

Wood Science and Nanotechnology: Overview and Our Efforts

Siqun Wang, Ph.D.
Department of Forestry, Wildlife and Fisheries
University of Tennessee

Wednesday, September 28, 2011, 12:20-1:10
160 Plant Biotechnology building



Center for Renewable Carbon
UT The University of Tennessee Institute of Agriculture

Definition of Science

<http://www.dictionary.com/>
n.

a. The observation, identification, description, experimental investigation, and theoretical explanation of phenomena.

b. Such activities restricted to a class of natural phenomena.

c. Such activities applied to an object of inquiry or study.

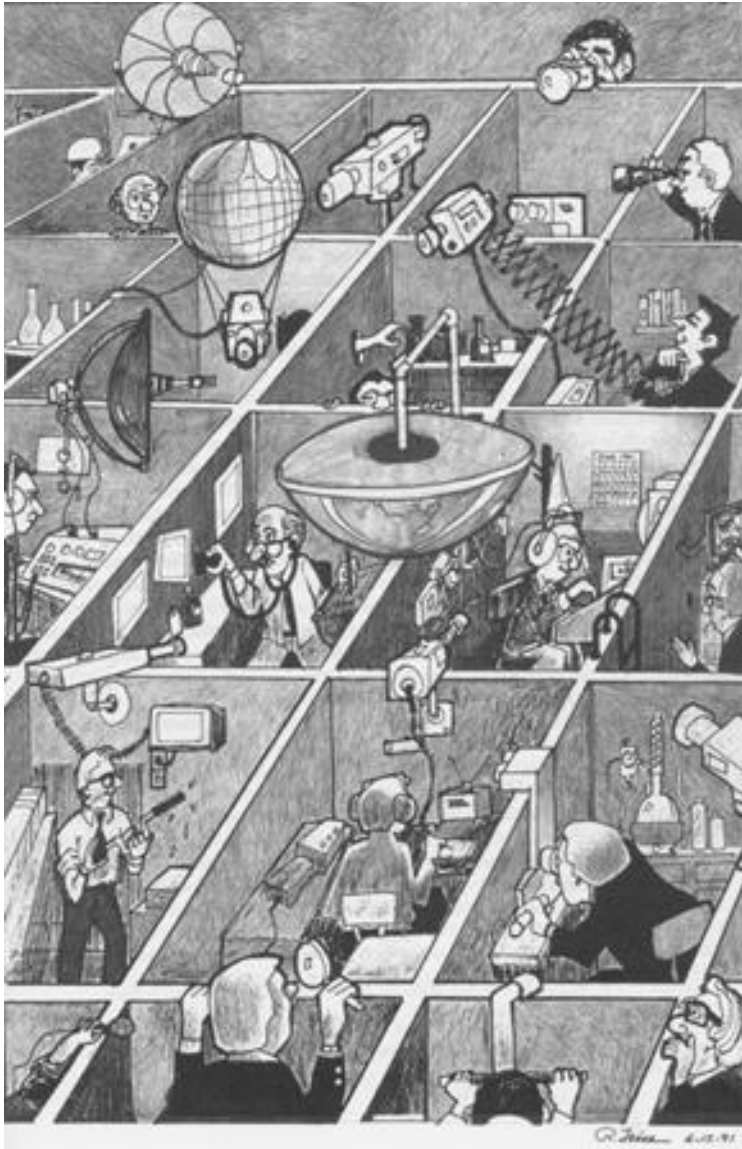
d. Methodological activity, discipline, or study: *I've got packing a suitcase down to a science.*

e. An activity that appears to require study and method: *the science of purchasing.*

f. Knowledge, especially that gained through experience.

g. **Science** Christian Science.

Definition of Science

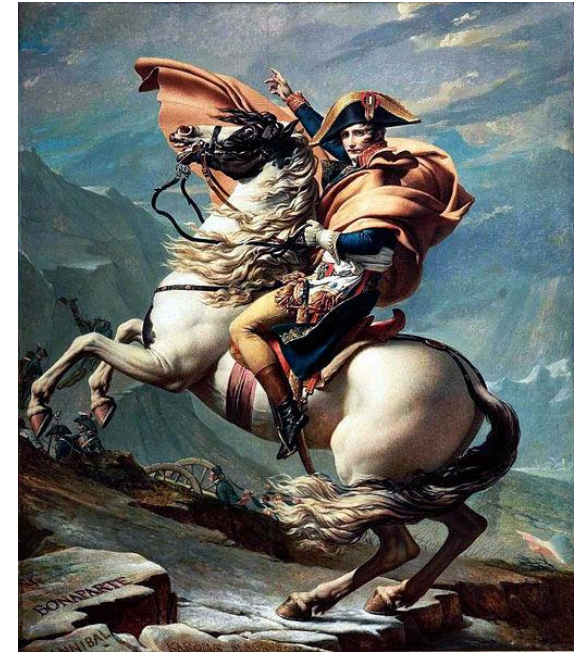


The science is to find out what have been done, what have not been done and to see what can be investigated.

Top Journals

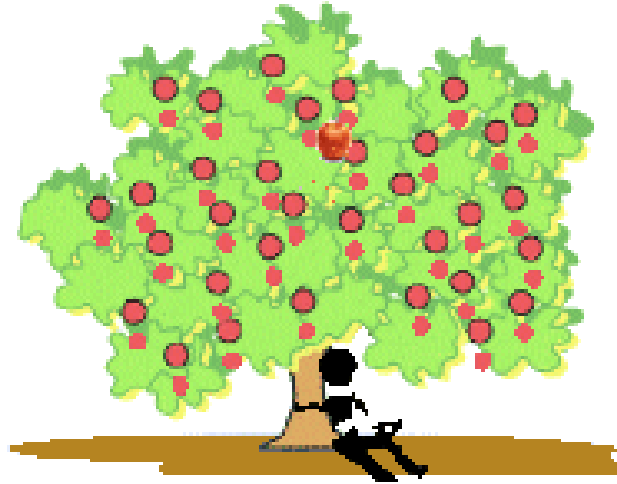


Napoleon



'Not want to be the general's soldiers is not a good soldier'

Newton (Isaac Newton, 1643~1727): Universal gravitation



How Pine Cones Open

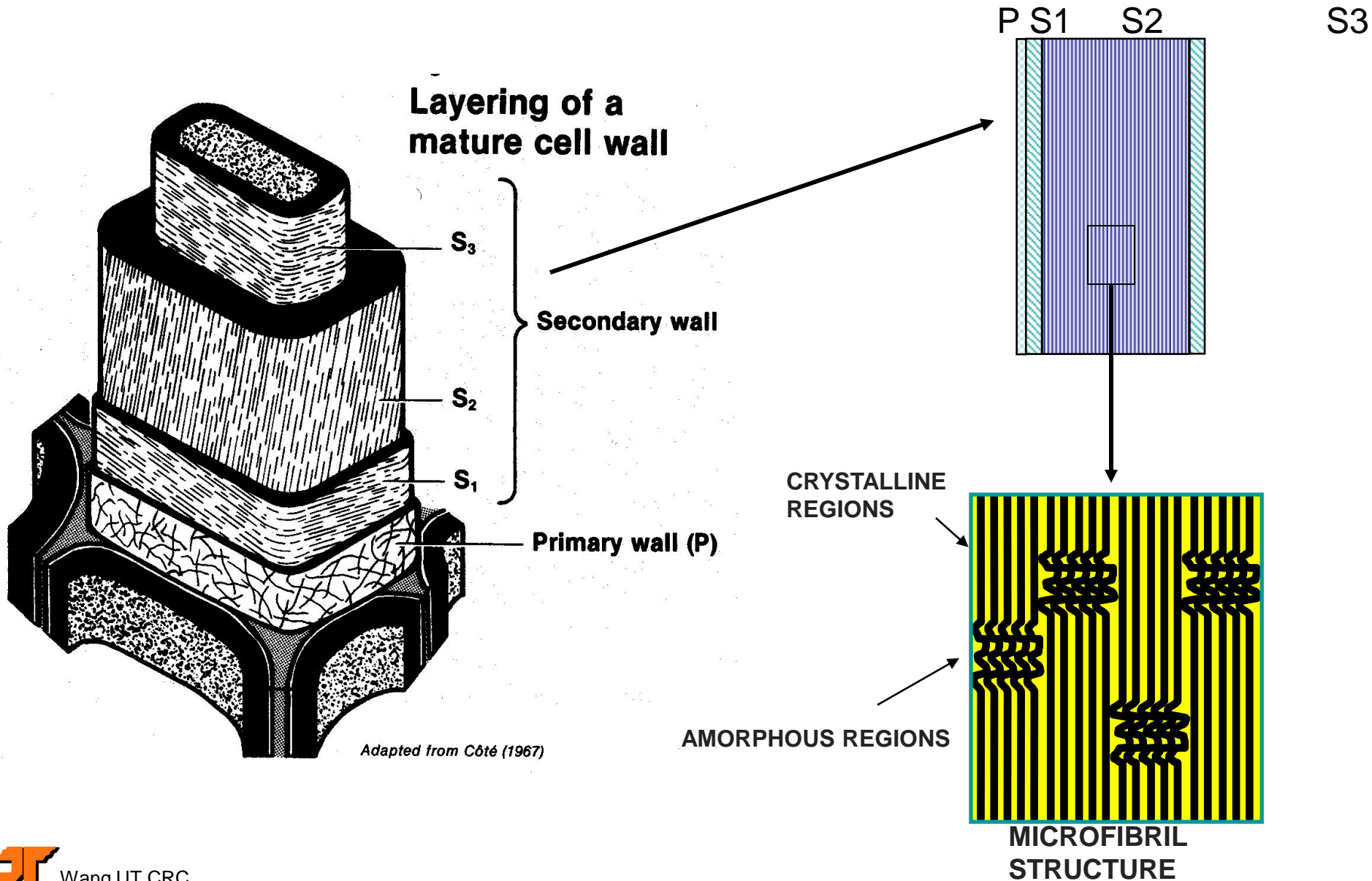


How Pine Cones Open

The scales of seed-bearing pine cones move in response to changes in relative humidity. The scales gape open when it is dry, releasing the cone's seeds. When it is damp, the scales close up. The cells in a mature cone are dead, so the mechanism is passive: the structure of the scale and the walls of the cells composing the scale respond to changing relative humidity.

Eichholz, G., *Jb. Wiss. Bot.* 17, 543-588 (1886).

Wood Structure



How Pine Cones Open

***Nature* 390, 668 (18 December 1997)**

COLIN DAWSON¹, JULIAN F. V. VINCENT¹ & ANNE-MARIE ROCCA²

¹ Centre for Biomimetics, University of Reading, Reading RG6 6AT, UK

² Defence Clothing and Textile Agency, Flagstaff Road, Colchester, Essex CO2 7SS, UK

Dissection of cones from the Monterey pine, *Pinus radiata*, revealed to us two types of scale growing from the main body of the cone — the ovuliferous scale and the bract scale. The larger ovuliferous scales respond to changes in relative humidity when removed from the body of the cone.

How Pine Cones Open

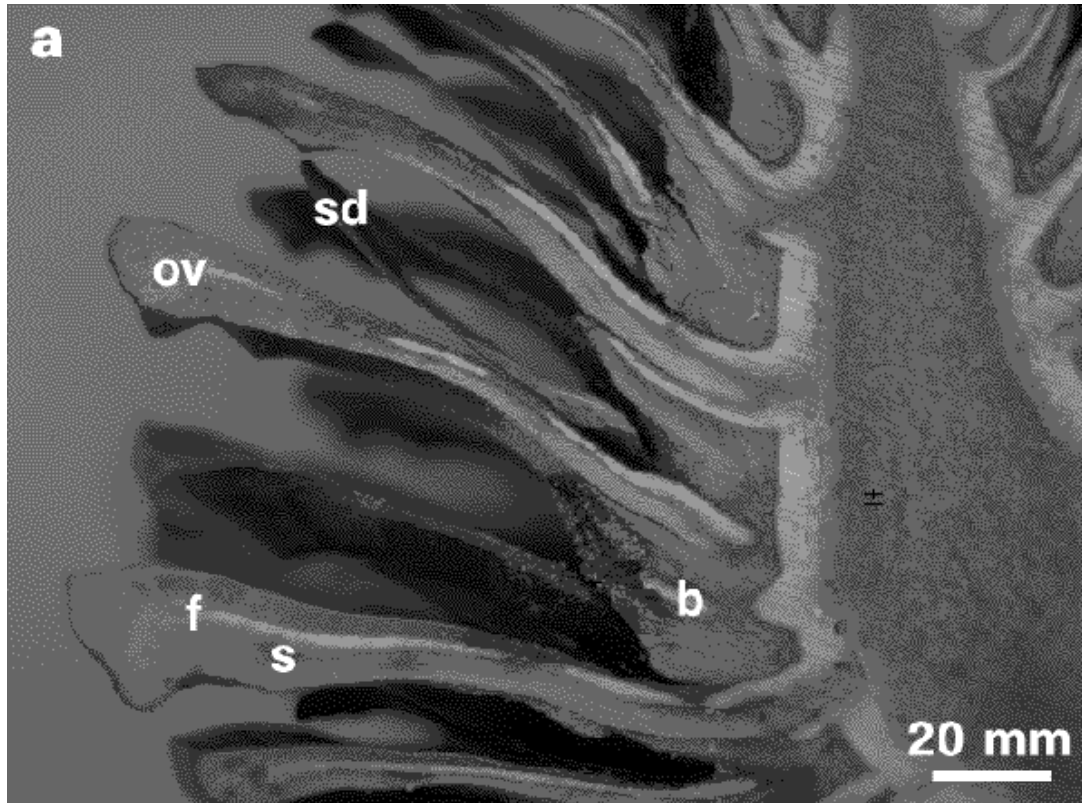
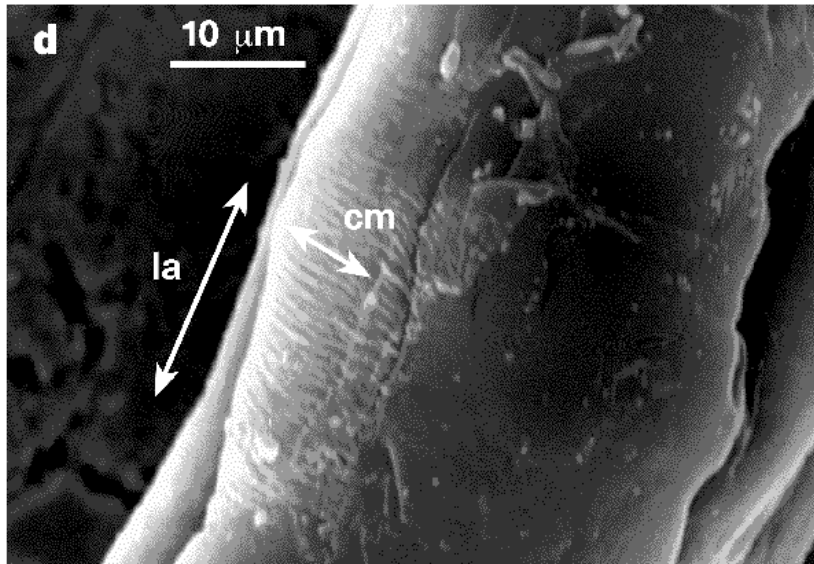
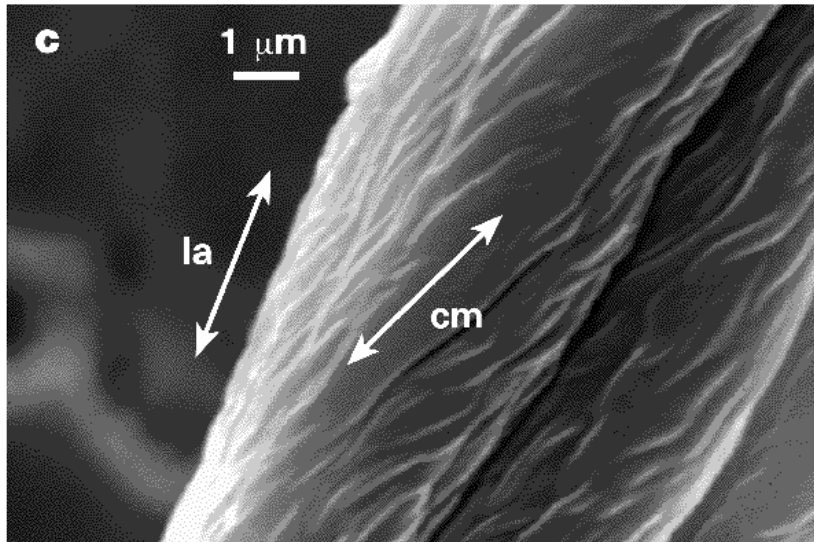


Figure 1. Morphology and behaviour of pine cone scales.

a, Median longitudinal section of female cone; **b**, bract scale; **sd**, seed; **ov**, ovuliferous scale with two-layer structure consisting of; **f**, fibres (white line within the scale) and **s**, sclerids.

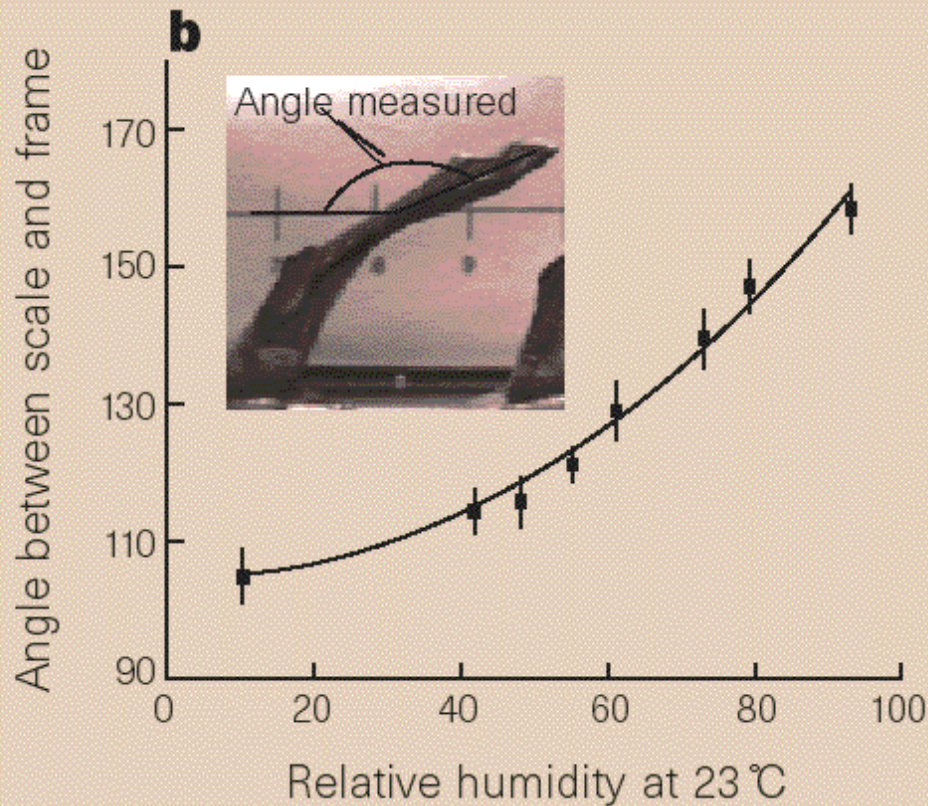
How Pine Cones Open



c, d, Scanning electron micrographs of fibres and sclerids, respectively.

θ , the angle between the long axis (la) of the cell and the direction of winding of cellulose fibres (cm), is high in sclerids and low in fibres.

How Pine Cones Open



b. Graph plotting the angle a scale makes to the base of the experimental apparatus against relative humidity. Inset: experimental apparatus and measured angle. Five scales were used to calculate mean \pm s.e.m.

Behaviour of single wood fibers under axial tensile strain

Nature 1971; 229:252-3

Page DH, El-Hosseiny F.,
Winkler K.

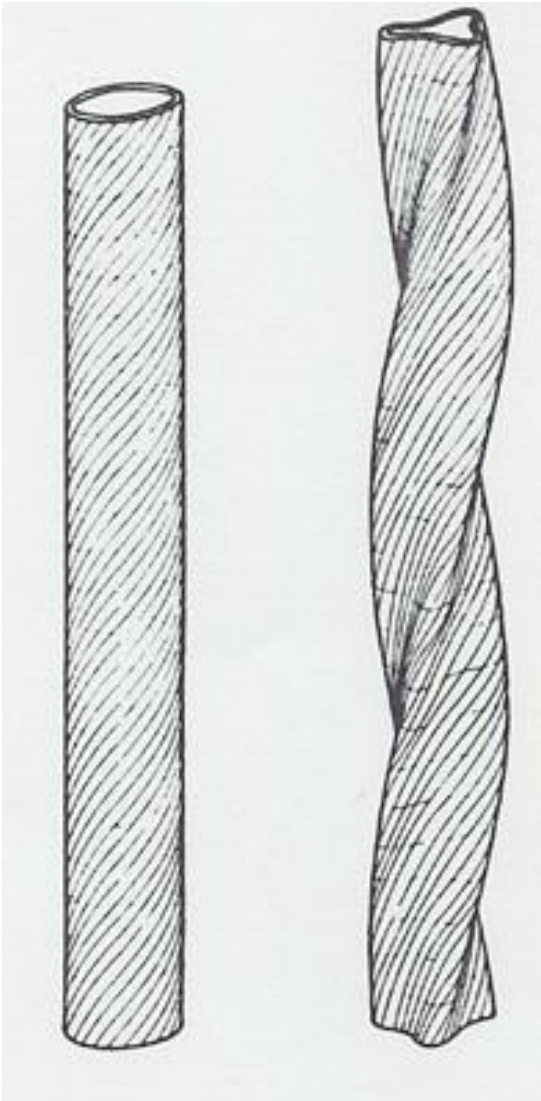


Behaviour of single wood fibers under axial tensile strain



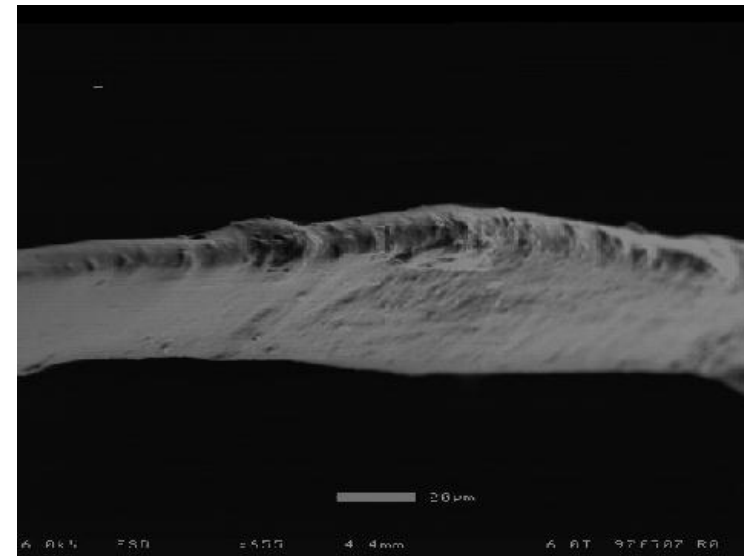
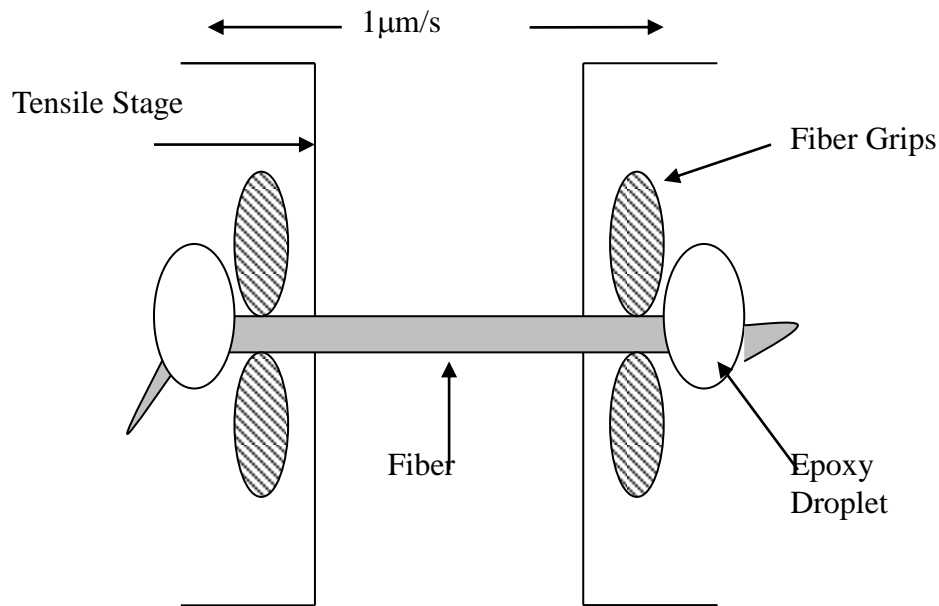
Fig. 1 Spruce wood fibre, pulped by the kraft process.
a, unstrained; **b**, strained.

Behaviour of single wood fibers under axial tensile strain



- ❑ Structure of wood fibers
 - fiber reinforced composite tube
- ❑ Theory of buckling of orthotropic shells
 - Buckling can occur because of induced shear stresses (aerospace industry)

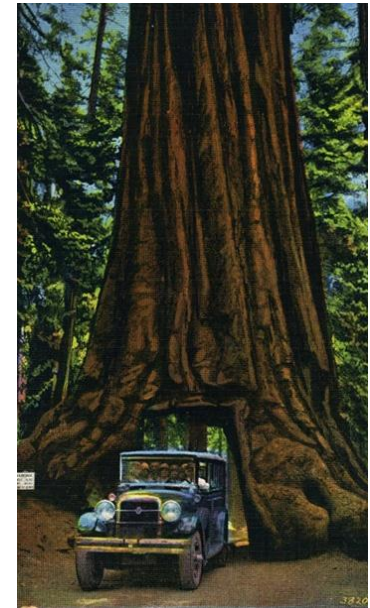
Mechanical properties of single wood fibers



Schematic of free fiber alignment grip assembly for use with microtensile testing stage. (adopted from S. Shaler)

Cellulose overview

- Cellulose is a carbohydrate polymer composed of glucose and constitutes about 45 percent of woody plant parts.
- The linear long-chain polymer, cellulose ($C_6H_{10}O_5$) $_n$, has a degree of polymerization, n which may be as large as 10,000.
- In cellulose, glucose units are connected through β linkage.
- Cotton is 90 percent pure cellulose.
- Wood is about 45% cellulose content.
- Biomass 1 billion ton per year in US.



Tunicates

Cellulose overview

- The pulp and paper industry is one of the largest industries in the United States, producing 64 million tons of pulp and 88 million tons of paper in 1991;
- Housing over 1 millions unit;
- Door panel (Audi A2) consisted of flax and sisal;
- Regenerated cellulose fibers (Lyocell, Rayon) ;
- Cellulose acetate (film, plastics, membrane)



Challenges in the future

Biofuel?



Cellulose/hemicellulose
Lignin as waste



Food or Bioproducts?



Use all components
No waste

Challenges in the Future

- **The Boeing airplane 787 Dreamliner is a milestone for advanced carbon fiber composites that make up over 50 percent of the materials of the airplane.**



Nanotechnology

What is Nano???

What is Nano???

What is Nano???

What is Nano???

What is Nano??

What is Nano???

Nanotechnologies are characterized by structural elements in the
~ 1 – 100 nanometer range.

$1 \text{ m} = 1000 \text{ mm} = 1,000,000 \text{ } \mu\text{m} = 1,000,000,000 \text{ nm}$

Nanotechnology

The Scale of Things – Nanometers and More

Things Natural

Ant
 ~ 5 mm

Dust mite
 ~ 200 μ m

Human hair
 ~ 60 - 120 μ m wide

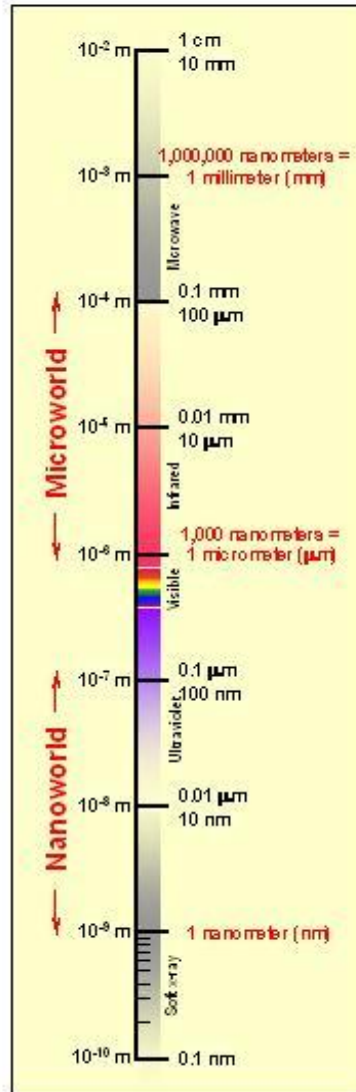
Fly ash
 ~ 10 - 20 μ m

Red blood cells with white cell
 ~ 2 - 5 μ m

ATP synthase
 ~ 10 nm diameter

DNA
 ~ 2 - 12 nm diameter

Atoms of silicon
 spacing \sim tenths of nm



Things Manmade

Head of a pin
 1-2 mm

Micro Electro Mechanical (MEMS) devices
 10 - 100 μ m wide

Pollen grain
Red blood cells

Zone plate x-ray "lens"
 Outer ring spacing ~ 35 nm

Self-assembled, Nature-inspired structure
 Many 10s of nm

Nanotube electrode

Carbon nanotube
 ~ 1.3 nm diameter

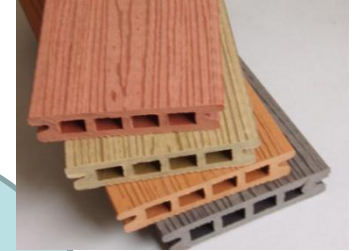
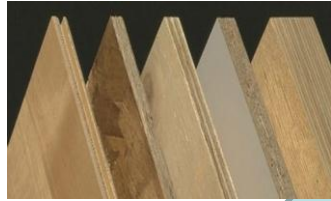
Carbon buckyball
 ~ 1 nm diameter

Quantum corral of 48 iron atoms on copper surface
 positioned one at a time with an STM tip
 Conal diameter 14 nm

The Challenge

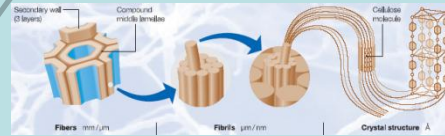
Fabricate and combine nanoscale building blocks to make useful devices, e.g., a photosynthetic reaction center with integral semiconductor storage.

Materials Research Group

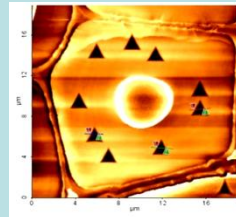


Wood-based
composites

Wood plastic
composites



Nanotechnology/
Nano-mechanics

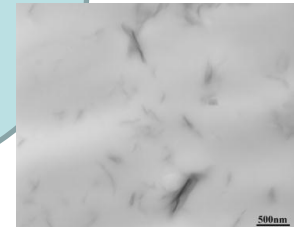
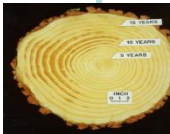
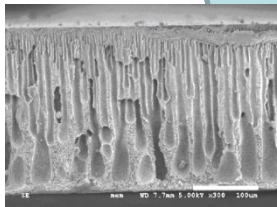


Non-wood
materials

Wood quality
and
modification

Advanced
materials

Nano-
composites



US, China, Chile, Japan,

Wood fiber refining

Siqun Wang

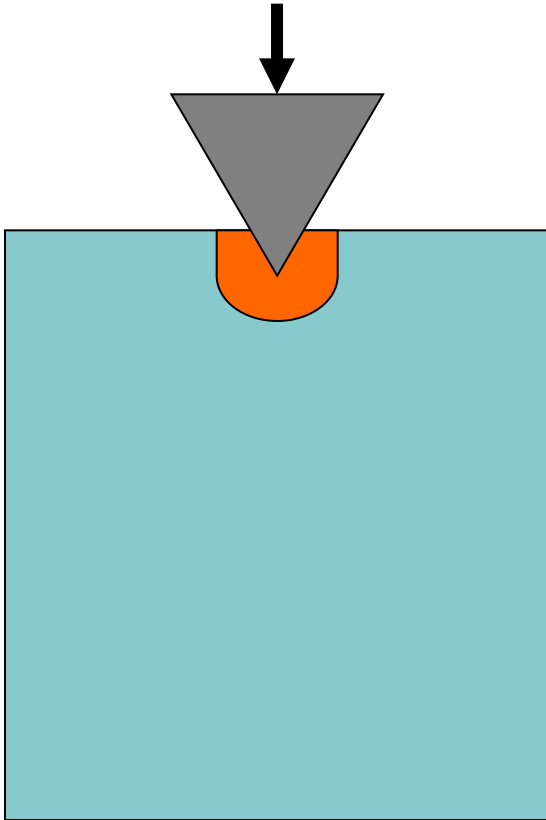
Materials:

- Refined wood fibers under different refining steam pressure

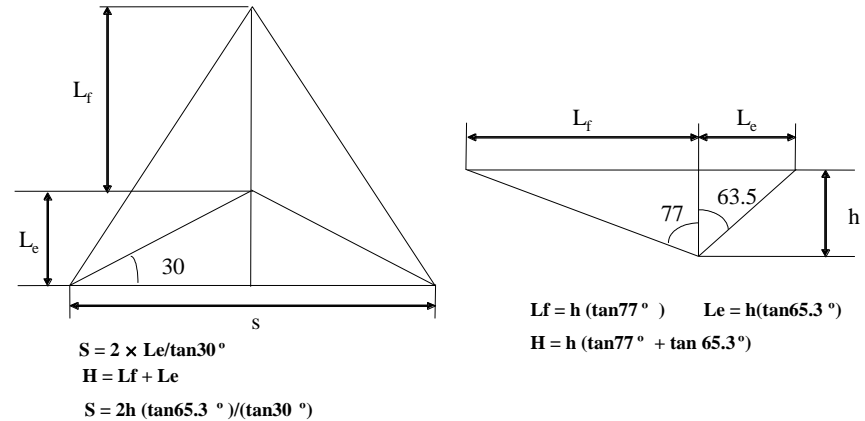


The image of refining fiber a) juvenile wood at 2 MPa, b) mature wood at 2 MPa, c) juvenile wood at 18 MPa, and d) mature at 18 MPa.

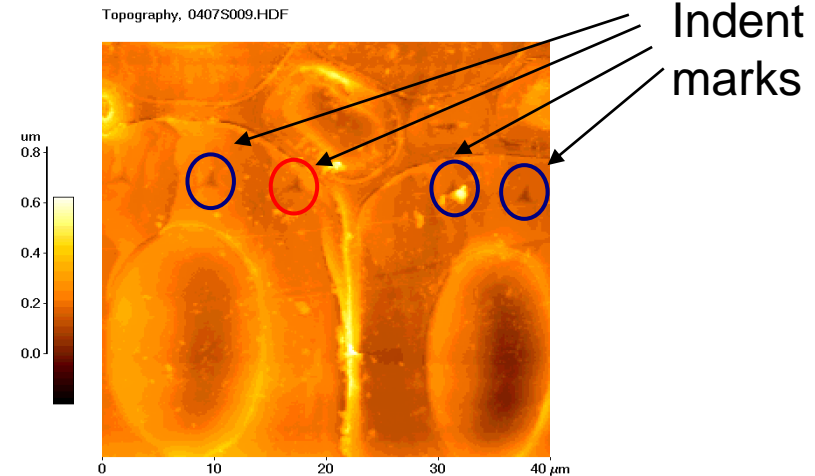
Nanoindentation



Schematic of the NANO II Indenter



Geometry of nano-indenter (Berkovich diamond tip)



Nanoindentation instrument and indentation procedure

Hardness (H):

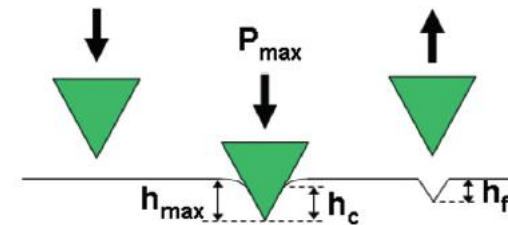
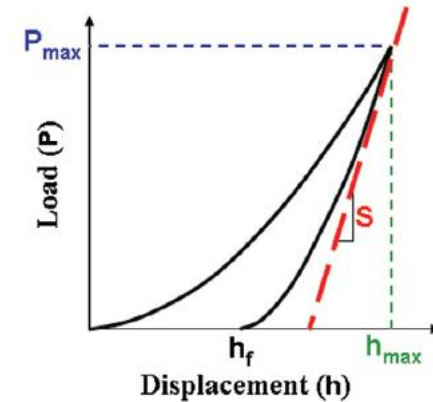
$$H = \frac{P_{\max}}{A} = \frac{P}{24.5h_c^2}$$

Elastic modulus (E_s):

(Oliver and Pharr)

$$E_r = \frac{dP}{dh} \frac{1}{2} \frac{\sqrt{\pi}}{\sqrt{A}}$$

$$E_s = (1 - \nu_s^2) \left(\frac{1}{E_r} - \frac{1 - \nu_i^2}{E_i} \right)^{-1}$$



Typical load-displacement curve

E_r is reduced elastic modulus, which accounts for the fact that elastic deformation occurs in both the sample and the indenter.

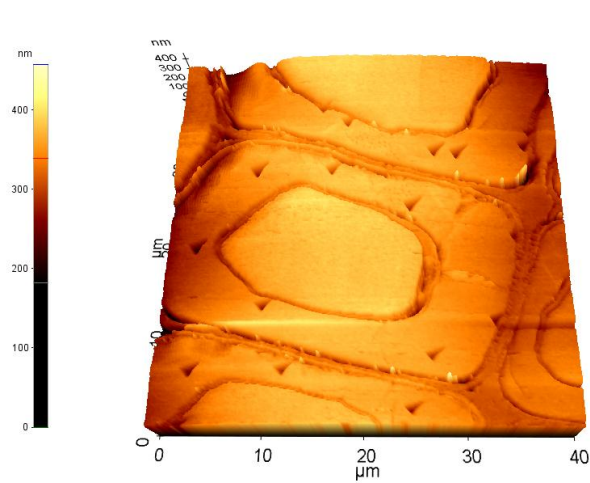
ν_s and ν_i (0.07) are the Poisson's ratios of the specimen and indenter, respectively.

E_i is the modulus of the indenter (1141 GPa).

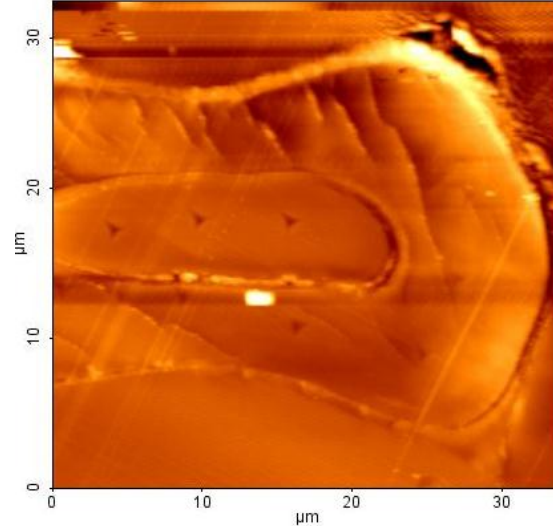
Results – Refined wood fibers

Siqun Wang

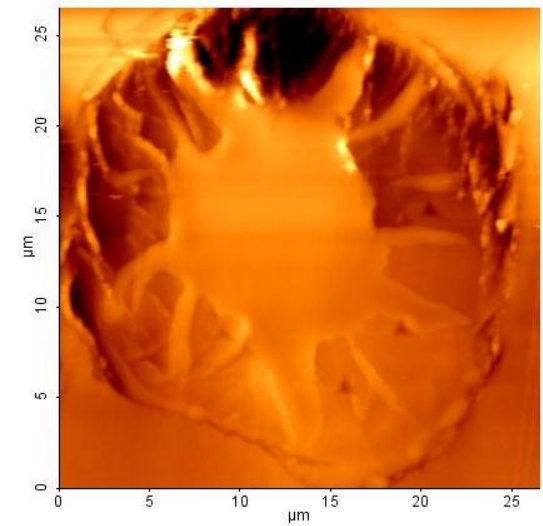
- Refined wood fibers under different refining steam pressure



2 Bars



12 Bars



18 Bars

Results – Refined wood fibers

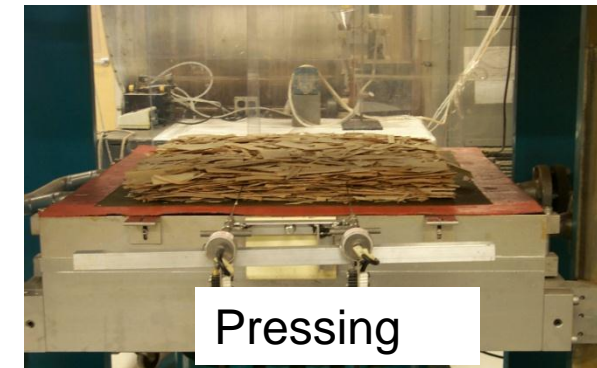
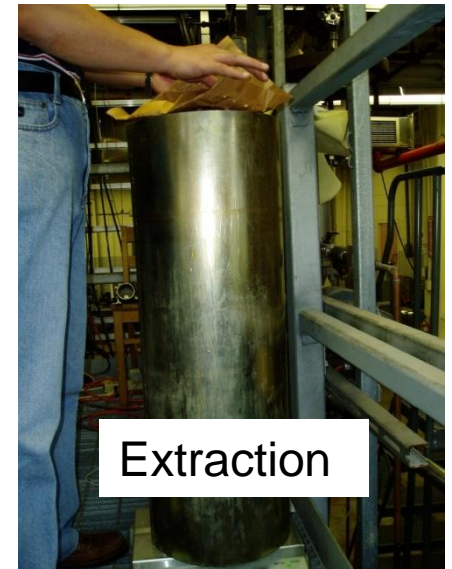
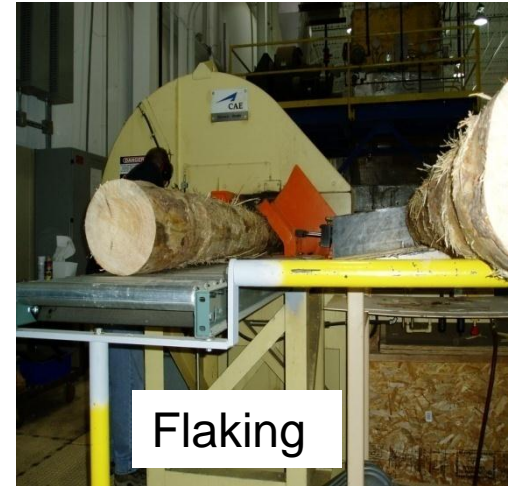
Siqun Wang

Summary of nanoindentation results of fiber cell wall

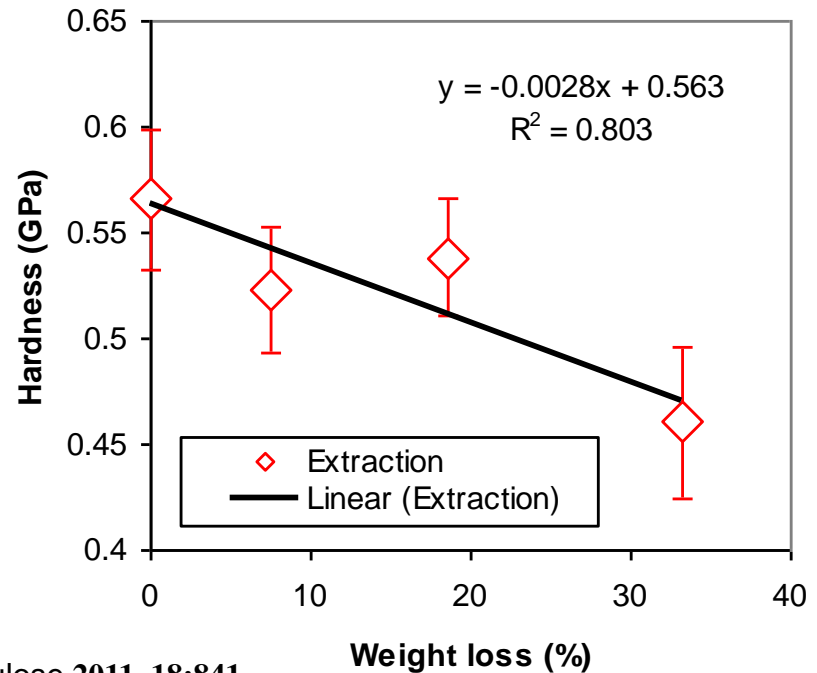
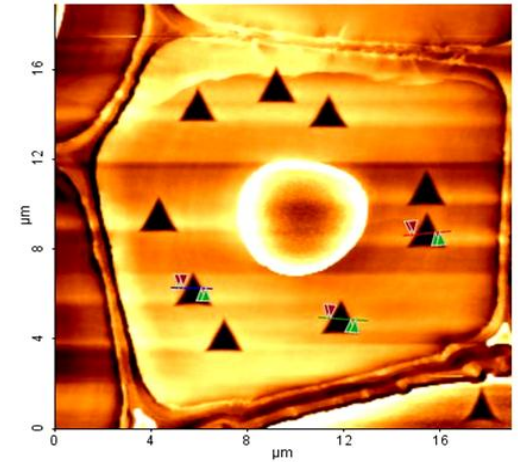
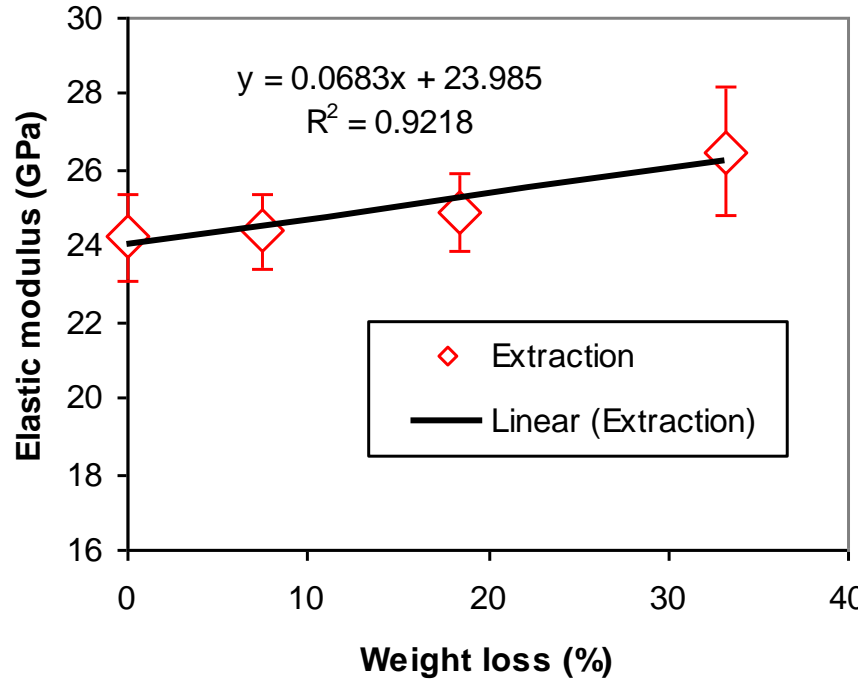
Property/pressure		2 bars	4 bars	6 bars	8 bars	10 bars	12 bars	14 bars	18 bars
Es GPa	Mean	21.35	18.62	15.96	16.83	15.32	14.05	13.09	12.22
	Stdev	2.59	2.97	2.41	2.53	2.51	2.87	3.42	3.29
	CV	12.13	15.95	15.10	15.03	16.38	20.43	26.13	26.92
H GPa	Mean	0.50	0.47	0.47	0.45	0.43	0.43	0.39	0.37
	Stdev	0.04	0.062	0.07	0.05	0.067	0.079	0.078	0.095
	CV	8.00	13.19	14.89	11.11	15.58	18.37	20.00	25.68
Ci %	Mean	7.58	8.72	8.87	8.63	8.24	9.68	12.30	13.08
	Stdev	0.86	1.56	1.25	1.29	1.09	1.79	3.89	3.91
	CV	11.35	17.89	14.09	14.95	13.23	18.49	29.25	29.89
n	Number	31	27	23	28	30	28	14	13

Note: Stdev: standard deviation; CV: coefficients of variation; Ci: indention creeps; n: the number of indents.

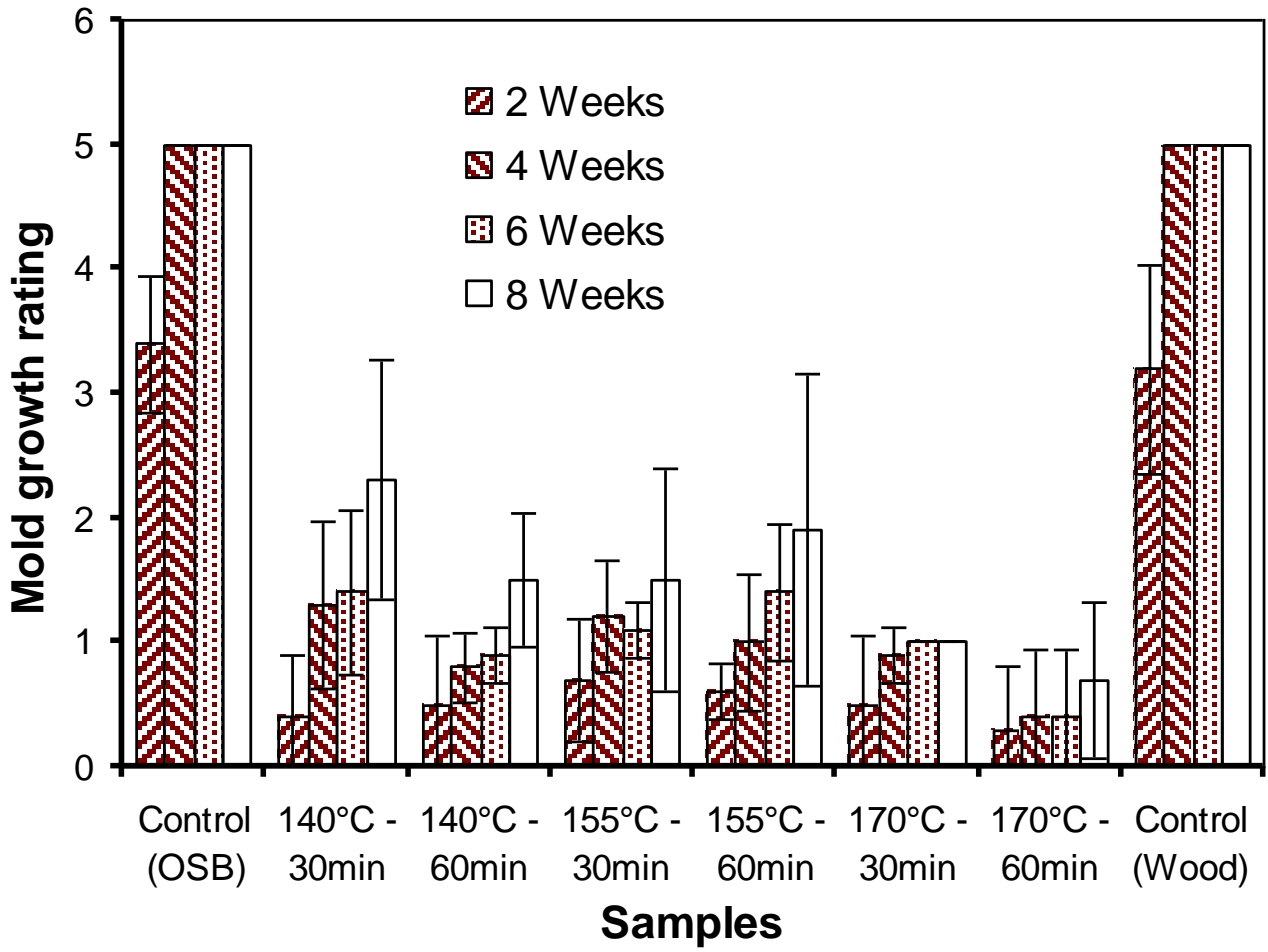
Enhanced OSB



Mechanical Properties of Oak Cell Walls



Mold rating of OSB samples that were exposed in a AWPA E24 test



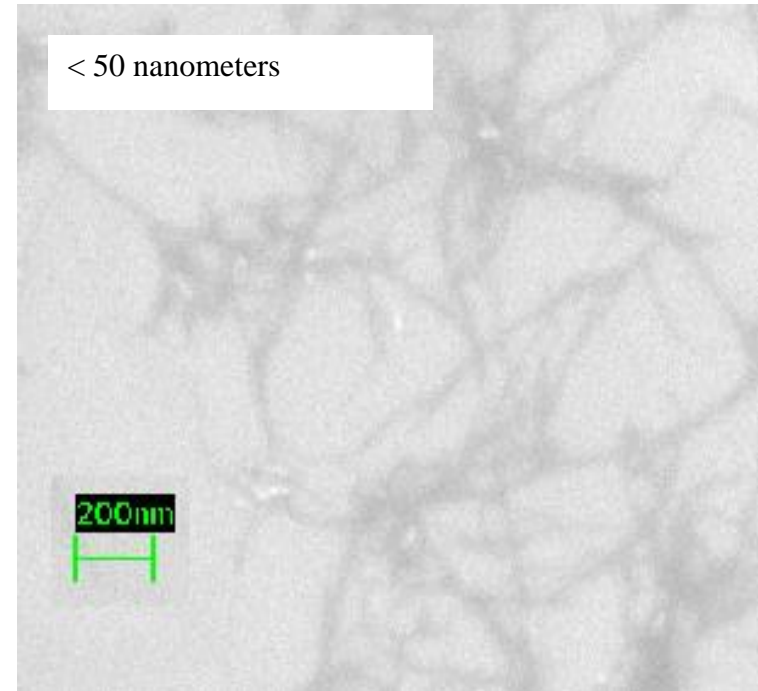
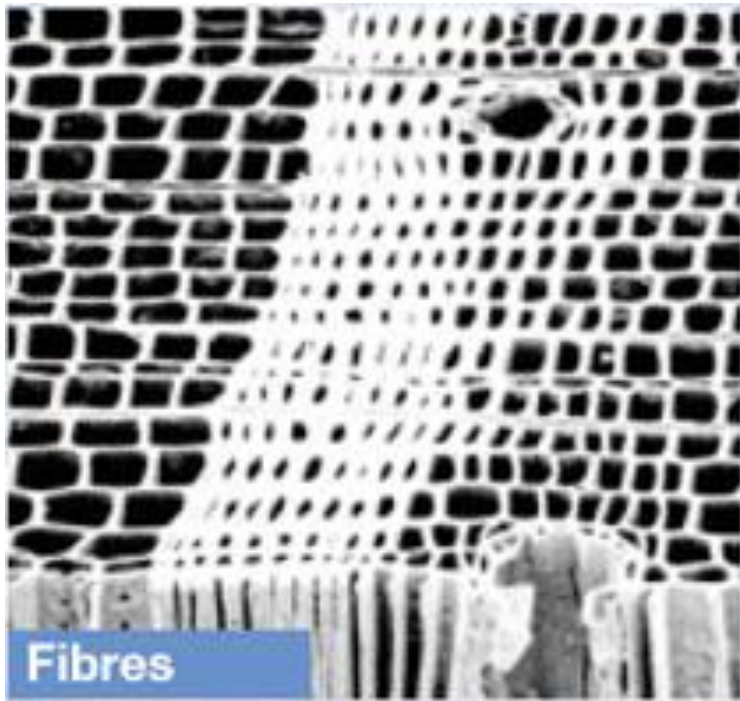
➤ Contained the following fungi: *Alternaria tenuissima*, *Aspergillus niger*, *Auerobasidium pullulans*, *Penicillium citrinum*, *Trichoderma* spp.

➤ Scale of 0 to 5, indicating mold coverings of 0, 5-10%, 10-30%, 30-70%, greater than 70% and 100% of the samples, respectively.

Hosseinaei, FPJ 2011, 61(1):31-

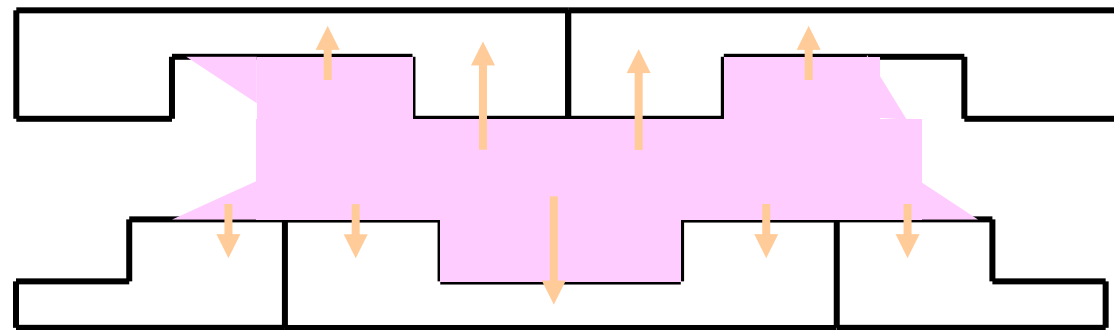
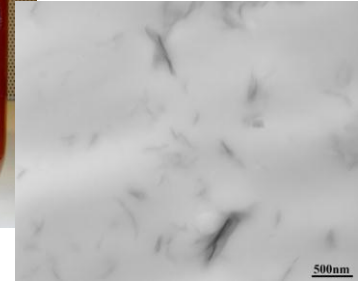
Microfibrillated cellulose (MFC)

Mechanical treatment: high pressure homogenizer, grinder treatment, fibrils in nano and micro scales.

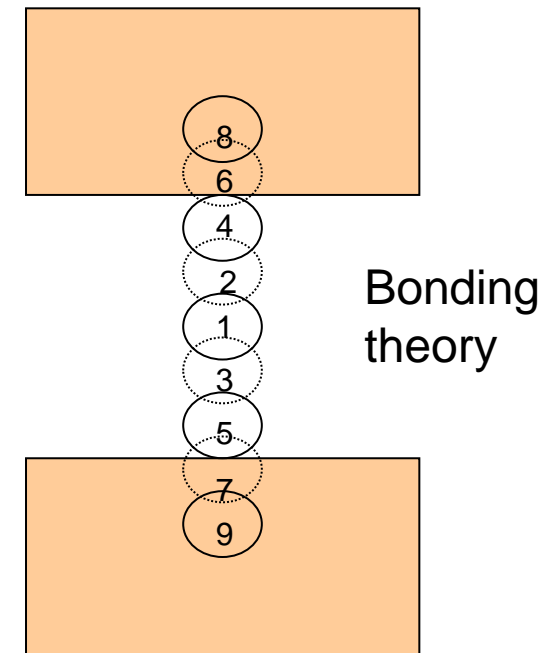


Microfibrillated cellulose (MFC)

- Reinforced adhesives (UT Patent in pending)

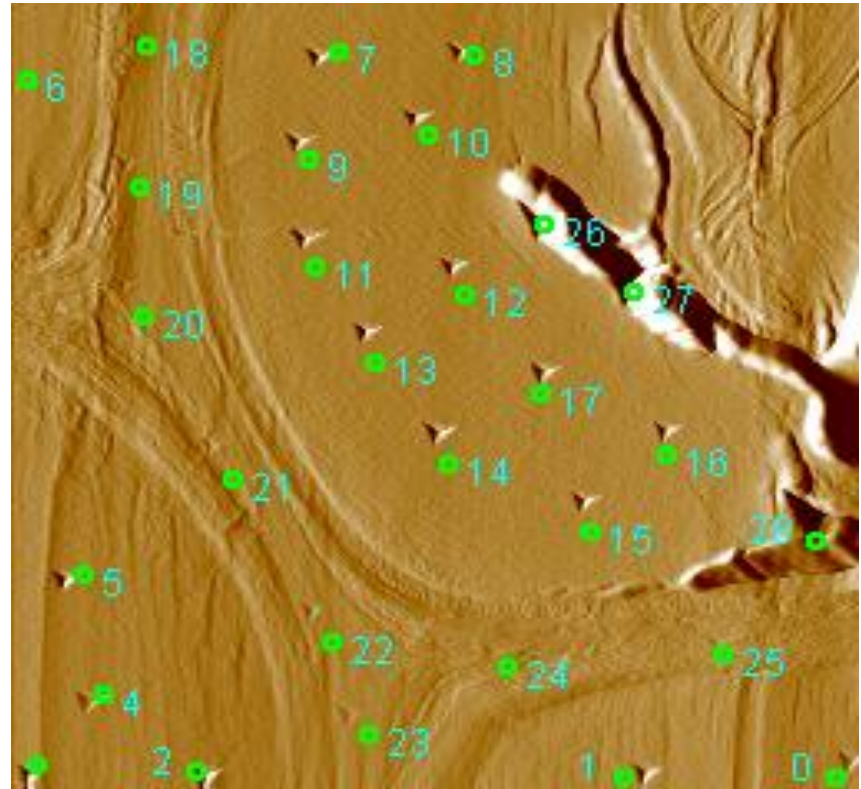
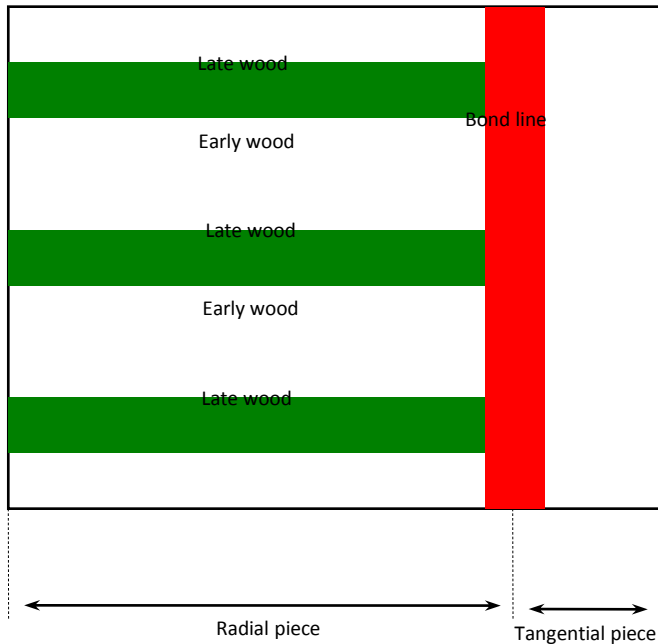


- Link 1: The adhesive film
- Links 2 and 3: Intraadhesive boundary layer
- Links 4 and 5: Adhesive-adherend interface
- Links 6 and 7: Adherend subsurface
- Links 8 and 9: Adherend proper



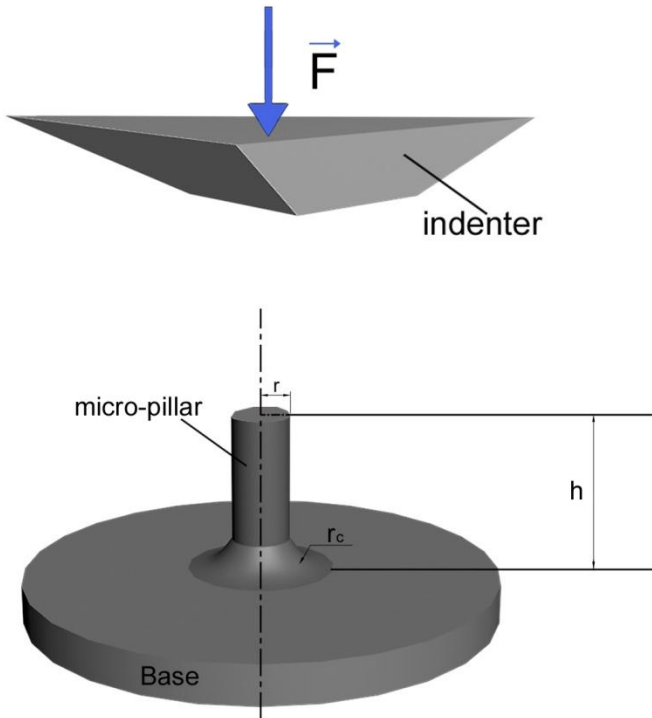
A. A. Marra, 1992

Interphase at bondline

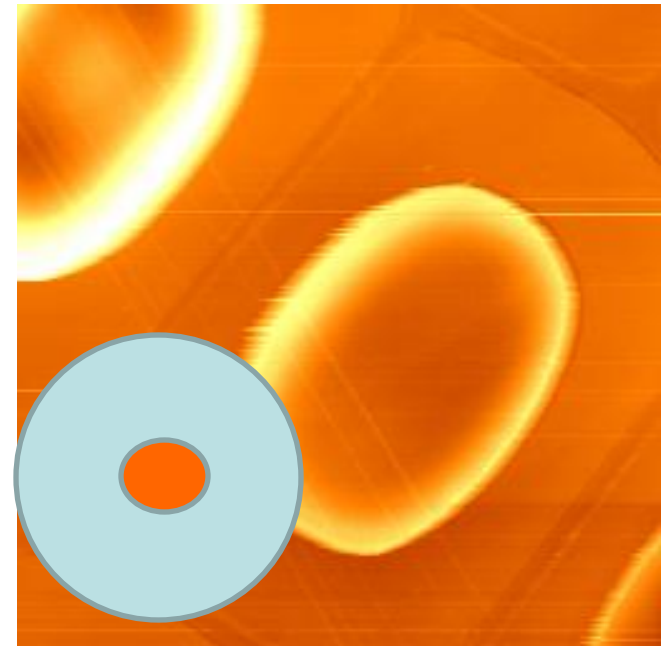


AFM images $20\ \mu\text{m} \times 20\ \mu\text{m}$ of wood cell walls showing the position of indents from nanoindentation

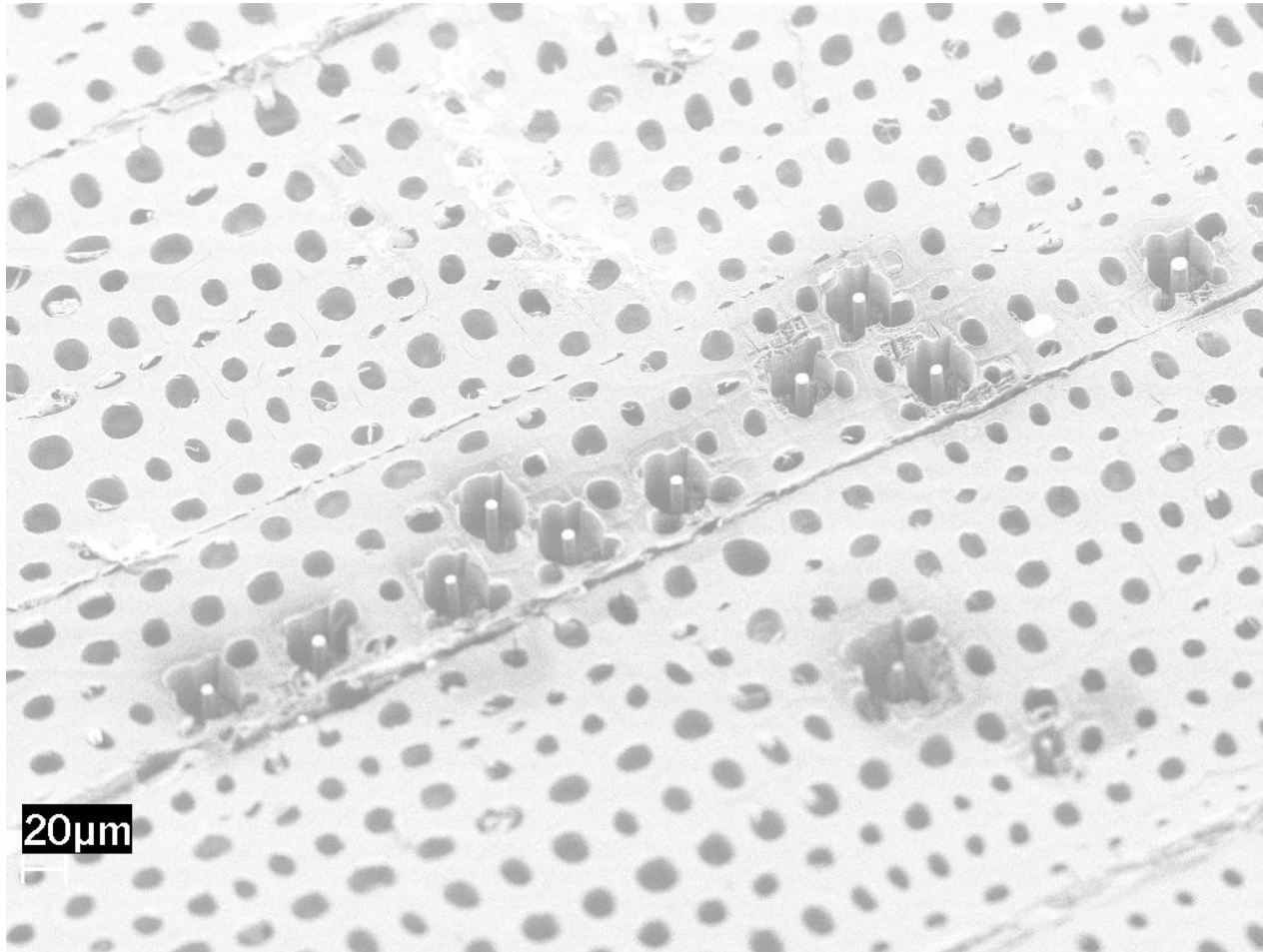
Micro-pillar compression test



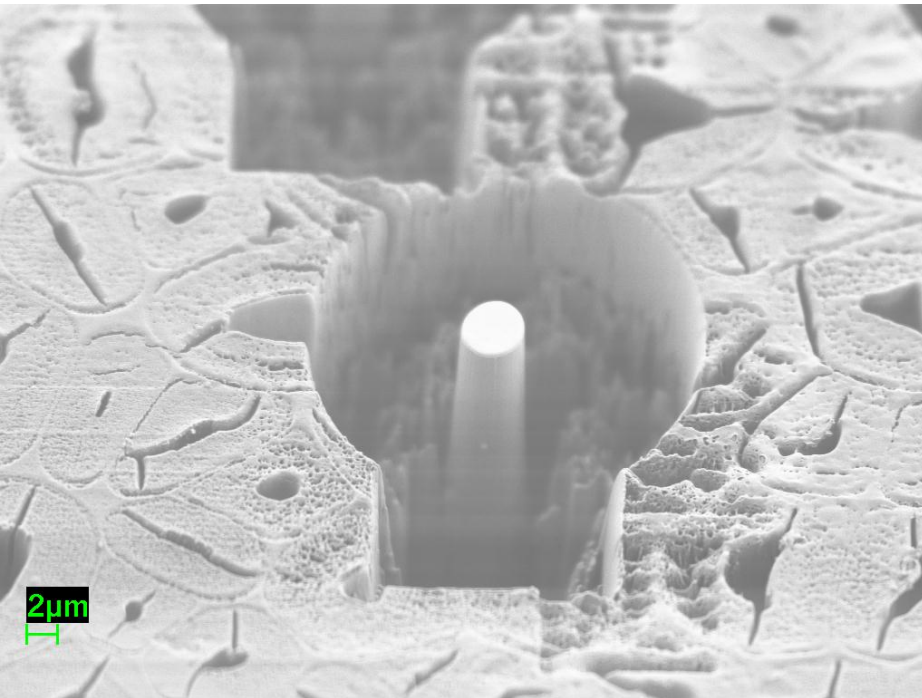
- Beam voltage 30 kV
- Beam current 7.617 nA
- Extraction voltage 6.33kV
- Emission current 2.4 kV



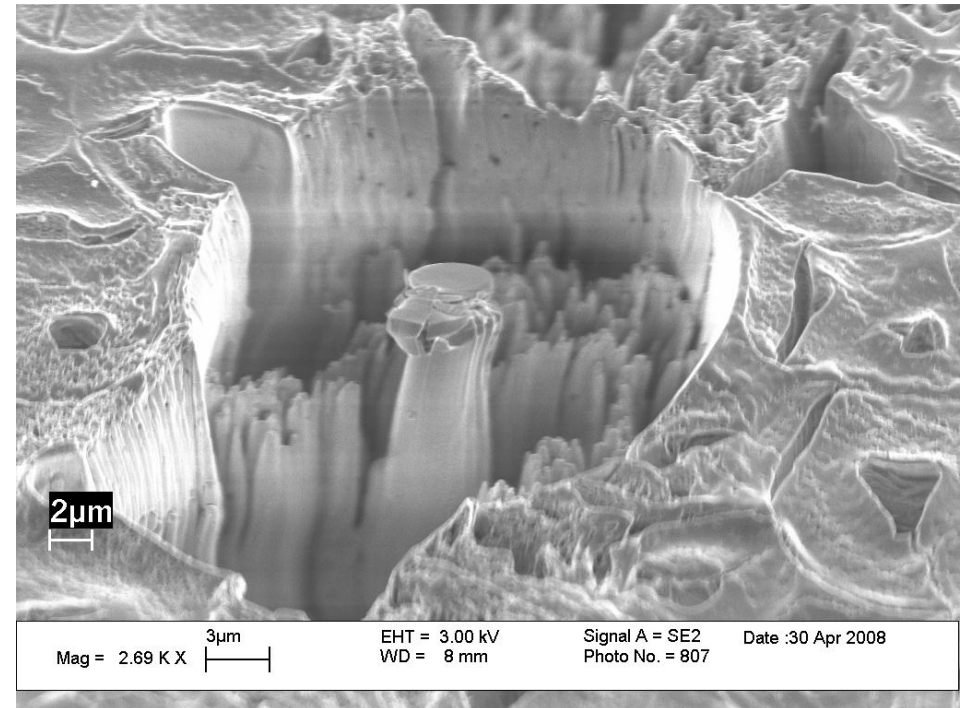
SEM image of loblolly pine specimen after FIB milling



Fracture behavior of wood pillars



a



b

SEM image of the keranji micro-pillar with 4.75 μm diameter at 36° tilt,
a- before testing, b – after testing

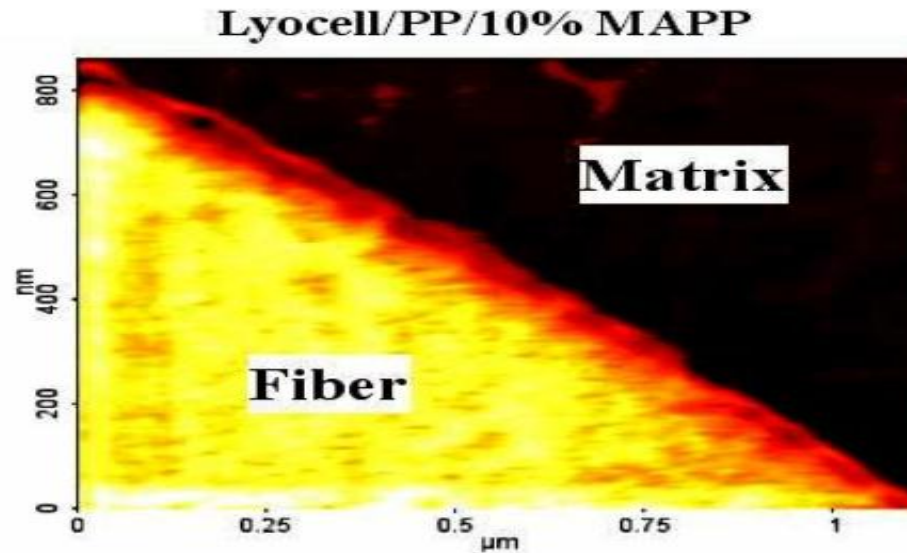
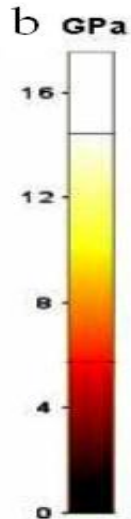
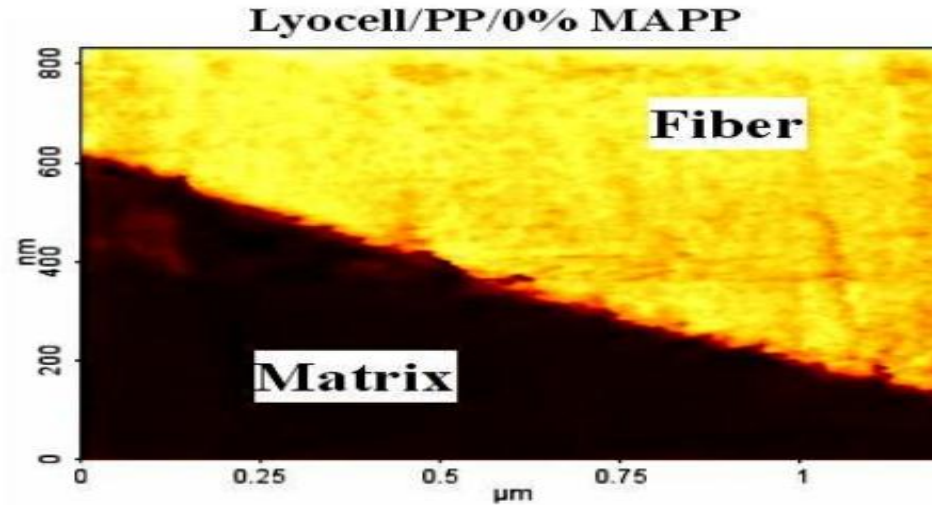
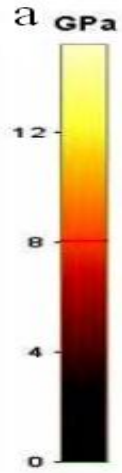
Compression strength and yield stress

Species	Yield stress (MPa)	Compression strength (MPa)
loblolly pine	111.3 (14.6)	125.0 (26.5)
keranji	136.5 (13.2)	160.0 (23.1)

(Numbers in parentheses are Standard deviation)

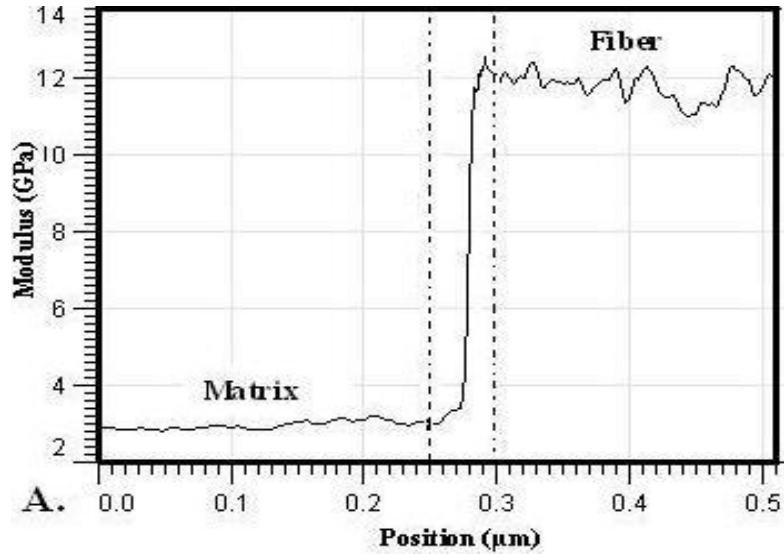
1. The density of keranji timber is 1.05 g/cm^3 while the one of loblolly pine is 0.51 g/cm^3 (Wood hand book, 1999).
2. The MFA of this keranji cell wall is 5.9° (Wu et al. 2008) and the corresponding MFA of loblolly pine cell wall is 15° (Tze et al. 2007).
3. The modulus of keranji cell wall is larger than the modulus of loblolly pine cell wall from nanoindentation test.

Imaging Interphase of Lyocell/PP Composites

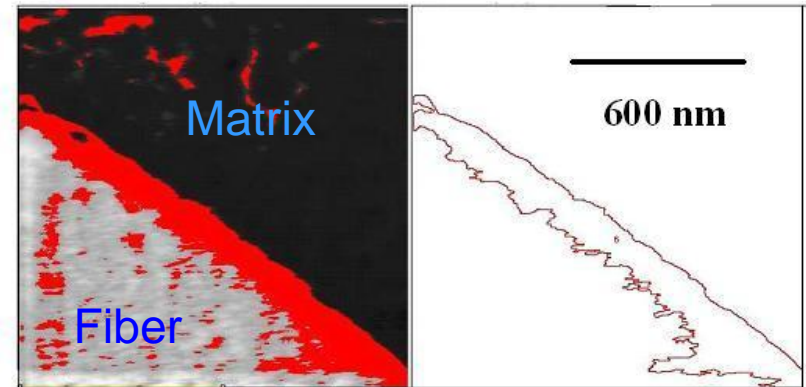
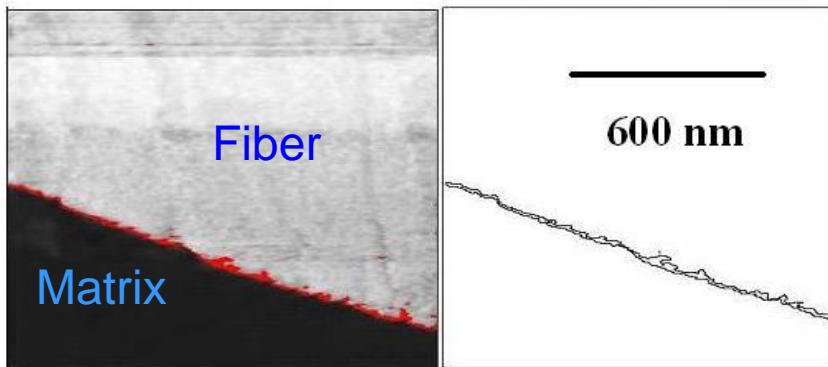
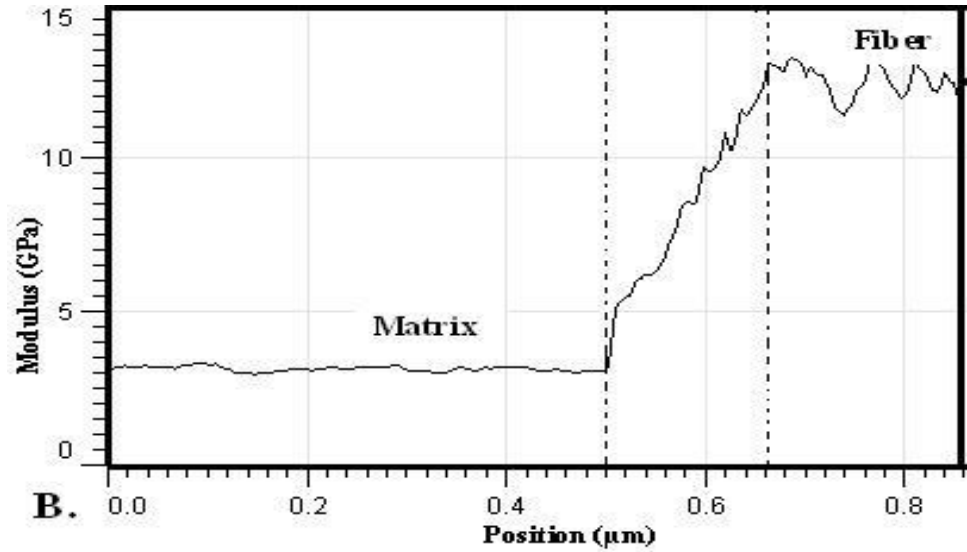


Line Profiles

PP/0 % MAPP composites



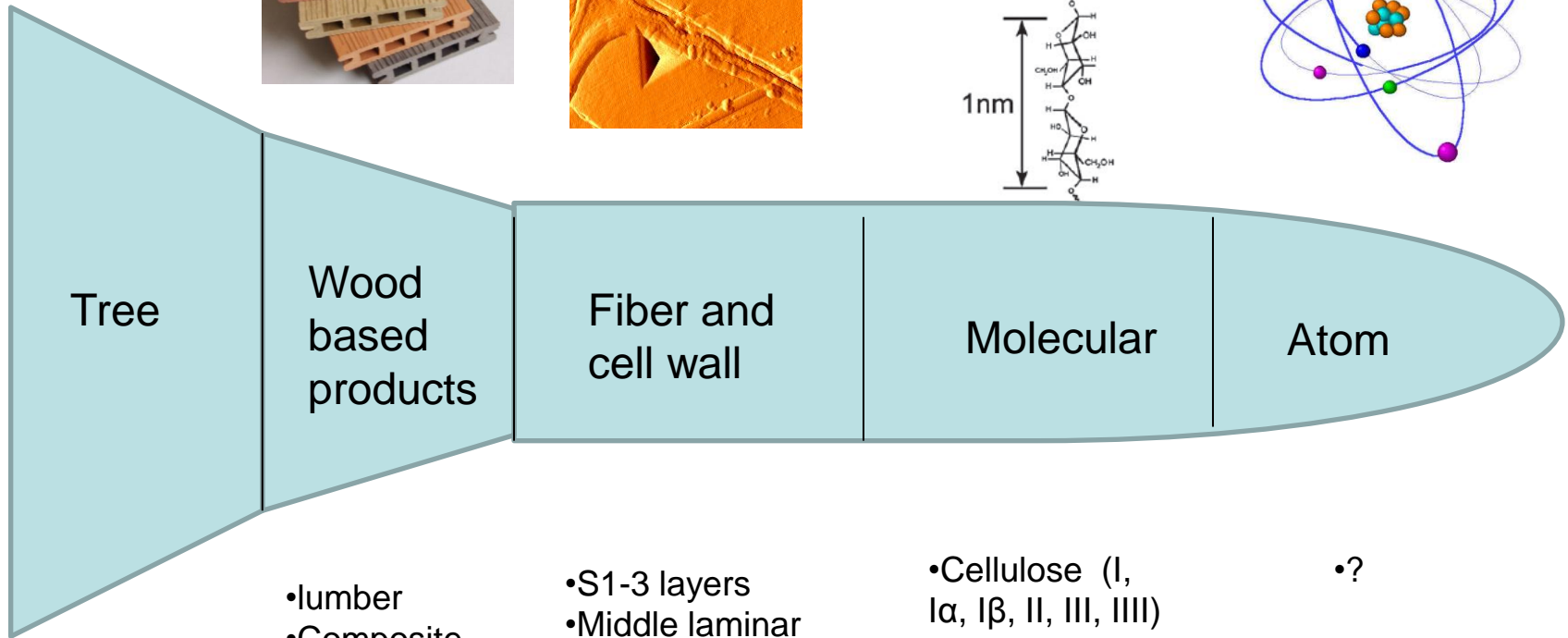
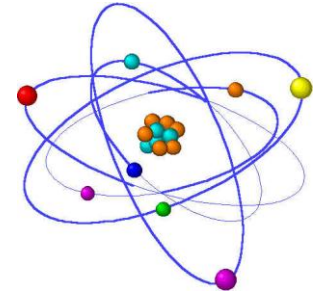
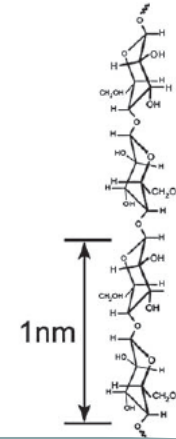
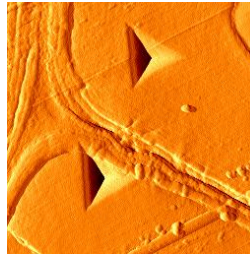
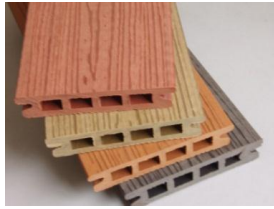
PP/10 % MAPP composites.



Measured Interphase Width

Composite Treatment (polymer, fiber)	Measured interphase width (nm)
0%MAPP	46 ± 5
2.5%MAPP	80 ± 11
10%MAPP	140 ± 15

Application in Wood Quality



Tree

Wood based products

Fiber and cell wall

Molecular

Atom

- Tree improvement
- Genetic
- Nano particle

- lumber
- Composite
- Pulp and paper

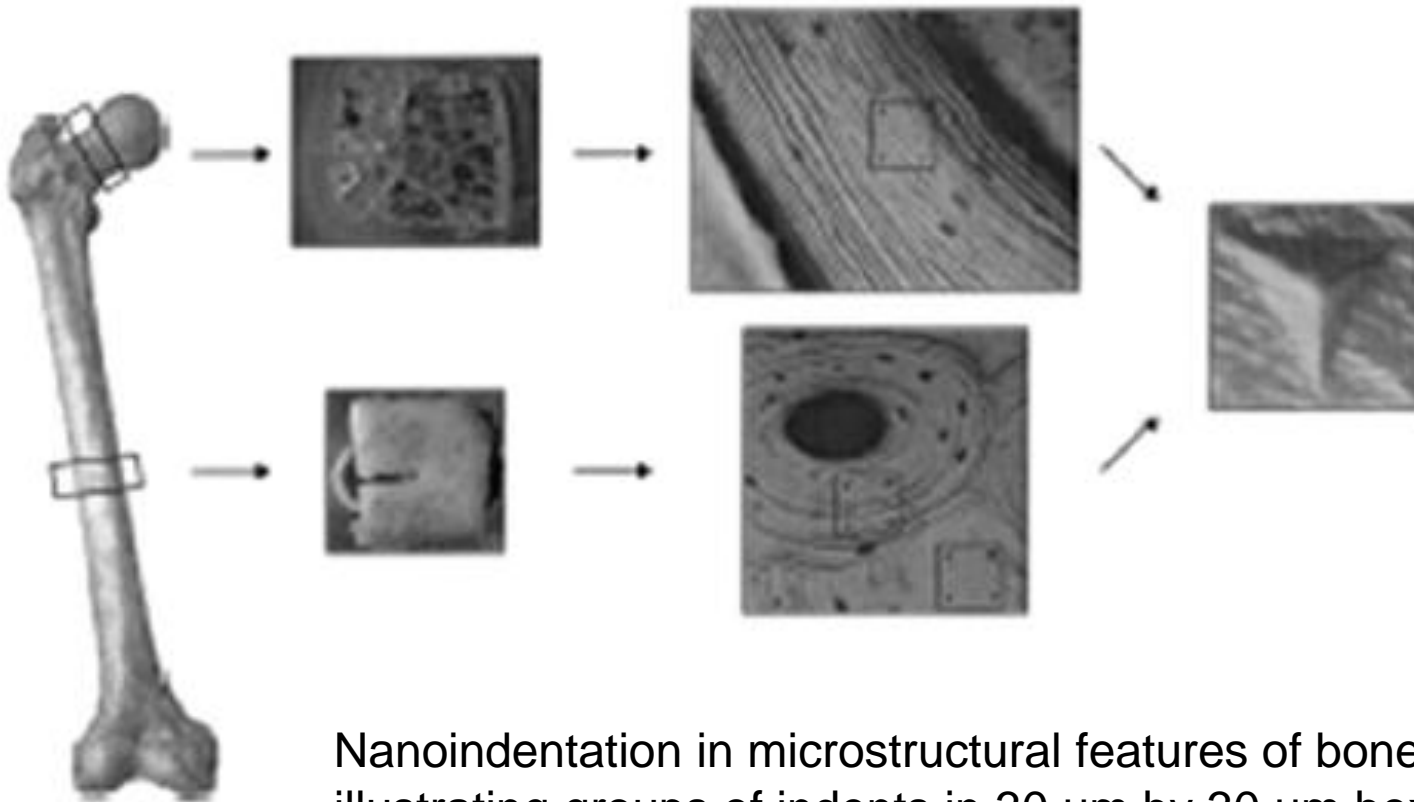
- S1-3 layers
- Middle laminar
- MFA

- Cellulose (I, I α , I β , II, III, IIII)
- Lignin (S/G ratio)
- hemicellulose

•?

Application in Wildlife Health

Mineralized tissues



Nanoindentation in microstructural features of bone, illustrating groups of indents in $30\ \mu\text{m}$ by $30\ \mu\text{m}$ boxes placed in trabecular bone (top) and in osteons and interstitial regions of cortical bone (bottom)

Nanotoday, 1(3), 2006

Application in Wildlife Health

soft tissues

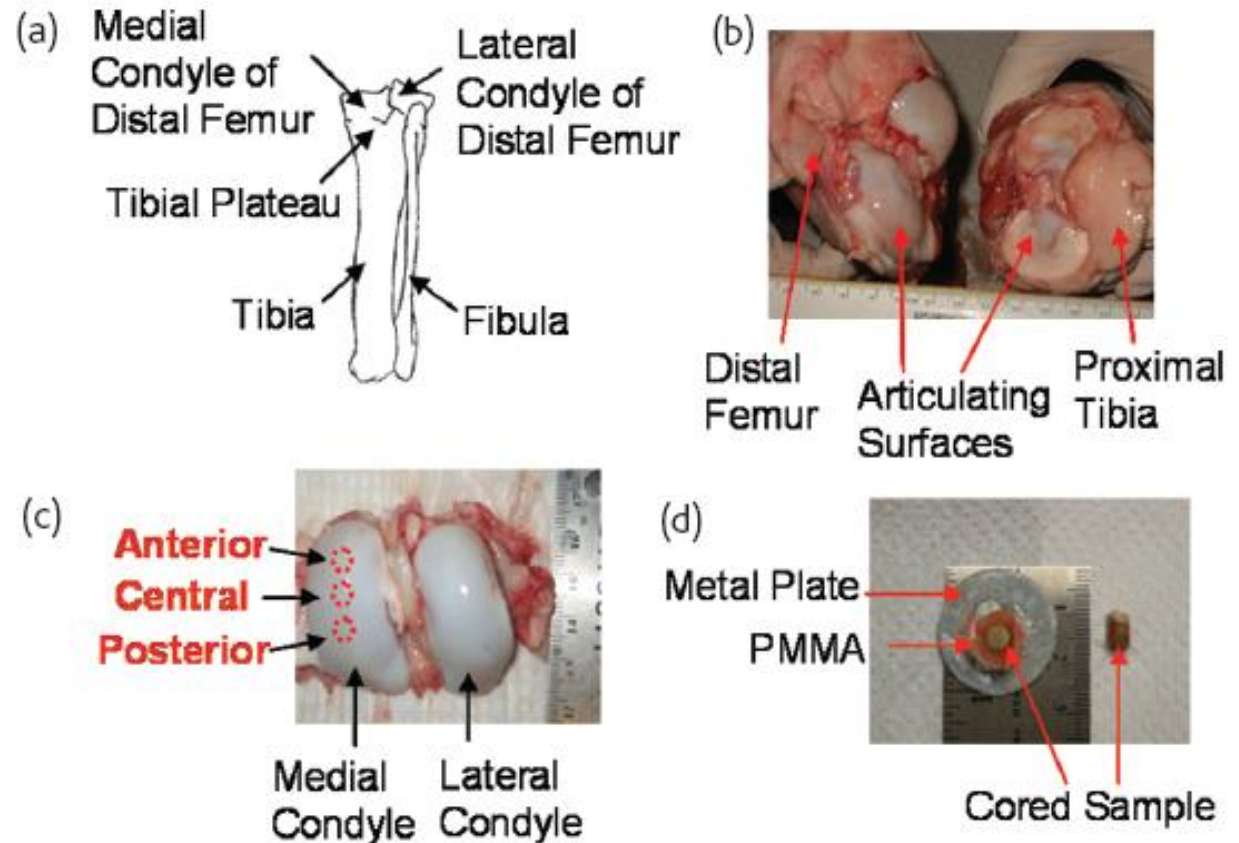


Fig. 9 Illustration of sample preparation for nanoindentation of cartilage plugs from a porcine femoral condyle. (a) Schematic of long bones. (b) Dissected joint. (c) Femoral condyle with core sites labeled. (d) Example core before and after potting in poly(methyl methacrylate) (PMMA) for indentation testing. Whole joints from small animals can also be mounted in a similar fashion.

Nanotoday, 1(3), 2006

Application in Wildlife Health

- Functional mechanical properties of repair cartilage in a rabbit knee;
- Correlation of the modulus of diseased artery tissues with the mineral content of the tissue (the degree of calcification);
- Fracture toughness of cartilage;
- Viscoelastic properties of healthy arteries, demineralized dentin, and the stratum corneum layer of skin;
- Structure-property relationships in specific regions of insect cuticle.

Application in Fisheries



No fishes left for research!



<http://www.utahspearfishing.com/>



web.utk.edu/~swang
www.renewablecarbon.org
swang@utk.edu