



Aalto University
School of Chemical
Technology

Modern applications of cellulose-based fibres and nanofibres

CHEM-E2140

Cellulose-based fibres

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Learning outcomes

After this lecture, the student will be able to:

- List the most prominent (potential) application areas of nanocellulose and lignin
- Describe the main challenges in utilizing nanocellulose and lignin
- Be aware of the contemporary case studies of nanocellulose and applications

Outline

- (1) Nanocellulose: recap from the previous lecture
- (2) Nanopaper and other materials from nanofibrillar cellulose
 - Gas separation applications
 - Transistor supports
- (3) Cellulose nanocomposites
 - Cellulose nanofibre (CNF) composites
 - Cellulose nanocrystal (CNC) composites
- (4) New materials from lignin
 - Phenol-formaldehyde resins and polyurethanes
 - Carbon fibres

Basic types of nanocellulose

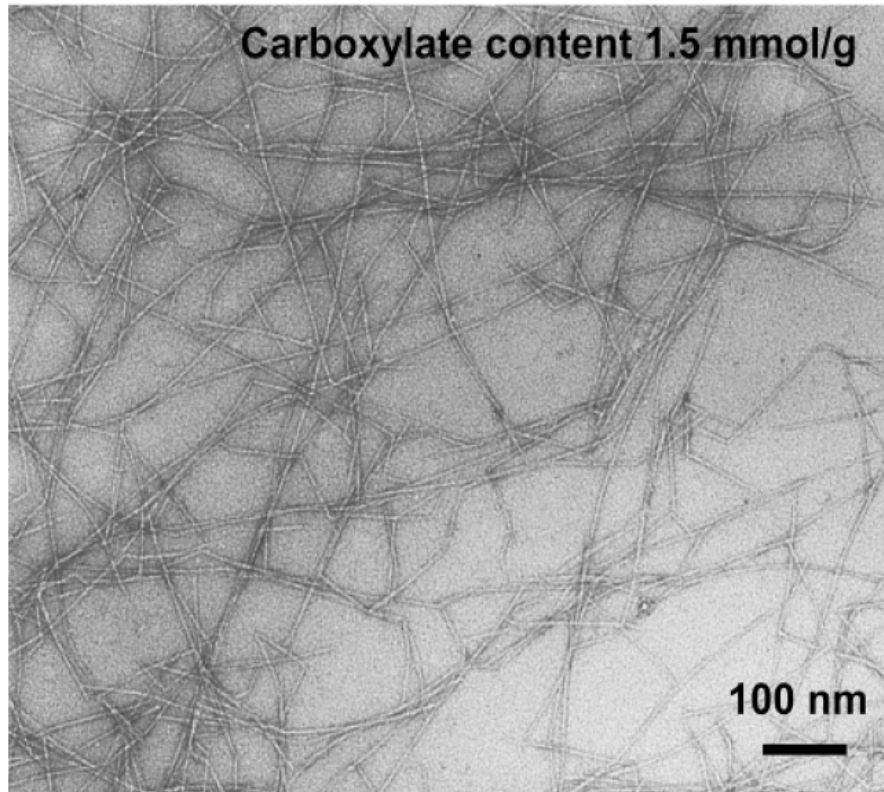
(1) Cellulose nanofibres (CNFs)

- Mechanically isolated microfibrils
- Chemically isolated microfibrils (TEMPO-oxidation)
- Bacterial cellulose

(2) Cellulose nanocrystals (CNCs)

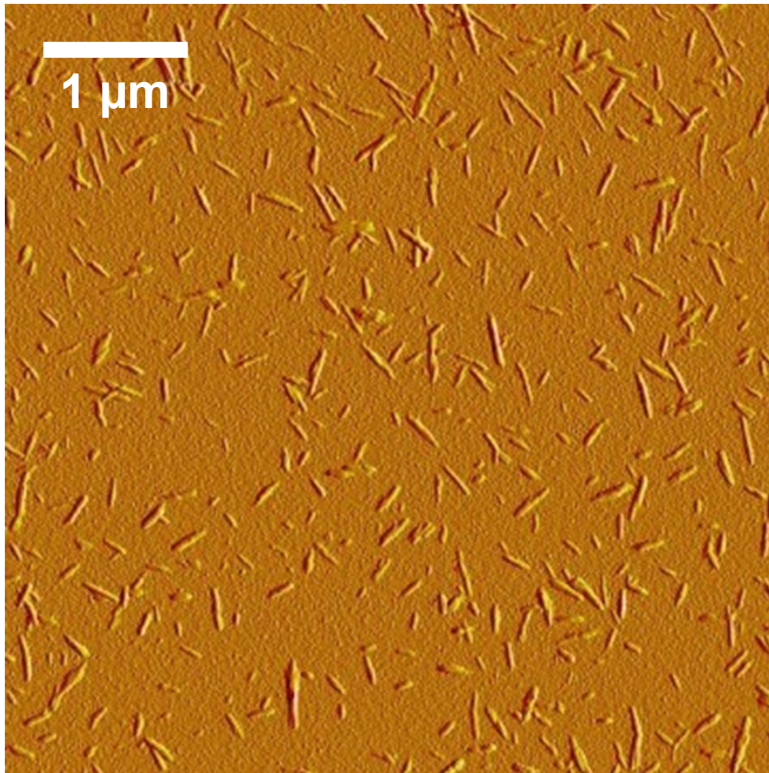
- Rods of highly crystalline cellulose, isolated by acid hydrolysis

Nanofibrillar cellulose (NFC)



- Long threads of isolated cellulose microfibrils
- Very high aspect ratio
- Length: 0.5-5 μm
- Width: 3-50 nm
- Highly charged when prepared by chemical isolation with TEMPO-oxidation
- Low charge density when prepared with mechanical isolation

Cellulose nanocrystals (CNCs)



- Rigid rods of crystalline cellulose
- Length: 50-1000 nm
- Width: 3-20 nm
- Usually charged with sulphate groups on the crystal surface
- Suspensions form spontaneously chiral nematic liquid crystal phases

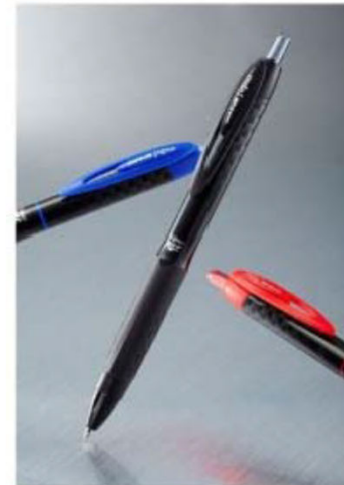
Existing commercial applications of nanocellulose



Adult diapers
(nanofibres, Japan)



Viscosity control in
oil drilling
(nanocrystals,
Canada)



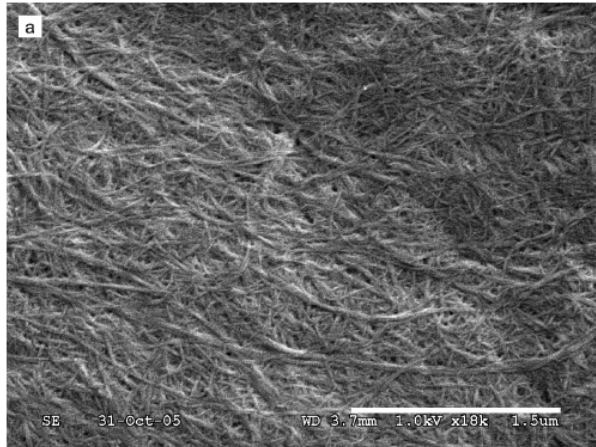
Ink dispersing in
ball point pens
(nanofibres, Japan)

Nanopaper (networks of cellulose nanofibres)

Films from cellulose nanofibres

- Prepared by casting a film of cellulose nanofibres (CNF) by getting rid of the water in CNF suspension / gel in one way or another
- The resulting film (a.k.a. *nanopaper*) is often unusually tough and strong
- The CNF film is often aimed at being optically transparent
- High density of nanopaper results in good gas barrier properties
- Maintaining strength, barrier properties etc. under humid conditions is a current research challenge with nanopaper

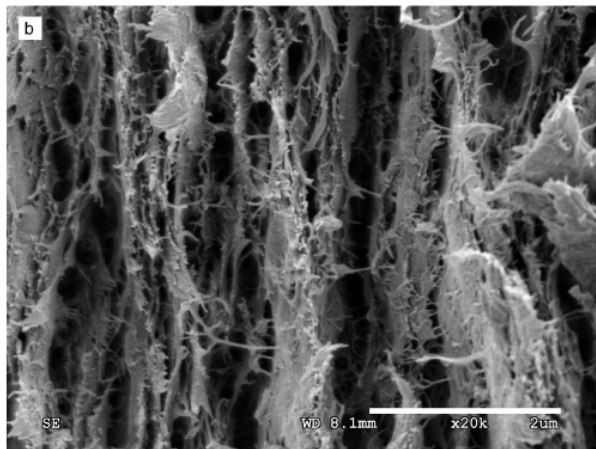
Nanopaper



Nanofibres obtained mechanically from bleached sulphite pulp after enzymatic pretreatment

The first nanopapers were prepared simply by vacuum filtration.

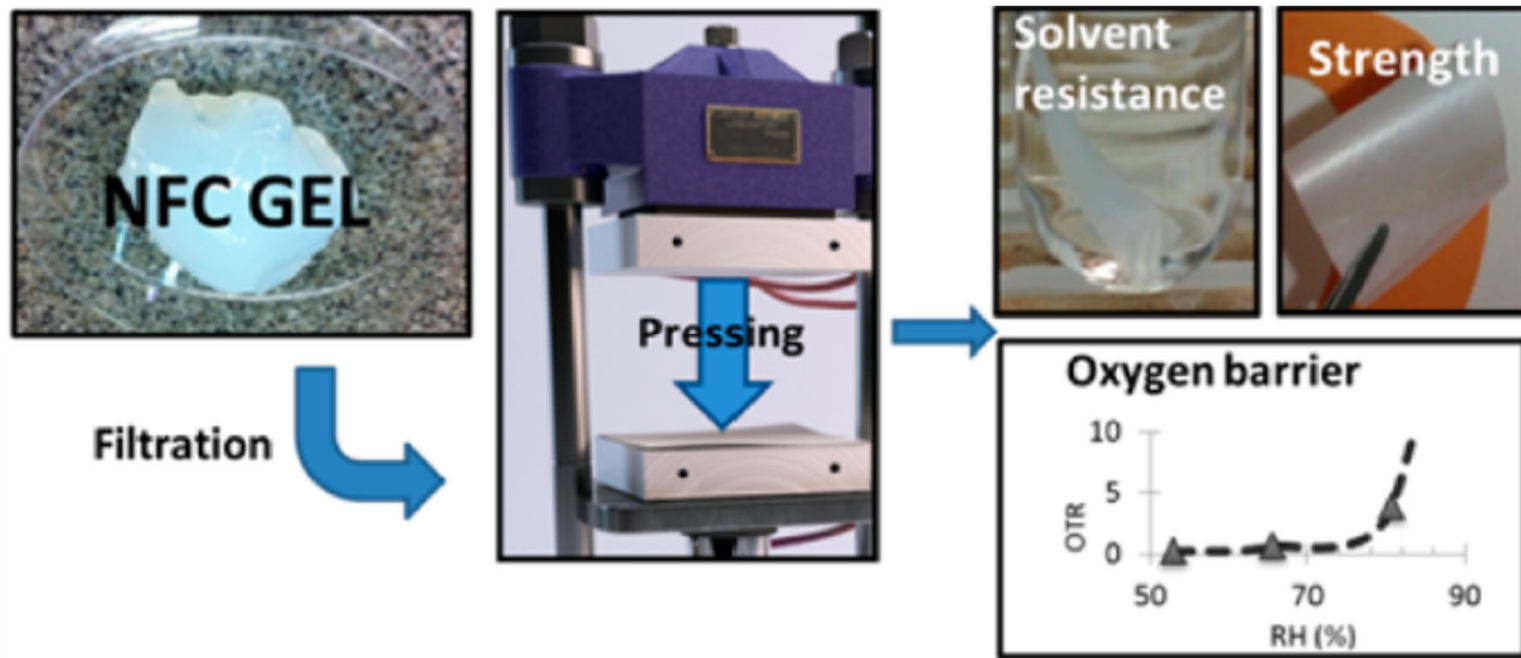
SEM image of the nanopaper surface



SEM image of the nanopaper fracture surface, exposing a layered structure.

Nanopaper preparation

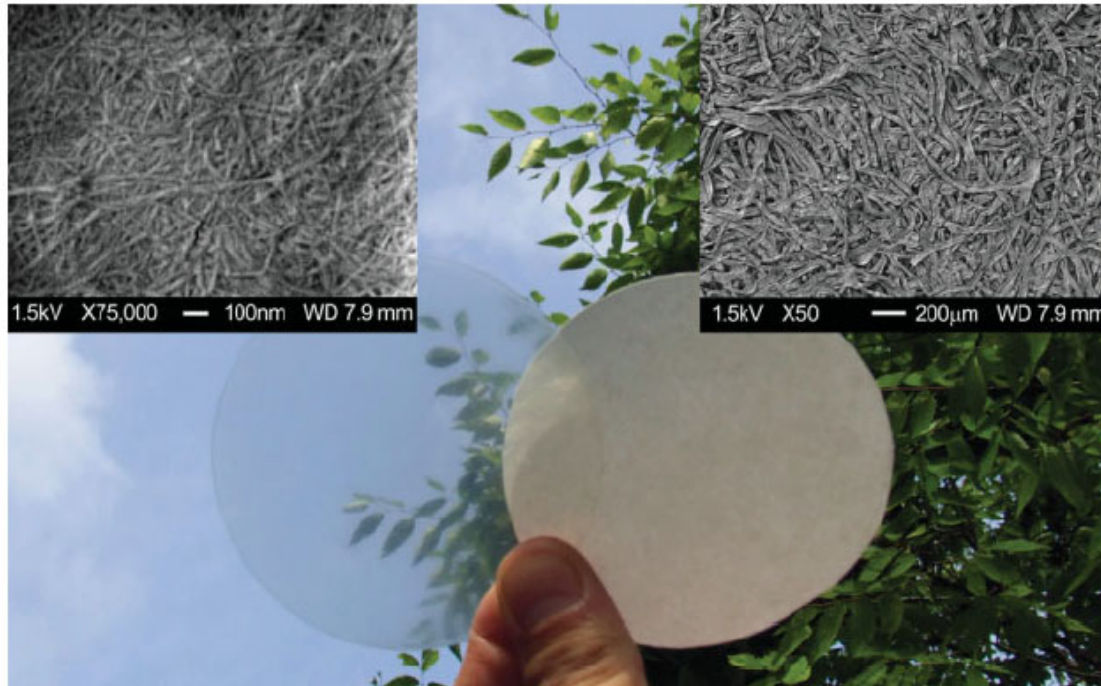
- Generally prepared by a batch process with filtering
- Hot pressing is applied to squeeze residual water out of the CNF network



Nanopaper

Nanofibers obtained mechanically from wood fibres after chlorite delignification

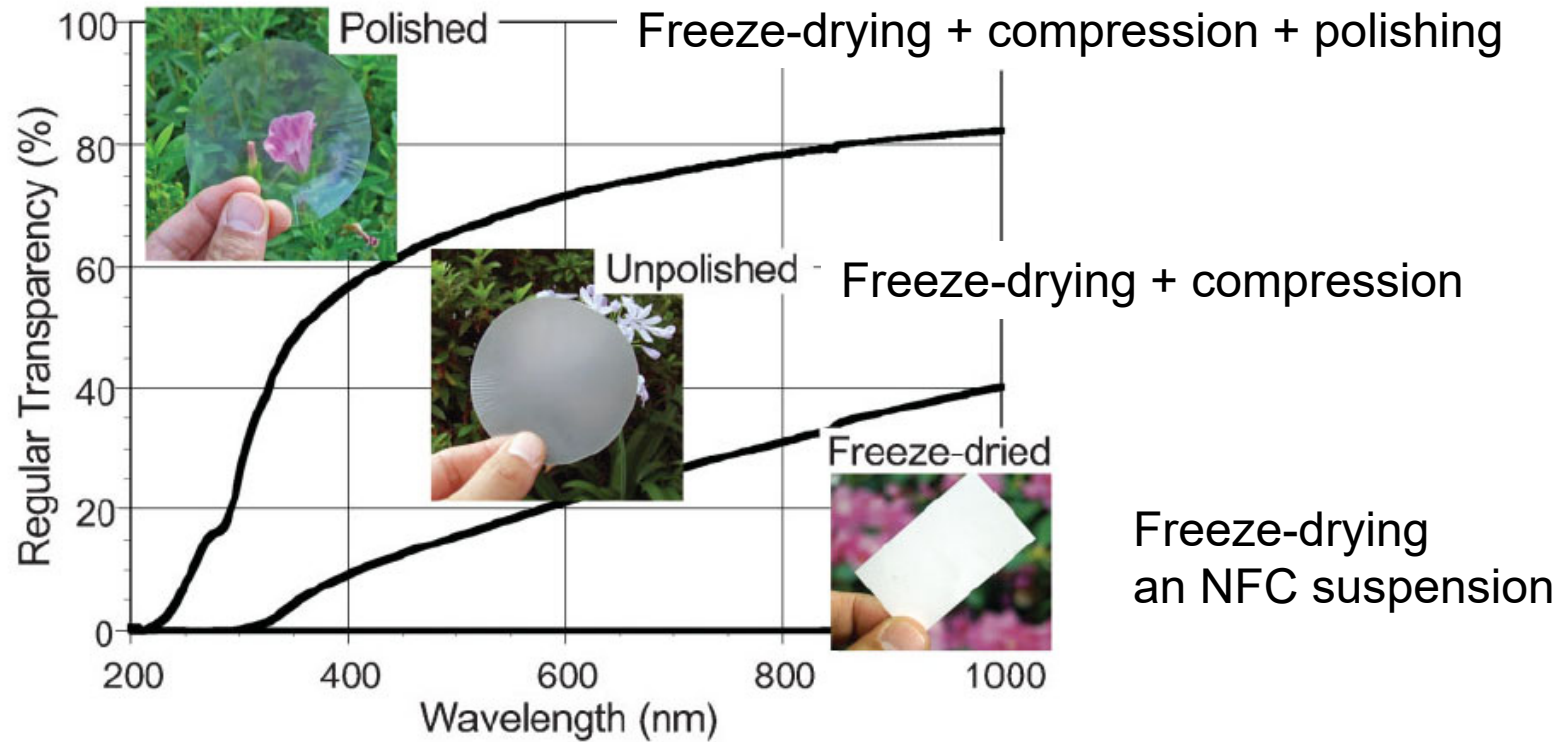
Nano-
paper



Paper

Figure 1. Optically transparent nanofiber paper (left) composed of 15 nm cellulose nanofibers (upper left, scale bar in inset: 100 nm) and conventional cellulose paper (right) composed of 30 μm pulp fibers (upper right, scale bar in inset: 200 μm).

Nanopaper

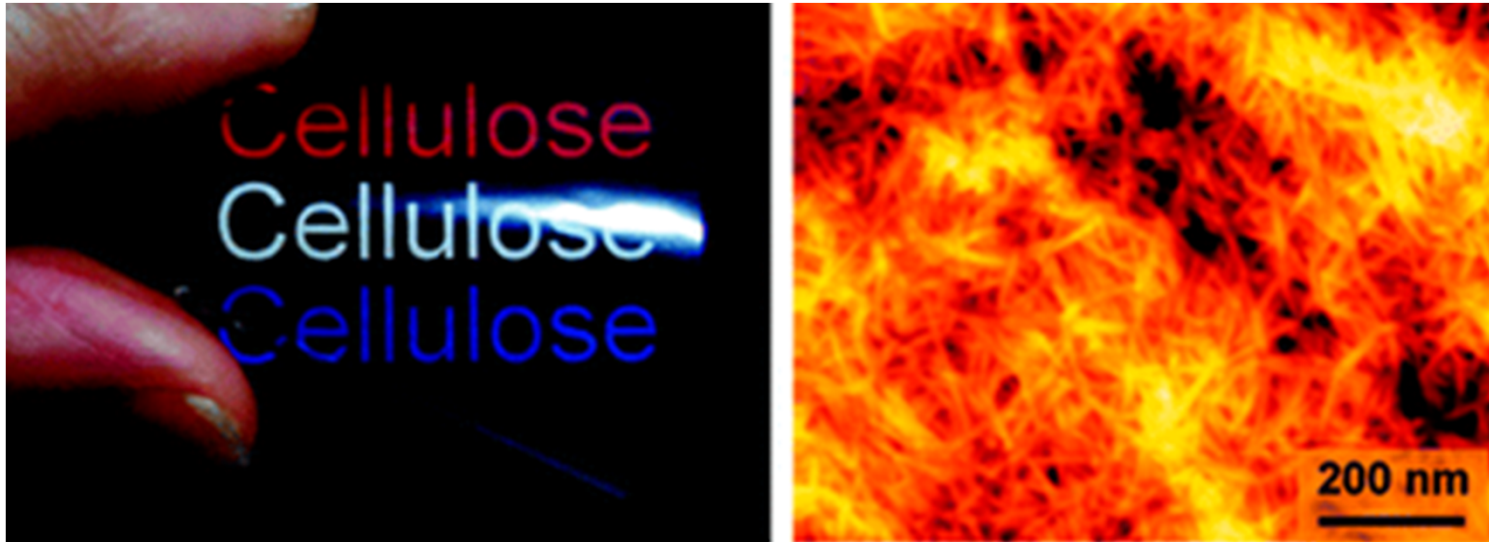


Surface roughness leads to light scattering
→ removed by polishing

Nogi et al. *Adv. Mater.* **2009**, 21, 1595.

Nanopaper

Nanofibres obtained from bleached kraft pulp with TEMPO-oxidation



Transparent films with high density (1.48 g cm^{-1})

Films from nanofibrillar cellulose

Nanofibres obtained from bleached kraft pulp with TEMPO-oxidation

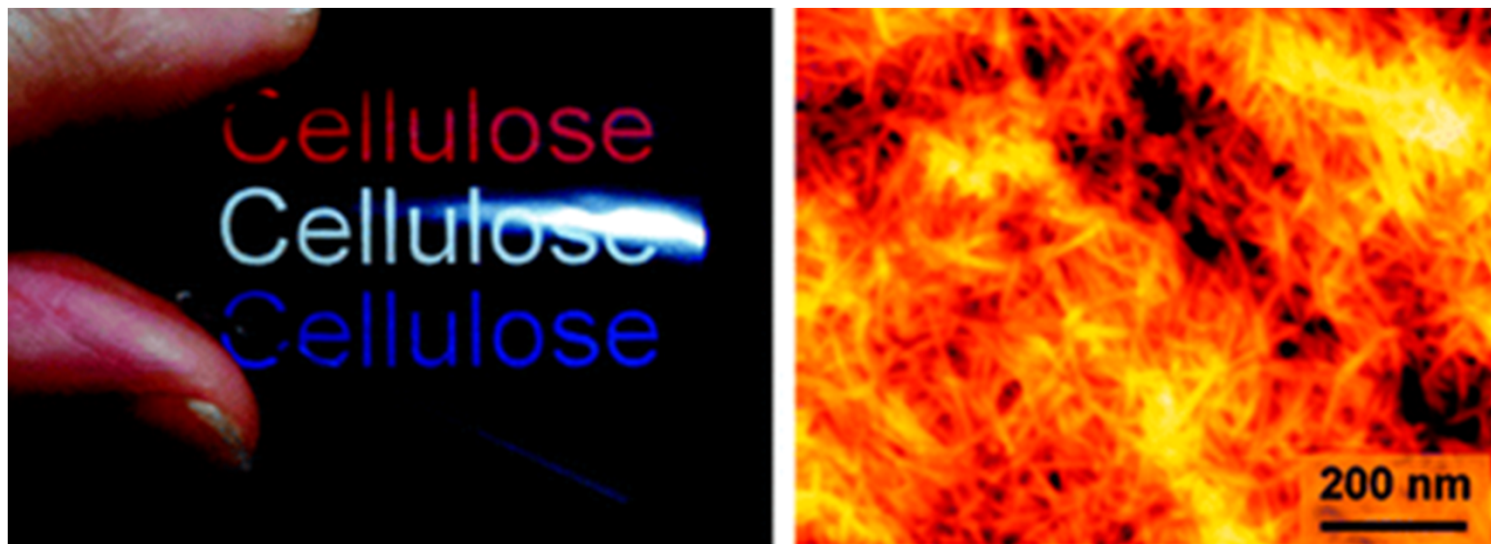


Table 2. Oxygen Permeability of the Original 25 μm Thick PLA Film and the Film Coated with 0.4 μm Thick TEMPO-Oxidized Cellulose Nanofibers

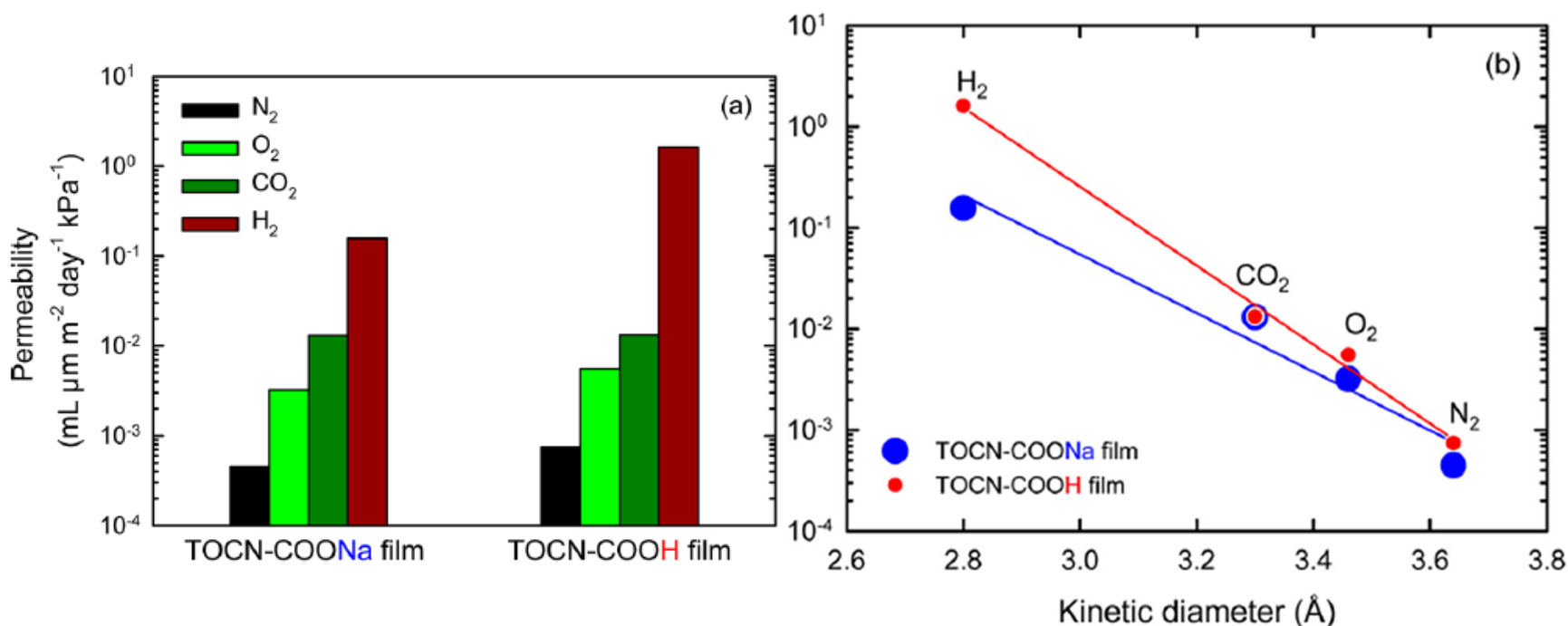
	O_2 permeability ($\text{mL m}^{-2} \text{ day}^{-1} \text{ Pa}^{-1}$)
polylactic acid (PLA) film	746
PLA film coated with TOCN	1

High gas
barrier properties

Fukuzumi et al. *Biomacromolecules* 2009, 10, 162.

Selective gas permeability of nanopaper

- NFC prepared by TEMPO-mediated oxidation (TOCN)
- The counter ion of carboxylic groups makes a difference, either a proton (TOCN-COOH) or sodium (TOCN-COONa)



→ Closer packing of fibrils in with Na^+ counterion (TOCN-COONa)

Fukuzumi et al. *Biomacromolecules* 2013, 14, 1705.

Selective gas permeability of nanopaper

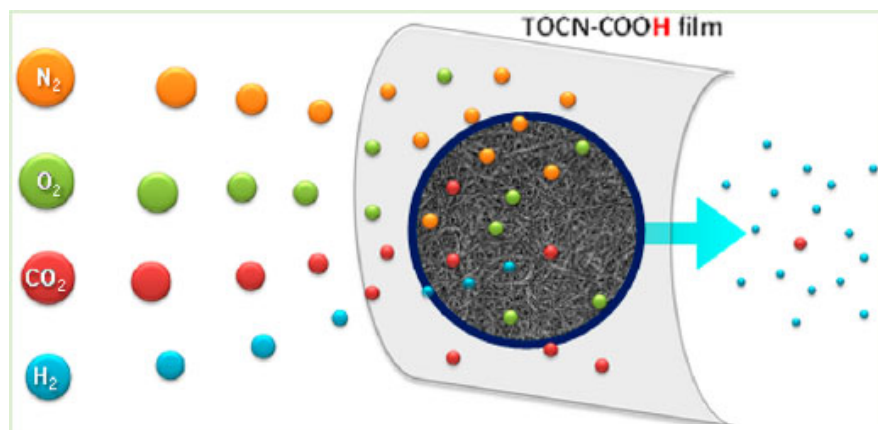


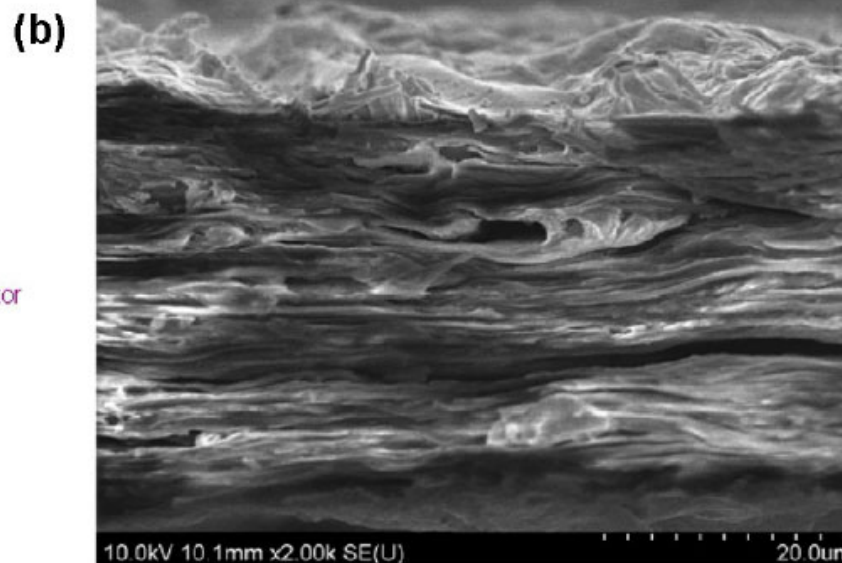
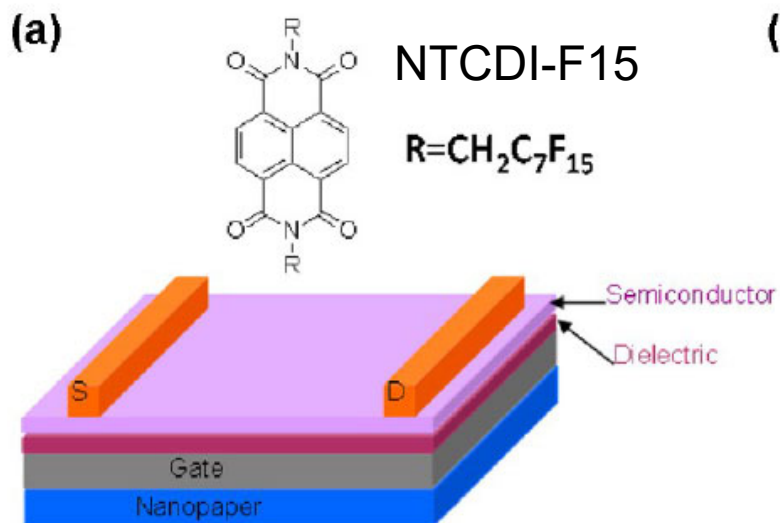
Table 1. Relative Gas Permeability Ratios of TOCN and Commercial Films

	H ₂ /N ₂	H ₂ /CO ₂	H ₂ /O ₂	O ₂ /N ₂	CO ₂ /N ₂
TOCN-COONa	350	12	49	7.2	29
TOCN-COOH	2200	24	290	7.4	92
cellophane	220	14	39	5.6	16
PET	190	5.3	30	6.2	35
PE	8.5	0.58	3.0	2.8	15

Fukuzumi et al. *Biomacromolecules* 2013, 14, 1705.

Nanopaper as a transistor support

Cross sectional SEM from transistor



Semiconductor: NTCDI-F15 semiconductor film

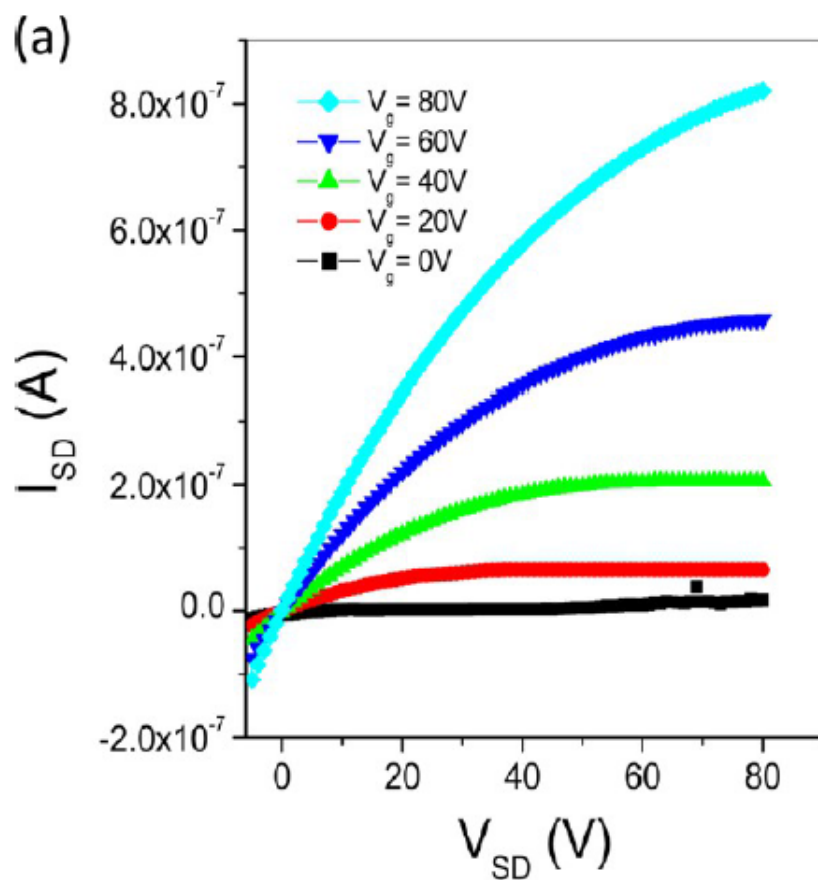
Dielectric: poly(methyl methacrylate) film

Gate electrode: single-walled carbon nanotubes

Nanopaper: film from TEMPO-oxidized NFC

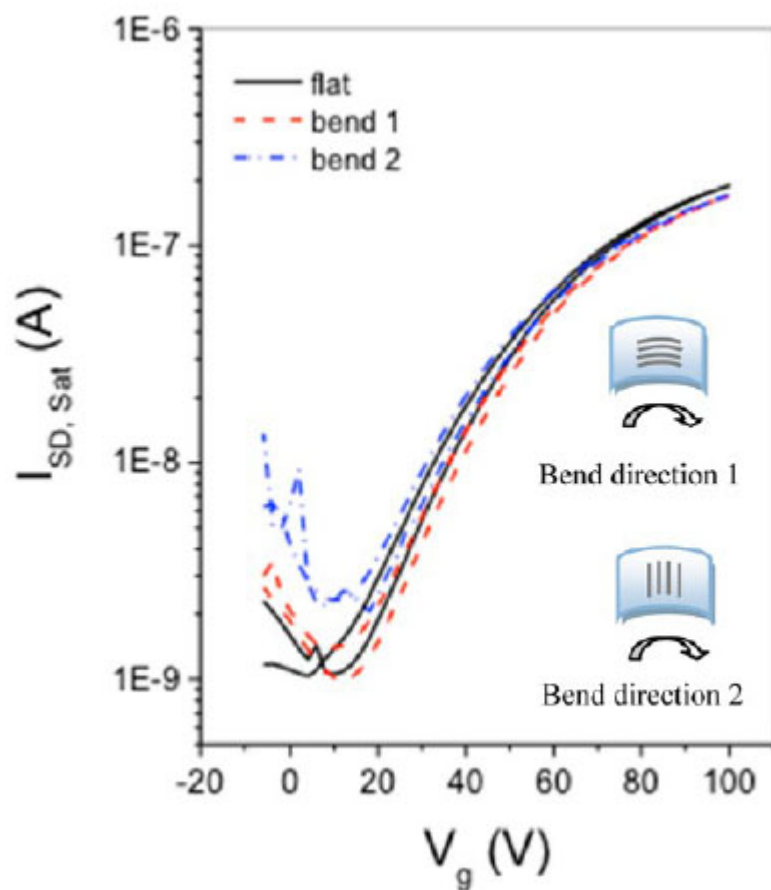
Huang et al. *ACS Nano* 2013, 7, 2106.

Nanopaper as a transistor support



- The constructed multilayer material works well as a field-effect transistor

Nanopaper as a transistor support



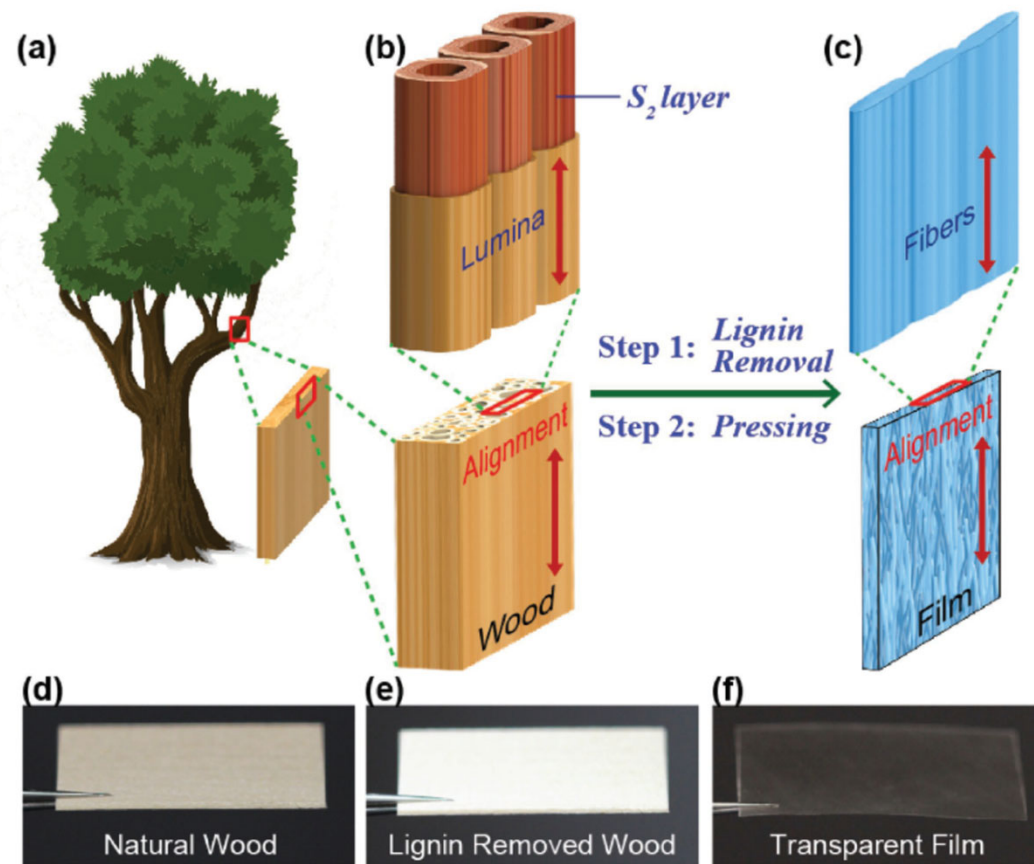
- Bending has little effect on the transistor performance of the material

Comparison of bending transistor supports

characteristics	nanopaper	traditional paper	plastic
surface roughness (nm)	5	5000–10000	5
porosity (%)	20–40	50	0
pore size (nm)	10–50	3000	0
optical transparency at 550 nm (%)	90	20	90
max loading stress (MPa)	200–400	6	50
coefficient of thermal expansion (CTE) (ppm K ⁻¹)	12–28.5	28–40	20–100
printability	good	excellent	poor
Young modulus (GPa)	7.4–14	0.5	2–2.7
bending radius (mm)	1	1	5
renewable	high	high	low

Huang et al. *ACS Nano* 2013, 7, 2106.

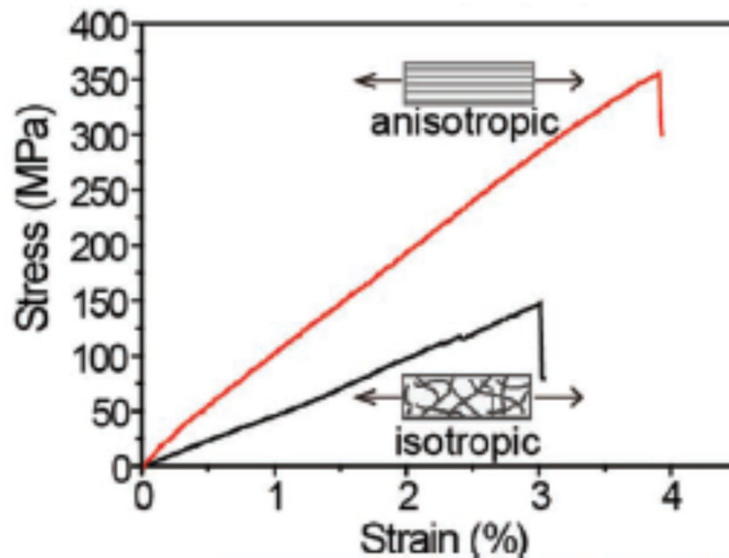
Nanopaper from aligned CNFs



Wood structure of aligned fibres *and* aligned microfibrils (secondary wall) is preserved upon delignification, resulting in nanopaper of aligned CNFs

Aligned CNF vs. isotropic CNFs

Tensile strength



Isotropic nanopaper sample here may be deliberately downplayed (inferior strength)

- Aligned CNFs lead to a stronger “nanopaper” (350 MPa tensile strength)
- Modern nanopapers usually have tensile strengths at ~200-300 MPa

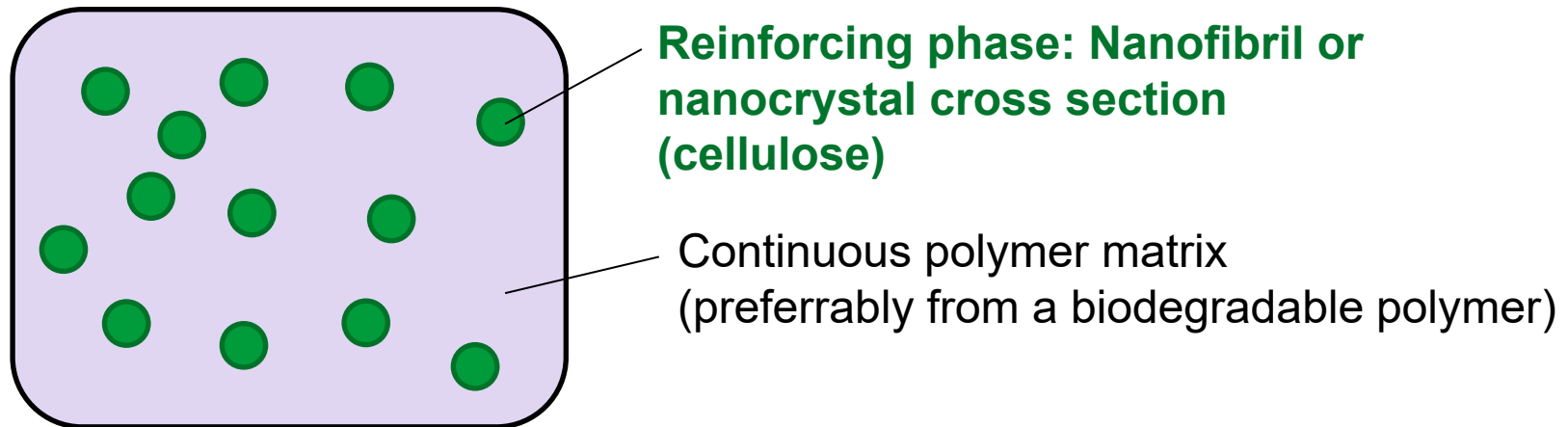
Cellulose nanocomposites

Cellulose nanocomposites

- Cellulose nanocomposites usually consist of cellulose nanofibres or cellulose nanocrystals embedded in a continuous polymer matrix
- The challenge is often to retain the nanometer dimensions of the cellulosic objects (i.e., prevent their aggregation)
- One of the big trends is to end up with materials that would be equal to plastics (or to surpass the properties of plastics)
- Another trend is to prepare stimuli-responsive composites for niche applications
- The research is still at a very early stage: most entries are fundamental efforts to understand the interactions of nanofibres with each other and/or other components

Nanocomposites from nanocellulose

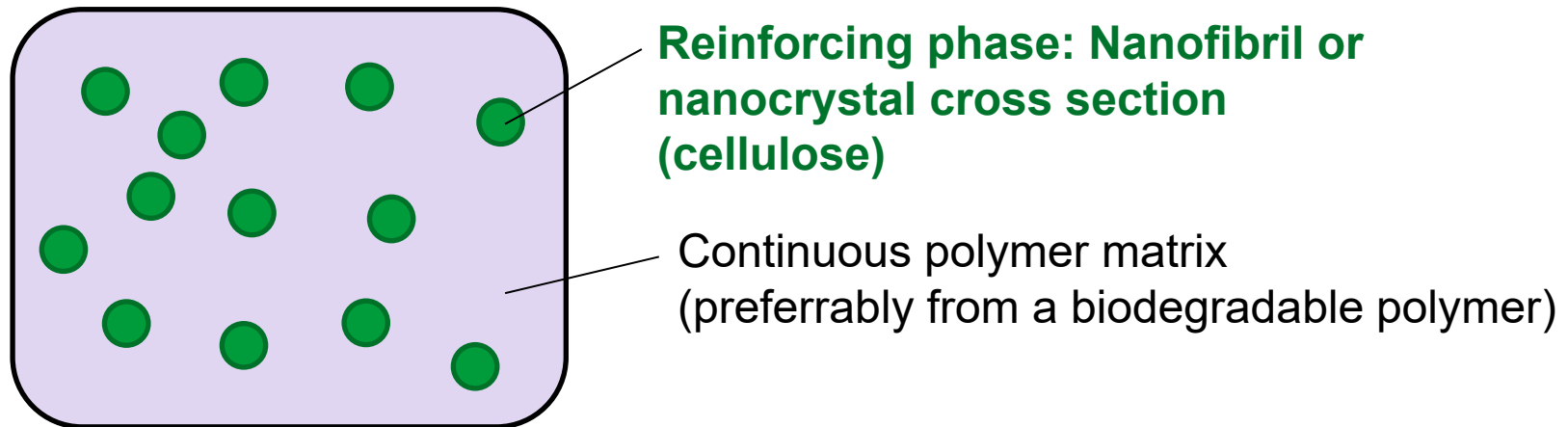
Schematic cross section
of a nanocomposite



OFTEN REFERRED TO SCENARIO: Poly(lactic acid) as a continuous matrix and nanofibrillar cellulose as the reinforcing phase. *Both* are bio-based and biodegradable.

Nanocomposites from nanocellulose

Schematic cross section
of a nanocomposite

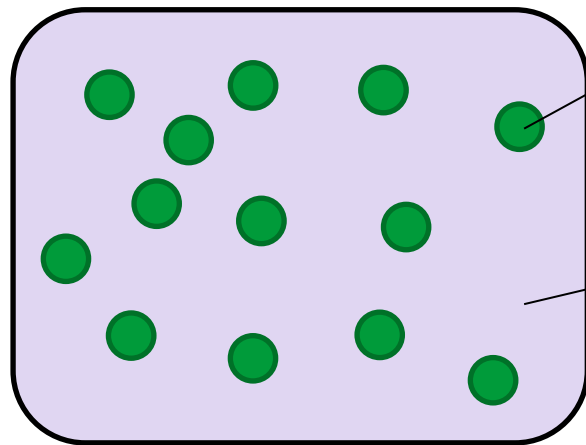


WHY CELLULOSE?

Poly(lactic acid) is brittle and weak on its own. Cellulose with strong mechanical properties would boost its strength.

Nanocomposites from nanocellulose

Schematic cross section
of a nanocomposite



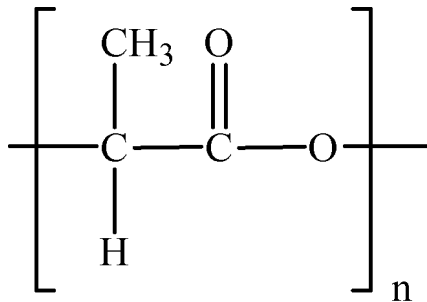
**Reinforcing phase: Nanofibril or
nanocrystal cross section
(cellulose)**

Continuous polymer matrix
(preferably from a biodegradable polymer)

WHY NANOCOMPOSITES?

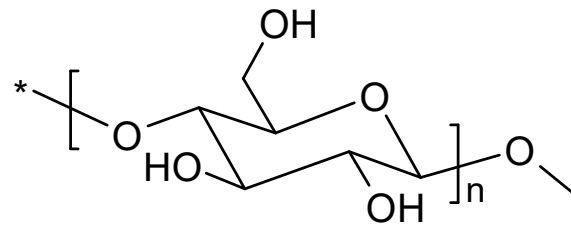
Nanocellulose has a very large surface area, that is, a lot of contact points with the continuous poly(lactic acid) matrix, plus it is very strong.

Nanocomposites from nanocellulose



Poly(lactic acid)

Dissolves in hydrophobic solvents

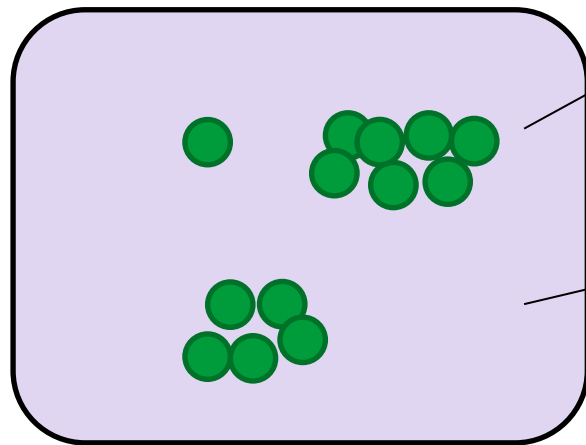


Cellulose

Dissolves in very few solvents

Nanocomposites from nanocellulose

Schematic cross section
of a nanocomposite



Reinforcing phase: Nanofibril or nanocrystal cross section (cellulose)

Continuous polymer matrix (preferably from a biodegradable polymer)

WHAT IS THE PROBLEM?

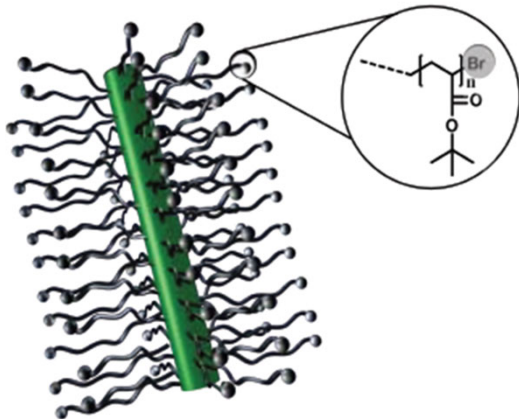
Cellulose aggregates easily with itself. It is incompatible with nearly anything else than the lignin/hemicellulose matrix in the plant cell wall.

→ Loss in surface area → No nanocomposite anymore

Nanocomposites from nanocellulose

How does one solve the problem?

One approach: modify the surface of nanocellulose



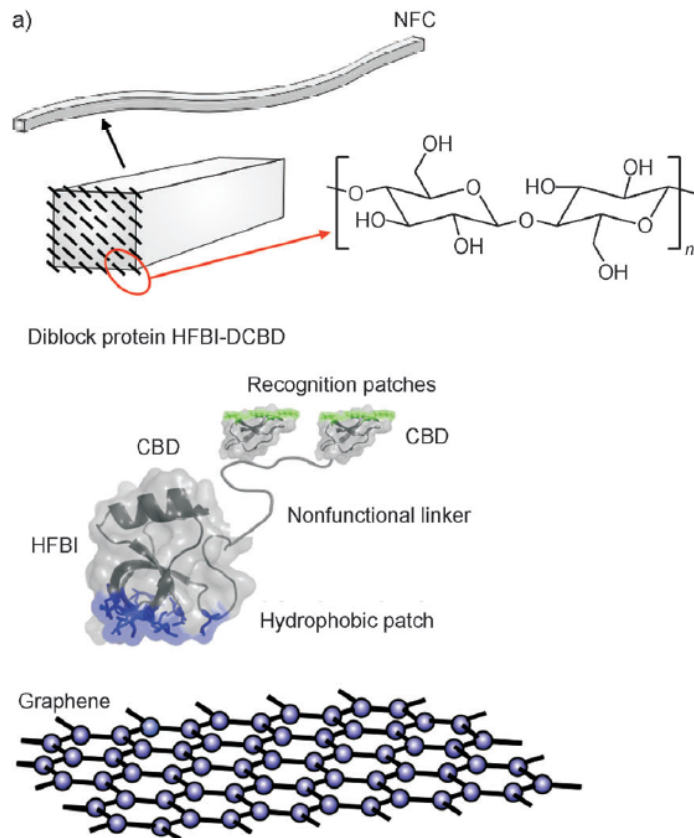
Surface modification:

- Surface of nanocellulose is more compatible with the surrounding polymer matrix in nanocomposites
- Crystalline core of cellulose stays intact
→ Strength properties of nanocellulose stay intact

At the moment, the methods to do this are expensive and not scalable.

Composites with nanofibrillar cellulose

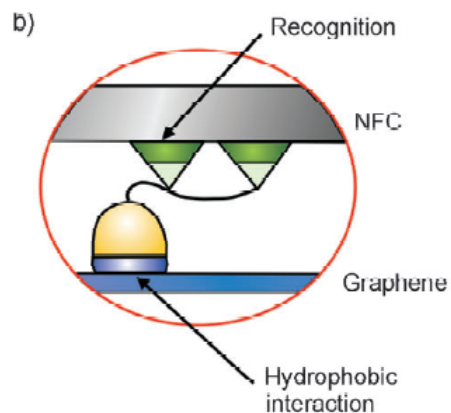
Graphene / protein / NFC composites



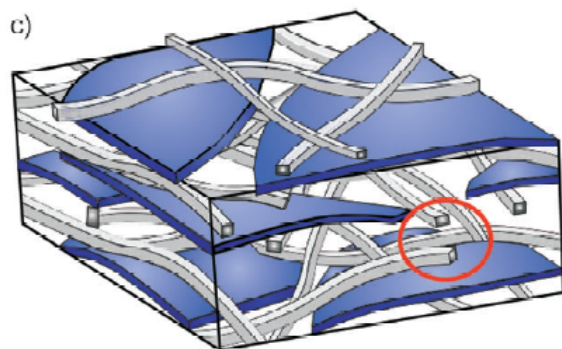
Materials:

- Nanofibrillar cellulose (NFC)
- Graphene
- Diblock protein: a protein with two binding sites – one to cellulose, one to graphene

Graphene / protein / NFC composites

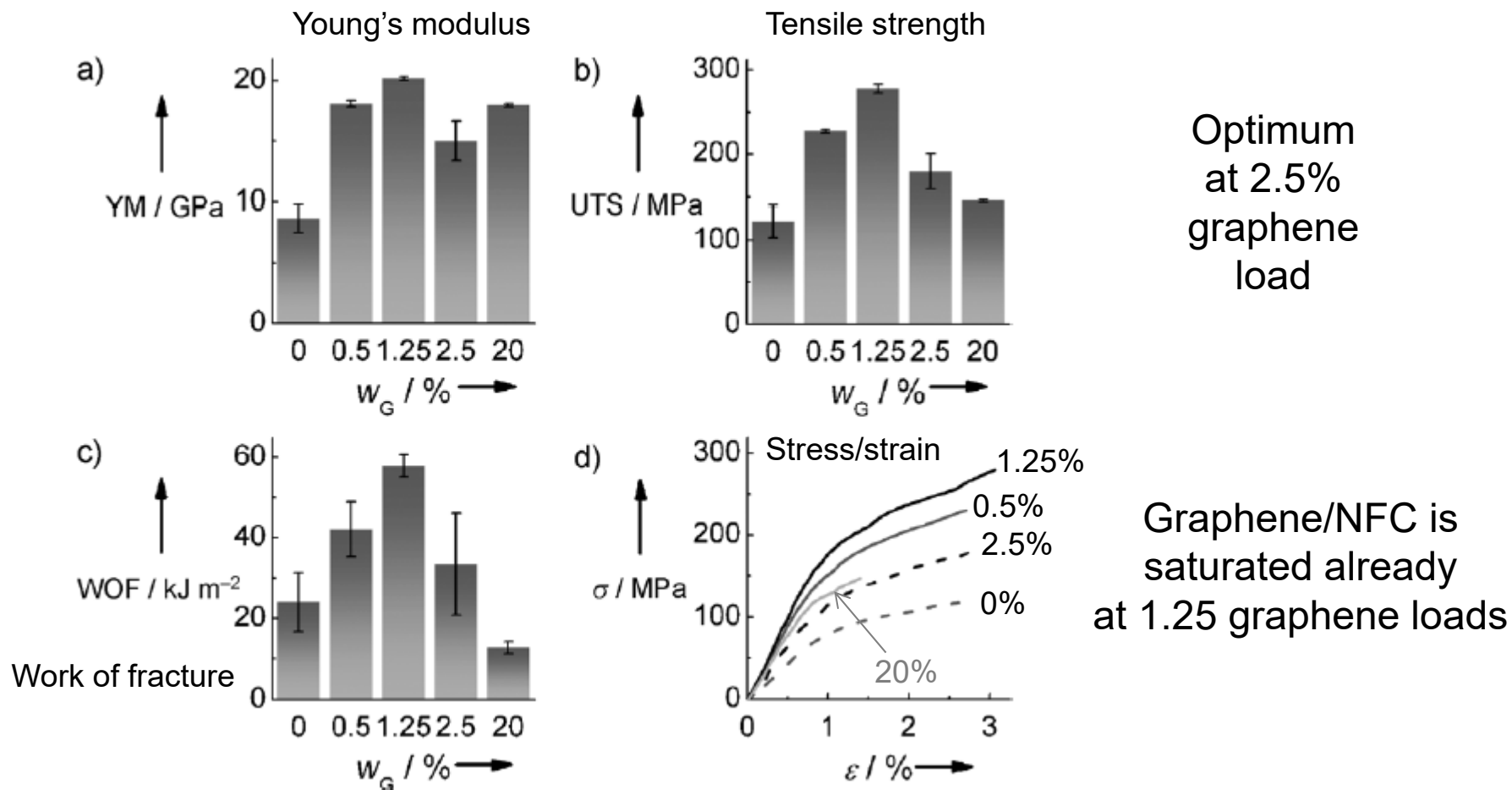


Diblock protein is able to manufacture an ordered nanocomposite of NFC and graphene.



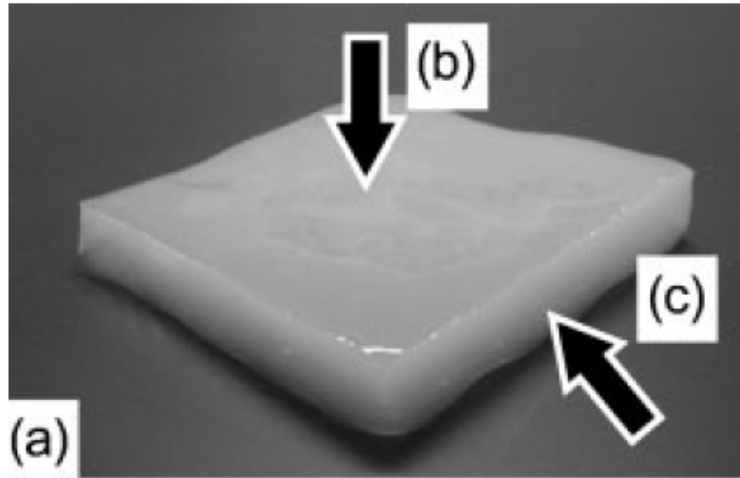
Graphene / protein / NFC composites

Mechanical properties as a function of the amount of graphene (W_G)



Laaksonen et al. *Angew. Chem. Int. Ed.* 2011, 50, 8688.

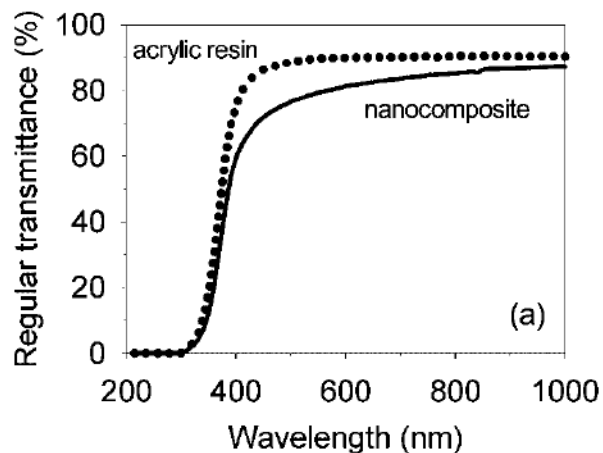
Acrylic resin / bacterial cellulose



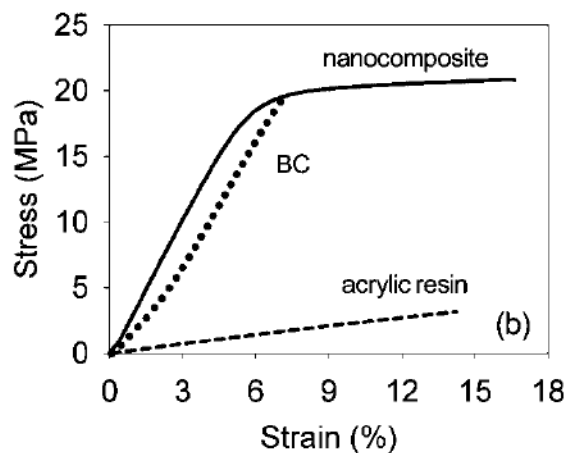
Bacterial cellulose pellicle

Water in a bacterial cellulose pellicle is replaced gradually with ethanol and impregnated with acrylic resin which is subsequently cured.

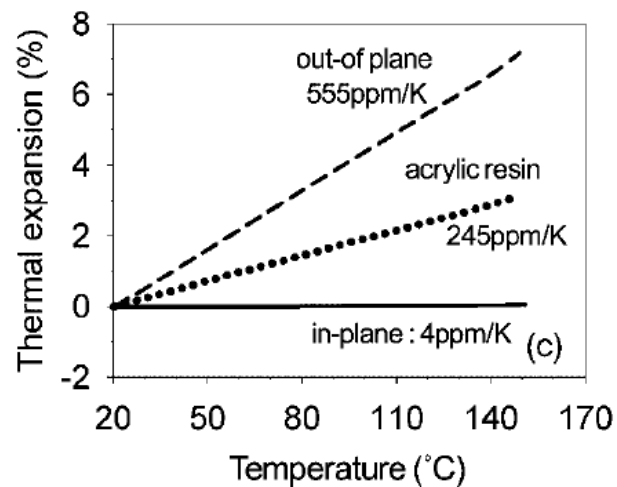
Acrylic resin / bacterial cellulose



Light transmittance of the resin is retained while the mechanical properties are enhanced.



Thermal expansion is very low.



Acrylic resin / bacterial cellulose



Figure 1. Luminescence of an organic light-emitting diode deposited onto a transparent BC nanocomposite. The luminescence area is $40 \times 25 \text{ mm}^2$. This work was carried out in collaboration with Mitsubishi Chemical Corporation and Pioneer Corporation.

Potential usage for foldable flat panel displays in the electronics device industry.



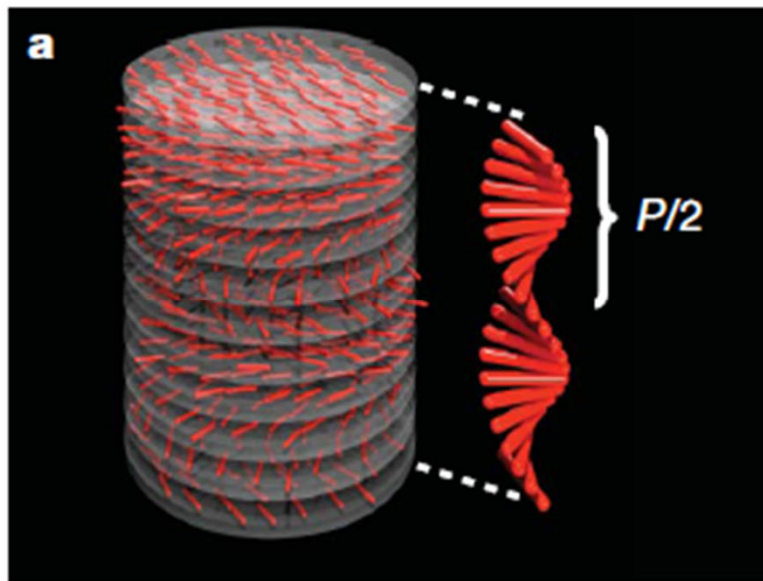
Most plastics have too large a thermal expansion for electronics devices.

Composites with cellulose nanocrystals

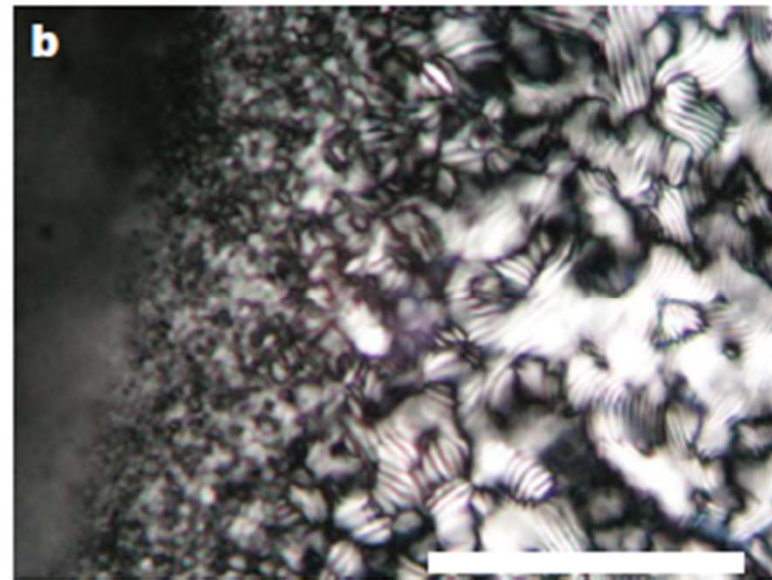
CNCs as chiral templates

- CNCs spontaneously form chiral nematic liquid crystal phases
- When $\text{Si}(\text{OEt})_4$ is added to the suspension, a composite forms

Schematics of chiral nematic liquid crystal suspension of CNCs



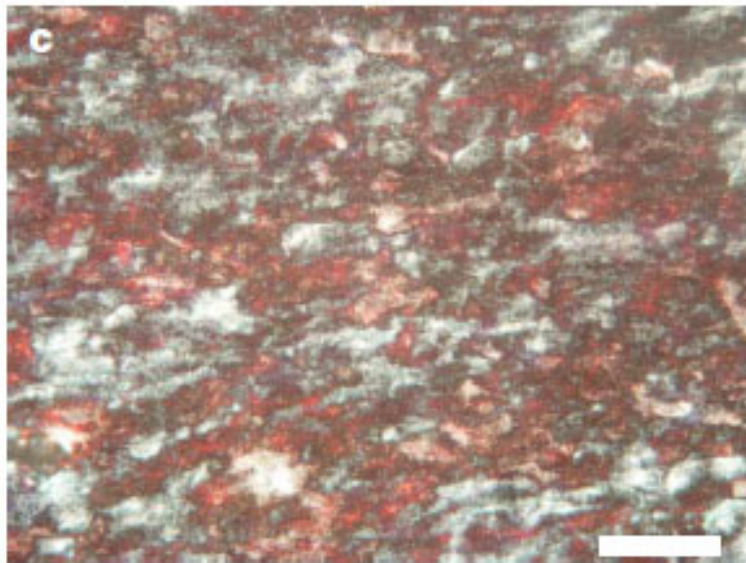
Polarized optical micrograph of composite suspension of $\text{Si}(\text{OEt})_4$ and CNCs



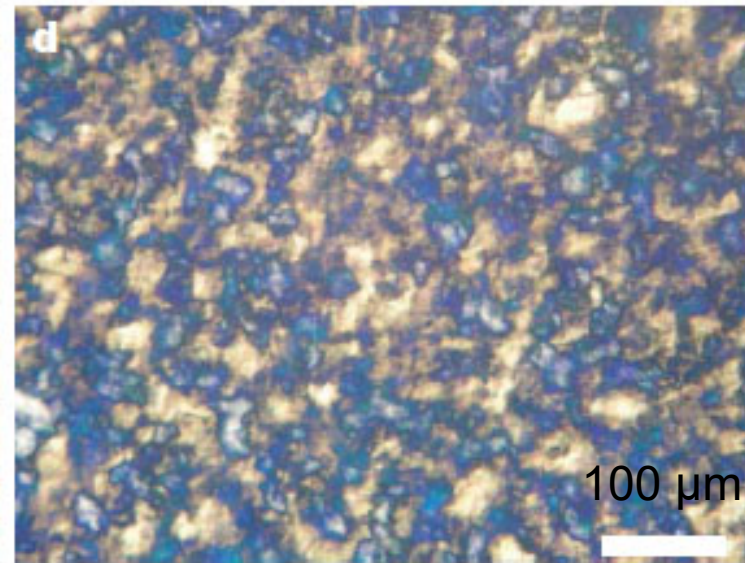
CNCs as chiral templates

- $\text{Si}(\text{OEt})_4$ hydrolyses to SiO_2 in CNC/water suspension
- CNCs can be removed by calcination, resulting in a mesoporous, chiral nematic film of SiO_2

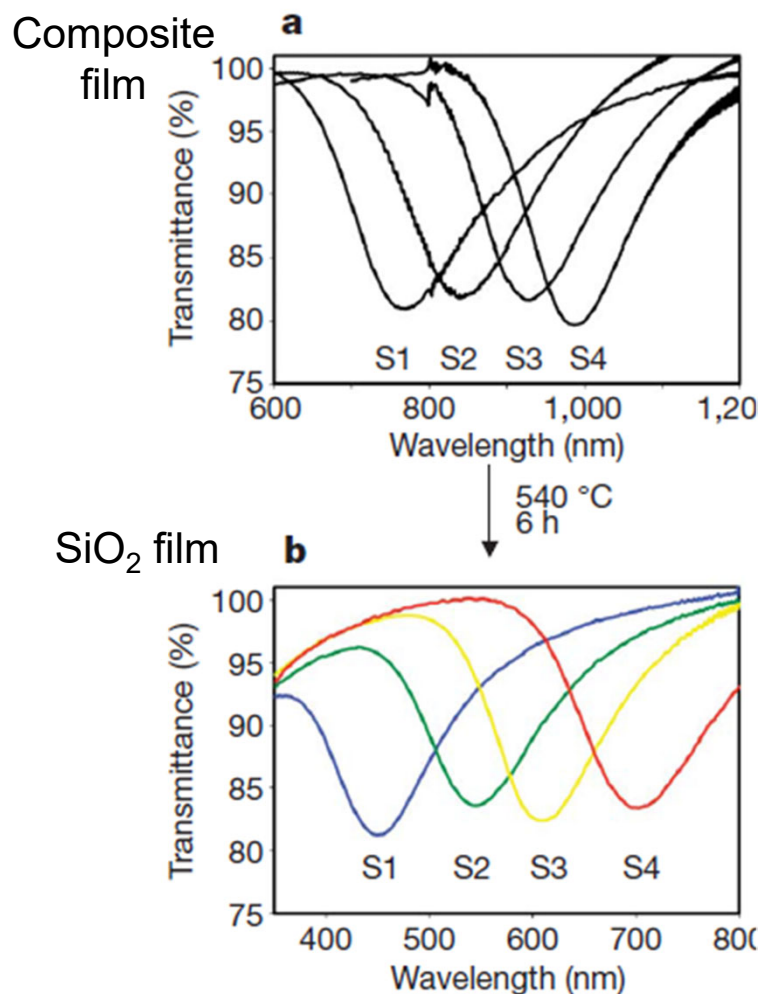
Polarized optical micrograph of composite film of SiO_2 and CNCs



Polarized optical micrograph of SiO_2 film after removing CNCs



CNCs as chiral templates

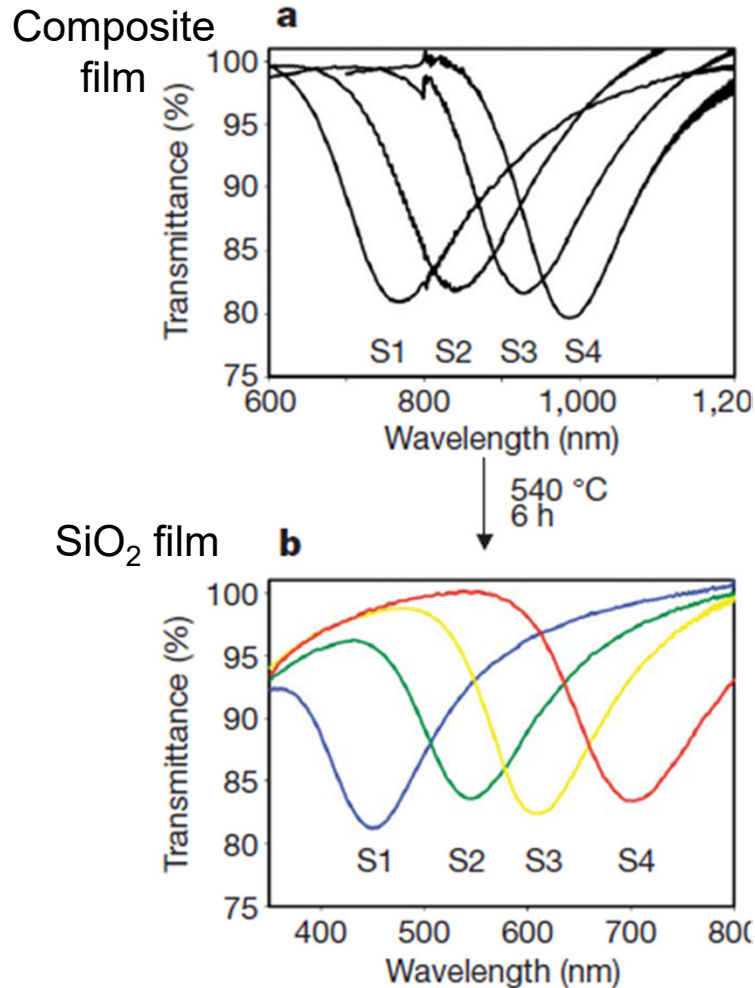


TUNING THE WAVELENGTH OF REFLECTED LIGHT

- Different ratios of Si(OEt)₄:CNCs in the initial composite mixture results in different *chiral pitch* of the liquid crystal
- Tuning the chiral pitch leads to different reflection wavelengths of the calcined silica films

Shopsowitz et al. *Nature* **2010**, 468, 422.

CNCs as chiral templates



Peak wavelength of light (λ_{max}) reflected normal to the surface of a chiral nematic structure:

$$\lambda_{max} = n_{avg} P$$

where

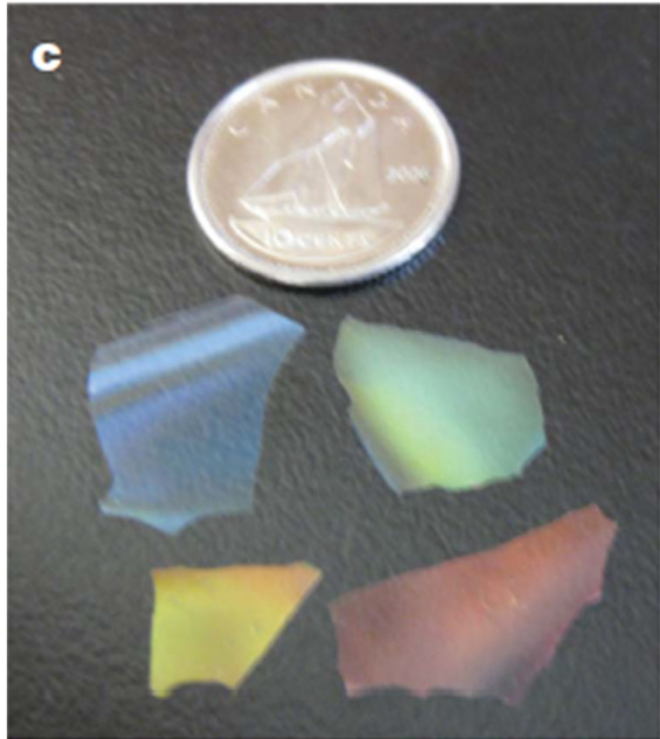
n_{avg} is the average refractive index

P is the helical pitch

Refractive indices of silica and cellulose are very similar (~ 1.5)

→ Chiral pitch, tuned by Si(OEt)₄:
CNC ratio, determines the colour

CNCs as chiral templates



Peak wavelength of light (λ_{max}) reflected normal to the surface of a chiral nematic structure:

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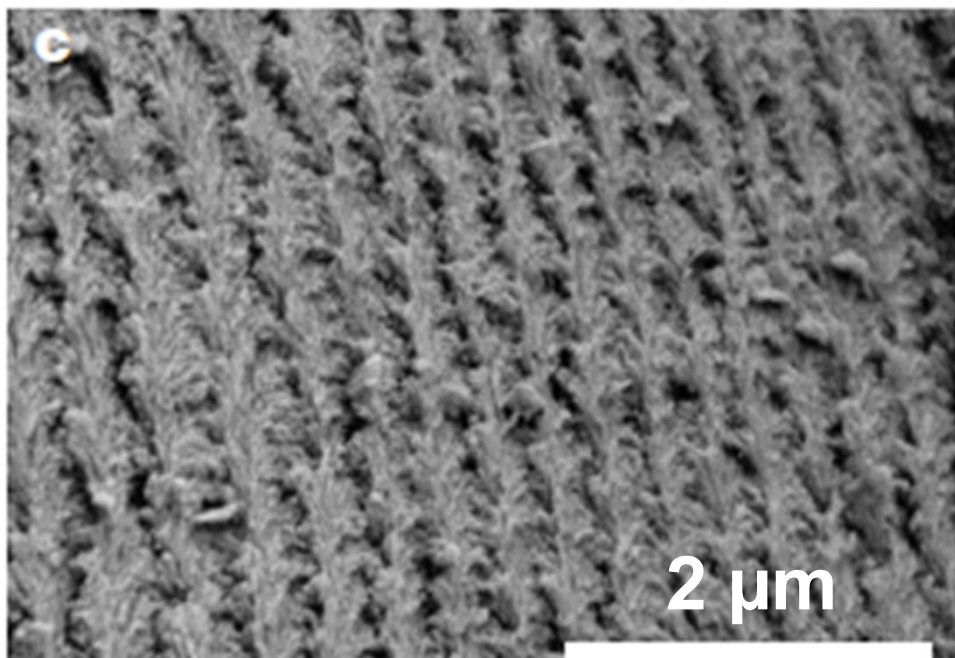
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Shopsowitz et al. *Nature* **2010**, 468, 422.

CNCs as chiral templates

SEM image of the SiO₂ film cross section, showing stacked layer from the helical pitch of chiral nematic phase

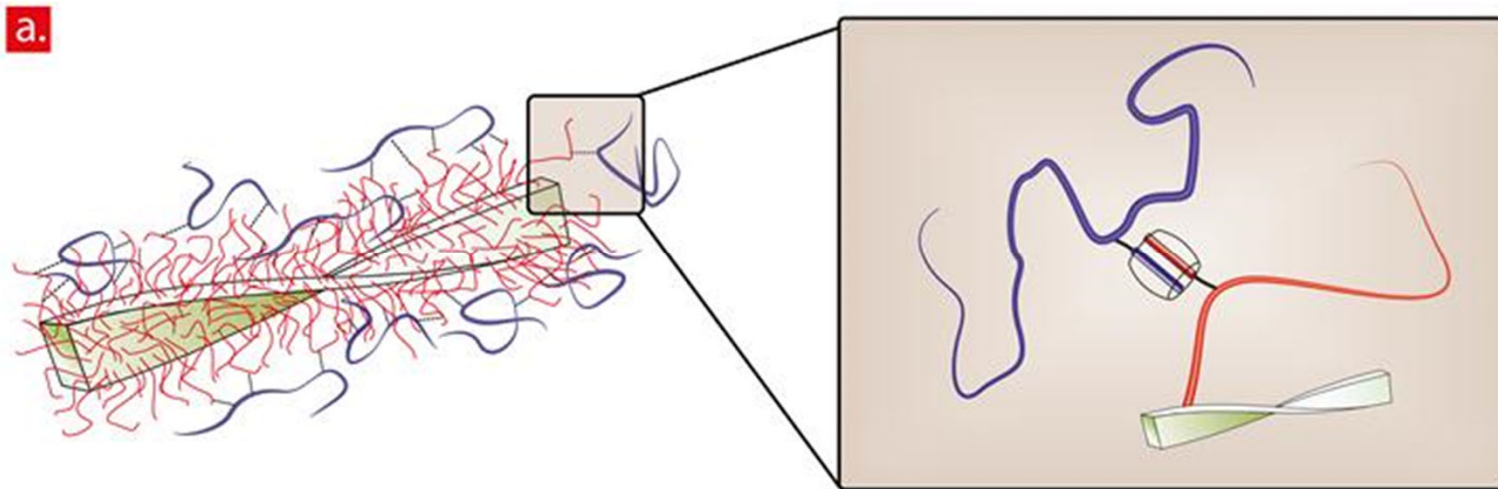


- Layer distance (chiral pitch) is a few hundred nanometers, i.e., in the wavelength of visible light

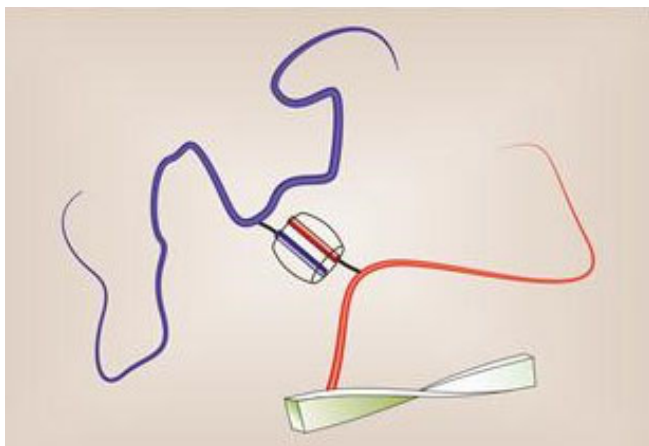
Self-healing hydrogels with CNCs

Basic idea:

- (i) Graft polymers on CNCs
- (ii) Blend grafted CNCs within a continuous polymer network
- (iii) Use strong cross linking agents that enable strength and self-healing

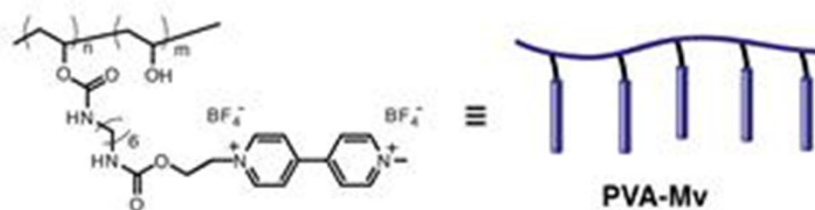


Self-healing hydrogels with CNCs



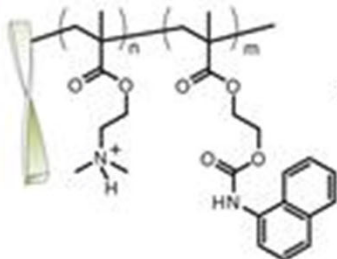
Cucurbit[8]uril: "handcuff" binder with both viologens and naphthyls as guests

Poly(vinyl alcohol) (PVA) containing methyl viologen (MV)

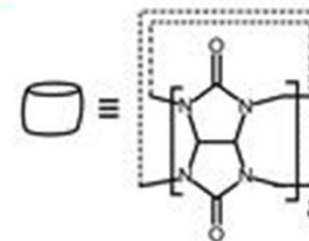


d.

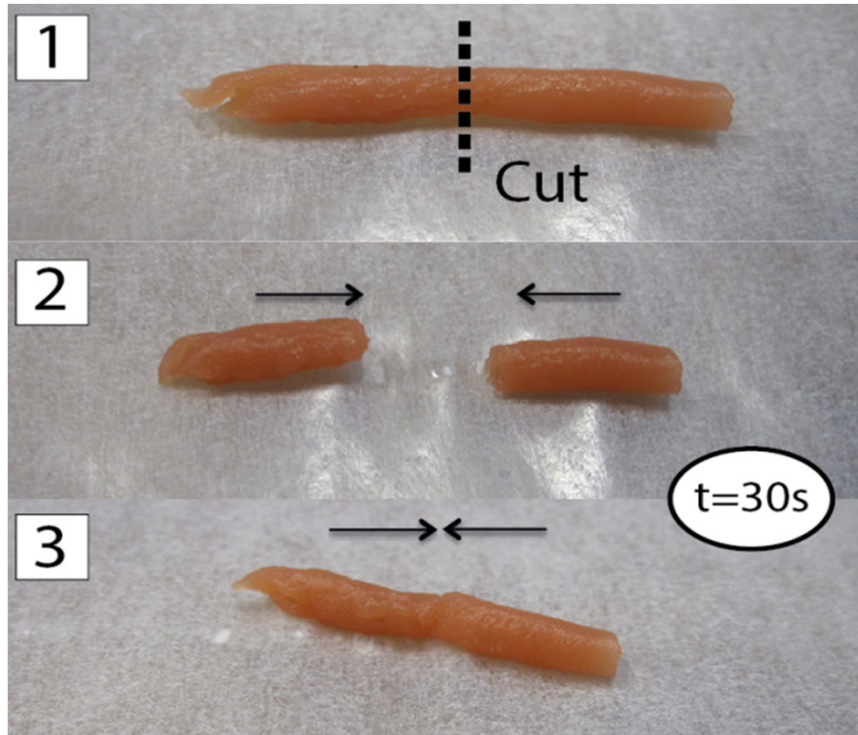
Poly(dimethylaminoethyl methacrylate) containing naphthyl methyl acrylate



e.



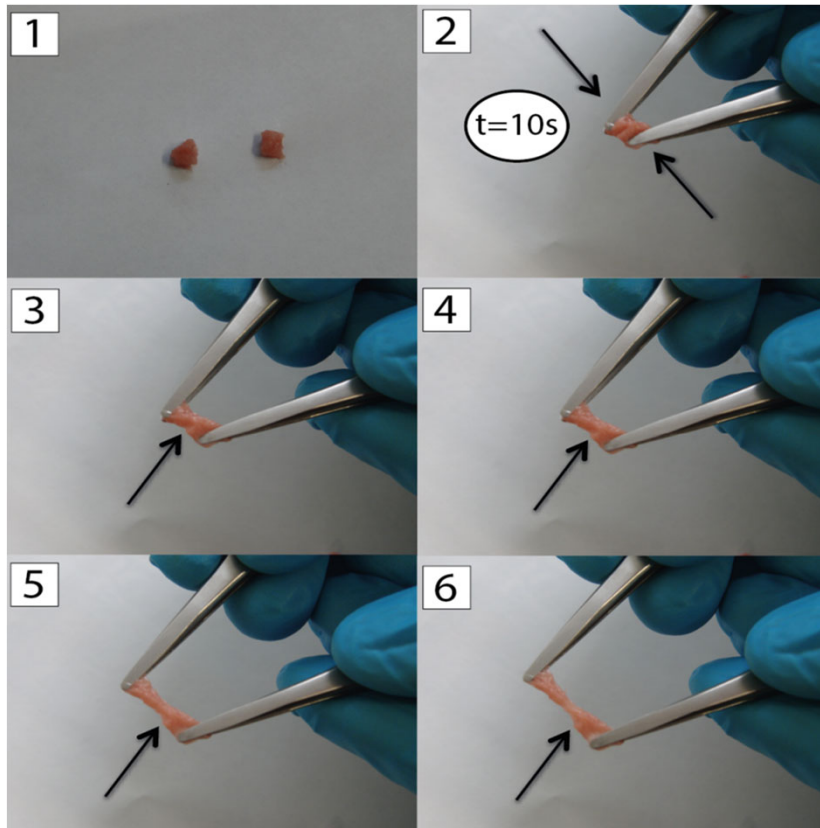
Self-healing hydrogels with CNCs



Self-healing immediately after cutting:

Supramolecular binding with cucurbit[8]uril is fast and strong.

Self-healing hydrogels with CNCs

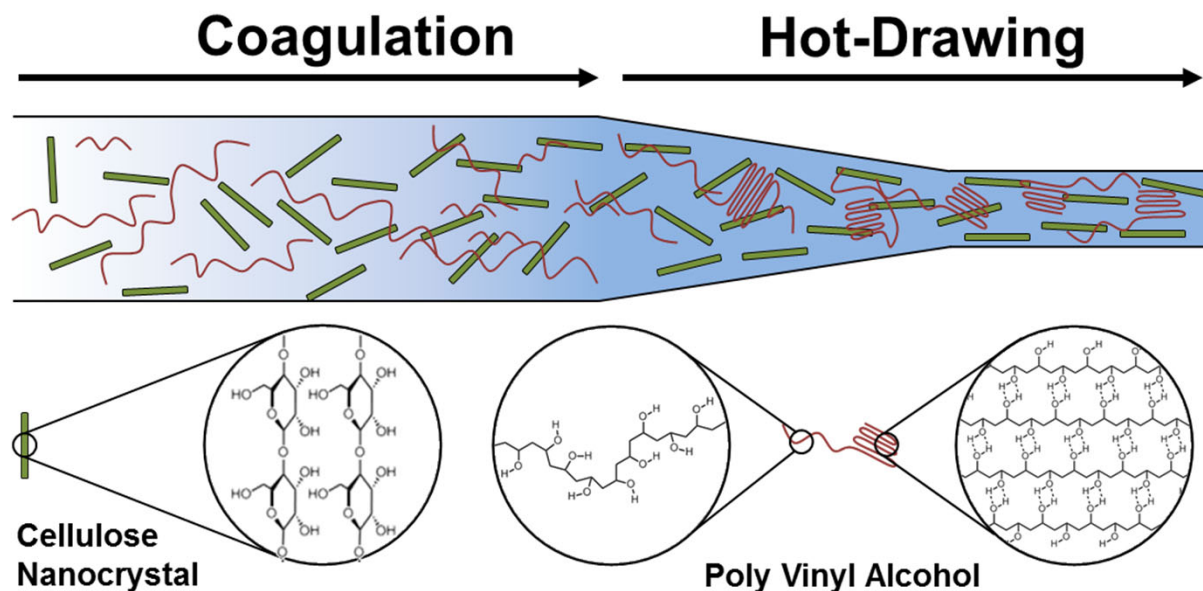


Self-healing after 4 months storage:

The mechanism with cucurbit[8]uril still works and it is still very fast.

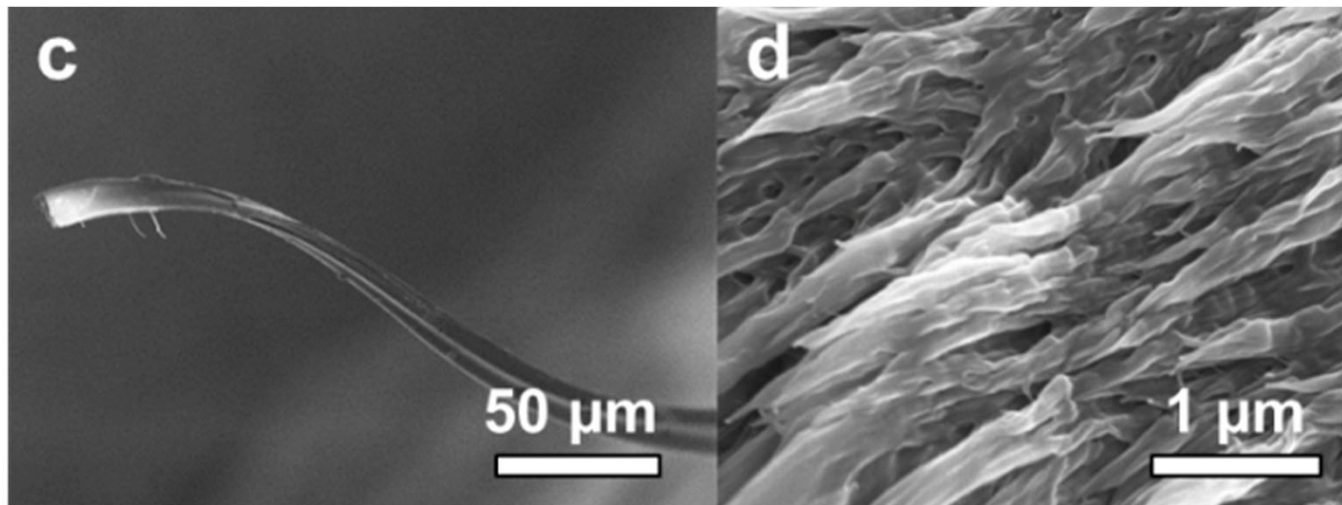
CNC composite fibres with polyvinyl alcohol

- PVA with loads of hydroxyl groups is a compatible matrix with CNCs
→ No compatibilizing modifications on CNCs required



CNC composite fibres with polyvinyl alcohol

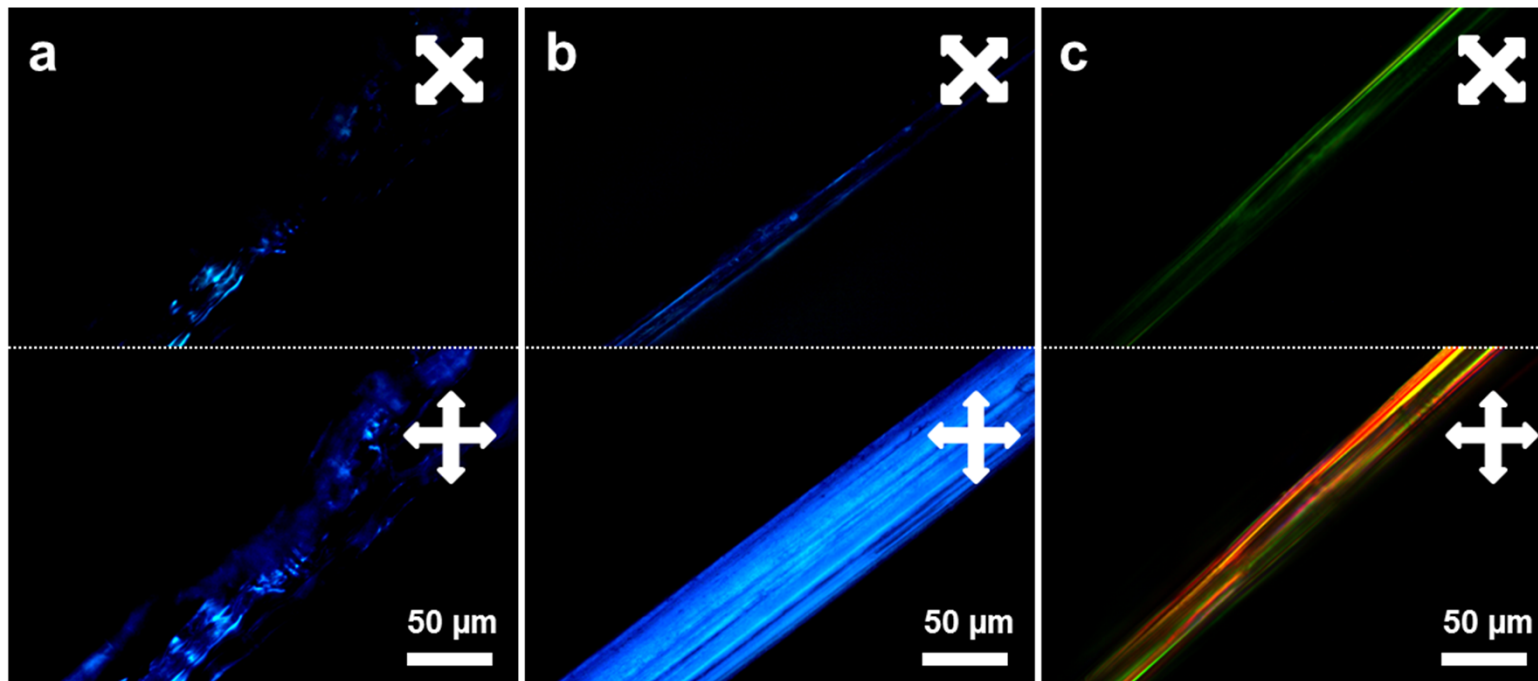
- Result: CNC/PVA composite fibers with tens of μm diameter



- CNC concentration upon fibre spinning is fairly high
 - Above the concentration for liquid crystal formation
 - Liquid crystal phase induces alignment of CNCs in resulting fibres

CNC composite fibres with polyvinyl alcohol

- Hot drawing further induces alignment and order in PVA/CNC fibres



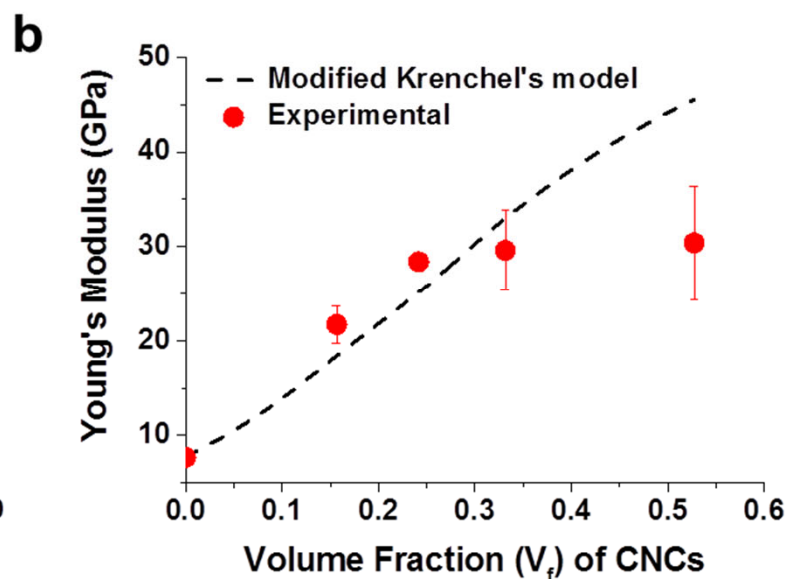
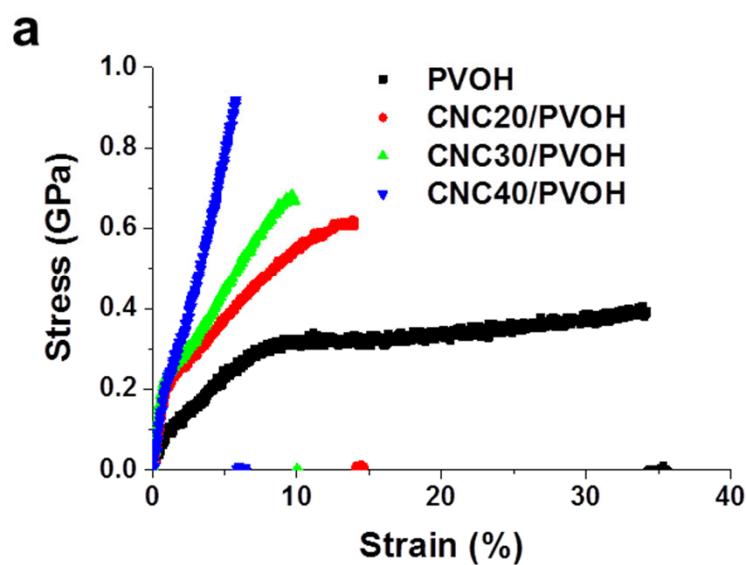
Undrawn PVA

Hot drawn PVA

Hot drawn PVA/CNC (60/40 ratio)

CNC composite fibres with polyvinyl alcohol

- Very high mechanical properties for the resulting PVA/CNC fibres: tensile strength of close to 1 MPa with 40% CNC loading



Conclusions on nanocellulose applications

- Materials incorporating nanocellulosics is a highly visible research area
- Some applications require just film formation (e.g., gas barriers, transistor supports), some require complex chemistry and recognition mechanisms (e.g., self-healing hydrogels)

Examples of versatility in research:

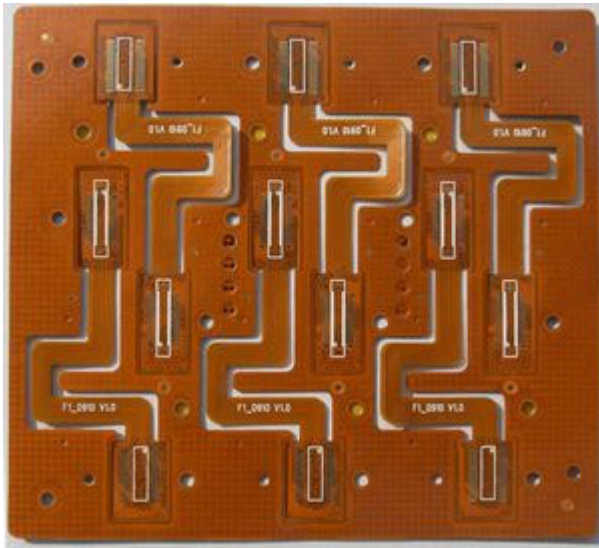
- Strong films and nanocomposites
- Magnetically responsive, water absorbing films
- Superhydrophobic and superoleophobic materials
- Templates for large scale chiral silicates

Materials applications from lignin:

- Phenol-formaldehyde resins
- Carbon fibres

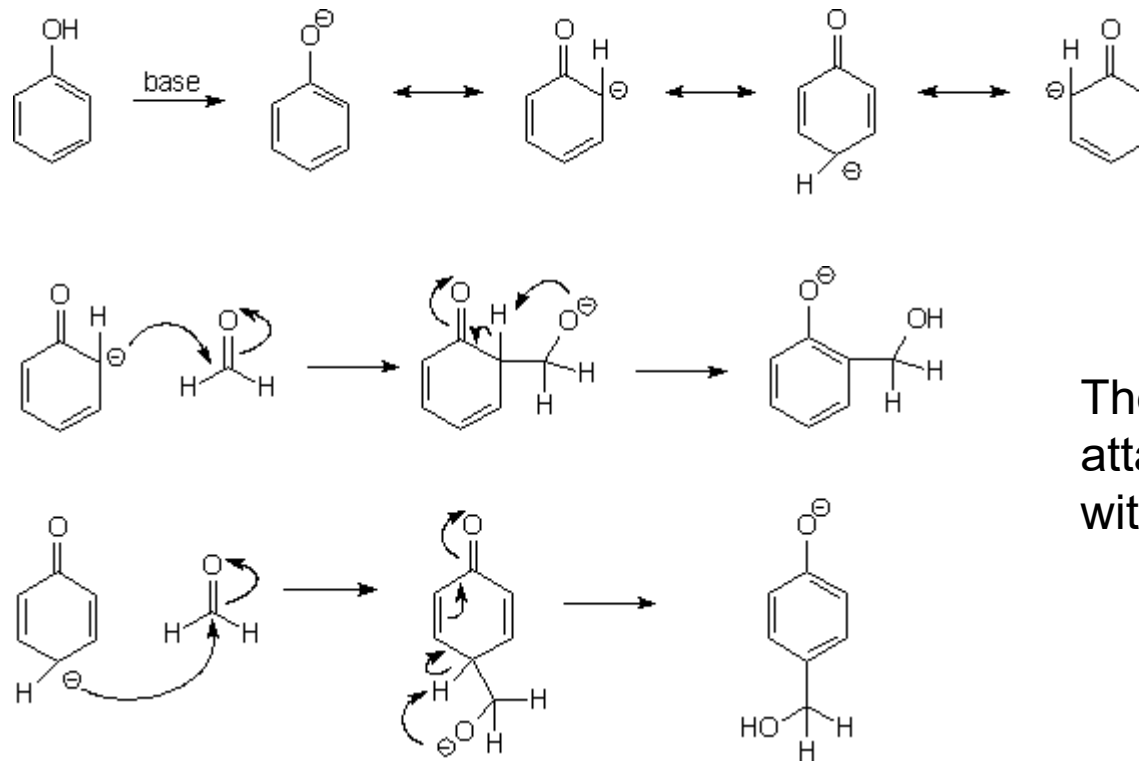
Phenol-formaldehyde resins

- Synthetic resins produced by reacting phenol and formaldehyde
- Main use in printed circuit boards (electronics)
- Other uses include coatings and adhesives



Phenol-formaldehyde resins

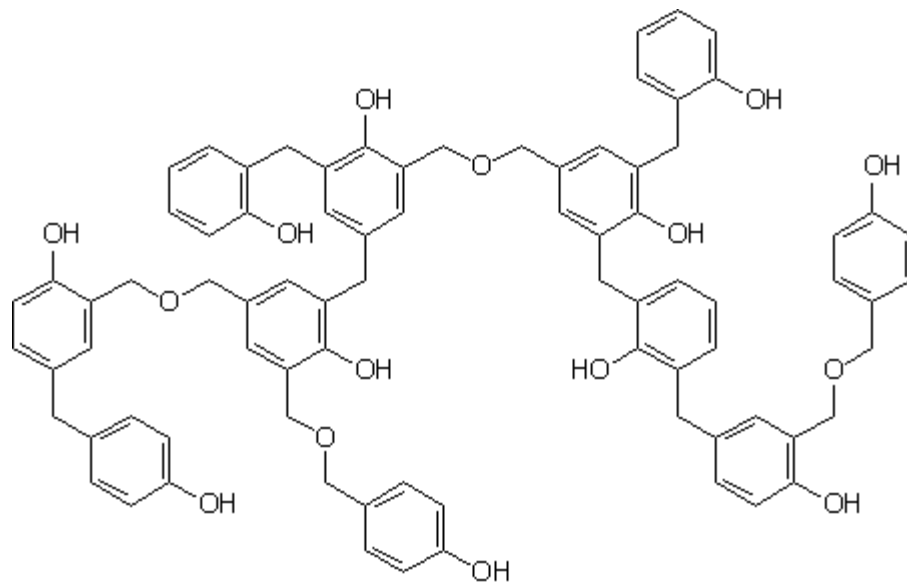
Traditional formation of (Novolac) resins from base-treated phenols:



The formaldehyde can attach on different sites within the phenol.

Phenol-formaldehyde resins

- The resulting resin is a highly cross-linked, irregular structure:

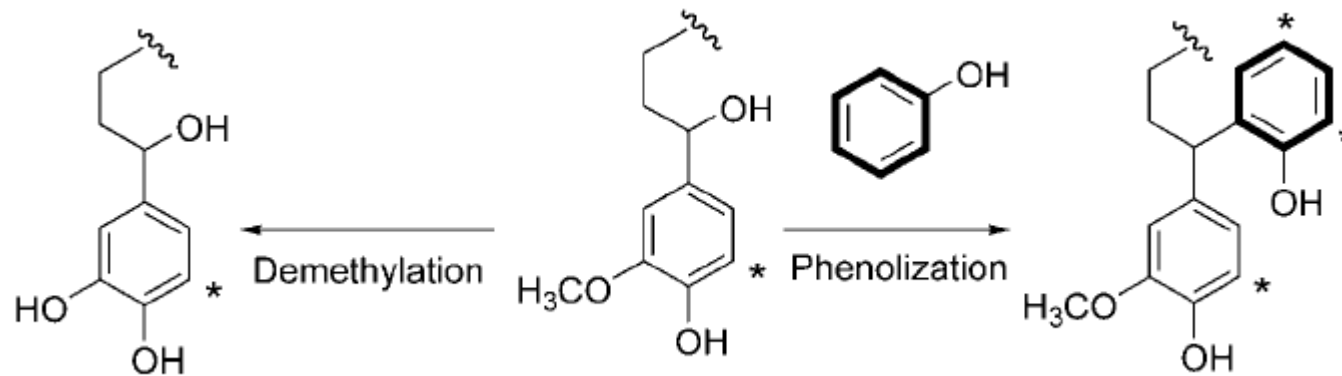


Fragment of a phenol-formaldehyde resin structure

Phenol-formaldehyde resins from lignin

- Lignin can be used to substitute phenol in the preparation of phenol-formaldehydes
- For resins, non-sulphur containing lignin is preferred (organosolv)
- For binder phenol-formaldehydes, 50% lignosulphonates or kraft lignin can be added instead of phenol without substantially modifying the characteristics
- The use of lignin is not only environmentally friendly but also cheaper

Phenol-formaldehyde resins from lignin



- Modification can be carried out to increase the number of phenolic reaction sites in lignin
- Two routes: demethylation and phenolization
- Resins prepared from modified lignin have been successfully used to glue plywood

Carbon fibres

- Fibres with a diameter of ca. 5-10 μm consisting of crystallized carbon (graphite)
- Properties: high stiffness and tensile strength, low weight and thermal expansion, chemically relatively inert
- Used in high-end applications (aerospace, motor sports)
- Relatively expensive compared with glass fibres

Carbon fibres – common preparation

From polymeric fibres:

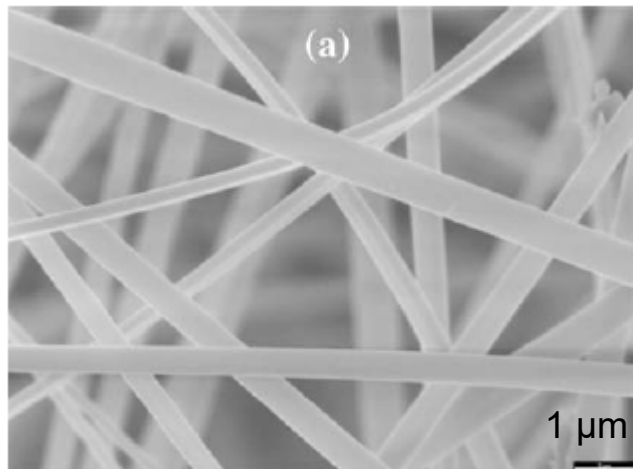
- (1) Oxidation in air at moderate temperature (e.g. 300°C)
- (2) The oxidized fibres are heated at ~2000°C in order for the graphite to form

Carbon fibres from lignin

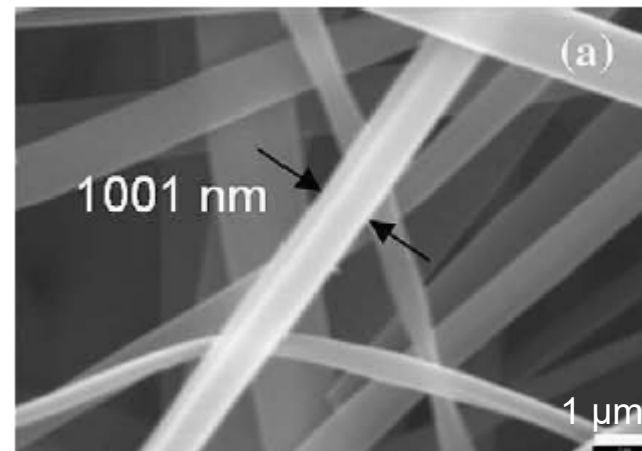
- Lignin can be spun into thin fibres by, e.g., electrospinning
- Glass transition temperature (T_g) of lignin is far below the temperatures required for carbonization
→ Lignin must be pretreated to prevent softening by, e.g., air oxidation
- Reactions during air oxidation increase the T_g of lignin
- As the temperature increases, at slow heating rates the T_g can increase faster than the temperature ($T_g > T$)
- At higher heating rates, the thermostabilization reactions are not able to maintain $T_g > T$, and the material enters the liquid-rubbery state, fusing together and losing fibrous characteristics

Carbon fibres from lignin

Electrospun fibres from Alcell lignin



Carbonized fibres from electrospun Alcell



- Lignin with high purity levels is required for good results
→ Normal kraft lignin does not generally meet quality demands

Summary on lignin applications

- Enormous quantities of lignin produced in pulping processes are mainly burned to create energy
- Many fields of applications exist for lignin: polymer additives, components in polymerization, precursors for small-molecular commodity chemicals, precursors for carbon fibres etc.
- However, large scale industrial applications are lacking

Conclusions

Nanocellulose:

- High potential: high strength, bio-based origin, biodegradability
- Difficulties: compatibility with composite matrix, realisation of potential
- Native properties of cellulose in the plant cell wall are underutilised

Lignin:

- Vast amounts produced in pulping processes world-wide
- Fundamental research is difficult because of structural heterogeneity
- Native structure of lignin is not utilised or rarely even characterized