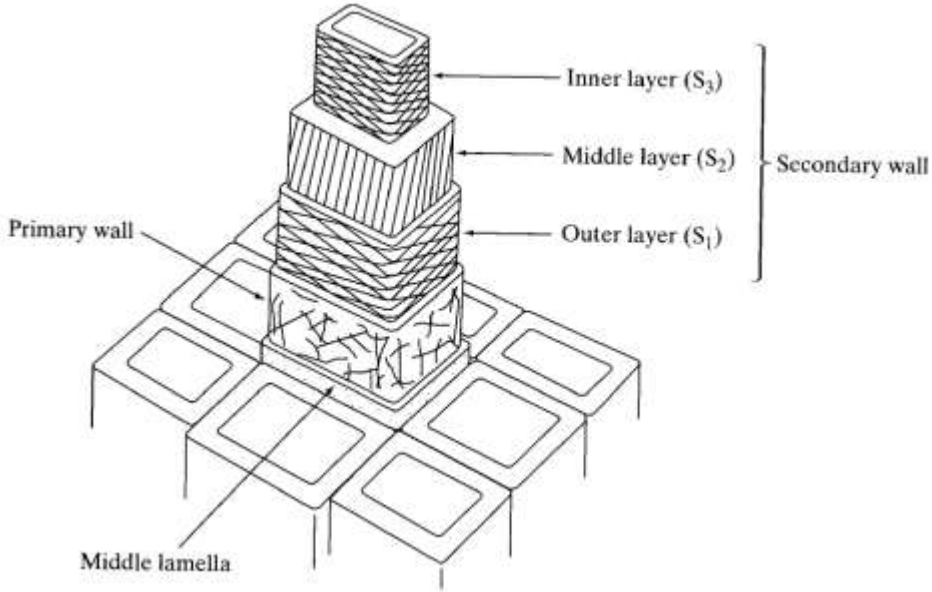


Eastern white pine in 3-D view, magnified 150x
(Source: 1980. Panshin, A.J. and C. de Zeeuw,
Textbook of Wood Technology, McGraw Hill, page 128).


[Pa]

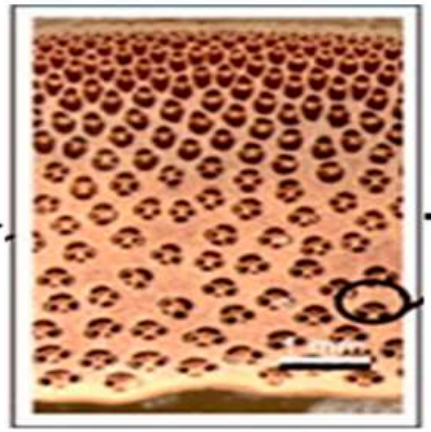
Wood: Microstructure hierarchy



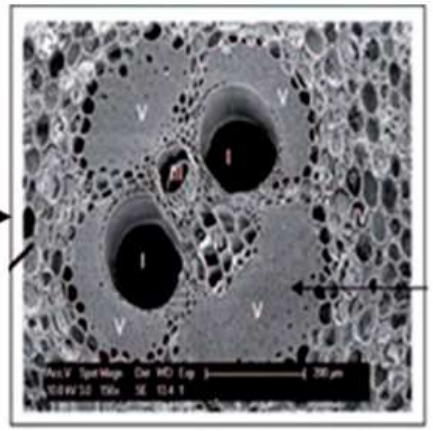


Wood: Microstructure hierarchy: Bamboo

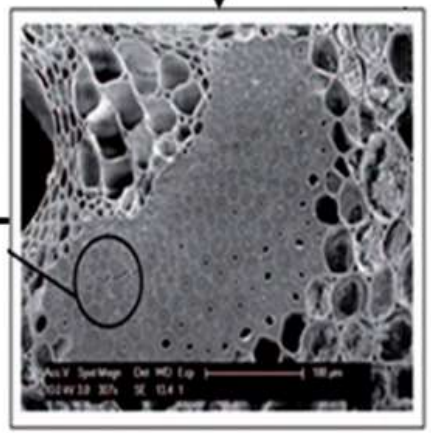
a). Bamboo culm



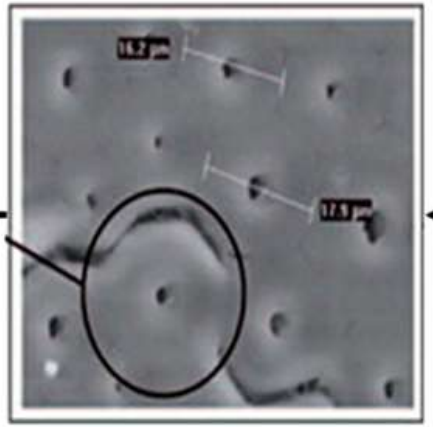
b). Cross-section of the culm



c). Vascular bundles



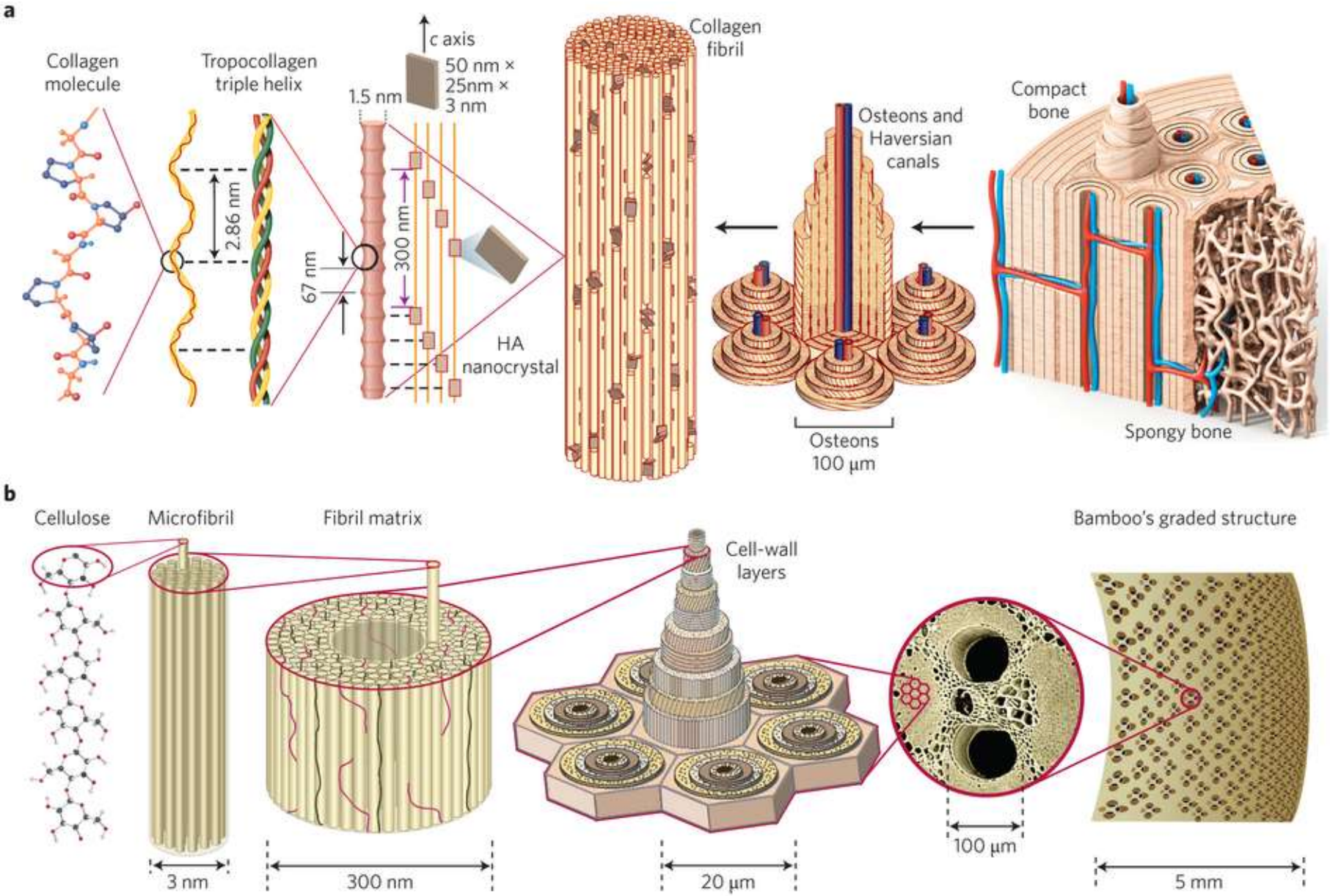
d). Bamboo fibre bundles



e). Elementary fibres

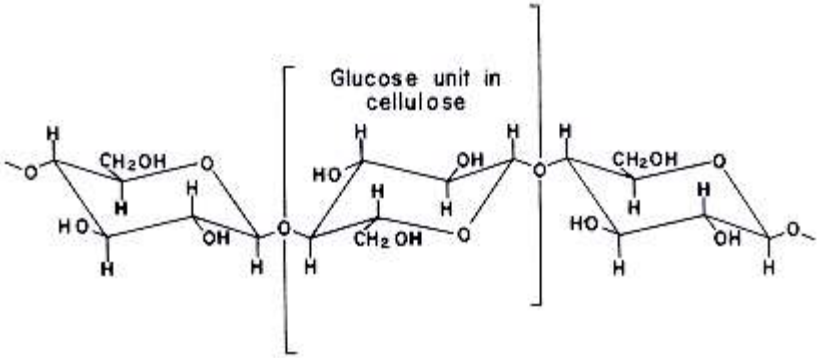
f). Model of polylamellae structure of thick-walled elementary fibre

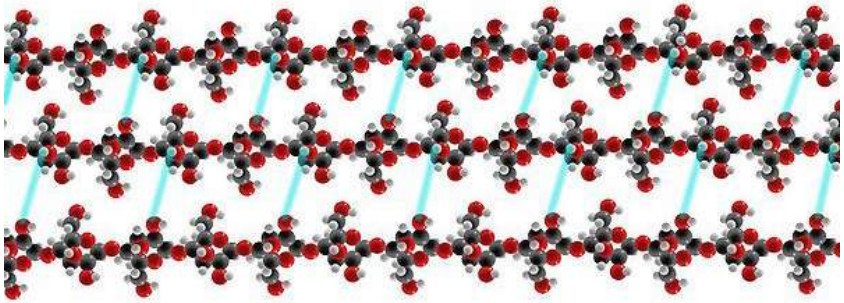
Comparison: Wood and Bone



Wood: Composition of cell wall of wood

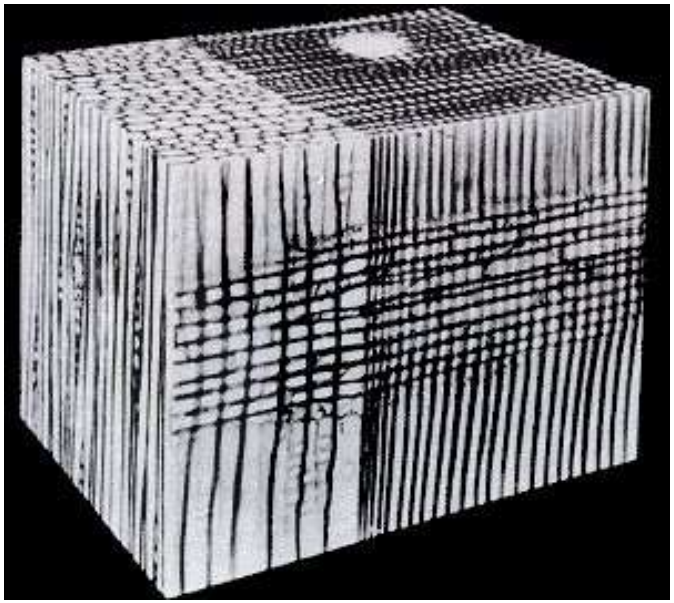
Material		Structure	Approx. wt %
Fibres	Cellulose $(C_6H_{10}O_5)_n$	Crystalline	45
Matrix	Lignin	Amorphous	20
	Hemicellulose	Semi-crystalline	20
	Water	Dissolved in the matrix	10
	Extractives	Dissolved in the matrix	5

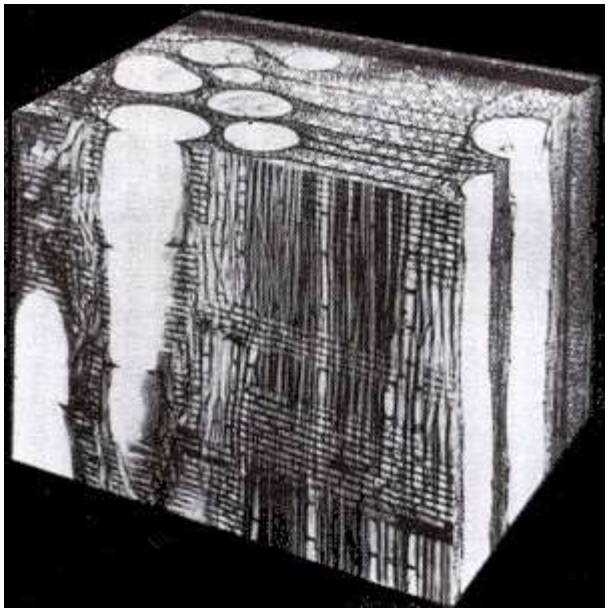




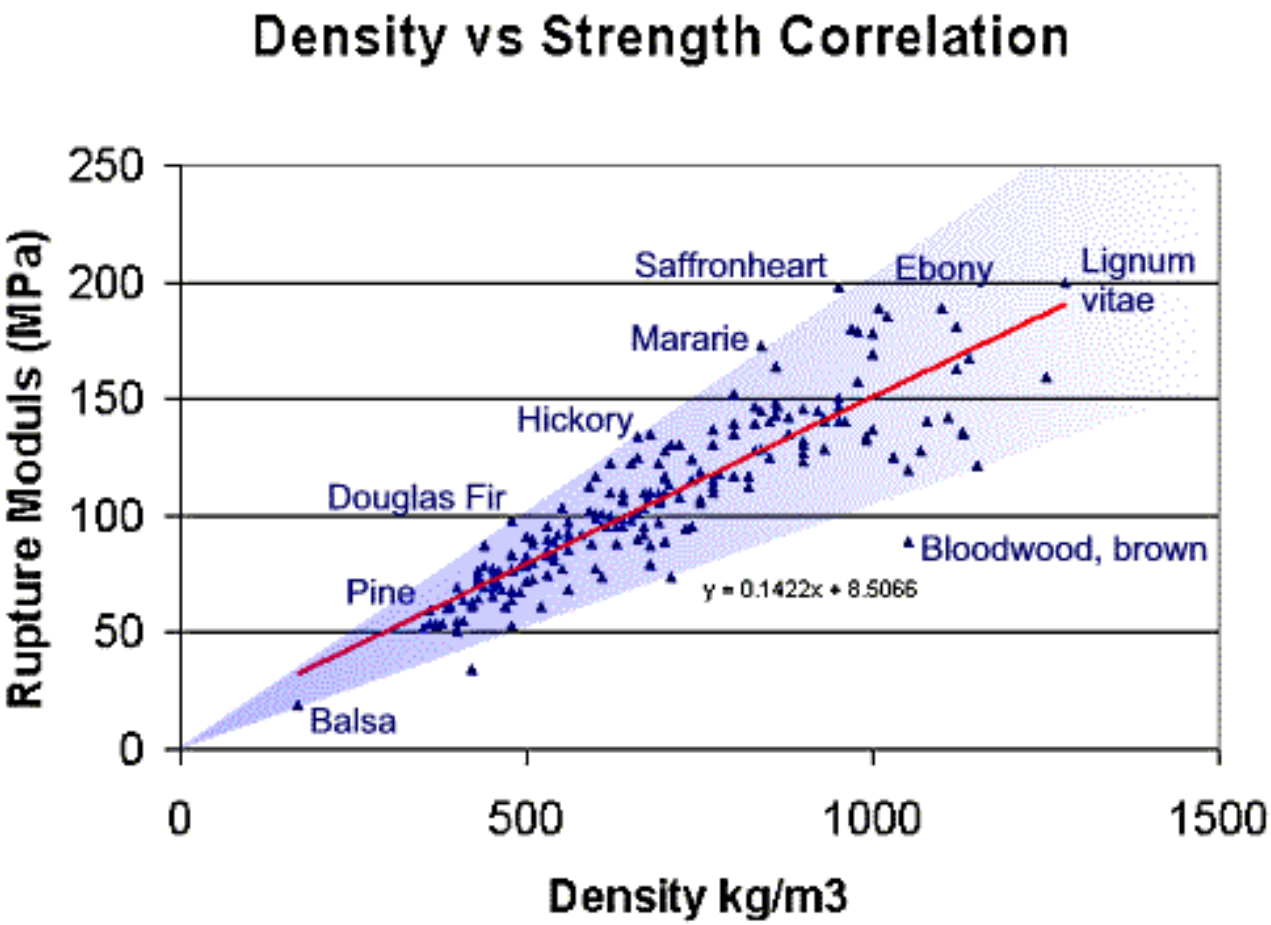
Wood

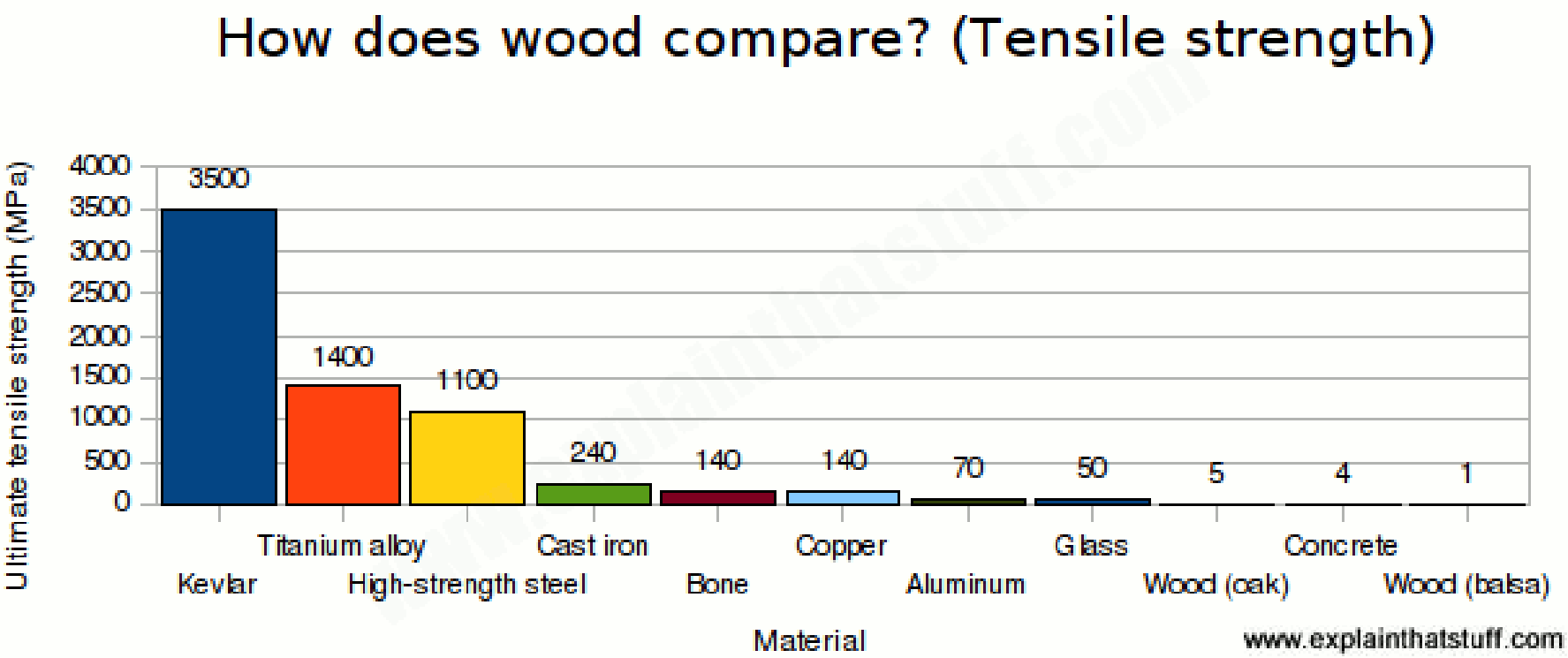
Softwood	Hardwood
Larger, longer cells Water transported by cells	Contains large-diameter vessels Water transported by these vessels



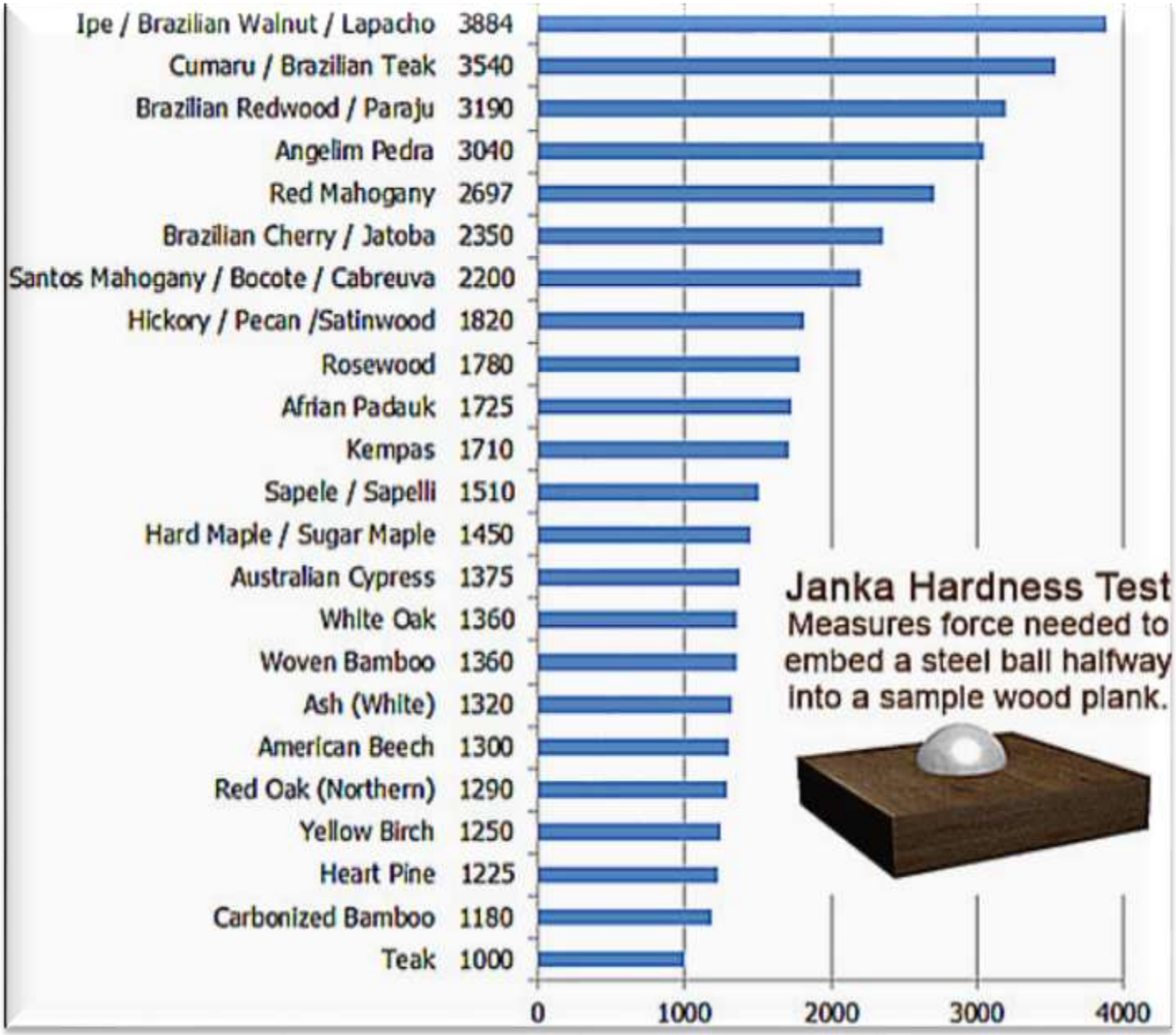


Wood: mechanical properties




How does wood compare? (Tensile strength)
Ultimate tensile strength (MPa)
4000
3500
3000
2500
2000
1500
1000
500
0
3500
1400
1100
240
140
140
70
50
5
4
1
Kevlar
Titanium alloy
High-strength steel
Cast iron
Bone
Copper
Aluminum
Glass
Wood (oak)
Concrete
Wood (balsa)
Material
www.explainthatstuff.com

Wood: mechanical properties: Hardness



Wood: mechanical properties: property map: specific strength

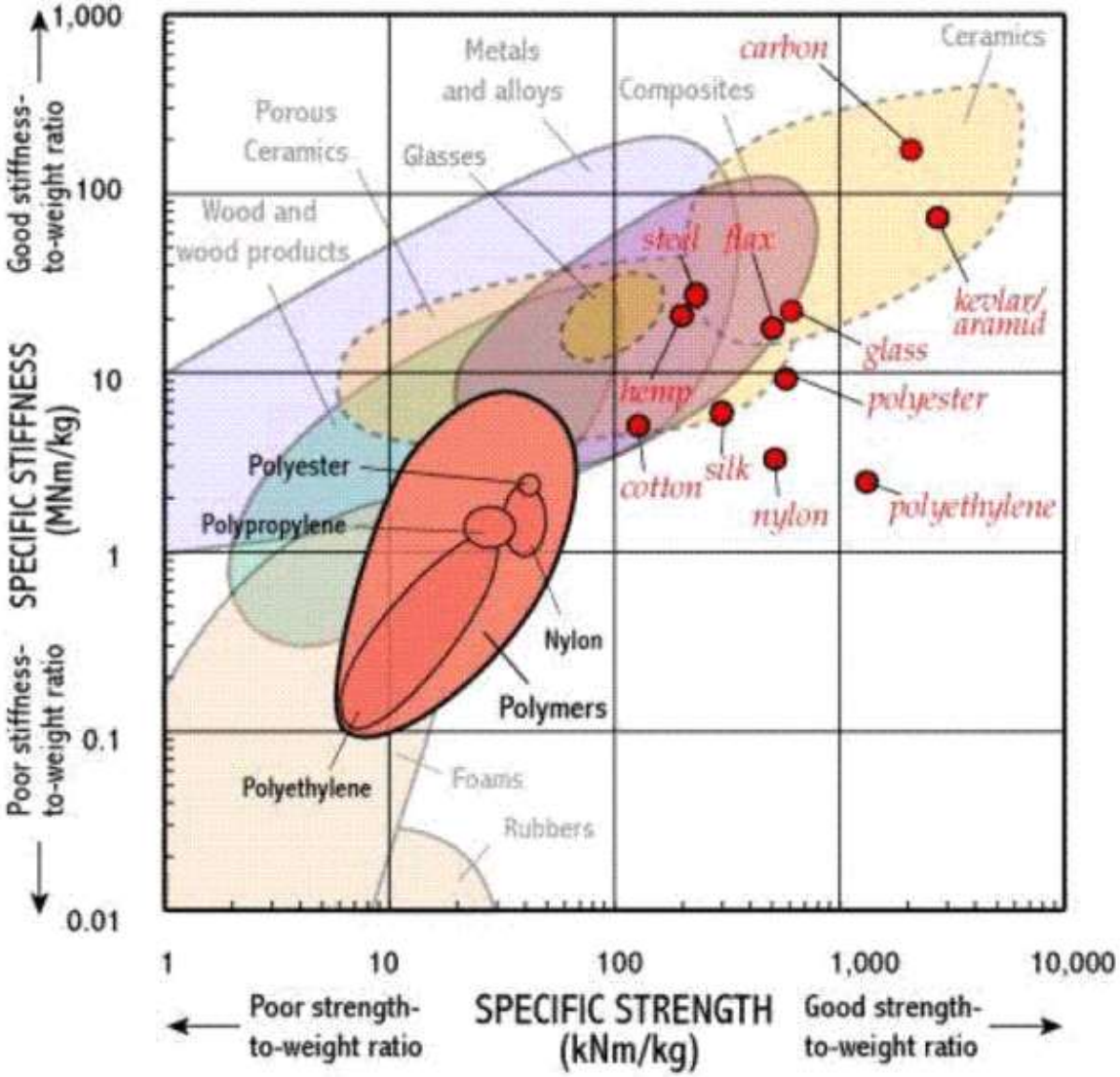


Figure 9-14: Structural materials stiffness and strength.