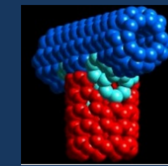
NANOCELLULOSE

An introduction, with experiments

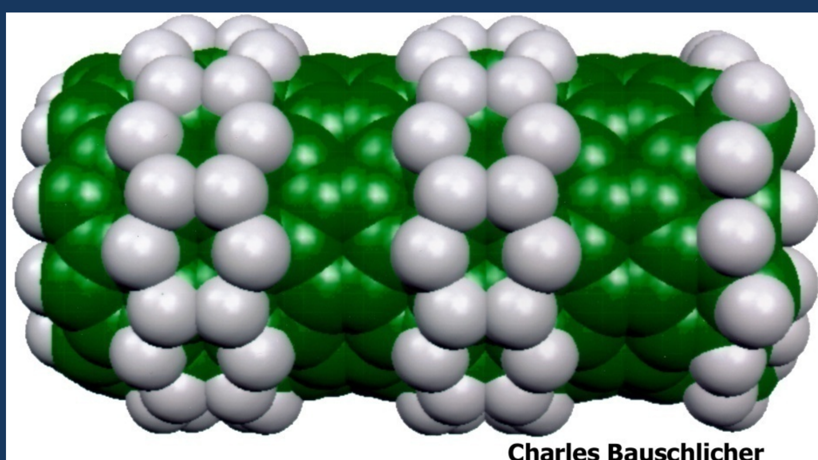
Nanotechnology 1959

- *I want to build a billion tiny factories, models of each other, which are manufacturing simultaneously. . . The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom. It is not an attempt to violate any laws; it is something, in principle, that can be done; but in practice, it has not been done because we are too big.*
- — Richard Feynman, Nobel Prize winner in physics



What is Nanotechnology?

Nanotechnology is the creation of **USEFUL/FUNCTIONAL** materials, devices and systems through control of matter on the nanometer length scale and exploitation of novel phenomena and properties (physical, chemical, biological) at that length scale



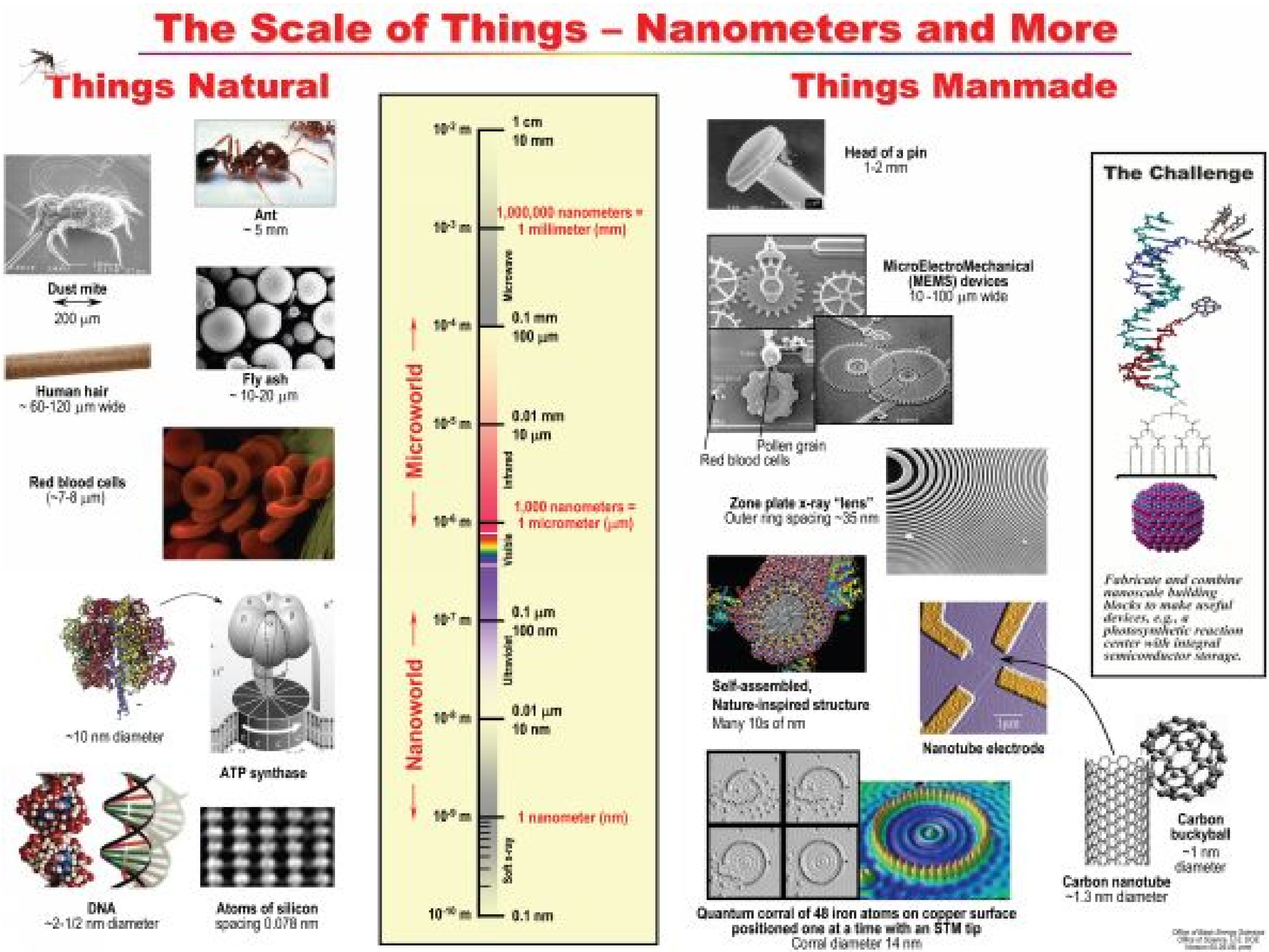
"If I were asked for an area of science and engineering that will most likely produce the breakthroughs of tomorrow, I would point to nanoscale science and engineering."

-Neal Lane
Former Assistant to the President for Science
And Technology

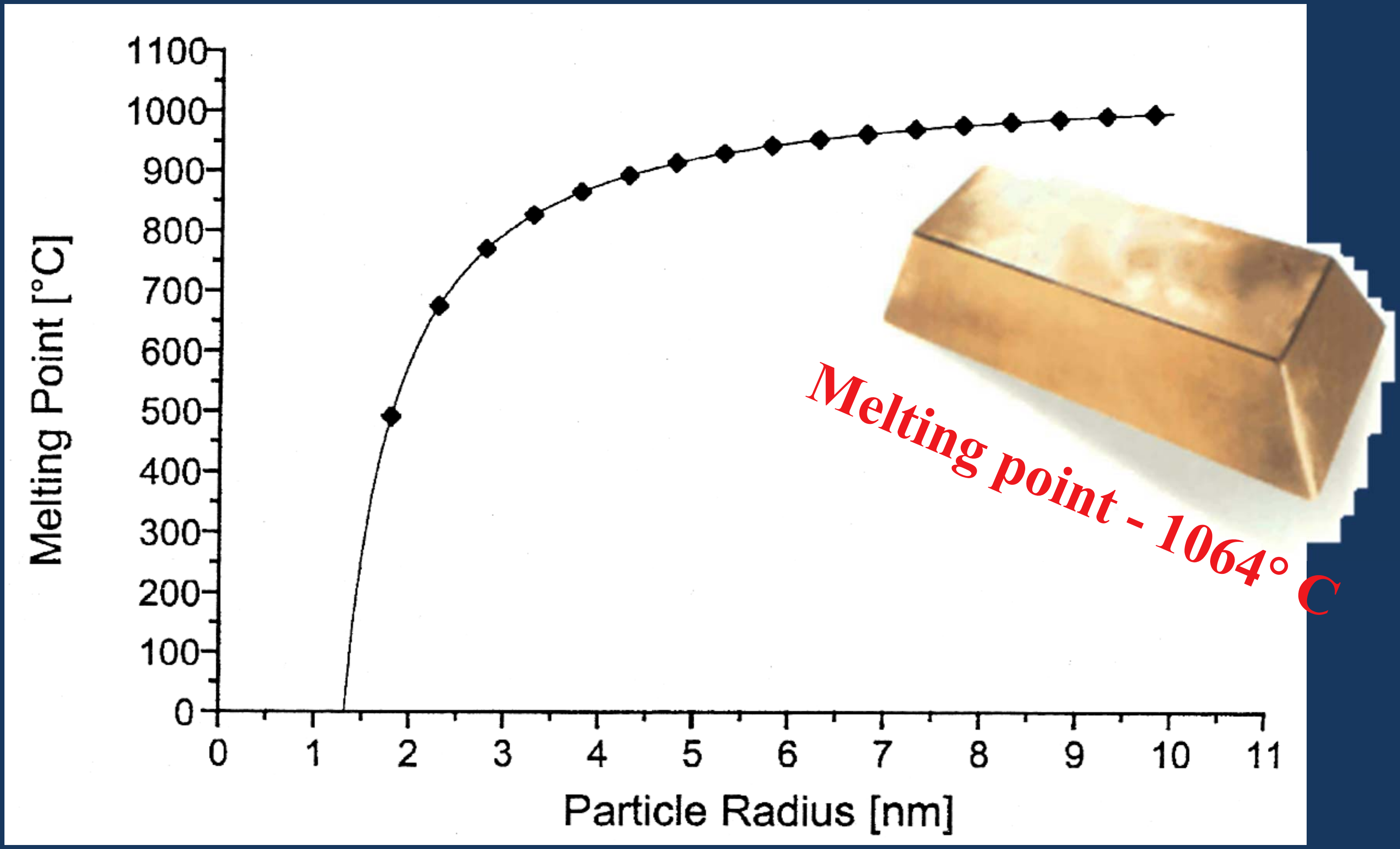
“NANO” DEFINITION

- SI (System International) unit prefix meaning 10^{-9}
- i.e. 1 nm = 1×10^{-9} m

- US Government
- 1 nm $\leq$ smallest dimension $\leq$ 100 nm

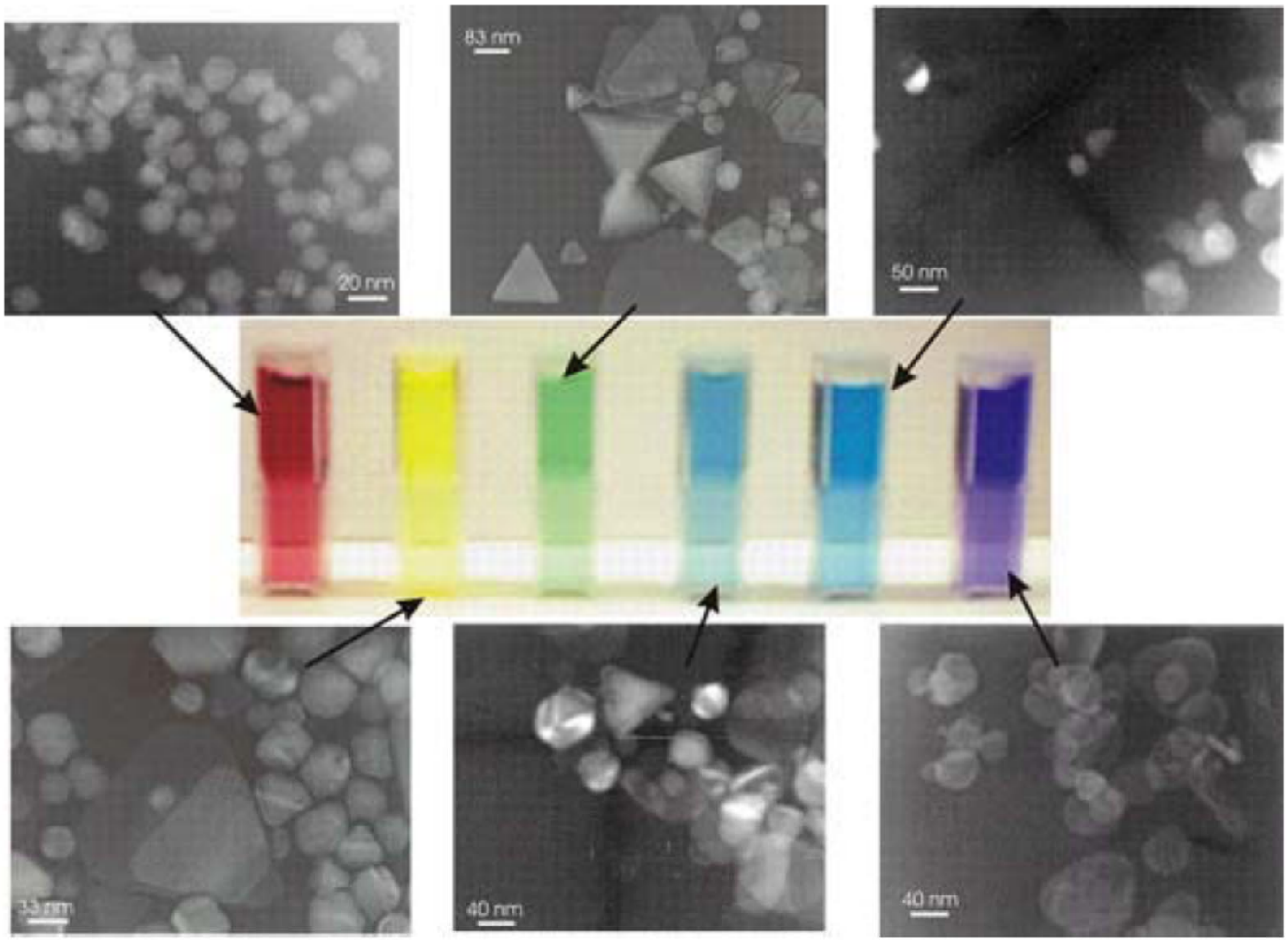

The Scale of Things – Nanometers and More
Things Natural
Things Manmade
Dust mite
200 µm
Ant
~ 5 mm
Human hair
~ 60-120 µm wide
Fly ash
~ 10-20 µm
Red blood cells
(~7-8 µm)
~10 nm diameter
ATP synthase
DNA
~2-1/2 nm diameter
Atoms of silicon
spacing 0.078 nm
10⁻² m
1 cm
10 mm
10⁻³ m
1,000,000 nanometers =
1 millimeter (mm)
Microwave
10⁻⁴ m
0.1 mm
100 µm
Microworld
10⁻⁵ m
0.01 mm
10 µm
Infrared
1,000 nanometers =
1 micrometer (µm)
10⁻⁶ m
Visible
10⁻⁷ m
0.1 µm
100 nm
Ultraviolet
Nanoworld
10⁻⁸ m
0.01 µm
10 nm
10⁻⁹ m
1 nanometer (nm)
Soft x-ray
10⁻¹⁰ m
0.1 nm
Head of a pin
1-2 mm
MicroElectroMechanical
(MEMS) devices
10 -100 µm 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
Quantum corral of 48 iron atoms on copper surface
positioned one at a time with an STM tip
Corral 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.
Carbon buckyball
~1 nm diameter
Carbon nanotube
~1.3 nm diameter

Melting Point of Gold



Source: K.J. Klabunde, 2001

Au and Ag nanoparticles change color with size



Nanocrystals in suspension. Each jar contains either silver or gold, and the color difference is caused by particle sizes and shapes, as shown in the structures
Courtesy of Richard Van Duyne Group, Northwestern University.

http://nanohub.org/resources/6583/about

2004_06_15_carbon_black.Par.0006.posterImage.jpg

Addition of nano-sized carbon to rubber

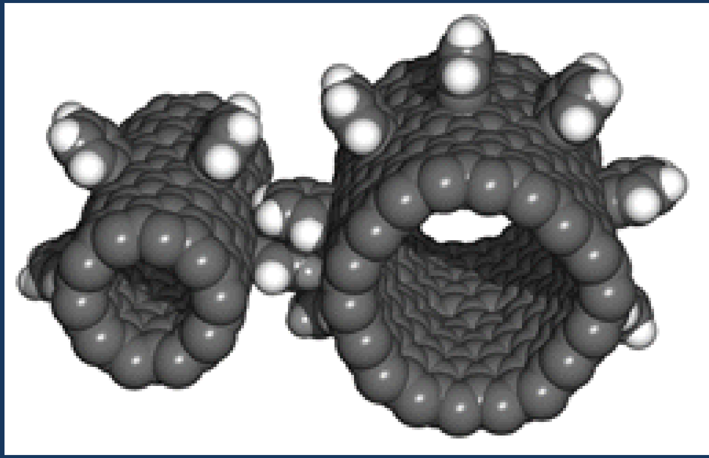
- Particle size 10-75 nm
- Strength can increase 10 X
- Stiffness increases 7 X (in accordance with modified Einstein equation)
- Abrasion resistance >1000 X
- White rubber uses silica nanoparticles

Parkinson, Brit. J. Appl. Phys. (1951) 2, 273

http://en.wikipedia.org/wiki/Carbon_black

Carbon Nanotubes

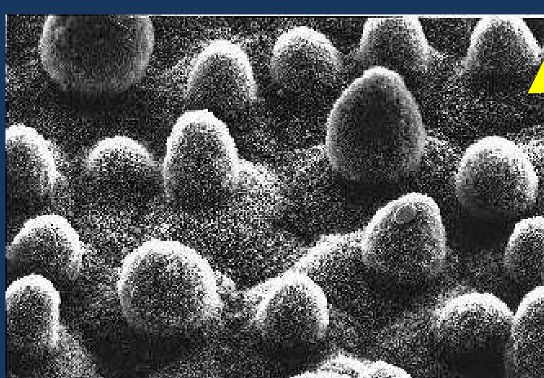
- CNT exhibits extraordinary mechanical properties: the Young's modulus is over 1 Tera Pascal. It is stiff as diamond. The estimated tensile strength is 30 Giga Pascal. These properties are ideal for reinforced composites, nanoelectromechanical systems (NEMS)



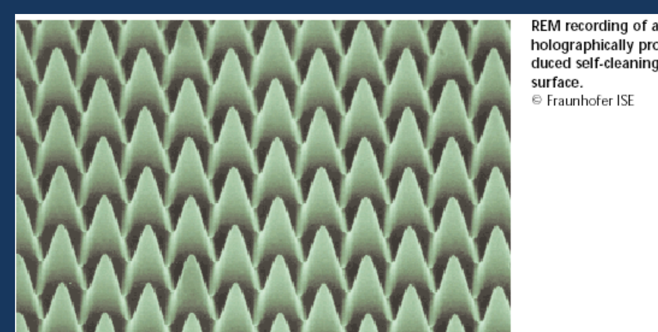
Price = $50 – $500/g
~ $20 K – $200 K/lb!

Self-Cleaning Surfaces: Lotus Effect

W. Barthlott, Univ. of Hamburg



Epicuticular wax

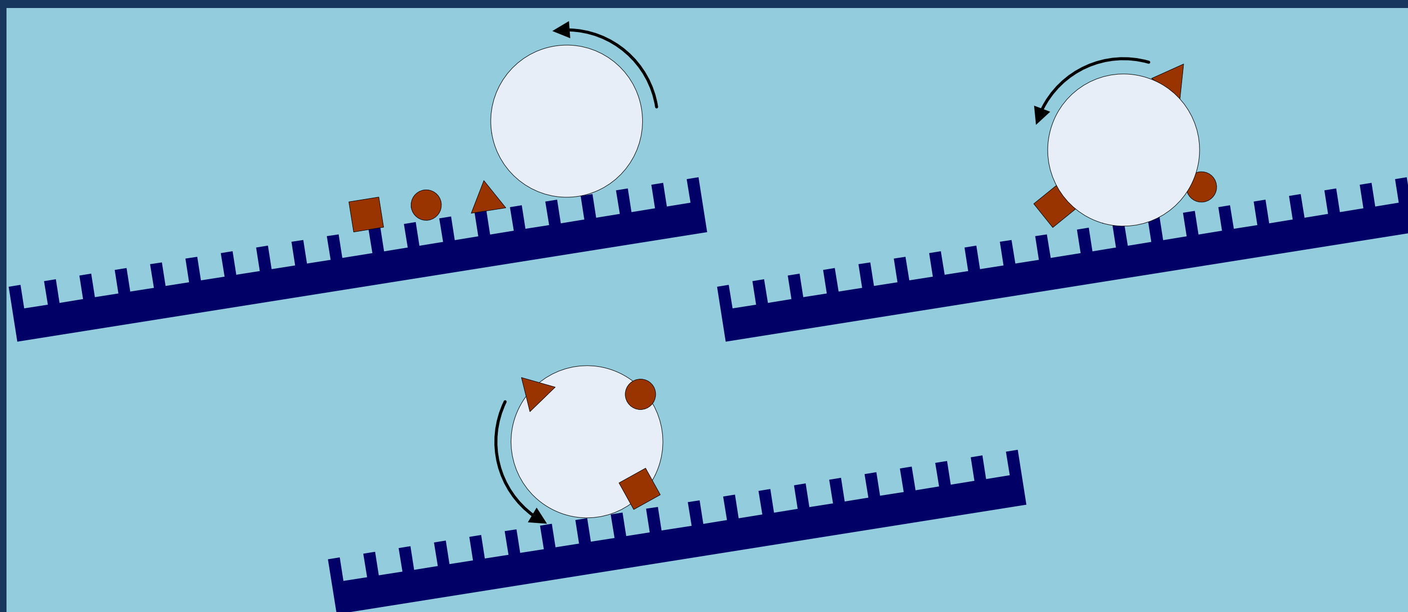


(Source: Metin Sitti, CMU)

Water on a lotus leaf

http://en.wikipedia.org/wiki/Image:LotusEffekt1.jpg

Diagram showing a droplet cleaning a superhydrophobic surface by rolling off



- Droplet does not slide, it rolls
- Particle removed if force of adsorption > static friction between the particle and surface
- static friction force very low due to minimized contact area between particle and surface

http://lotus-shower.isunet.edu/the_lotus_effect.htm

http://www.eddiebauer.com/eb/product.asp?cm_cg
=T319&product_id=31472&.rand=disabled

Stain & Wrinkle-Resistant Solid Color Shirt with Nano-Tex®
Finally, a dress shirt that looks great, feels great, and is wrinkle-resistant and stain-repellent. A classic handsome shirt with a helpful modern twist.

EddieBauer.com

nano techwire.com
nanotechwire.com

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2/9/2005 11:08:47 PM

Nanotec Pty Ltd Announces it's wood protection product "Nanoseal Wood".

Nanotec Pty Ltd based in Sydney, Australia announced today the start of the marketing of it's wood protection product "Nanoseal Wood". Nanoseal Wood is a water based, ultra hydrophobic, colloidal solution with self assembling properties to form the functional surface structure.

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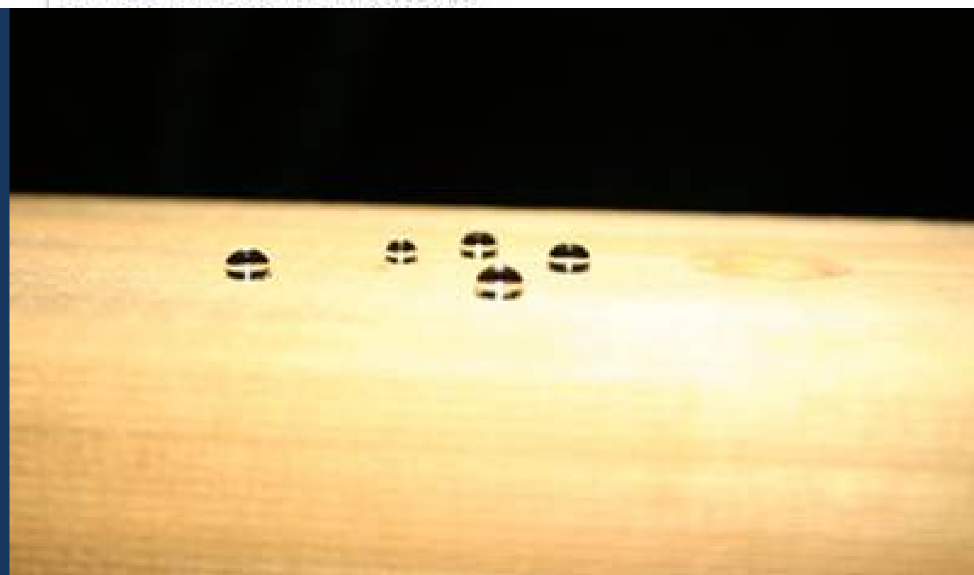
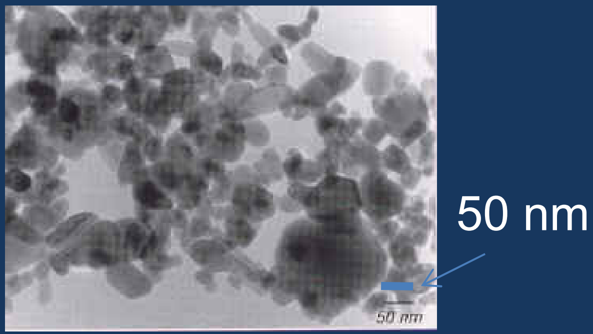


Clear Sunscreen

- Large ZnO particles
  - Block UV light
  - Scatter visible light
  - Appear white
- Nanosized ZnO particles
  - Block UV light
  - So small compared to the wavelength of visible light that they don't scatter it
  - Appear clear

"Traditional" ZnO sunscreen is white

Nanoscale ZnO sunscreen is clear



Zinc oxide nanoparticles

Sources: http://www.apt powders.com/images/zno/im_zinc_oxide_particles.jpg
http://www.abc.net.au/science/news/stories/s1165709.htm
http://www.4girls.gov/body/sunscreen.jpg

nano*sense.org/documents/presentations/NIMDWorkshopOct2005.ppt*

Nanovations Lignol

UV protection for wood using nanoparticles

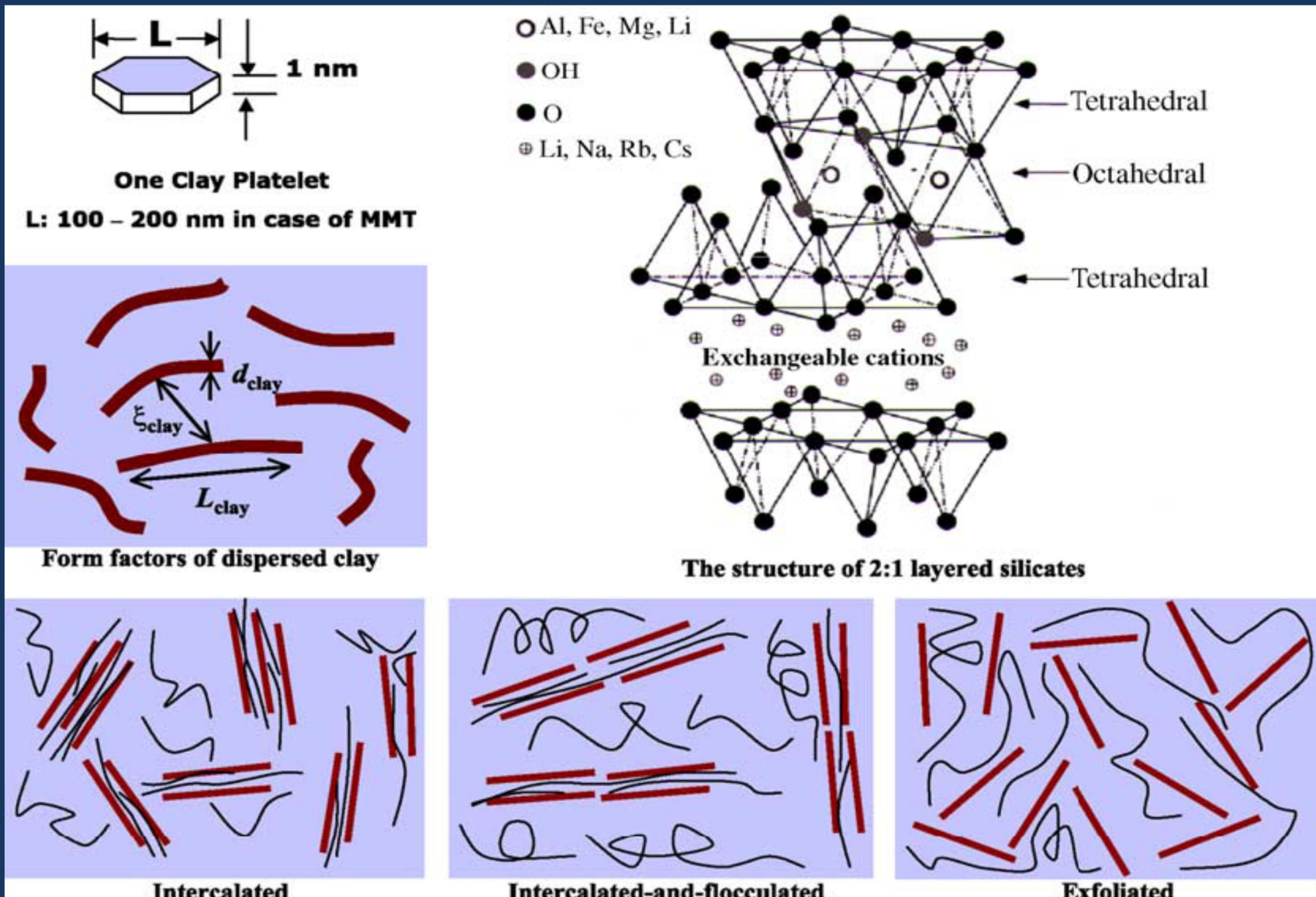
http://www.nanovations.com.au/Wood.htm

Building 3D Structures with DNA Bricks

Clay nanocomposites

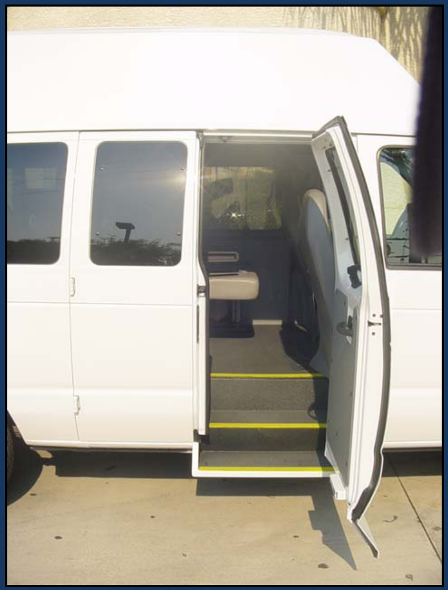
- Developed by Toyota in 1990
- Applications:
  - Fire-resistant plastics
  - Barrier films
  - Appliance, construction, electrical, food packaging and transportation sectors

http://nanocor.com/



Reproduced from Sinha Ray, Okamoto and Okamoto by permission of American Chemical Society, USA.

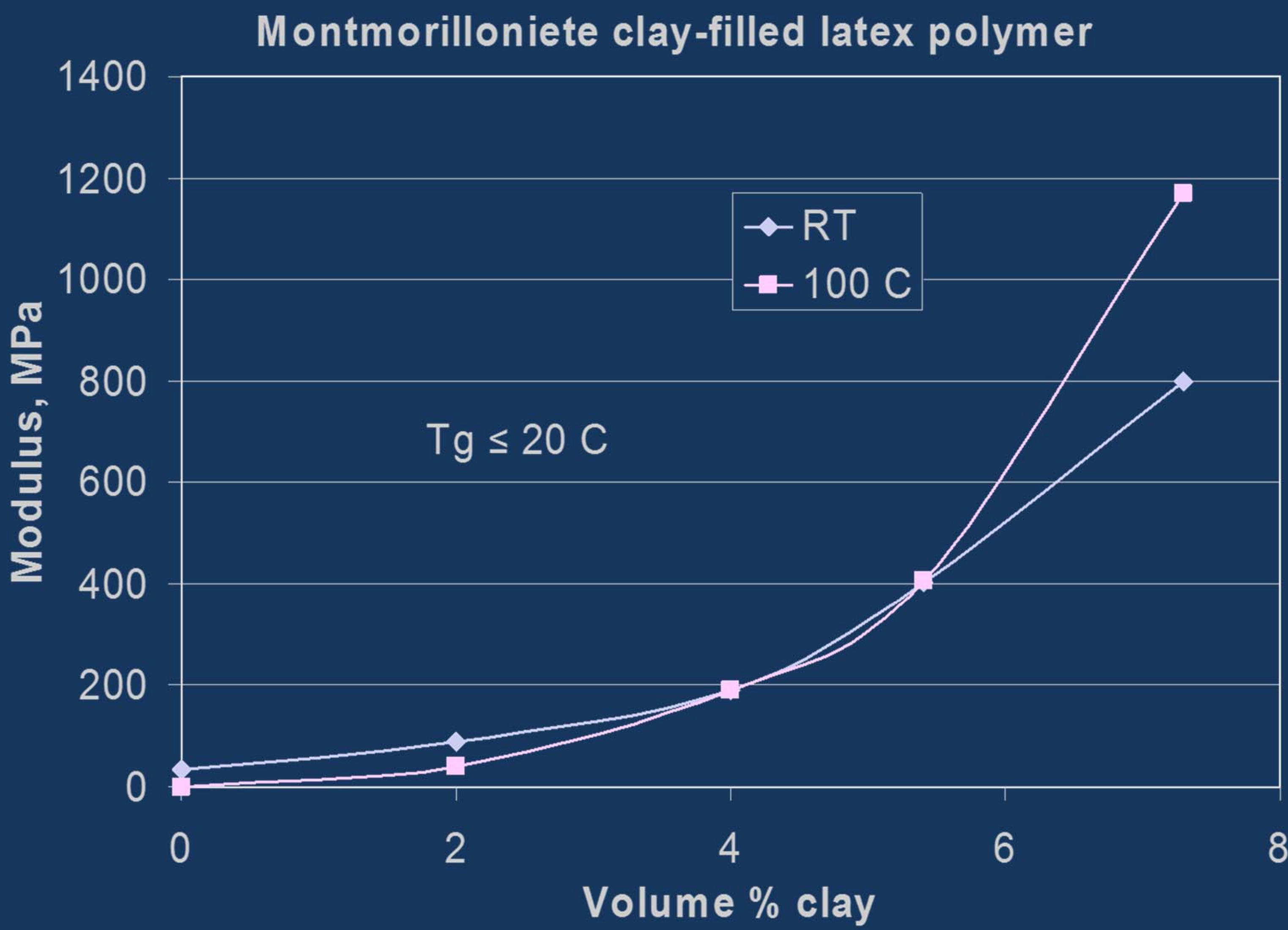
S. Ray and M. Okamoto, Prog. Polym. Sci. 28 (2003) 1539–1641



The step-assist on the 2002 GMC Safari (shown) and Chevrolet Astro vans is the automotive industry's first exterior applications for thermoplastic polyolefin-based nanocomposites. The part won General Motors the 2001 Grand Award for plastics innovation from the SPE's Automotive Division. (Photo courtesy of Wieck Photo Database).

http://www.specialchem4polymers.com/resources/articles/article.aspx?id=579

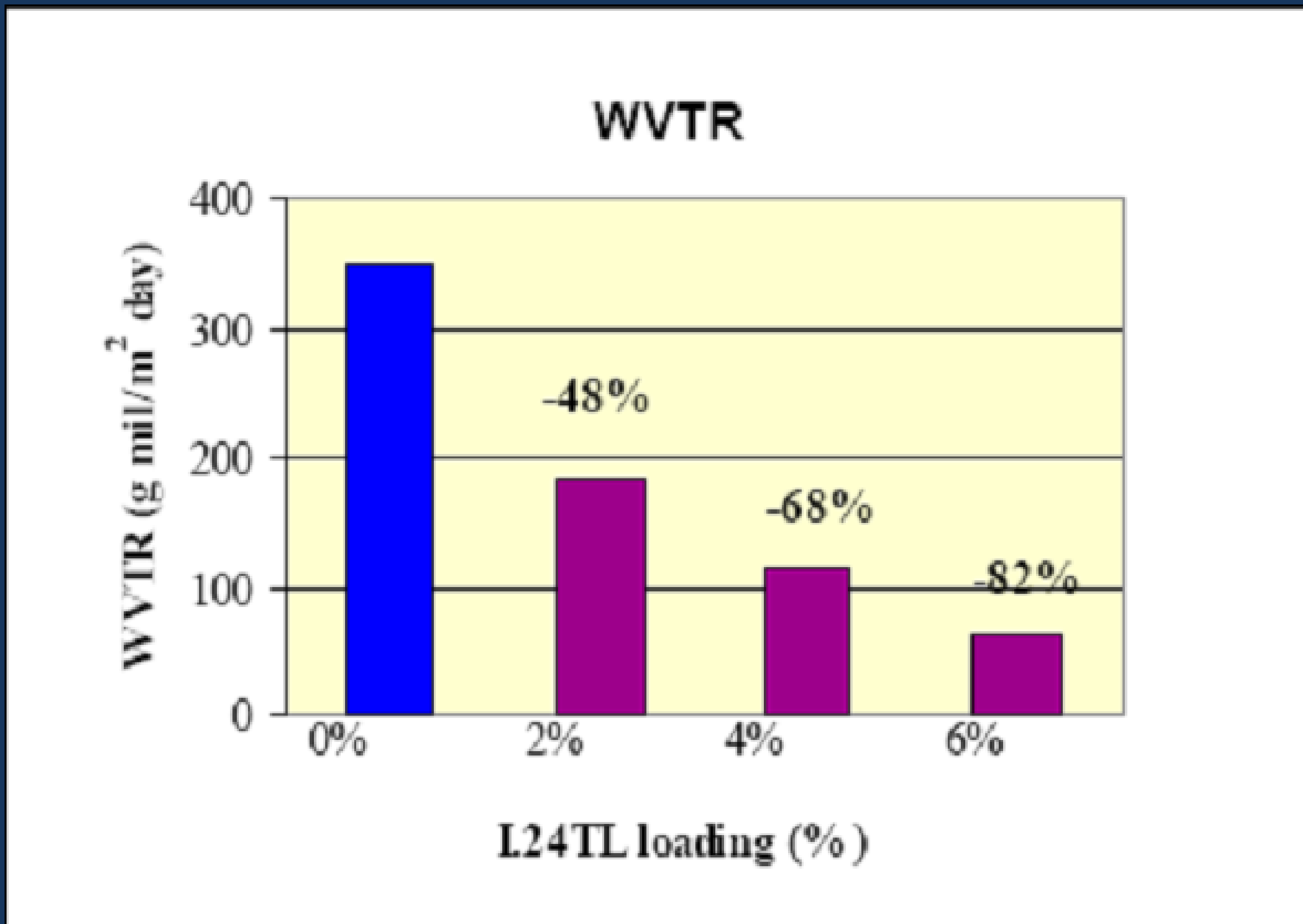
Exfoliated clay in a water-dispersible latex copolymer



Y. Rao and J. M Pochan, Macromol. (2007) 40:290-296

Barrier Film for packaging

Nano-PA6 using Nanomer 1.24 TL - *In situ polymerization*

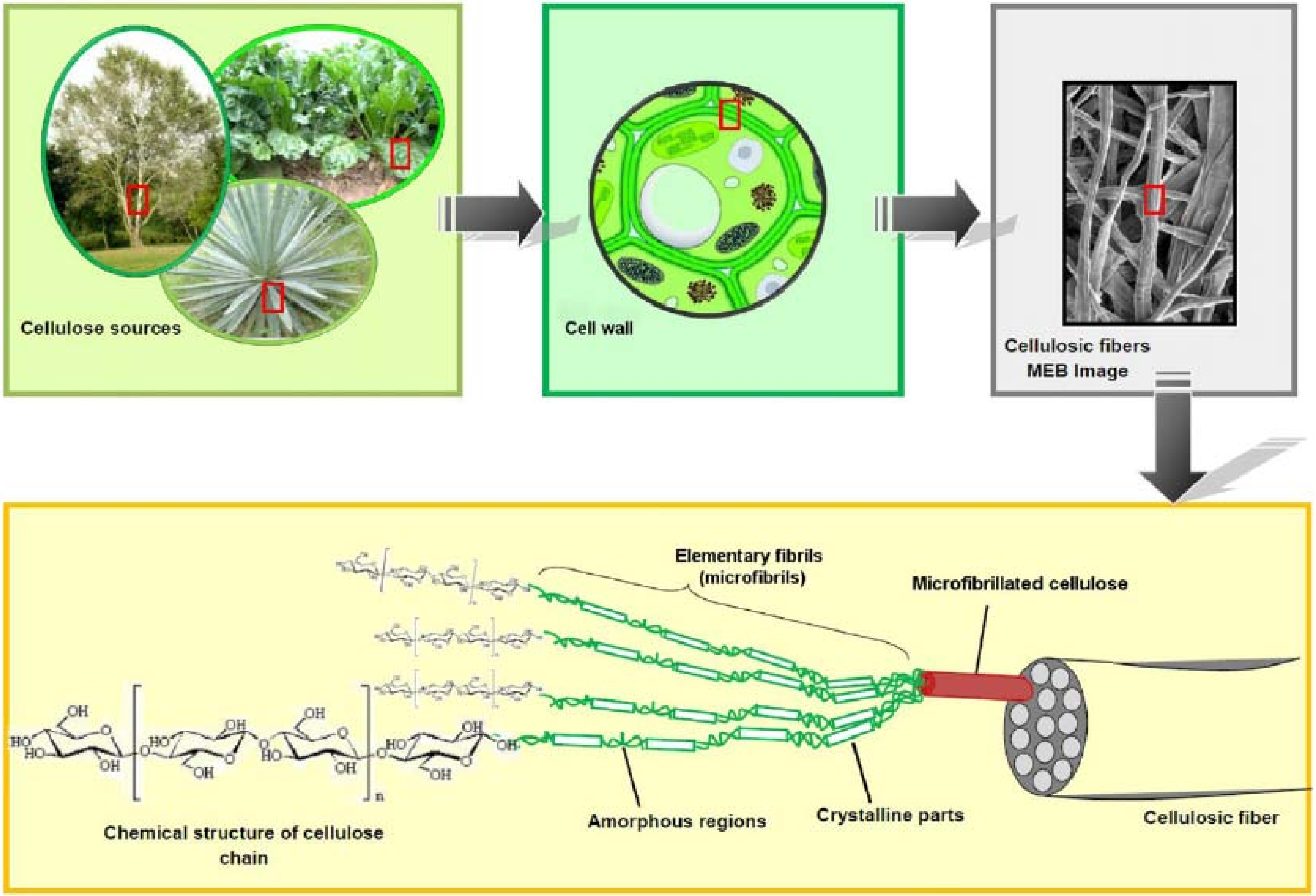


http://nanocor.com/

CHALLENGES

- Dispersion of nanoparticles
- Production scale-up of nanoparticles
- Coupling of filler to matrix
- Improving knowledge base to allow intelligent design of products which capture the advantages of nanomaterials

Angew. Chem. nt. Ed. 2011, 50, 5438–5466

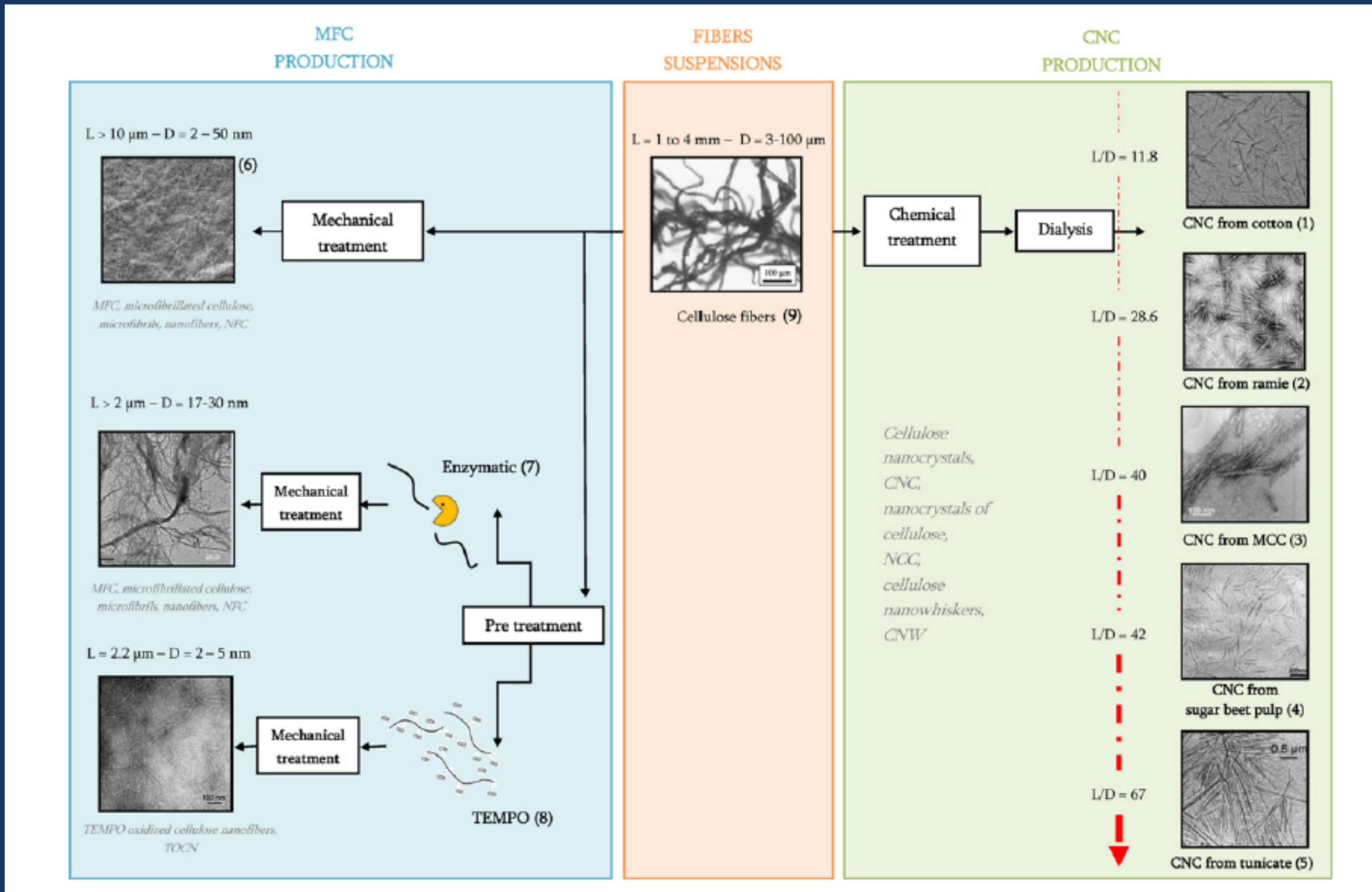


N. Lavoine et al. / Carbohydrate Polymers 90 (2012) 735–764

[redacted]

The cellulose sub-elementary fibril in plants is the most abundant nanomaterial on Earth!

Prof. Hiroyuki Yano
Kyoto University



N. Lavoine et al. / Carbohydrate Polymers 90 (2012) 735–764

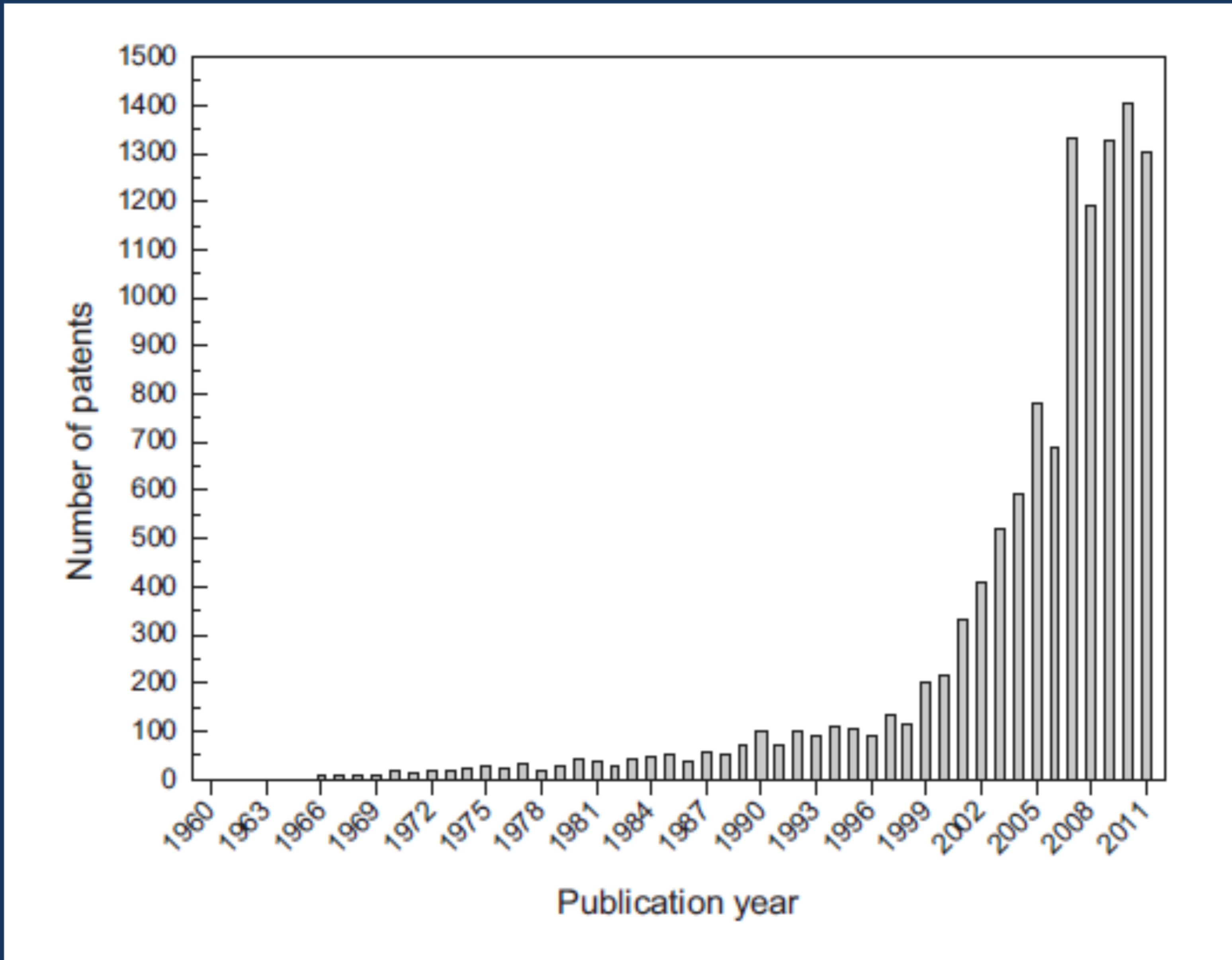
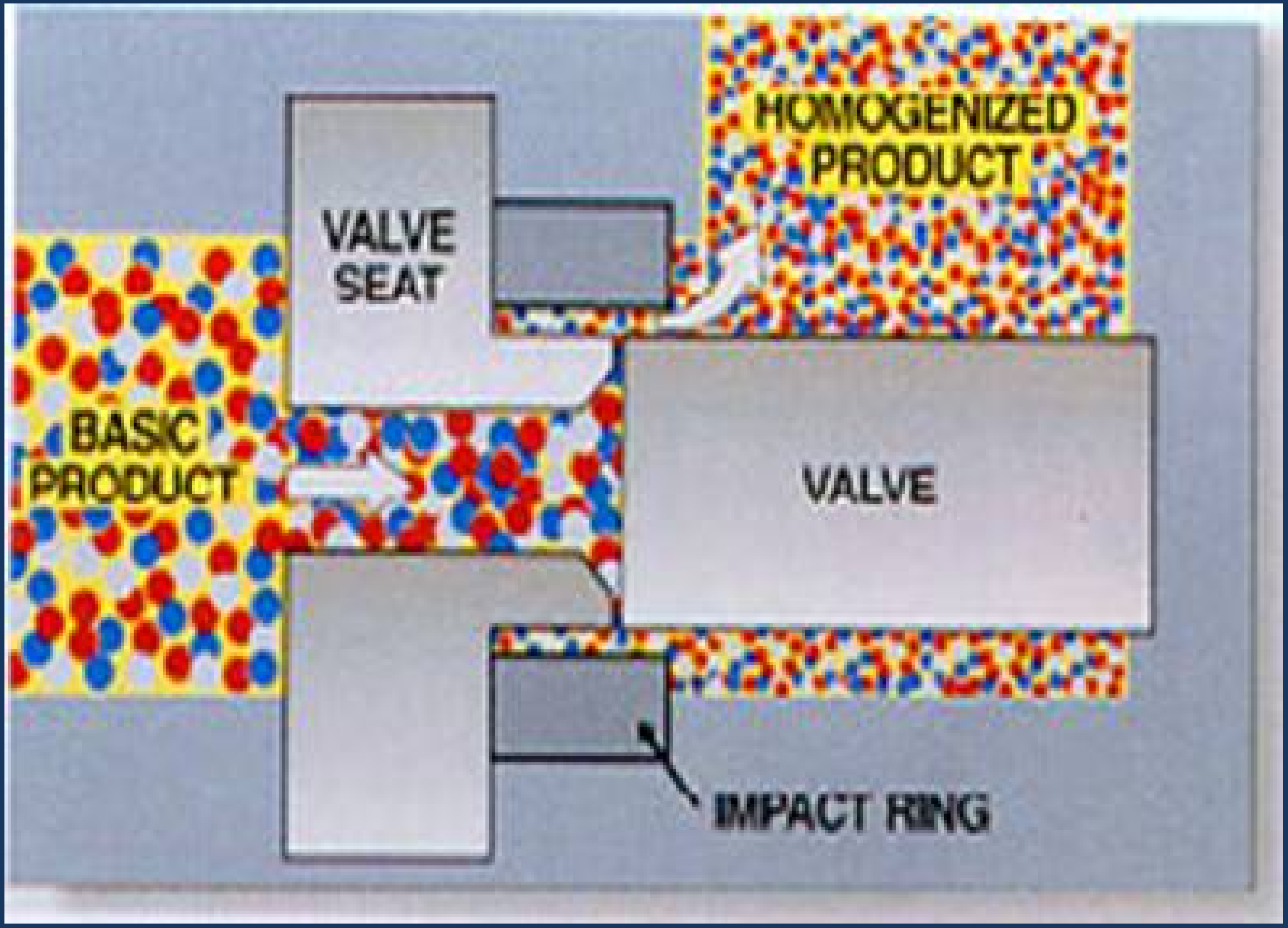


Fig. (3). Evolution of the annual number of patents on microcrystalline cellulose. Descriptors: microcrystalline cellulose.

Charreau, et al. 2013, Rec. Pat. Nanotech. 7,56

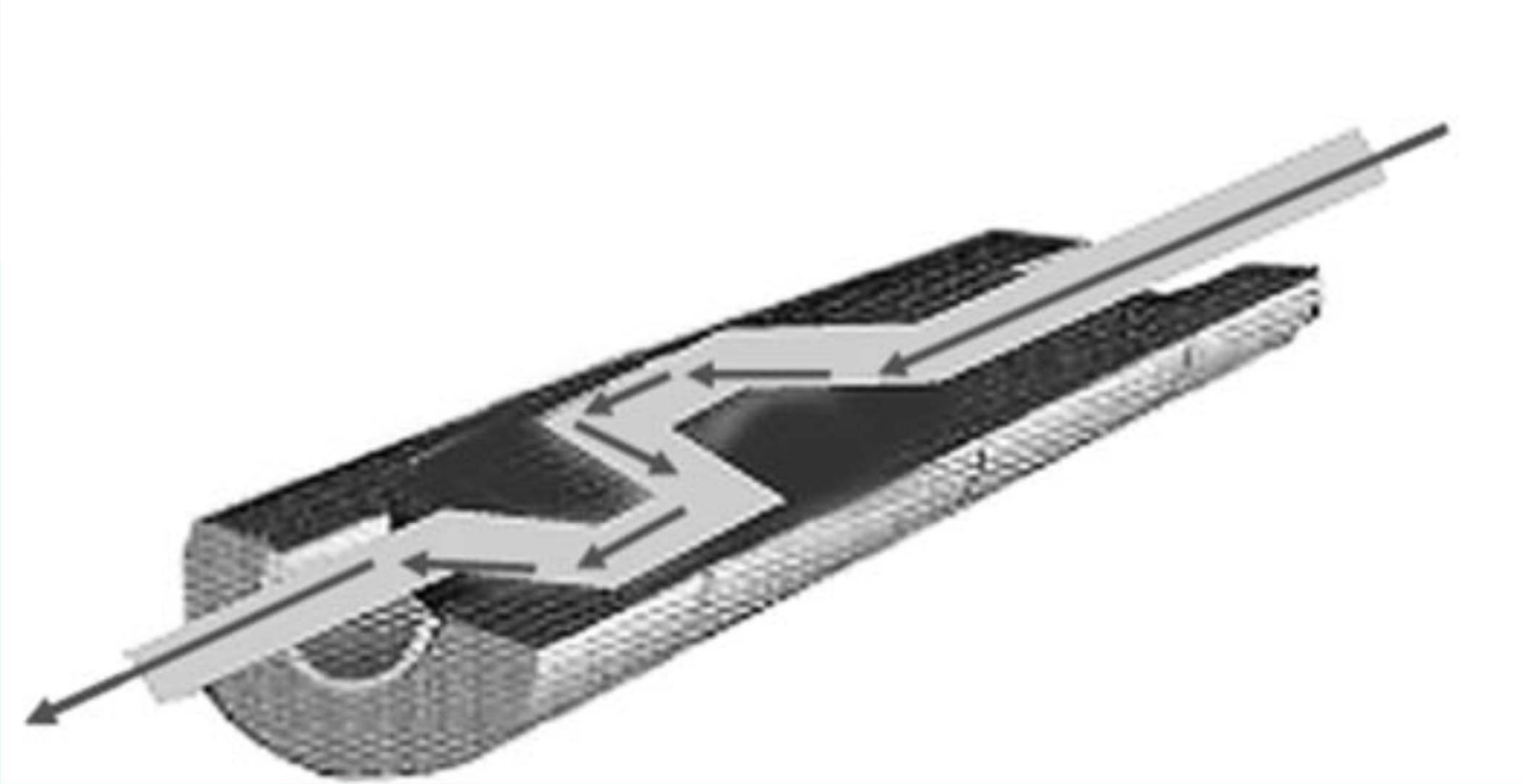
CELLULOSE NANOFIBER (CNF)

Microfluidizer/ high pressure homogenizer



http://www.pharmainfo.net/pharma-student-magazine/nanoemulsions-0

Microfluidizer



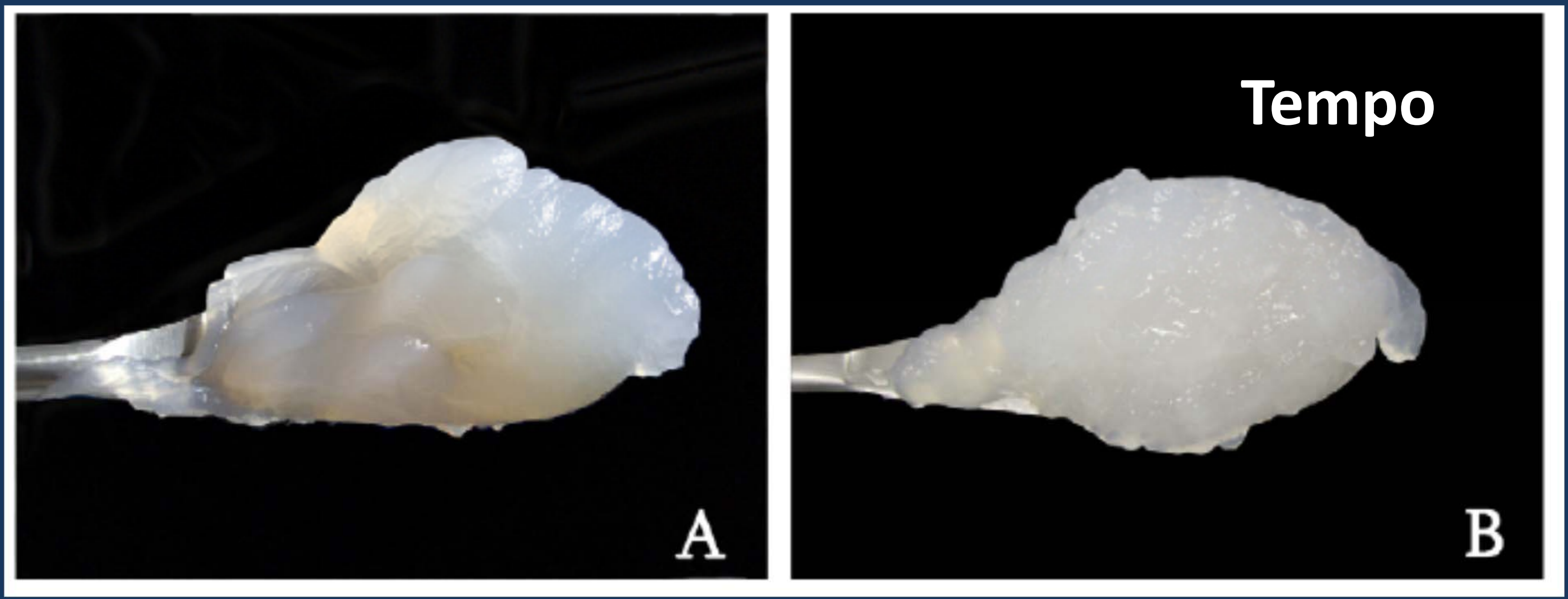
Klemm, et al., Angew. Chem. Int. Ed. 2011, 50, 5438 – 5466

Supermasscolloider
Masuko Grinder

MASUKO SANGYO CO.,LTD

http://www.masuko.com/English/product/Masscolloder.html

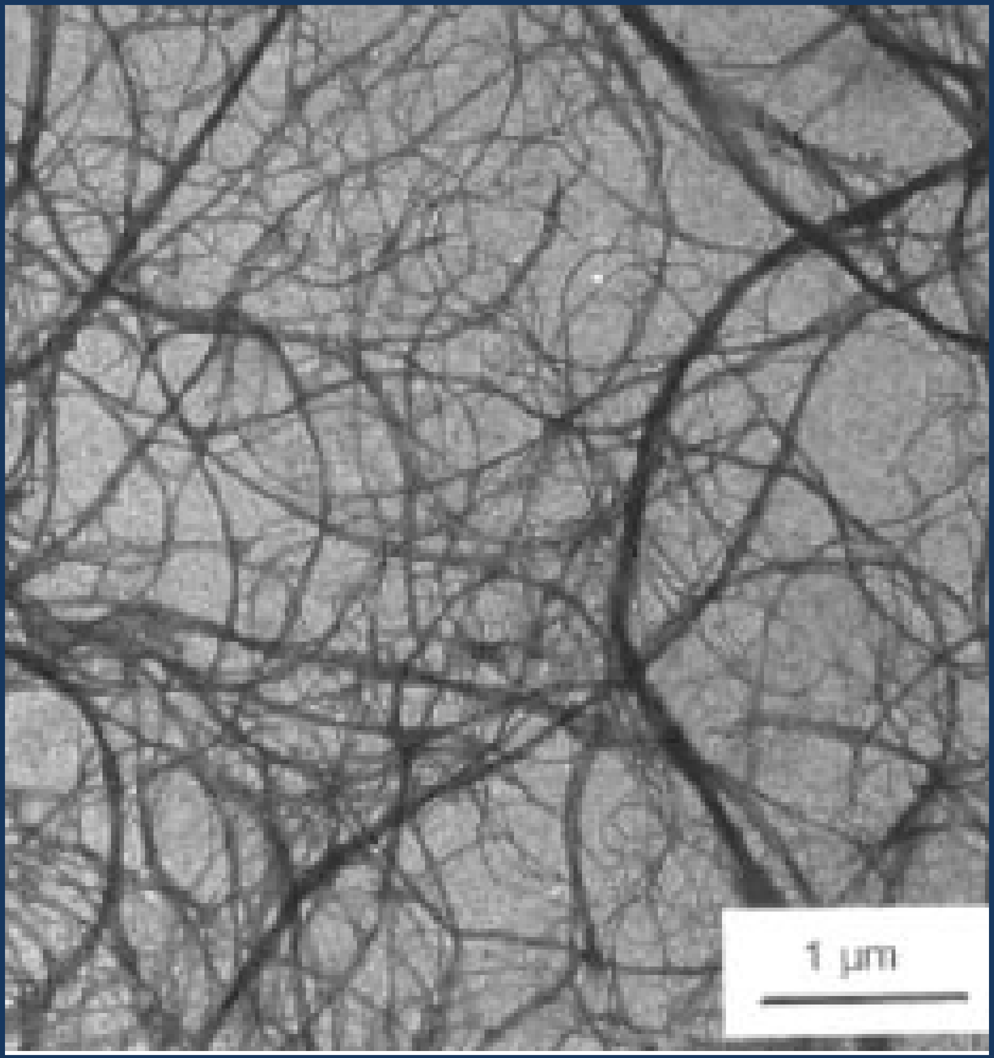
Results at ~2% solids



http://www.kemira.com/en/industries-applications/paper/chemical-pulp/Pages/default.aspx

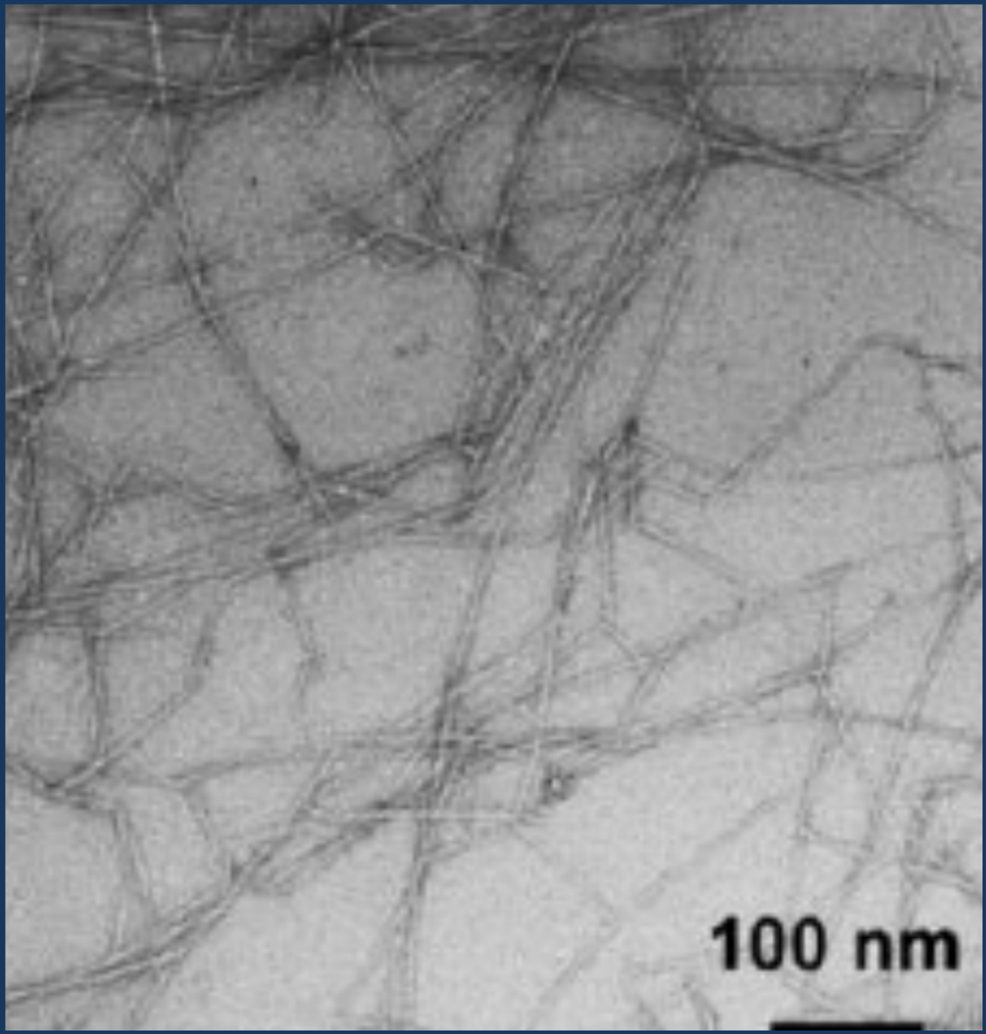
N. Lavoine et al. / Carbohydrate Polymers 90 (2012) 735–764

Microfibrillated cellulose



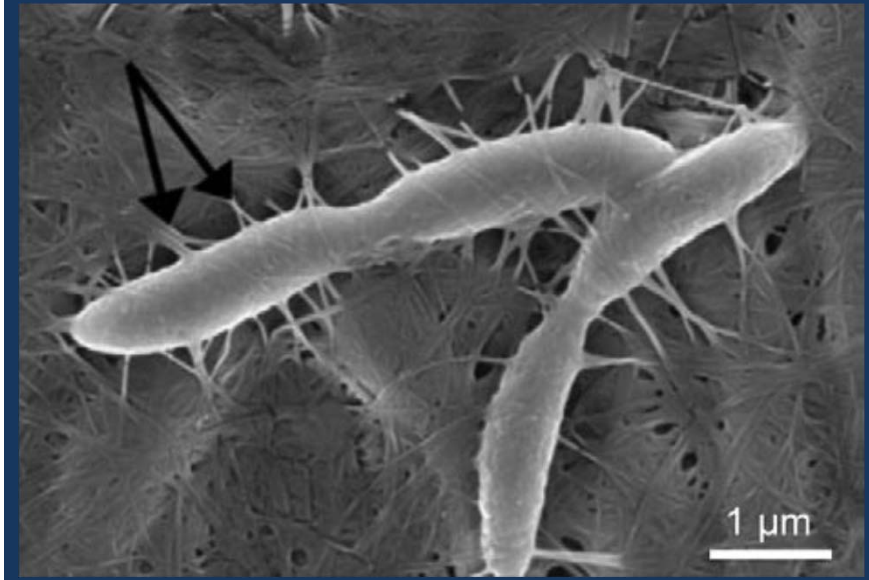
Dufresne, et al. J. Appl. Poly. Sci. 64 (1997) 1185

Nanofibrillated cellulose

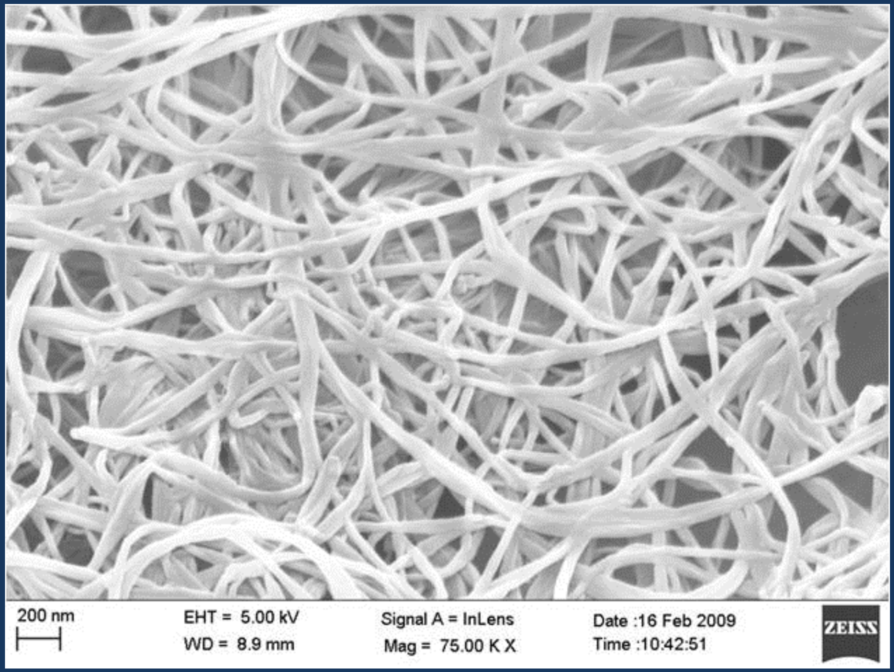


Saito, et al. Biomacromolecules 8 (2007) 2485

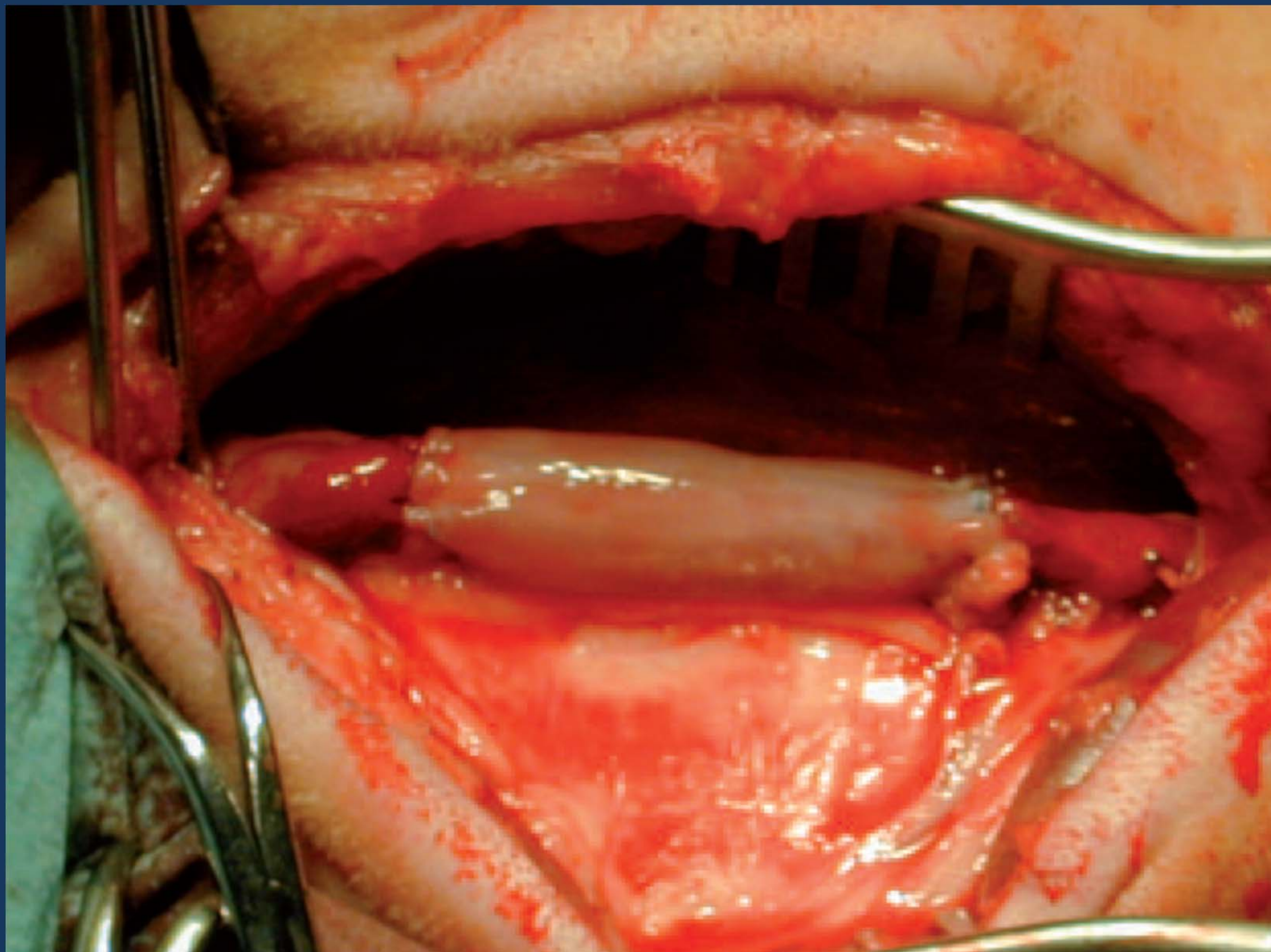
Bacterial Cellulose



Klemm, et al., Angew. Chem. Int. Ed. 2011, 50, 5438 – 5466



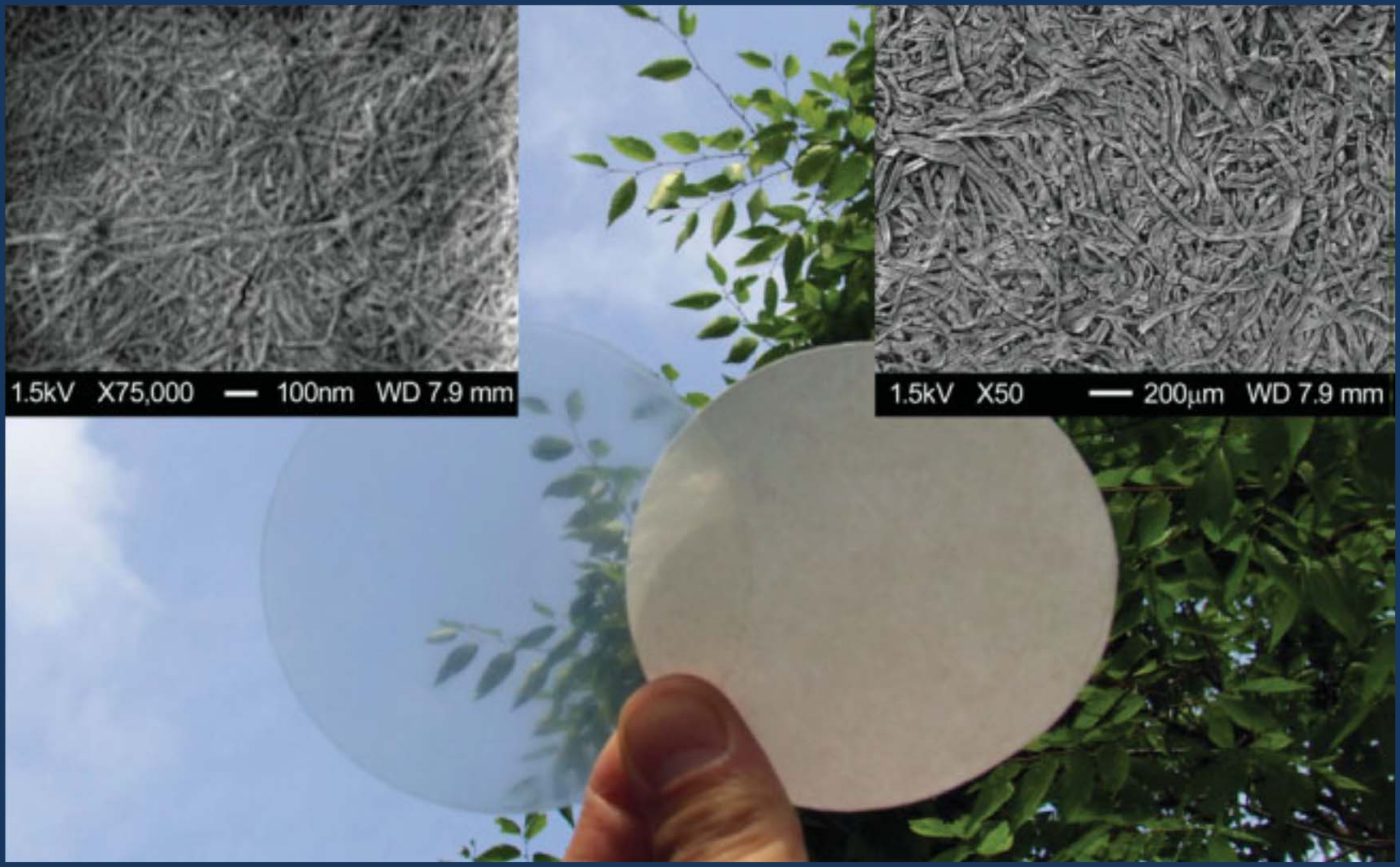
http://microbialcellulose.blogspot.com/2010/12/functional-and-green-end-of-life.html



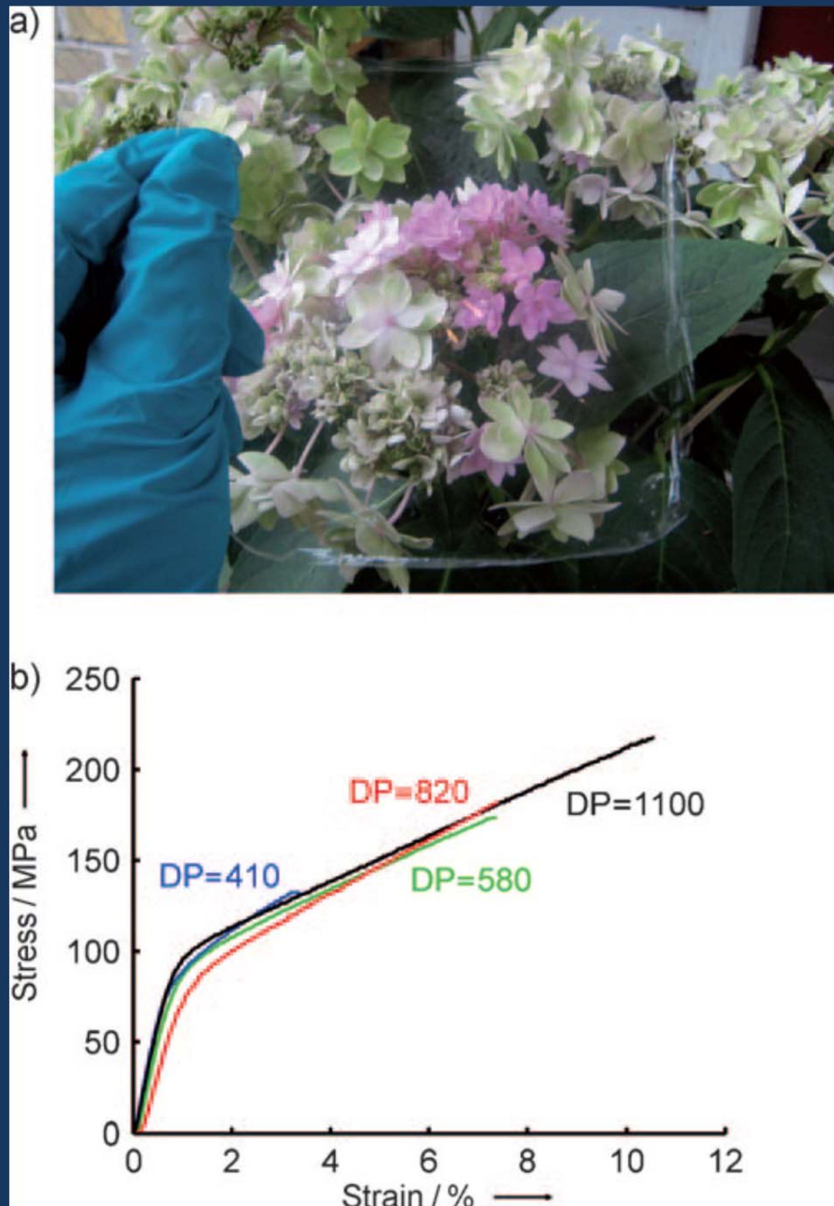
BNC tube used as a long-segment vascular graft (5 cm) for
the right carotid artery of a sheep (courtesy: Priv.-Doz. Dr. J. Wippermann,
Department of Cardiothoracic Surgery, University Hospital, Cologne, Germany).

Klemm, et al., Angew. Chem. Int. Ed. 2011, 50, 5438 – 5466

Nanopaper vs. Paper



Nogi, et al. Adv. Mater. 2009, 20, 1–4



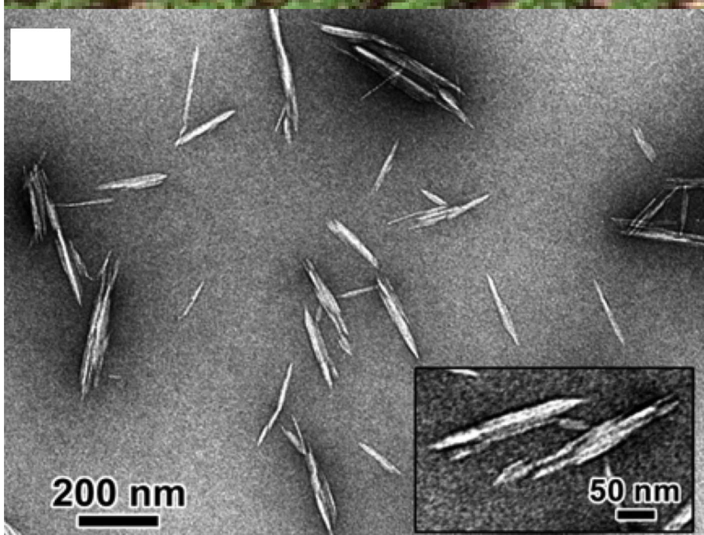
Klemm, et al., Angew. Chem. Int. Ed. 2011, 50, 5438 – 5466

Pilot plant at Inventia in Sweden

http://www.innventia.com/en/Our-Ways-of-Working/Demonstration-and-pilot/Pilot-plant-for-nanocellulose/

SOURCES OF:
CELLULOSE NANOCRYSTALS
NANOCRYSTALLINE CELLULOSE
CELLULOSE WHISKERS
CELLULOSE NANOWHISKERS

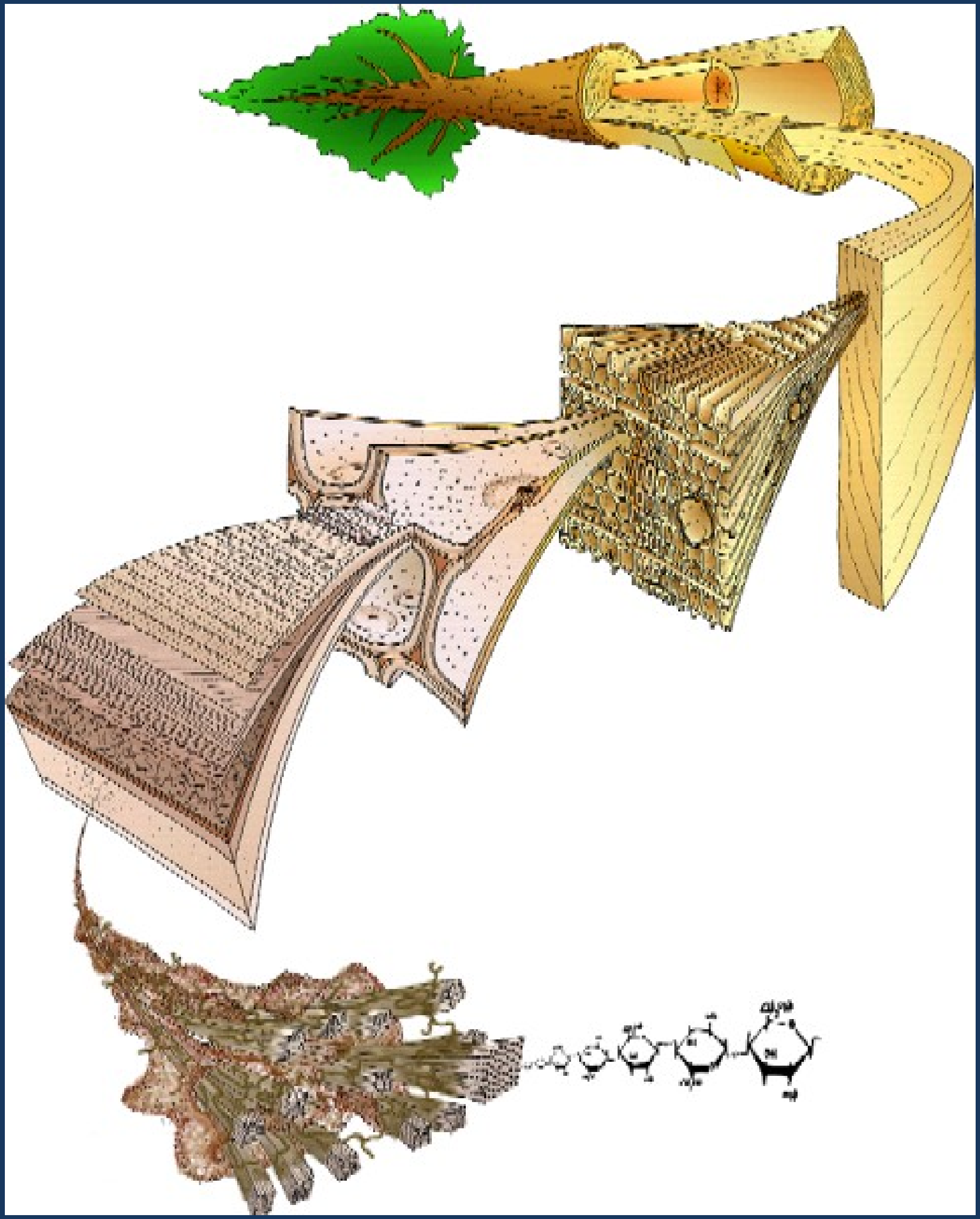
Cotton



Biomacromol. 9 (2008) 57

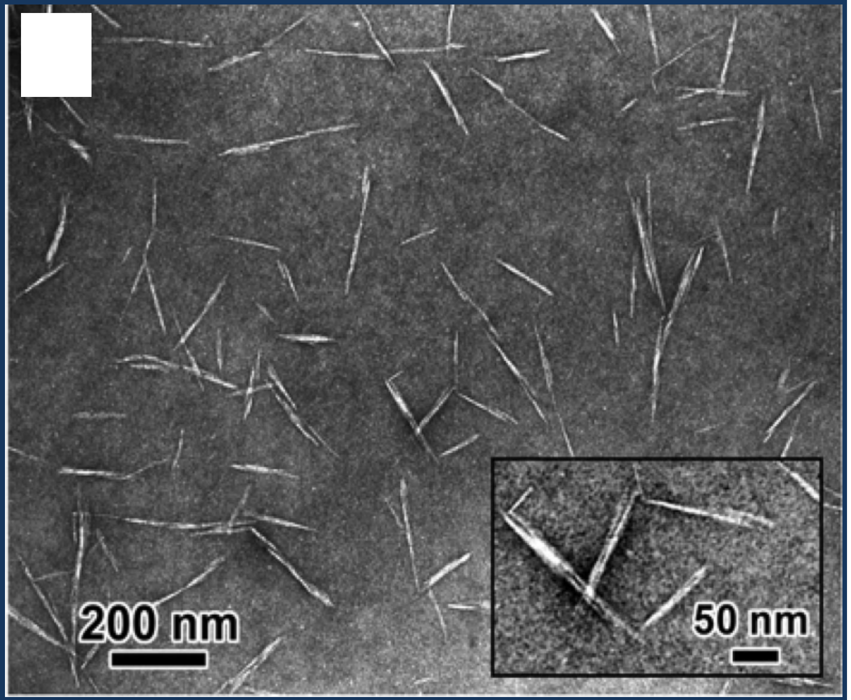
http://www.cottoninc.com/Cotton-Sustainability-Media/Cotton-Environmentally-Friendly-Fiber-Trade-Ad/

http://www.cals.ncsu.edu/agcomm/difference/cotton/



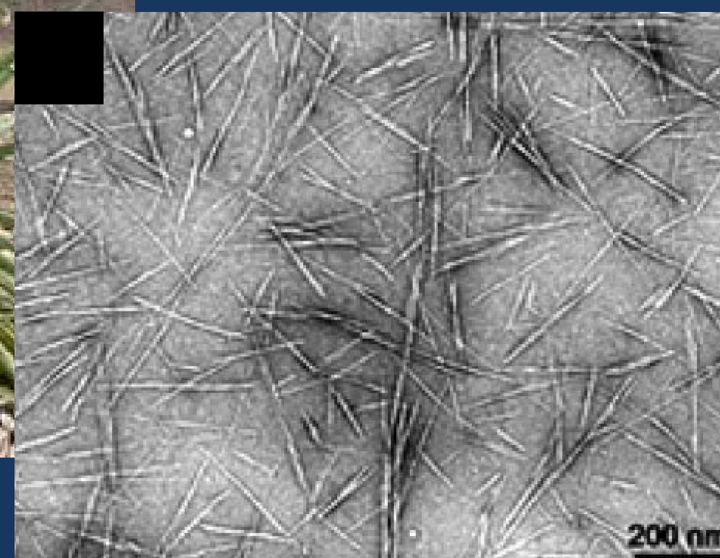
Copyright University of Canterbury, 1996. Artwork by Mark Harrington
http://www.nzwood.co.nz/why-wood/forests-and-wood/wood-structure-and-features/

Wood



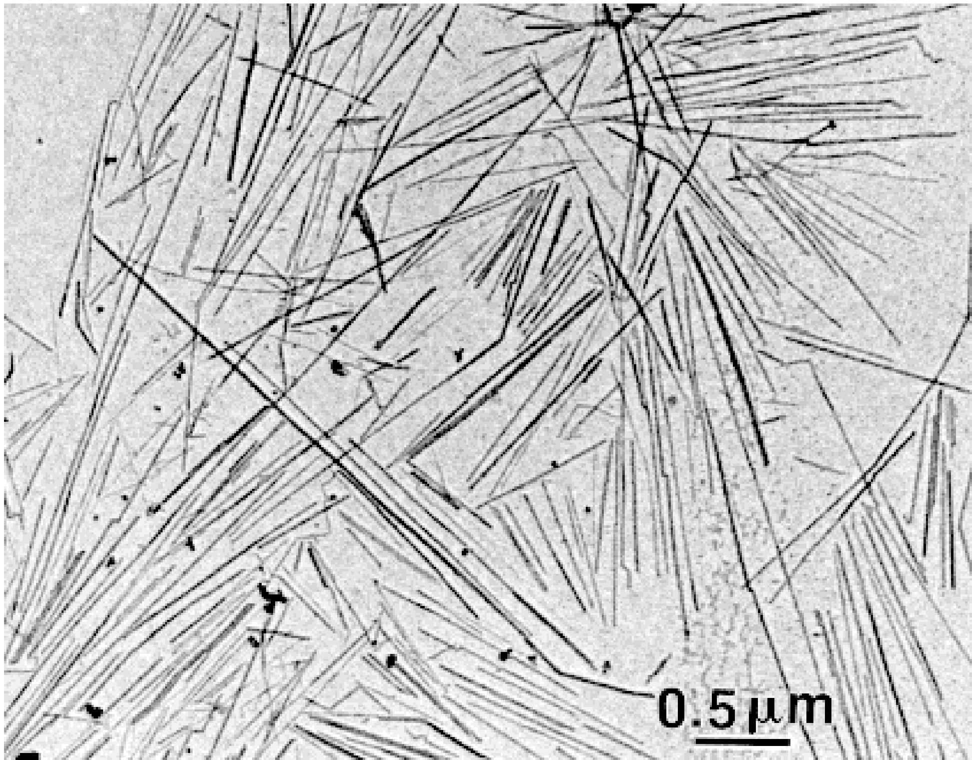
Biomacromol. 9 (2008) 57

Sisal



http://www.industreecrafts.org/Natural%20fibres%20-%20Sisal.htm

Chem. Rev. 110 (2010) 3479



J. Nanosci Nanotech 6 (2006) 322

http://www.animalpicturesarchive.com/list.php?qry=styela%20clava

Sea squirts (tunicates)

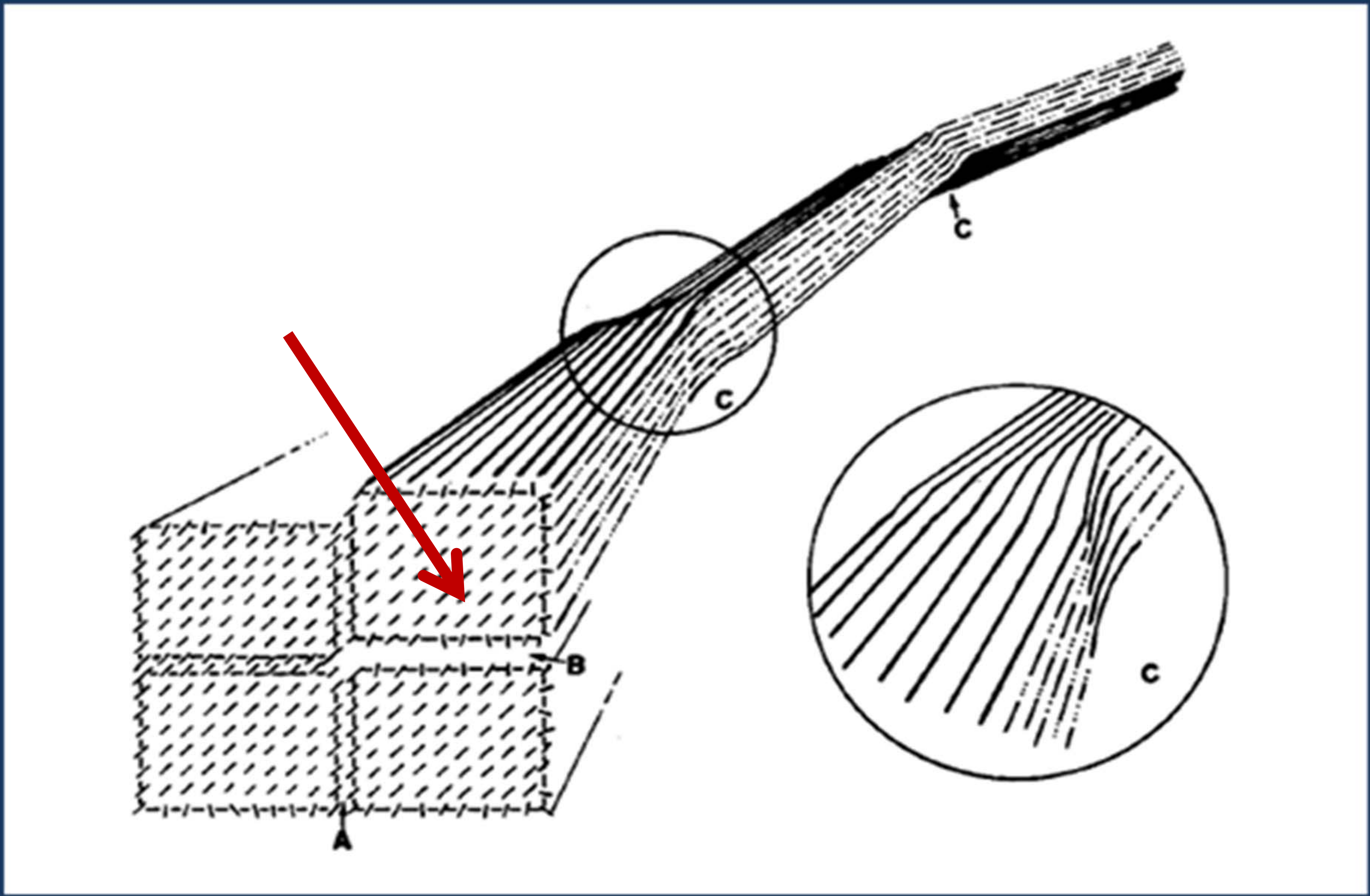
http://www.wascuba.org/tunicates/styelaclava.htm

HEMP

http://themoderatevoice.com/15688/hemp-ban-reefer-madness-indeed/

J. Appl. Poly. Sci. 109 (2008) 3804

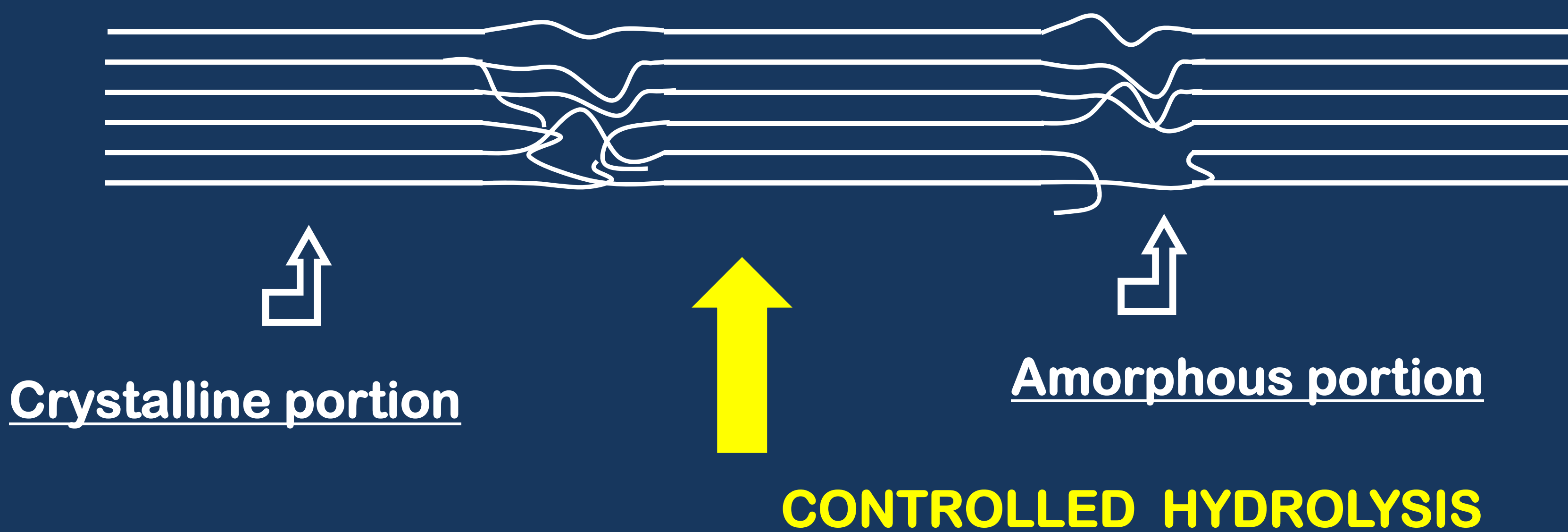
Cellulose microfibrils = assemblies of cellulose nanofibrils



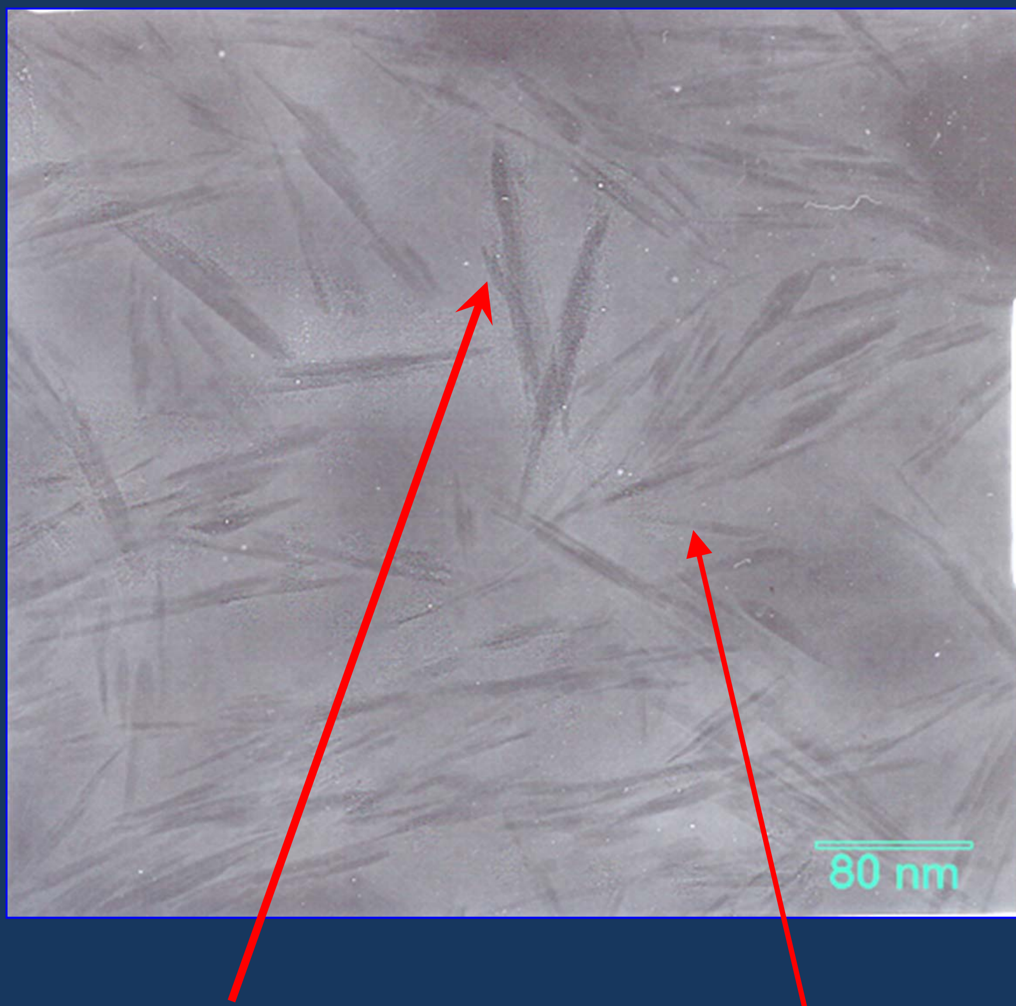
Rowland SP, Roberts EJ. Journal of Polymer Science, Part A-1: Polymer Chemistry 1972;10:2447

CELLULOSE NANOCRYSTAL PRODUCTION

- Native cellulose - Semi crystalline Polymer (~70% crystalline).



TEM image of CNC



Agglomeration

Single strand

- L/d=Aspect ratio
- Diameter=5-20nm
- Length=200-350 nm
- Aspect ratio=10-70

Cellulose nanocrystal size and geometry depends upon source

Source	Length	Cross section	Aspect ratio
Tunicate	100 nm – microns	10-20 nm	5 to > 100 (high)
Algal (Valonia)	> 1000 nm	10 to 20 nm	50 to > 10 nm (high)
Bacterial	100 nm – microns	5-10 x 30-50 nm	2 to > 100 (medium)
Cotton	200-350 nm	5 nm	20 to 70 (low)
Wood	100–300 nm	3 – 5 nm	20 to 50 (low)

Beck-Candanedo, et. al. Biomacromol. (2005) 6:1048-1054

Cellulose nanocrystals have a high surface area

	m^2/g
E-glass fibers*	~1
Paper fibers	4
Graphite	25-300
Fumed silica	100-400
Fully exfoliated clay	~ 500
Cellulose nanocrystals**	250-500
Carbon nanotubes***	~ 100 - ?

*http://www.jm.com/engineered_products/filtration/products/microfiber.pdf
** Winter, W. presentation at ACS meeting, San Diego, March 2005
***http://www.ipme.ru/e-journals/RAMS/no_5503/staszczuk/staszczuk.pdf.

Stronger than steel, Stiffer than aluminum

Material	Tensile strength GPa	Modulus GPa
Cellulose crystal	7.5[1] (~3)	145[2]
Glass fiber	4.8	86
Aluminum wire	0.62	73
Steel[3]	0.54	200
Graphite whisker	21	410
Carbon nanotubes[4]	11-63	270-970

1. Marks, *Cell wall mechanics of tracheids* **1967**
2. **Sturcova, et al. (2005) Biomacromol. 6, 1055**
3. **http://www.ezlok.com/TechnicalInfo/MPCarbonSteel.html**
4. **Yu, et al *Science* (2000) *287*, 637**

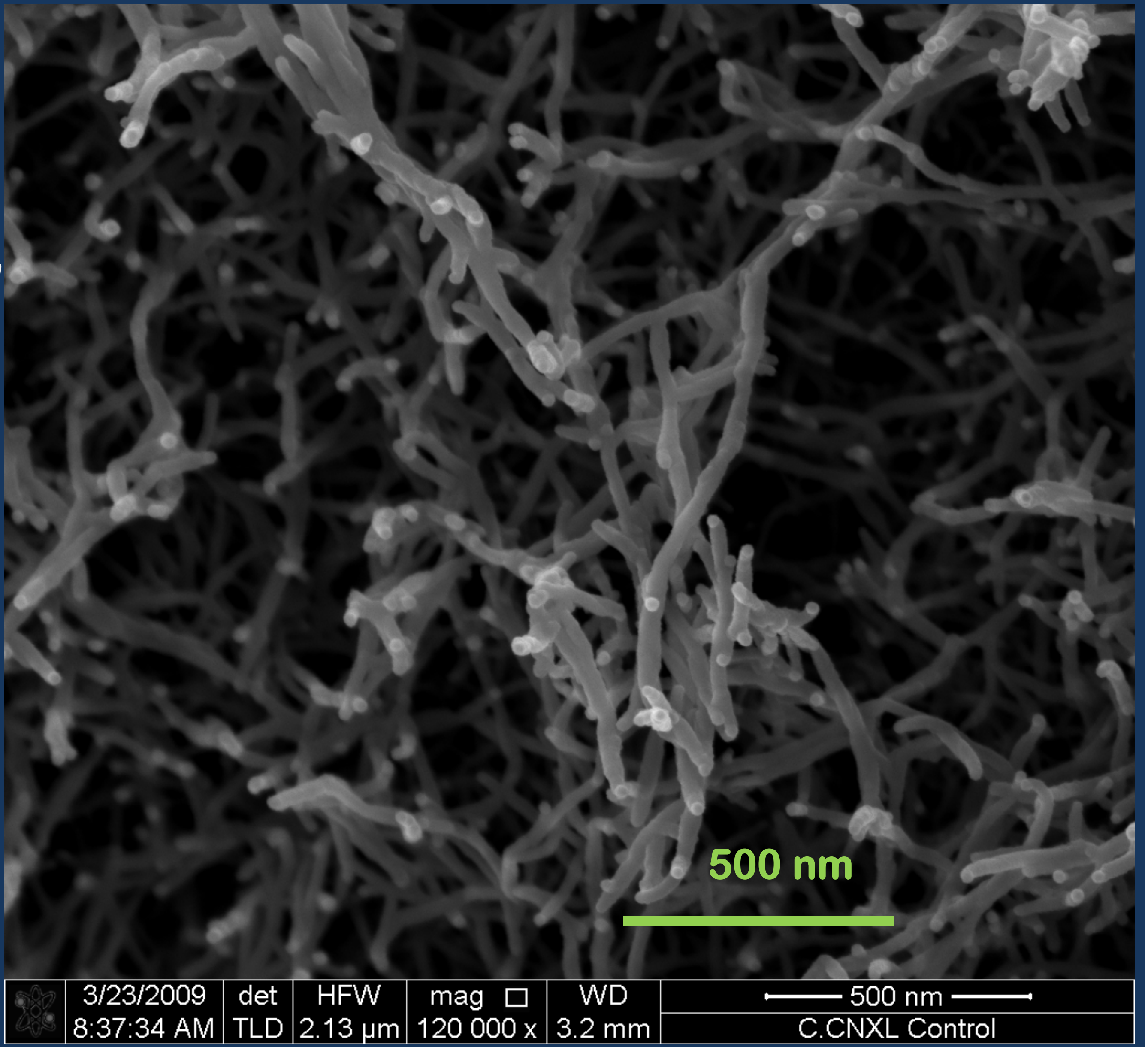
Transmission electron Microscope (TEM) image of cellulose nanocrystal aerogel

Images courtesy of Anahita Pakzad, grad student in lab of Reza Shahbazian Yassar, Michigan Technological University

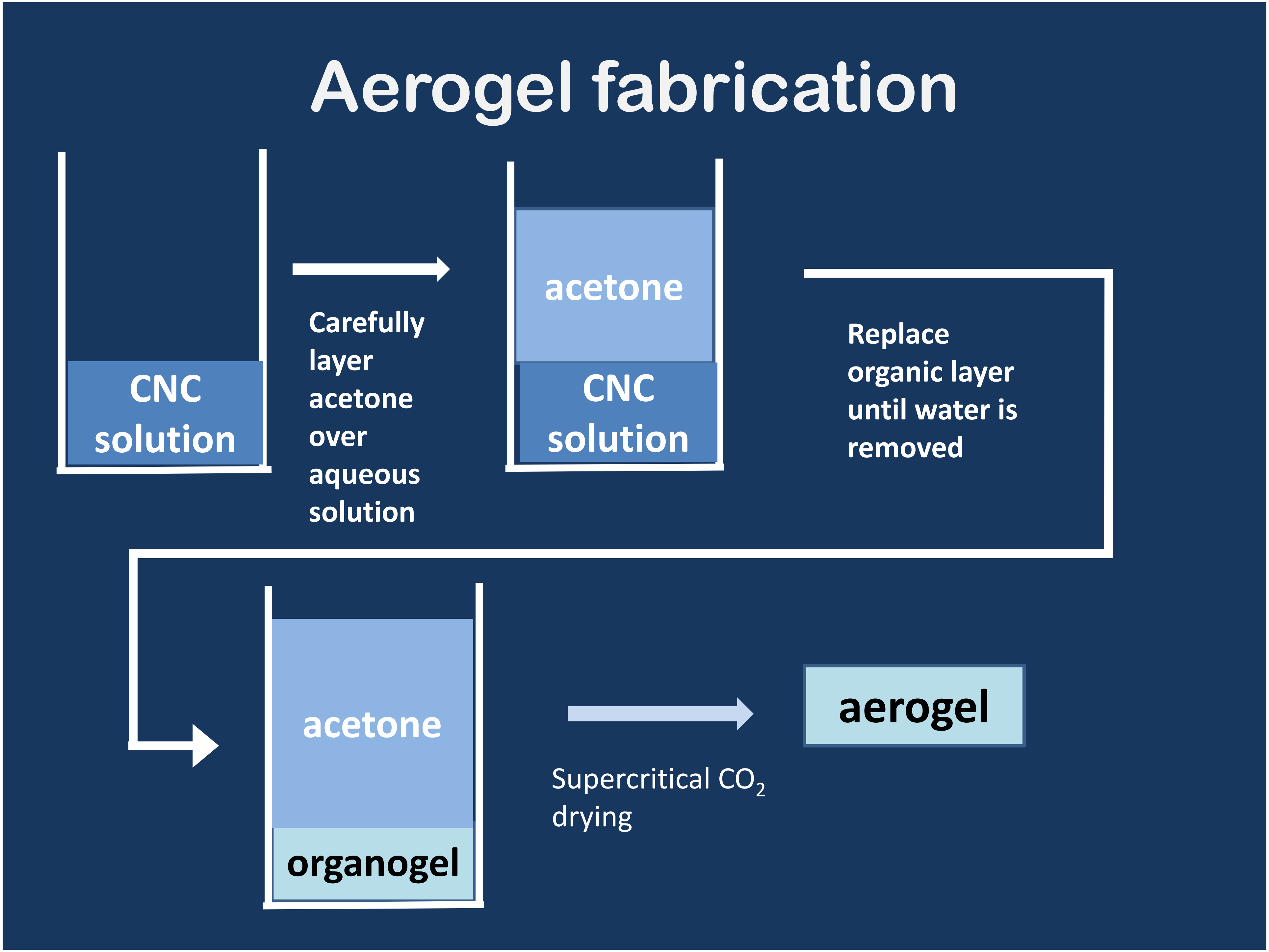
Cellulose Nanocrystal Aerogel

- High porosity
  - 200-600 m^2/g
- Low density
  - ~0.05 g/cm^3
- Low thermal conductivity

SEM image courtesy of Bruce Arey, Pacific Northwest National Labs, Richland, WA

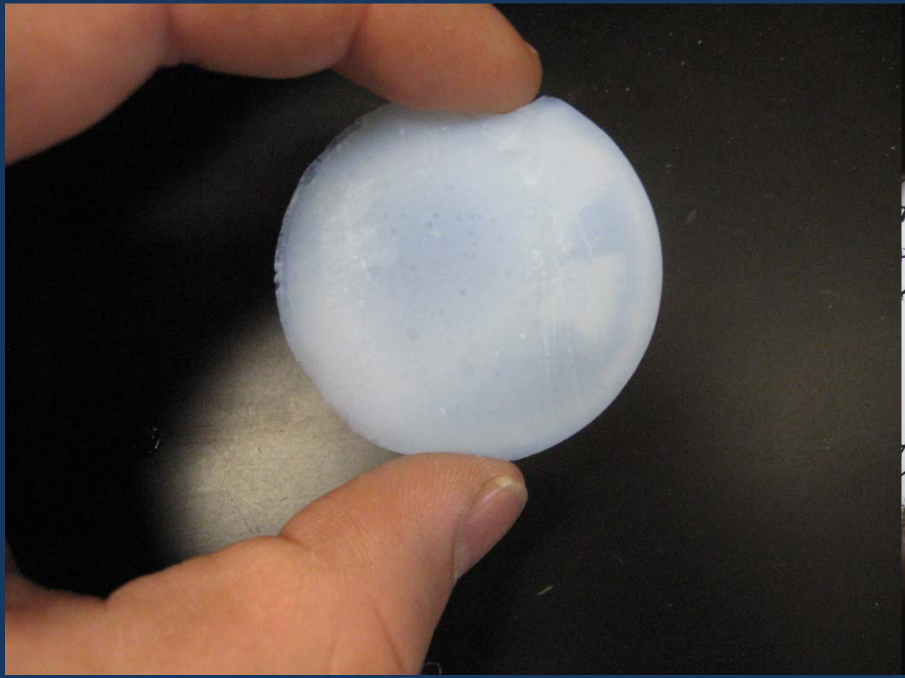


R. J. Moon, A. Martini, J. Nairn, J. Simonsen, and J. Youngblood, Chem. Soc. Rev. **40**, 3941 (2011)


Aerogel fabrication
CNC solution
Carefully layer acetone over aqueous solution
acetone
CNC solution
Replace organic layer until water is removed
acetone
organogel
Supercritical CO_2 drying
aerogel

CNC aerogels

Blue in reflected light | Red in transmitted light



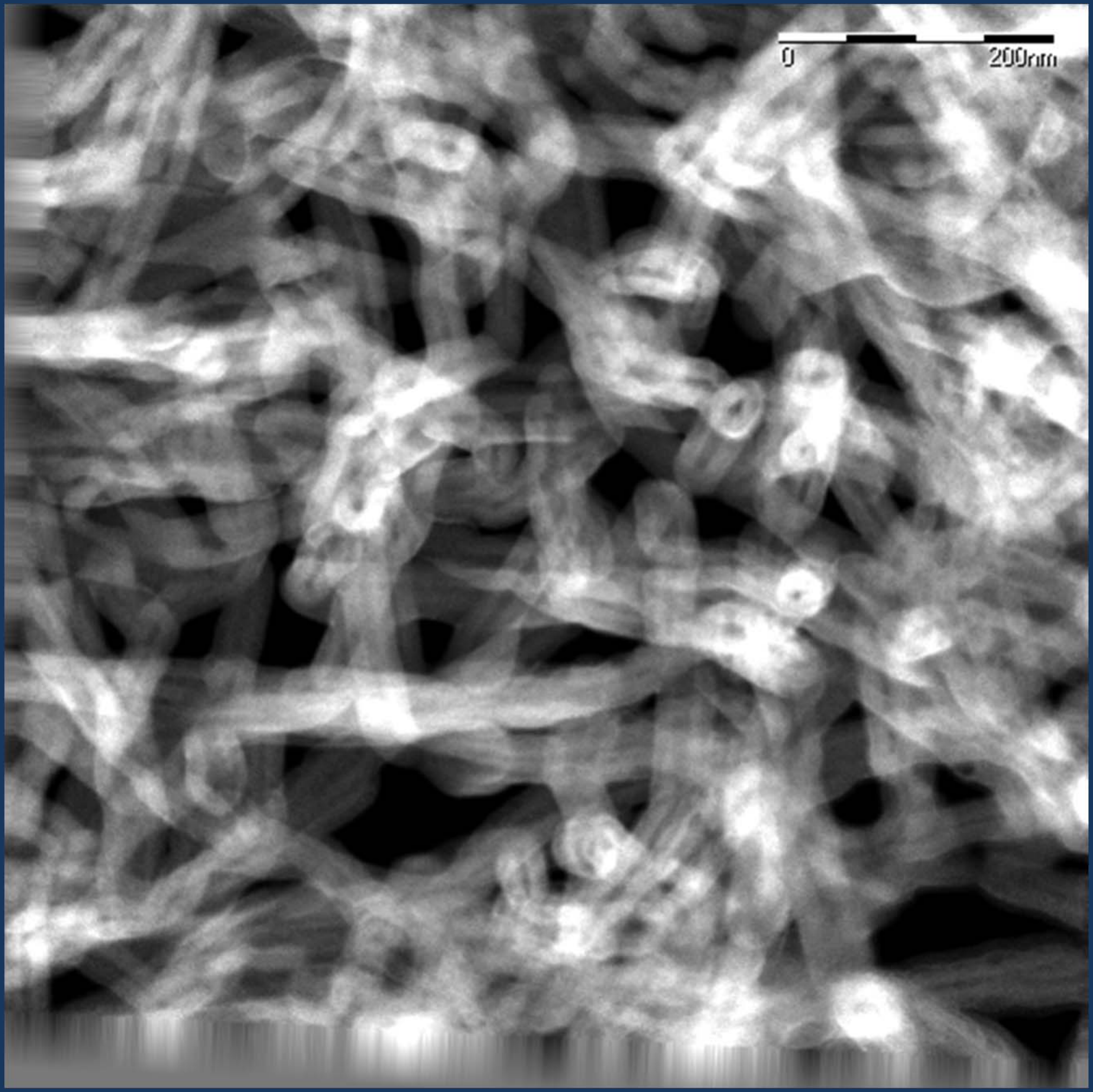
Rayleigh scattering

$$x = \frac{2\pi r}{\lambda}$$

x = scattering parameter
r = characteristic dimension = $(\text{volume})^{1/3}$
λ = wavelength of light

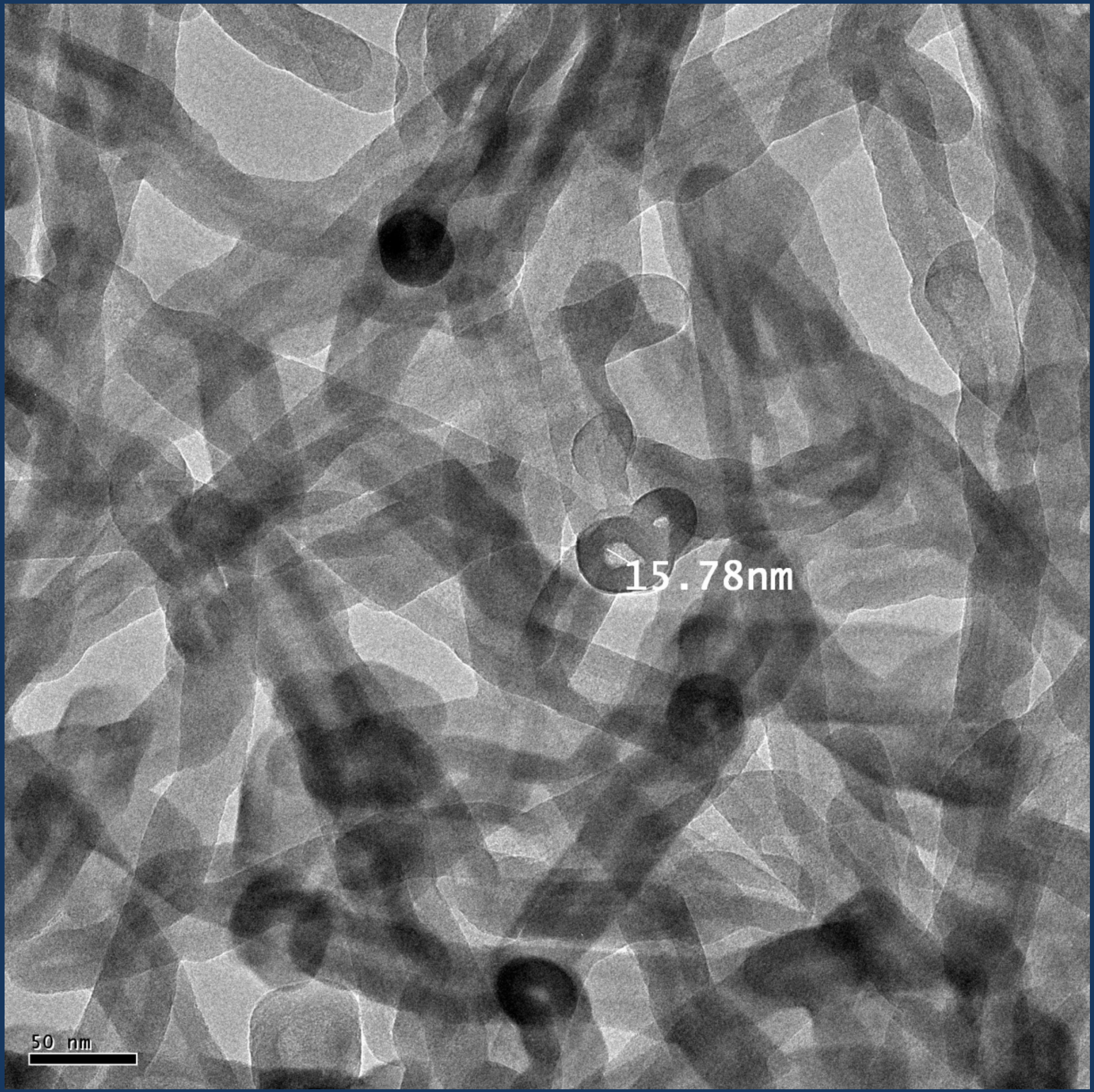
$x << 1$

TEM Tomography of CNC aerogel coated with Al_2O_3 by ALD



TEM images by Peter Eschback, and Teresa Sawyer, OSU

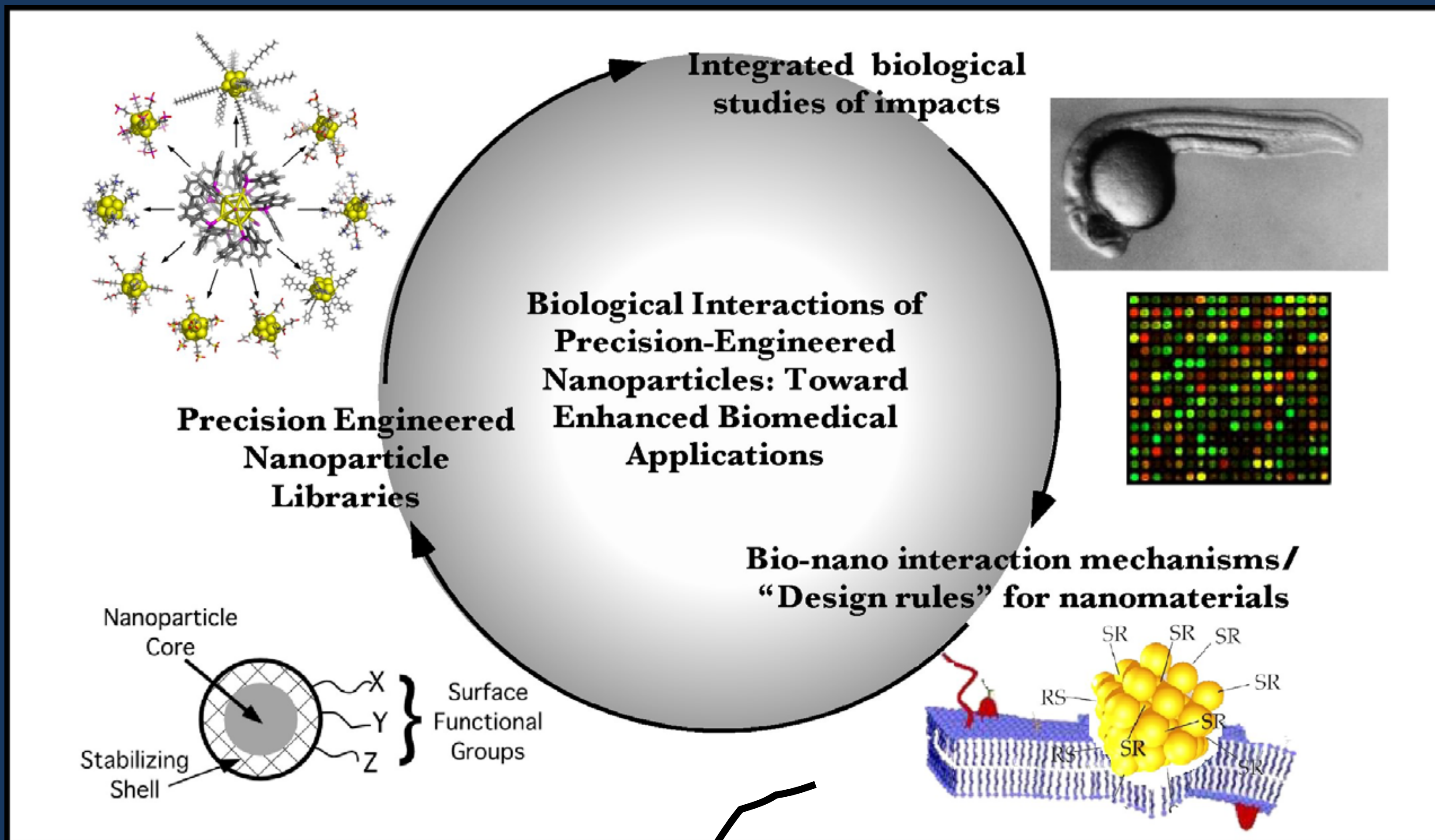
Focused ion beam sliced the coated aerogel
Both CNC and Al_2O_3 are observed



http://www.melodea.eu/Bio-based.aspx

Environmental Health and Safety of nanocellulose

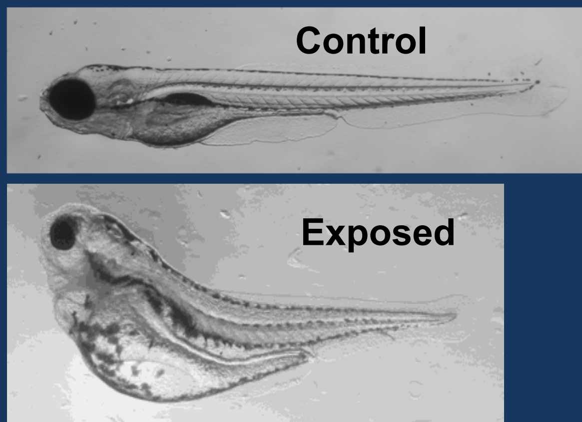
Iterative Process to Gain Knowledge



Nanomaterial-Biological Interactions Knowledgebase

Slide courtesy of Dr. Stacy Harper, OSU

CNCs are not toxic

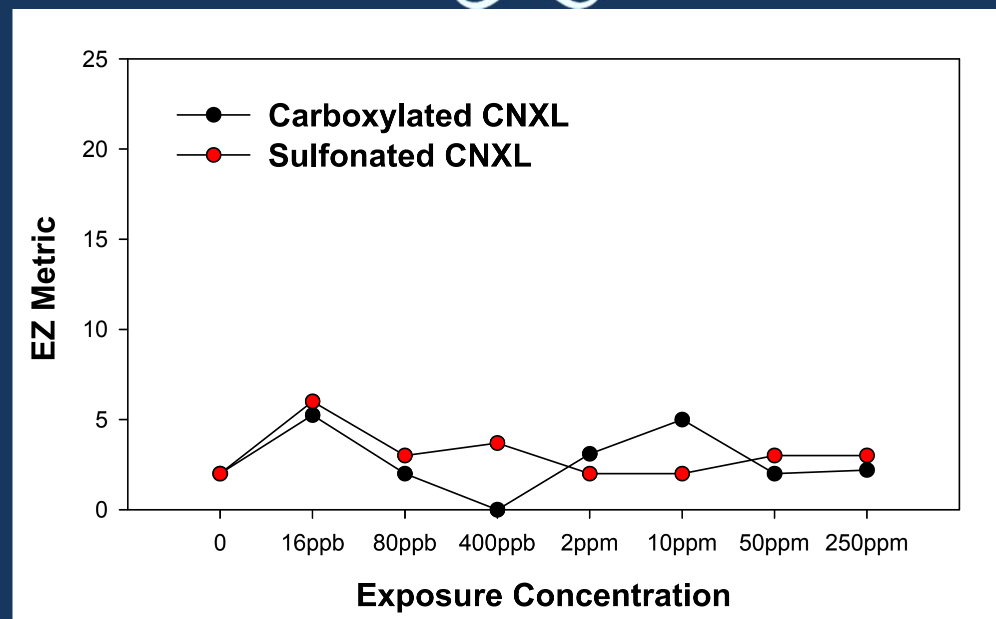


Developed using OSU's NANOMATERIAL-BIOLOGICAL INTERACTIONS KNOWLEDGEBASE

frequency of effect
x hierarchical ranking

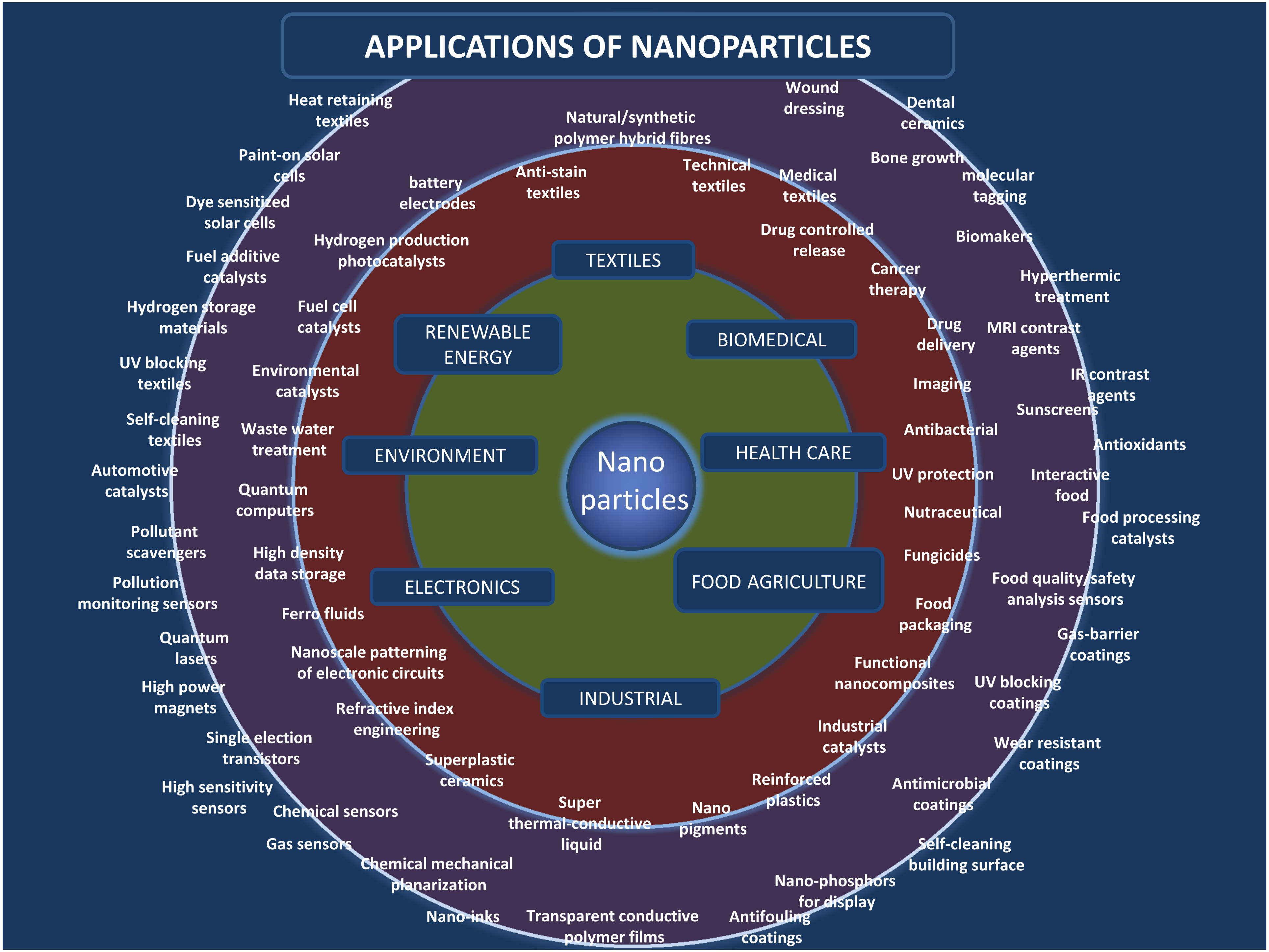
'EZ' Metric

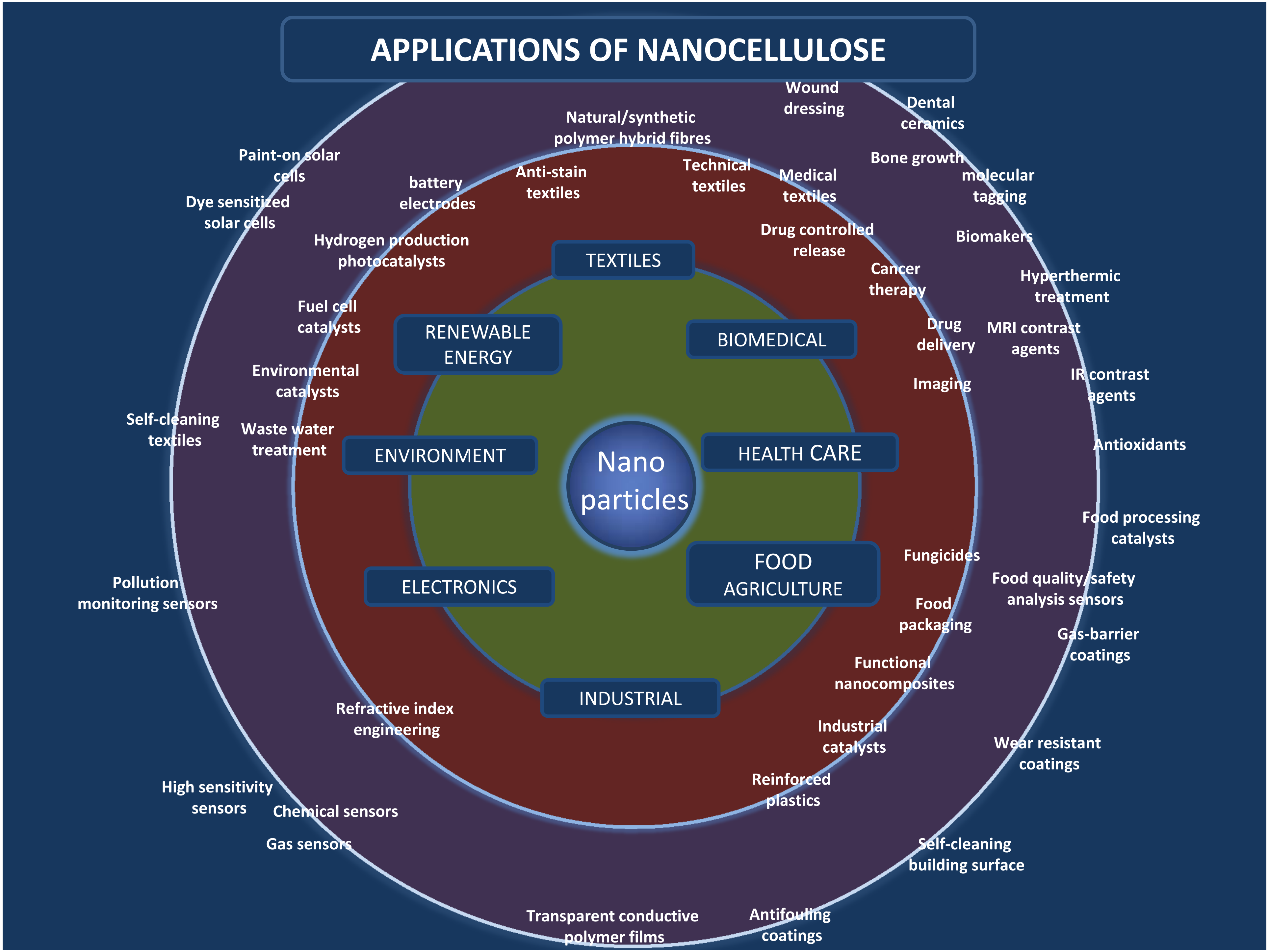
Normalized to scale 0-24



EZ Metric	toxic potential	interpretation
≤ 5	low	likely benign
5 to 15	moderate	suspect nanomaterial
> 15	high	requires further testing

Slide courtesy of Dr. Stacy Harper, OSU


APPLICATIONS OF NANOPARTICLES
Nano particles
TEXTILES
BIOMEDICAL
HEALTH CARE
FOOD AGRICULTURE
INDUSTRIAL
ELECTRONICS
ENVIRONMENT
RENEWABLE ENERGY
Heat retaining textiles
Natural/synthetic polymer hybrid fibres
Wound dressing
Dental ceramics
Paint-on solar cells
battery electrodes
Anti-stain textiles
Technical textiles
Medical textiles
Bone growth
molecular tagging
Dye sensitized solar cells
Hydrogen production photocatalysts
Drug controlled release
Biomakers
Fuel additive catalysts
Cancer therapy
Hyperthermic treatment
Hydrogen storage materials
Fuel cell catalysts
Drug delivery
MRI contrast agents
UV blocking textiles
Environmental catalysts
Imaging
IR contrast agents
Sunscreens
Self-cleaning textiles
Waste water treatment
Antibacterial
Antioxidants
Automotive catalysts
Quantum computers
UV protection
Interactive food
Nutraceutical
Food processing catalysts
Pollutant scavengers
High density data storage
Fungicides
Pollution monitoring sensors
Food quality/safety analysis sensors
Ferro fluids
Food packaging
Quantum lasers
Nanoscale patterning of electronic circuits
Gas-barrier coatings
Functional nanocomposites
UV blocking coatings
High power magnets
Refractive index engineering
Industrial catalysts
Single election transistors
Wear resistant coatings
Superplastic ceramics
Reinforced plastics
High sensitivity sensors
Antimicrobial coatings
Chemical sensors
Super thermal-conductive liquid
Nano pigments
Gas sensors
Self-cleaning building surface
Chemical mechanical planarization
Nano-phosphors for display
Nano-inks
Transparent conductive polymer films
Antifouling coatings


APPLICATIONS OF NANOCELLULOSE
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Waste water treatment
Antioxidants
Food processing catalysts
Fungicides
Pollution monitoring sensors
Food quality/safety analysis sensors
Food packaging
Gas-barrier coatings
Functional nanocomposites
Refractive index engineering
Industrial catalysts
Wear resistant coatings
Reinforced plastics
High sensitivity sensors
Chemical sensors
Gas sensors
Self-cleaning building surface
Transparent conductive polymer films
Antifouling coatings

COMMERCIALIZATION OF NANOCELLULOSES

CNC:

- Canada
  - CelluForce, 1 ton/day, $41 million manufacturing facility
  - Blue Goose Biorefineries
    - Nanocrystals, nanofibers
- Germany
  - Nanocrystal production (Melodea, two years)

COMMERCIALIZATION OF NANOCELLULOSES

CNF:

- Finland
  - Manufacturing planned for Nokia cell phone cases
- Sweden
  - Manufacturing facility for paper additives
- Japan
  - Pilot plant for TEMPO cellulose nanofibers
  - Biorefinery pilot plant (Hiroshima)
- Switzerland, US
  - Manufacture of bacterial cellulose biomedical products
- USA
  - Announcement expected soon

RECENT EXPERIMENTS

Poly(vinylidene fluoride)-co-hexafluoropropylene (PVDFHFP) copolymer nanocomposites with cellulose nanocrystals

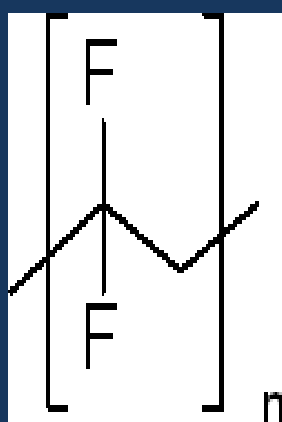
Jeremiah Kelley, Jie Ding, John Nairn, John Simonsen
(Mike Lerner)

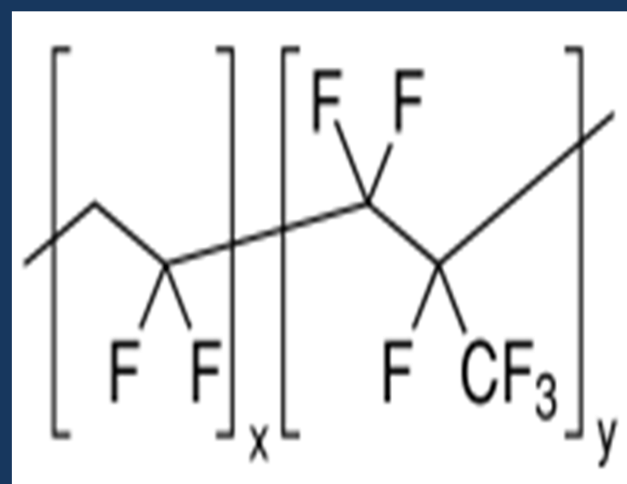
Oregon State University

PVDFHFP

- A copolymer of poly(vinylidene fluoride) (PVDF)
- Introduction of HFP units decreases crystallinity

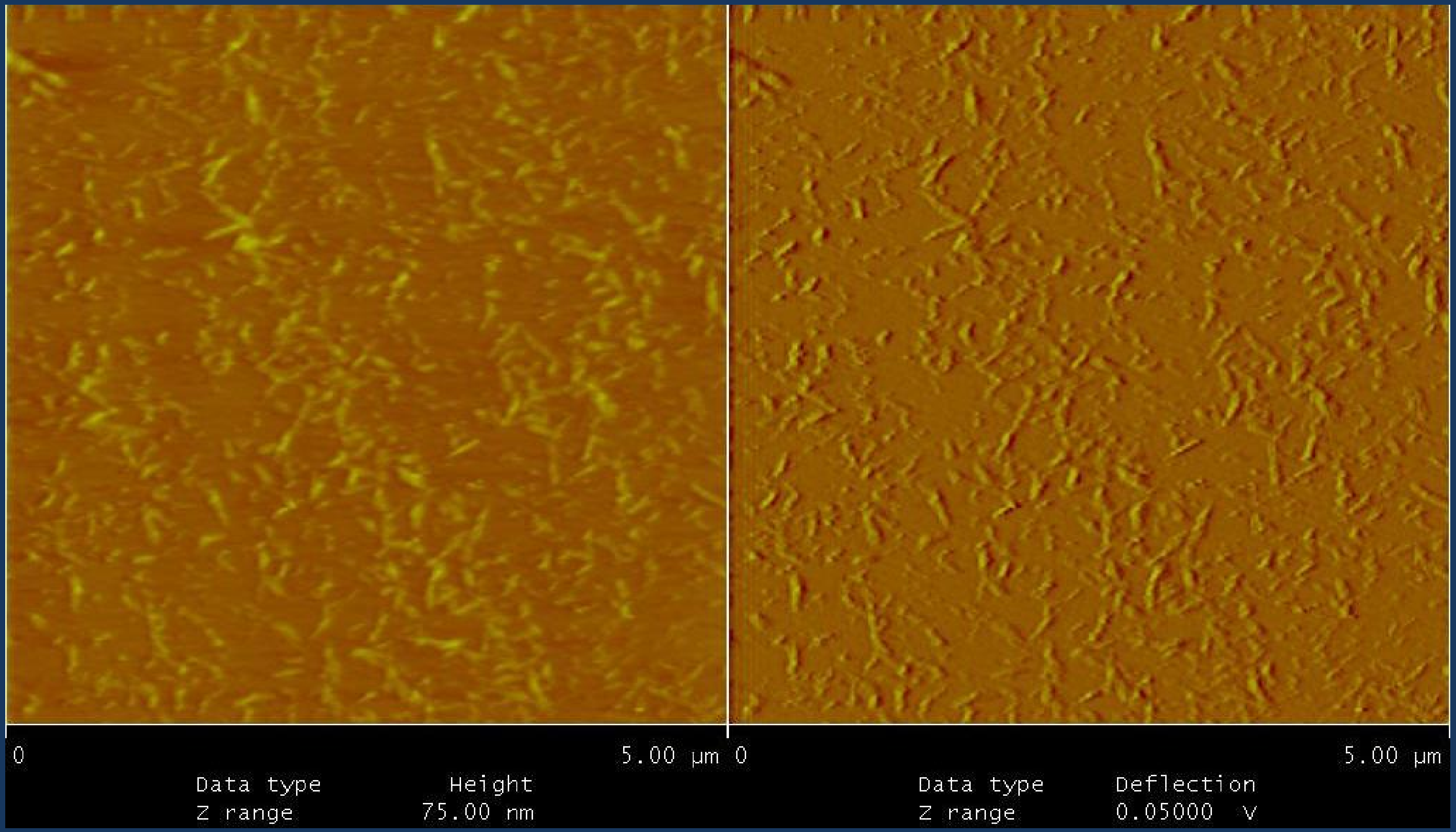
PVDF





PVDFHFP

AFM Images of cellulose nanocrystals



Average diameter (d) = 9 (3) nm, length (l) = 189 (40) nm, and l/d (ρ) = 23 (8)

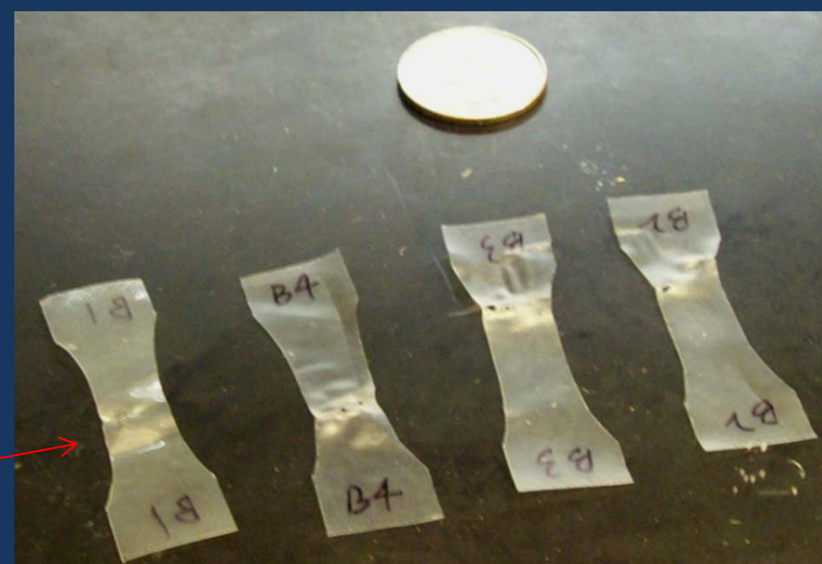
TENSILE TESTING

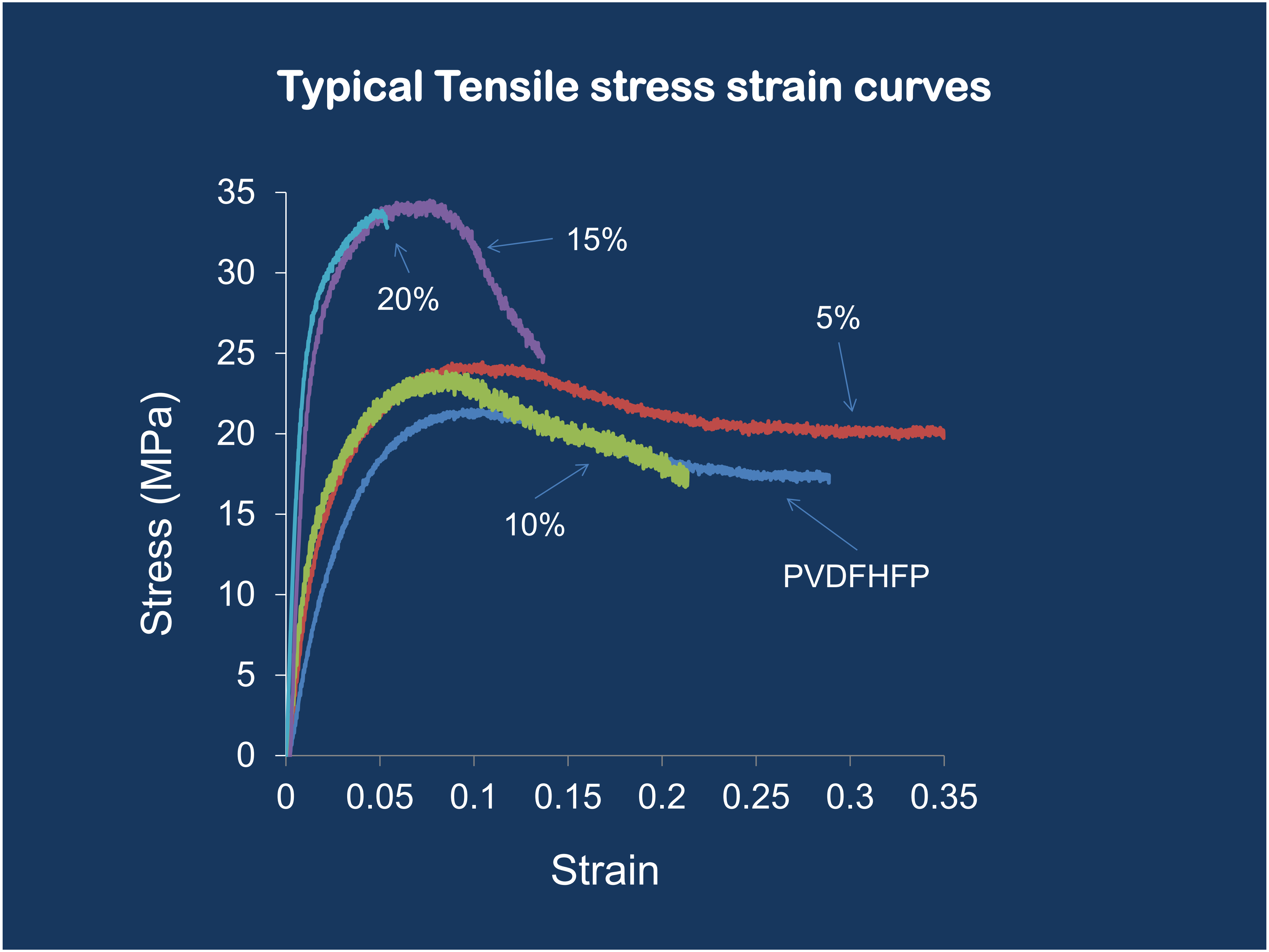
Tensile Testing

- Instron tensile testing machine
- Dogbone samples
  - 0.05 mm x 30 mm x 15 mm for PVDFHFP composites
  - 5 mm/min extension rate
  - Toughness = work to fracture (T)

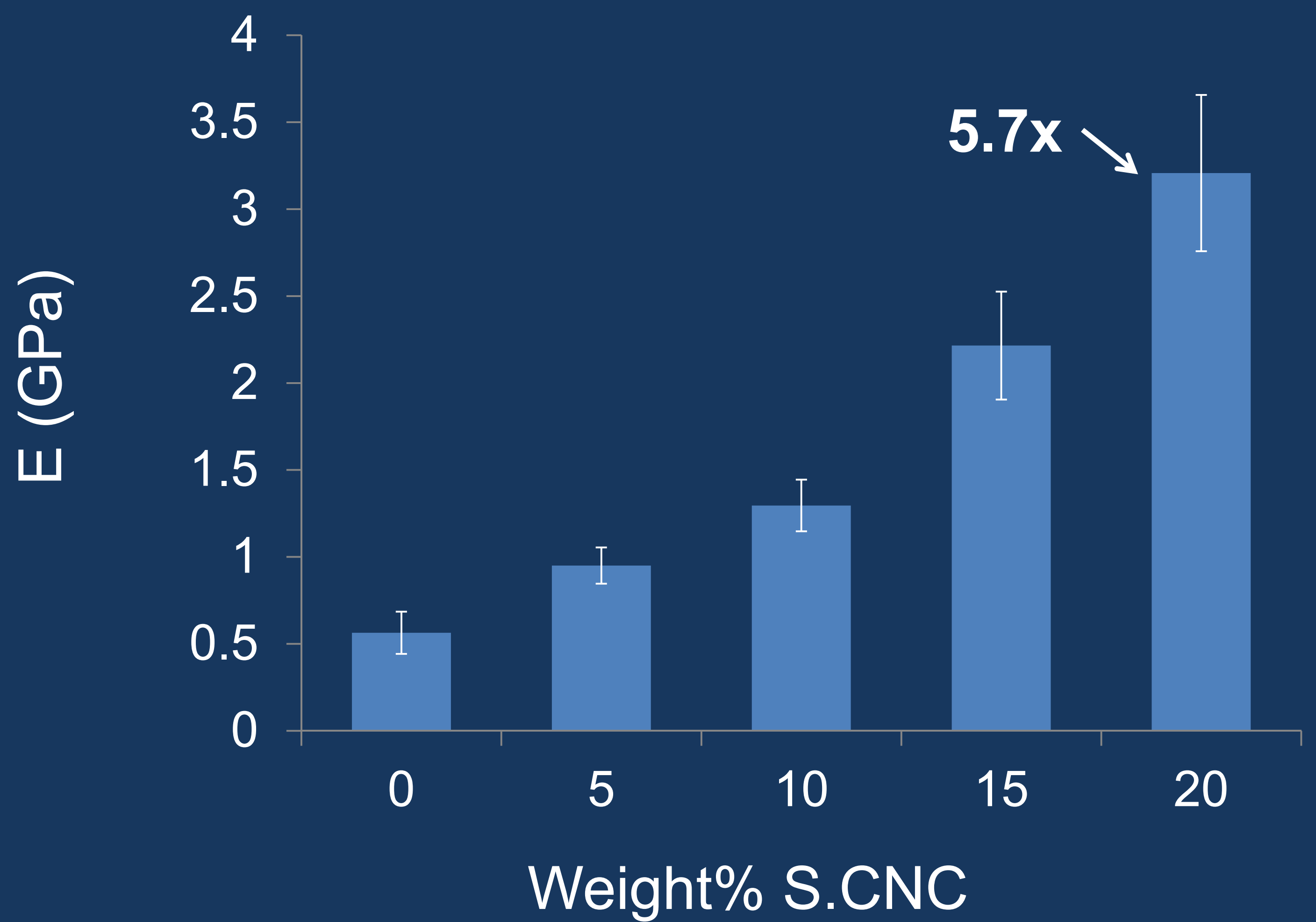
$T = \int \sigma d\varepsilon$, where σ is stress and ε is strain

PVDFHFP/CNC composites

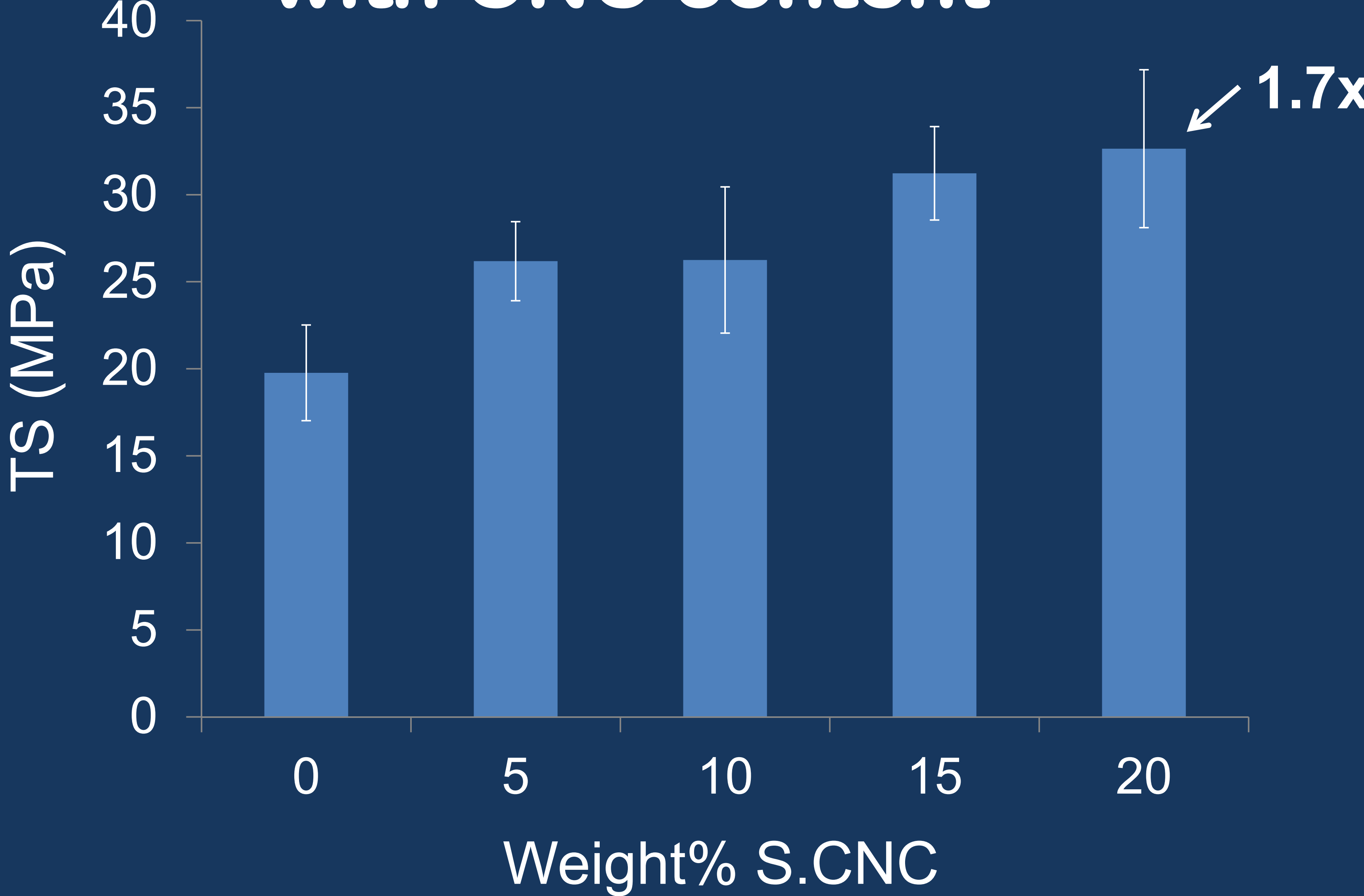



Typical Tensile stress strain curves
35
30
25
20
15
10
5
0
Stress (MPa)
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
Strain
15%
20%
5%
10%
PVDFHFP

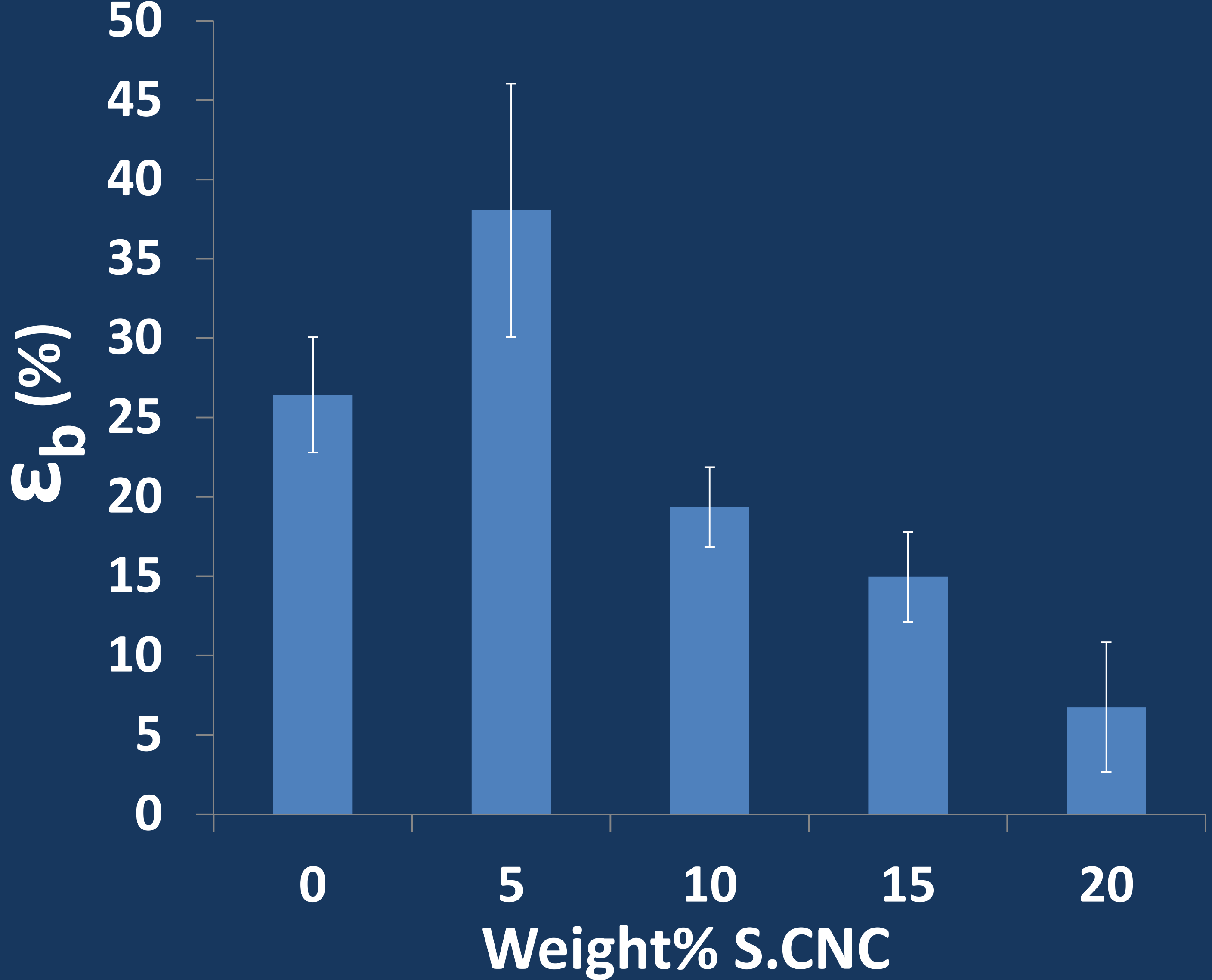
Large modulus increase with CNC content



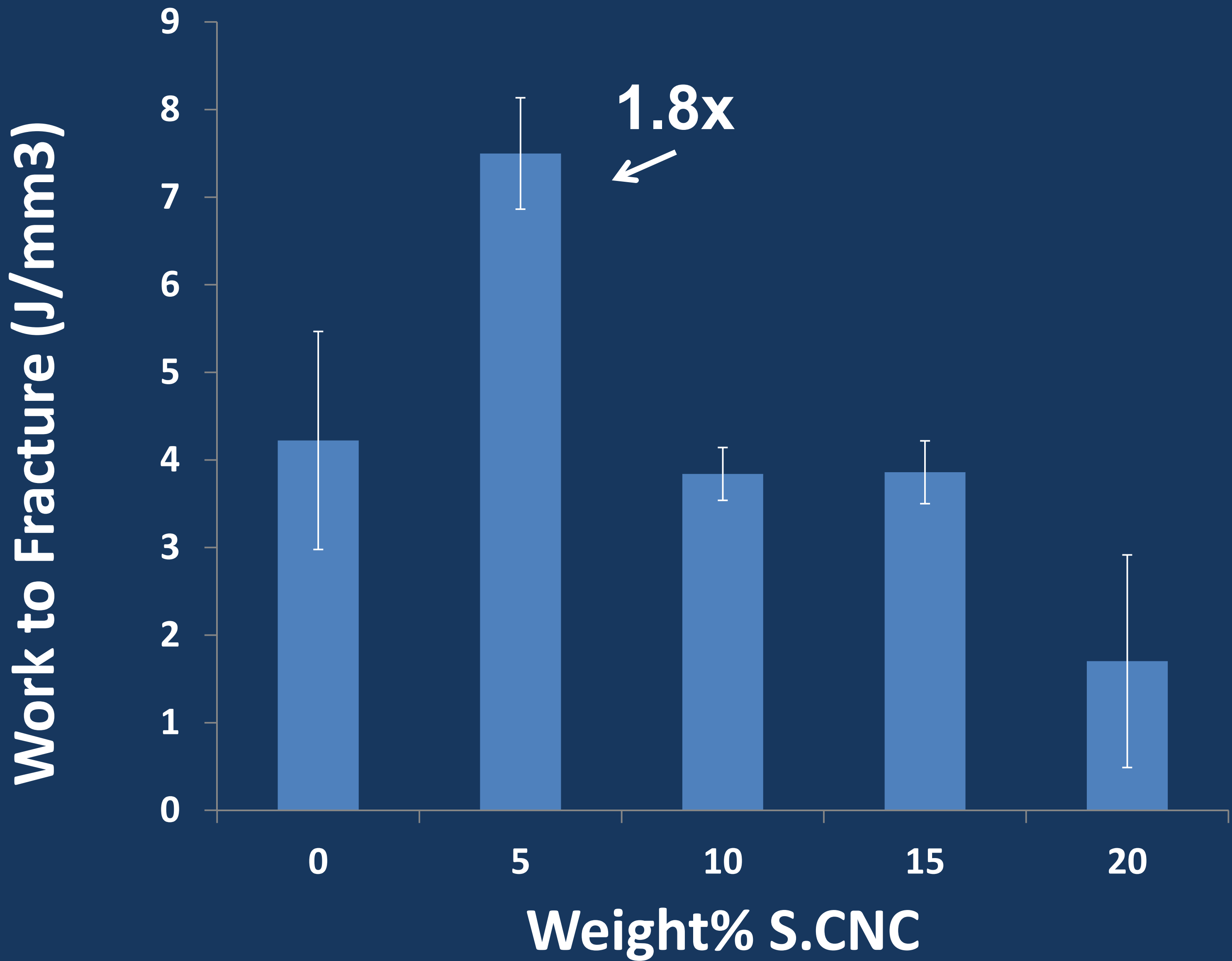
Tensile Strength (TS) increases with CNC content



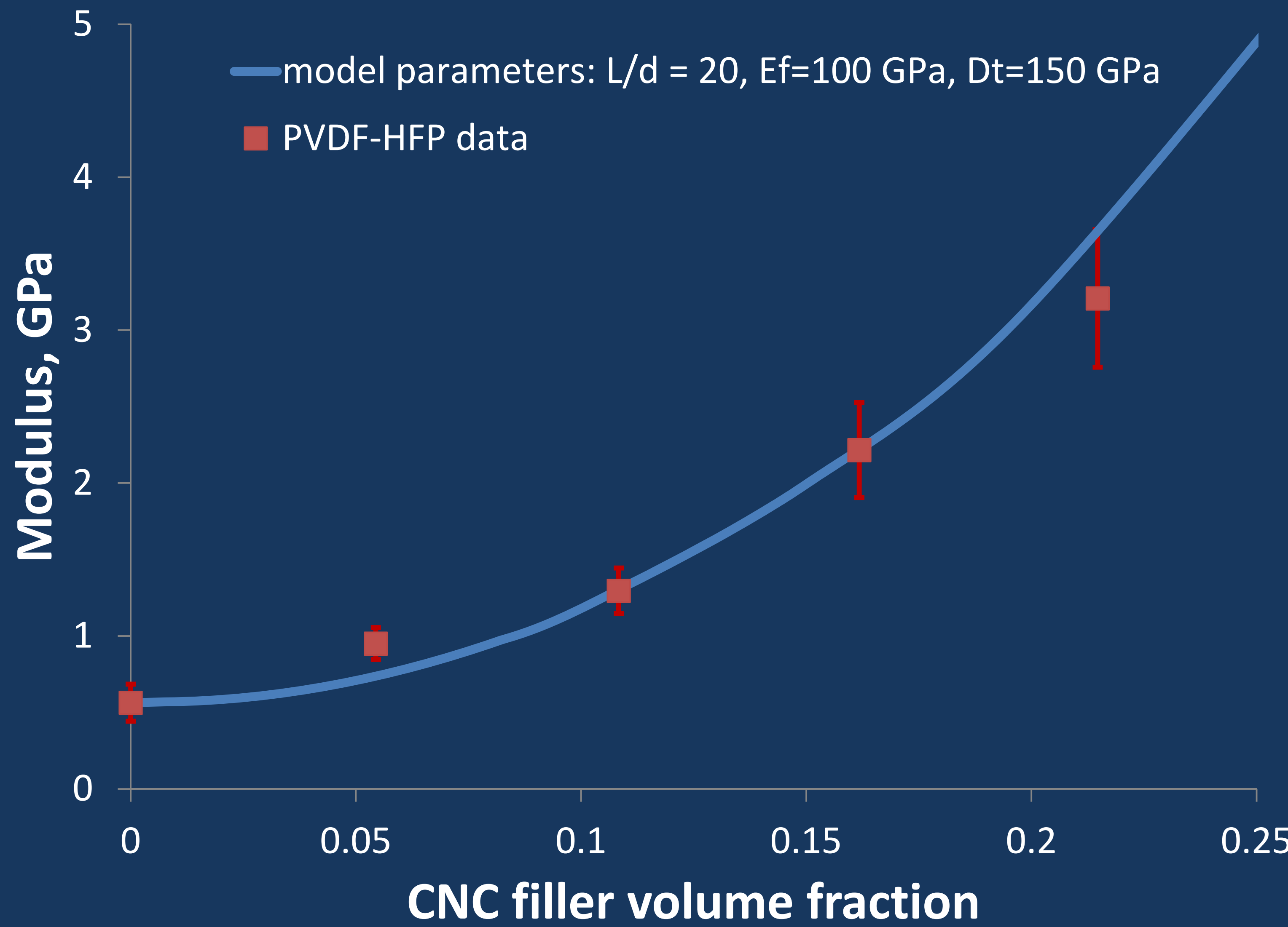
Strain to Break shows embrittlement at high CNC content



Work to Fracture peaks early



The Nairn model of Composite modulus



Model developed by Prof. John Nairn, OSU

Thermal Analysis

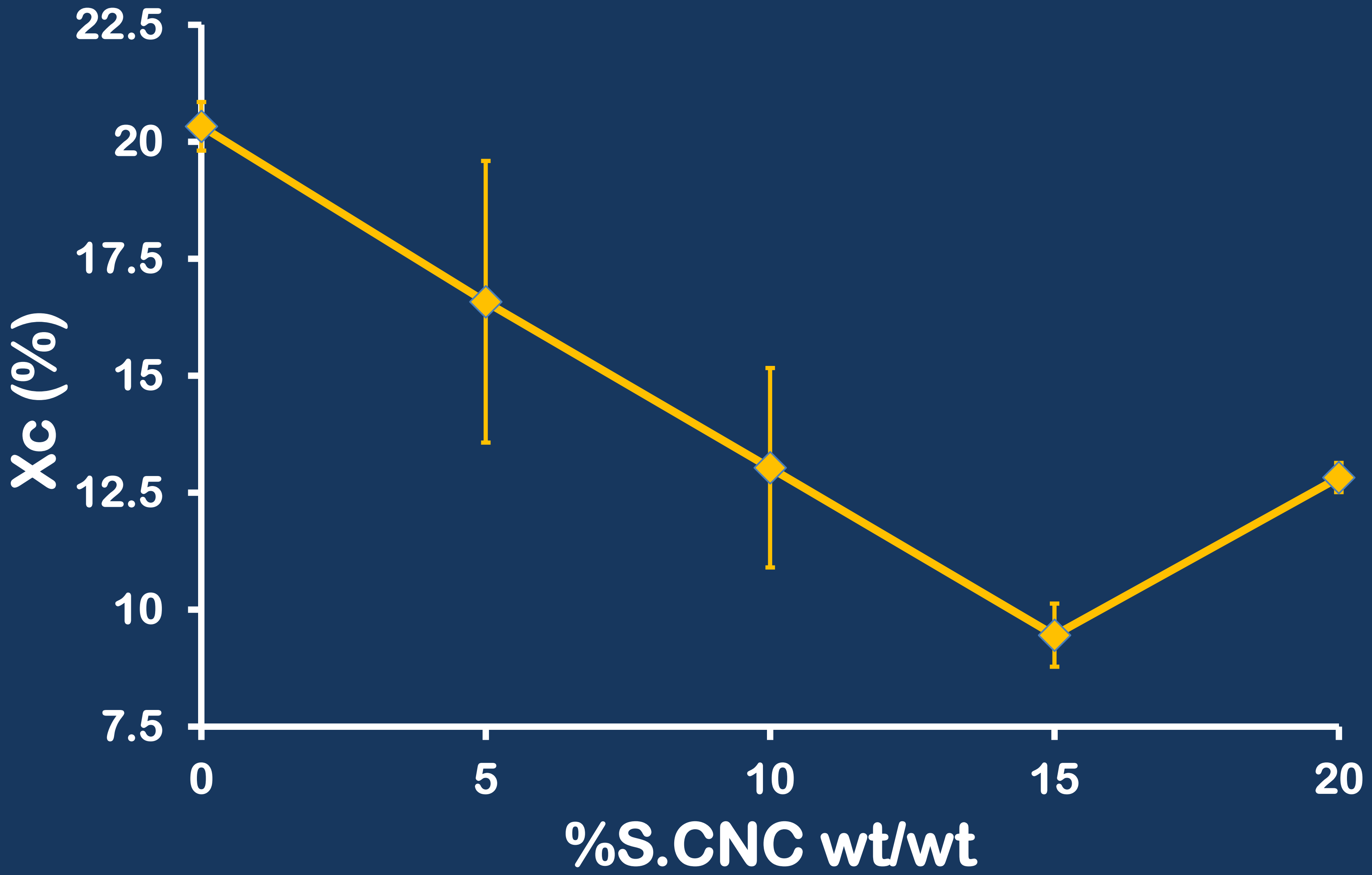
- Differential scanning calorimetry (DSC) scan over a temperature range of 30 °C to 160 °C using a scan rate of 10 °C/min and ~5 mg samples
  - % crystallinity (%X_c) calculated

$$\% X_c = (W_m * \Delta H_{m,0})^{-1} \Delta H_m * 100$$

$\Delta H_{m,0}$ = melting enthalpy of crystalline PVDFHFP (104 J/g)

W_m = weight fraction of matrix

% Matrix Crystallinity decreases with CNC content



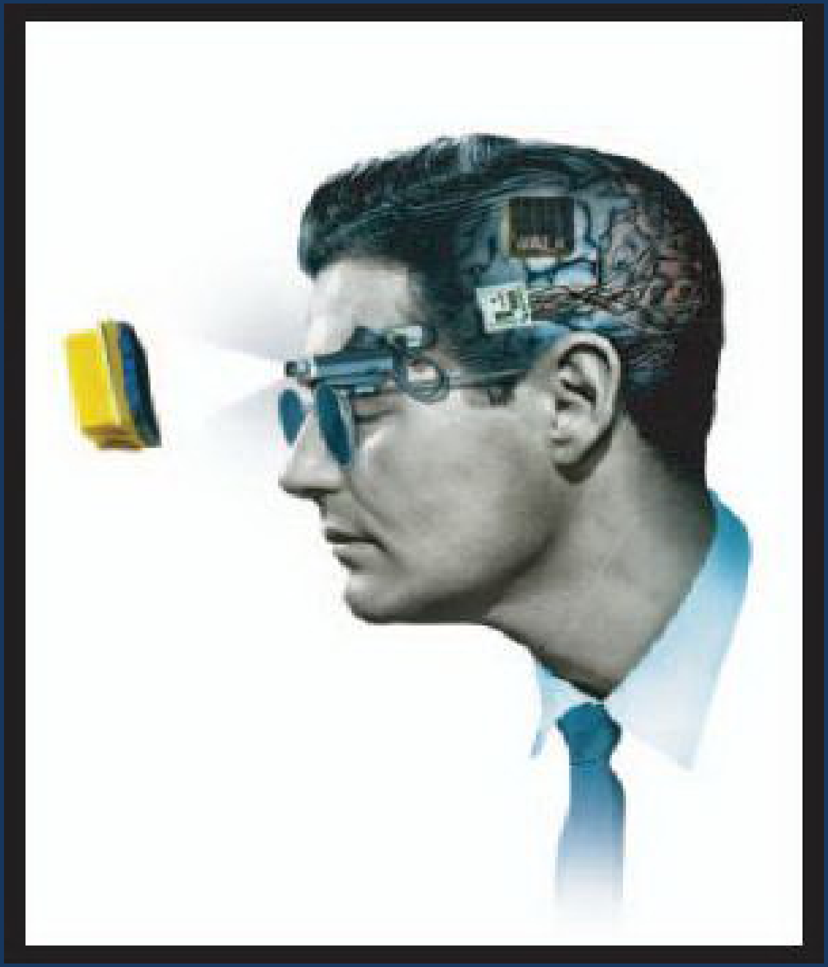
Conclusions

- Modulus, strength and work to fracture can all be improved
- Further investigation into anti-nucleation effect warranted
- How do we explain the compatibility of CNCs with this polymer?

Intracortical microelectrodes

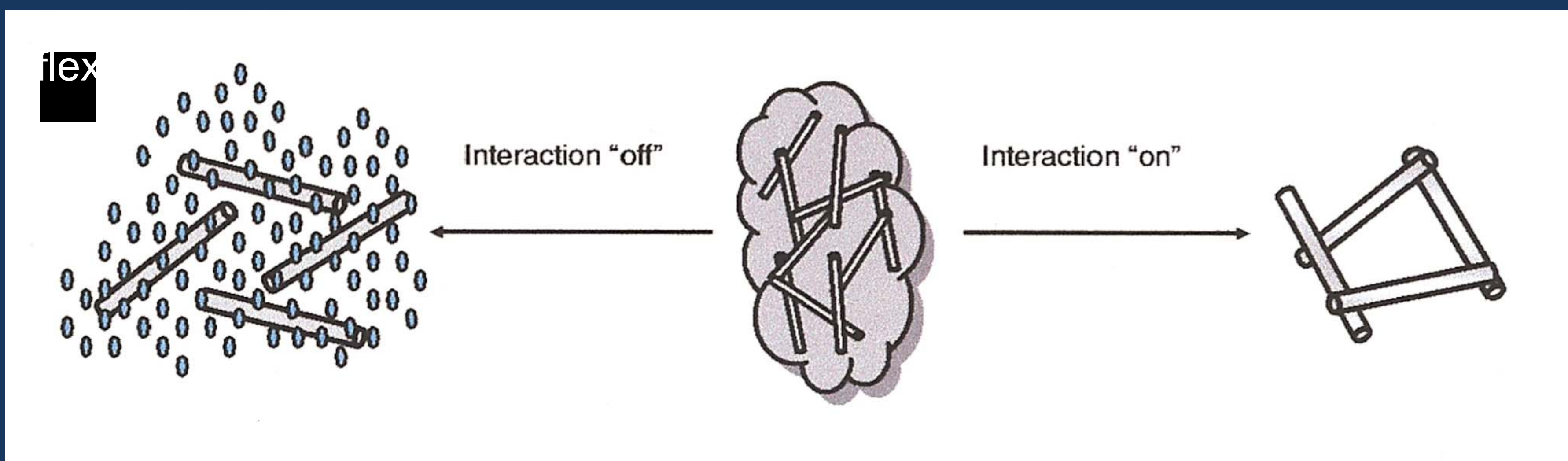
Bio-inspired switchable nanocomposite for intracortical microelectrodes

Christoph Weder's research group, Case Western Reserve



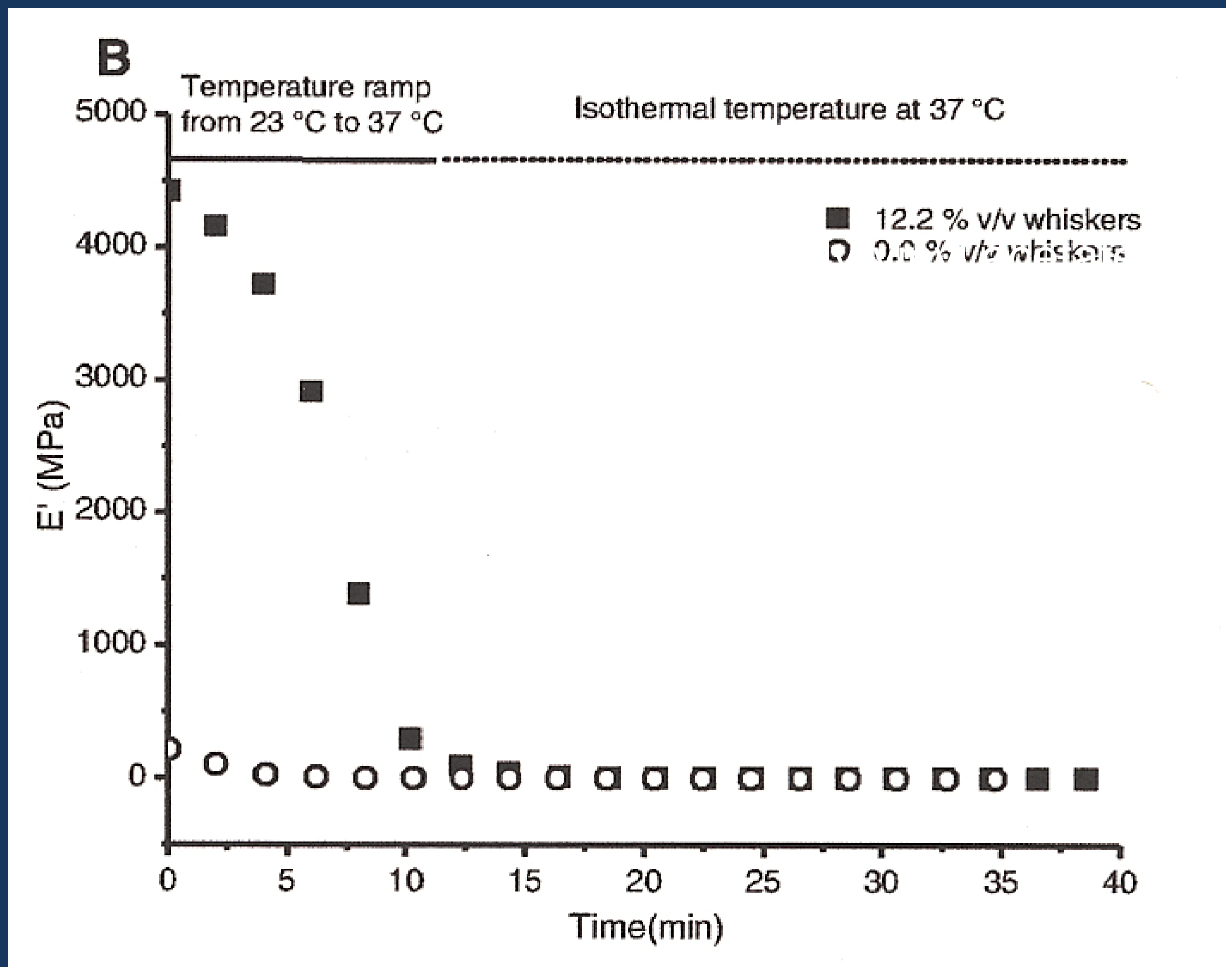
Troyk, P., et al. "A Model for Intracortical Visual Prosthesis Research." Artificial Organs 27.11 (2003): 1005-15)

Sea cucumber-inspired nanocomposite



Capadona, et al. Science 319, 1370 (2008)

Immersed in artificial cerebrospinal fluid



Capadona, et al. Science 319, 1370 (2008)

Questions?