



Forest Based Biorefinery

“Chemical and Engineering Challenges and Opportunities ”

Cellulose Technology

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Åbo Akademi
2010



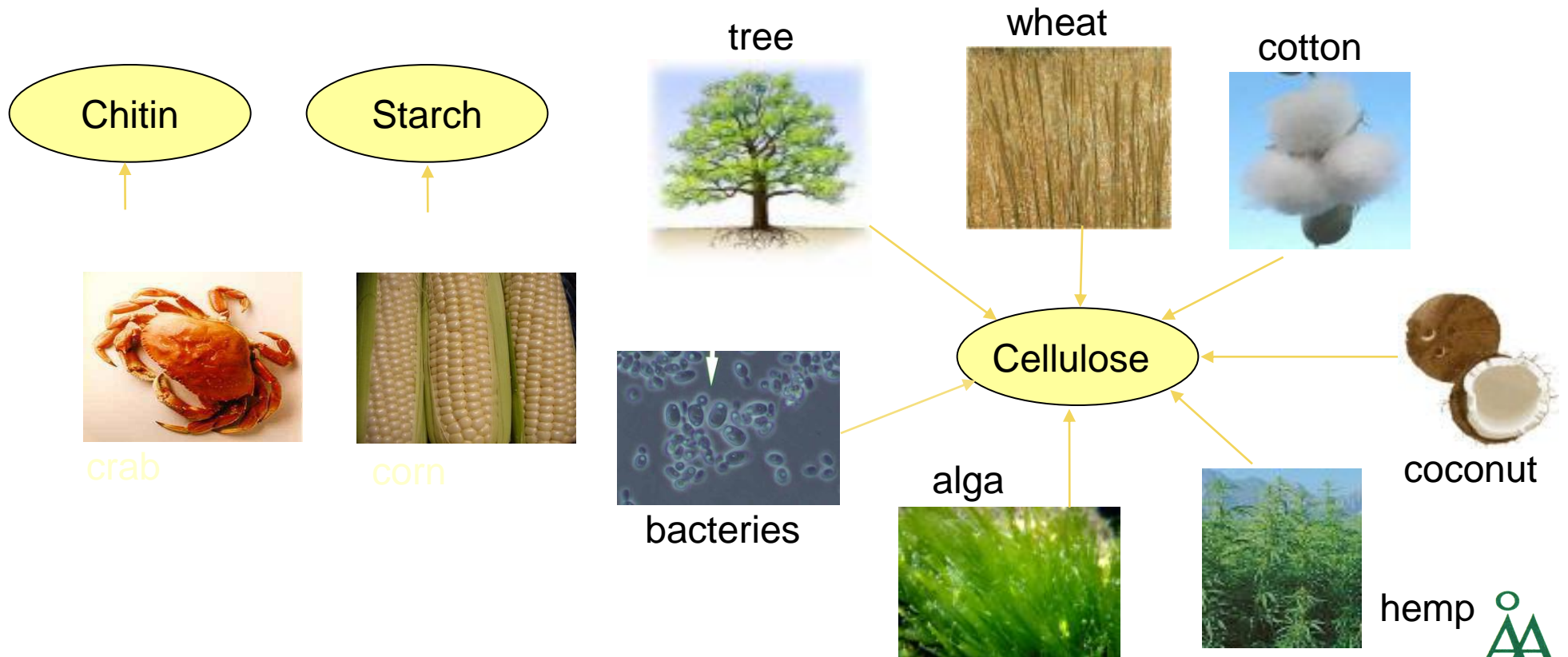
European Polysaccharide
Network Of Excellence

Laboratory of Fibre and Cellulose Technology

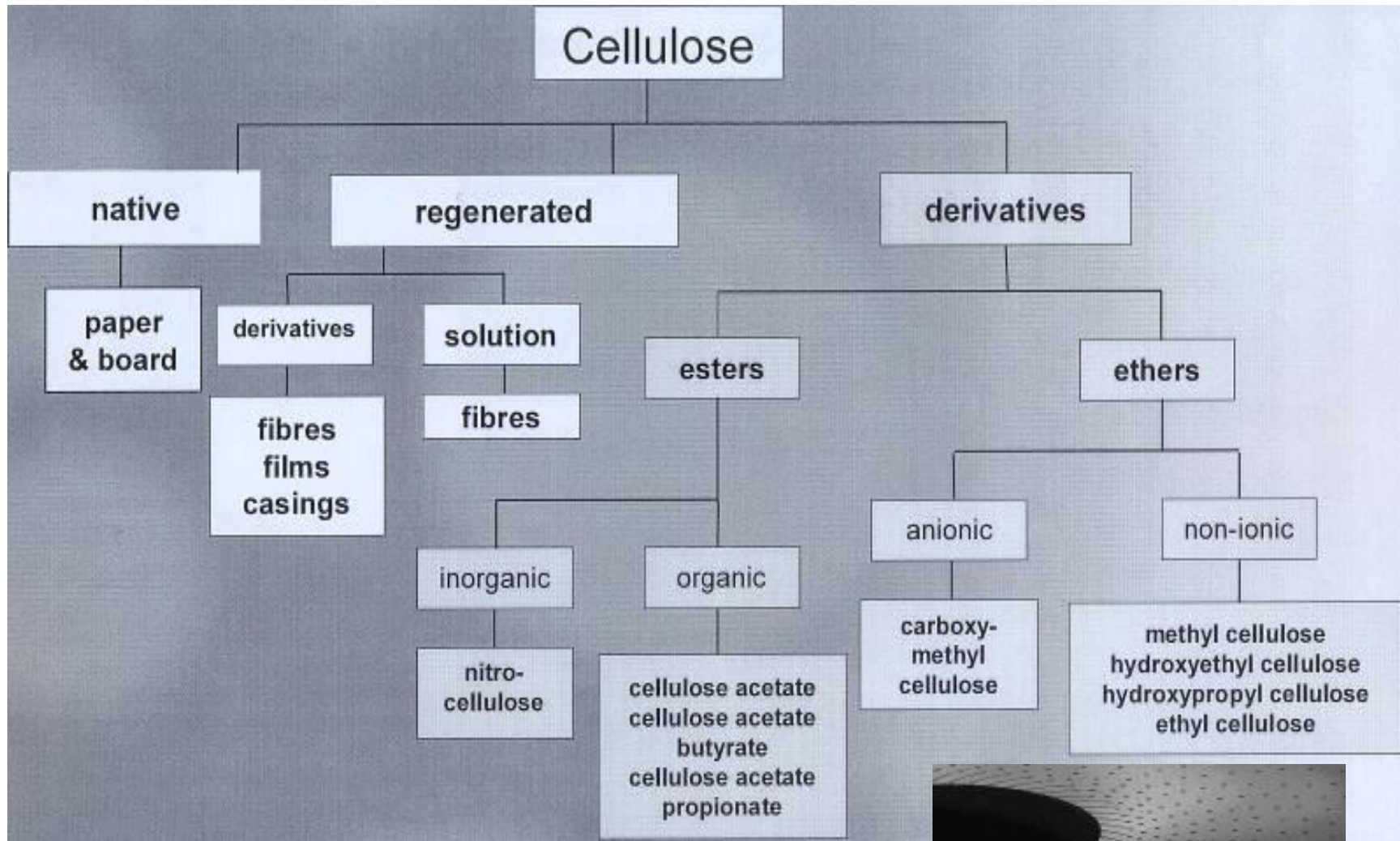


Polysaccharides

- Natural polymers such as starch, cellulose, chitin, carrageenan
- Produced by plants and animals



What is Cellulose Technology ?



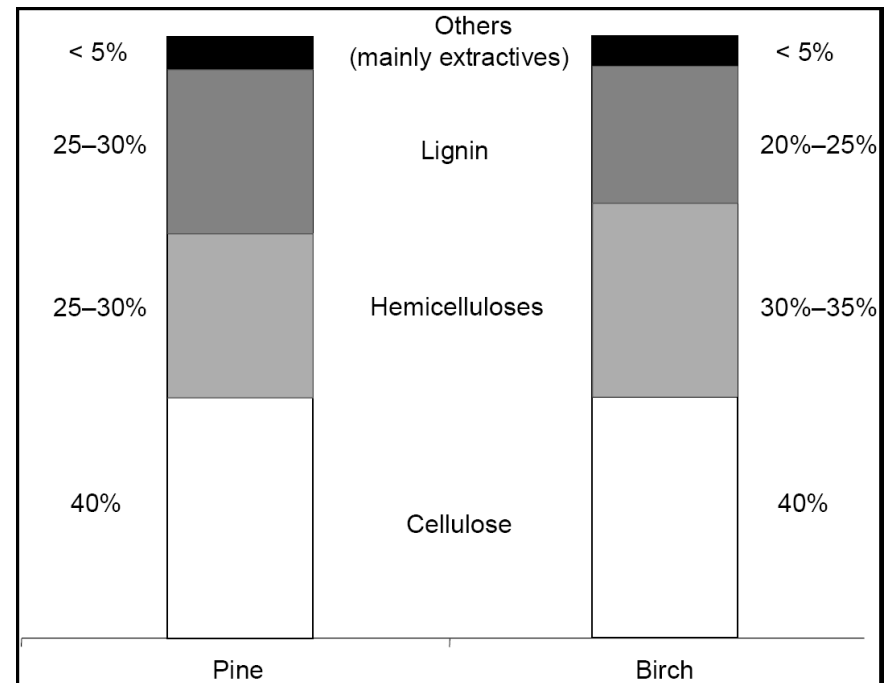
Cellulose

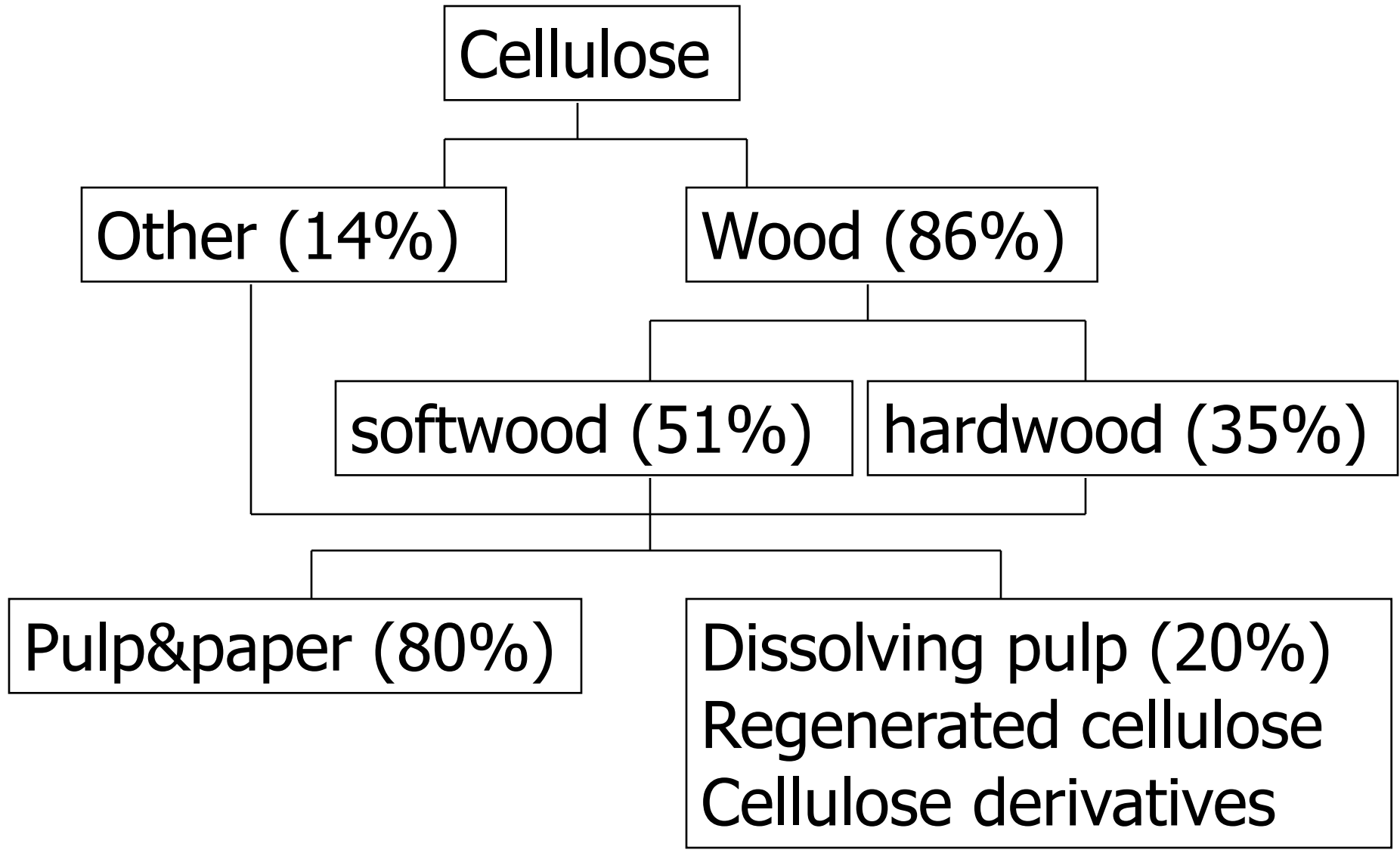
- 50 % of biomass on earth
- 100-150 billion-ton per year
- One tree: ~14 g of cellulose per day
- Vegetal (plants)
- Seaweed (valonia, microdycon)
- Biosynthesised by bacteria (acetobacter xylonium)

Cellulose sources

Plant material	Cellulose content (dried material, %)
Corn	17-20
Bamboo, Straw, Sugar Cane	40-50
Flax, Hemp, Ramie	70-75
Cotton	95-99

Wood is the main source



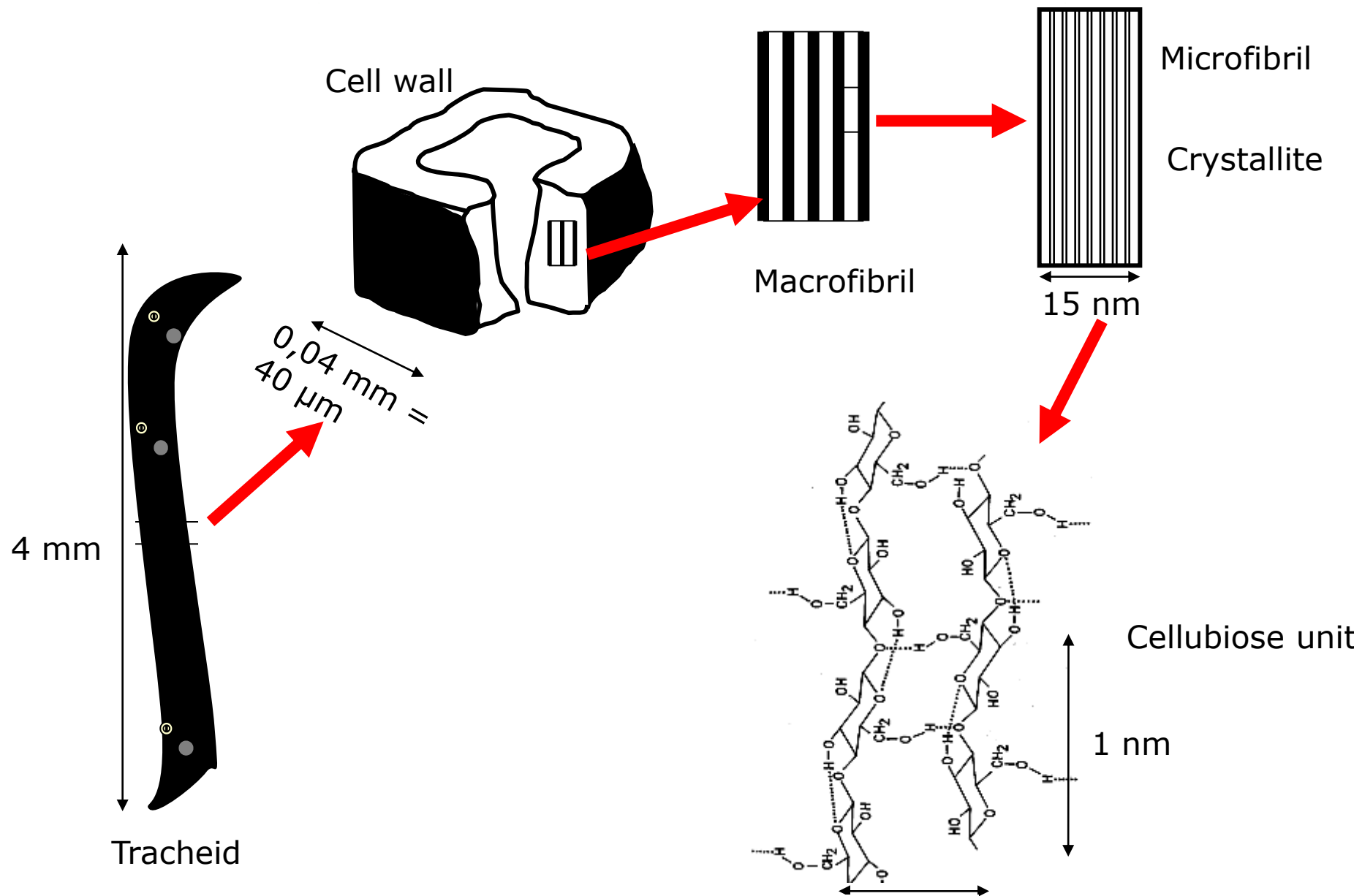


Dissolving pulp processes

- Target: remove hemicelluloses and lignin
- Chemical pulping processes:
 - Bisulphite
 - Sulphite-soda
 - Prehydrolysis kraft
- Bleaching (TCF)

Degree of polymerization of cellulose from different raw materials

Vegetal species	DP
Algae Valonia	26 000
Cotton	10 000
Flax, Hemp	9 000
Spruce	8 000
Wood pulp	500 - 1000



Cellulose chemistry and nanostructure

Cellulose chemistry

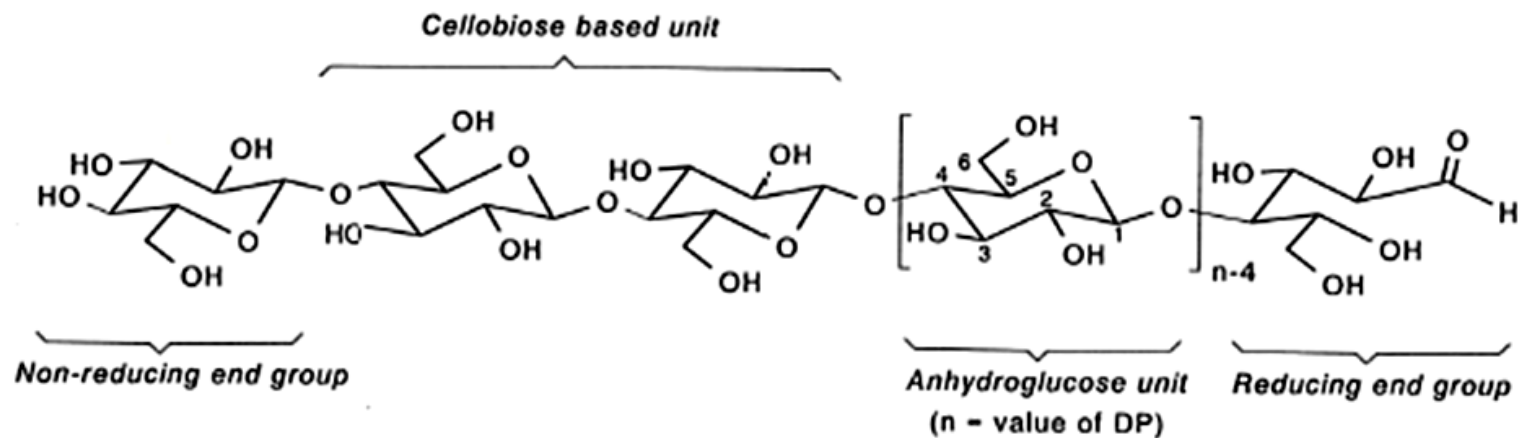
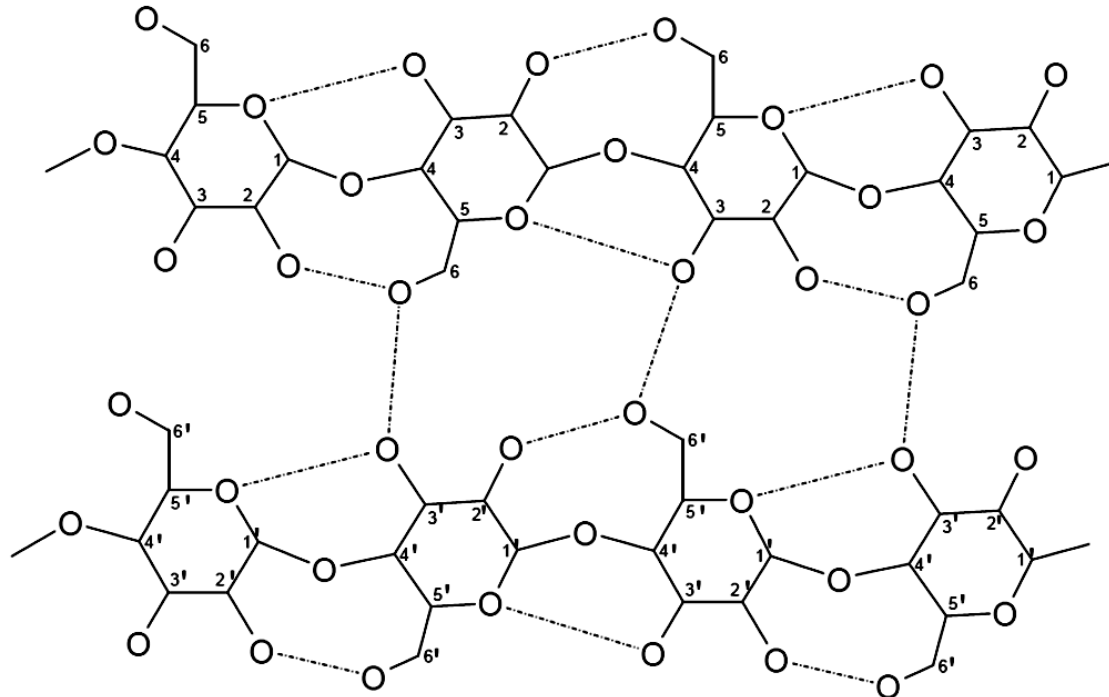
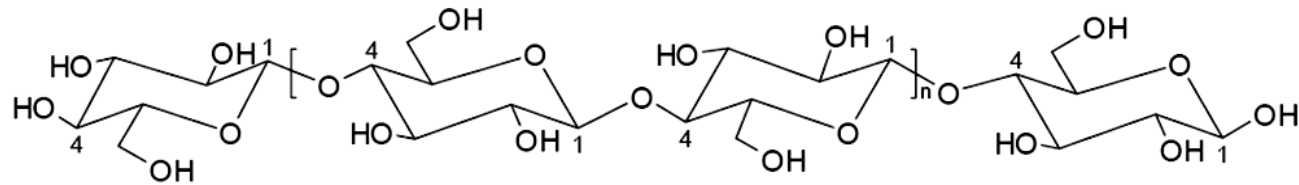
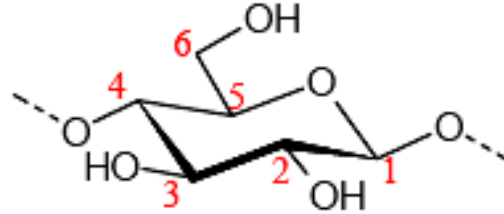


Figure 2.1.1. Molecular structure of cellulose.

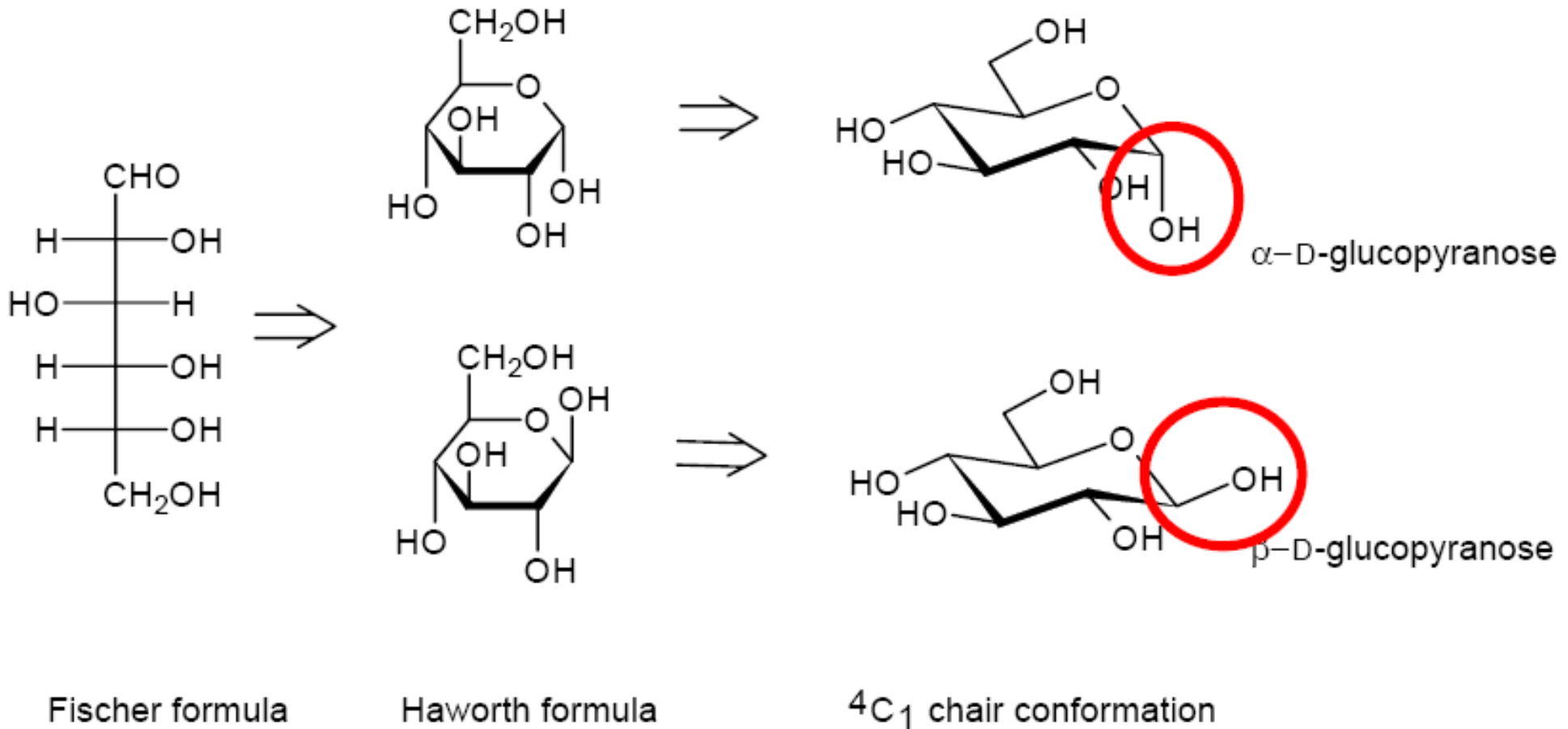
Comprehensive Cellulose Chemistry Vol 1
D. Klemm, et al. (Eds.)
Wiley-VCH, Chichester, 1998

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Cellulose chemistry

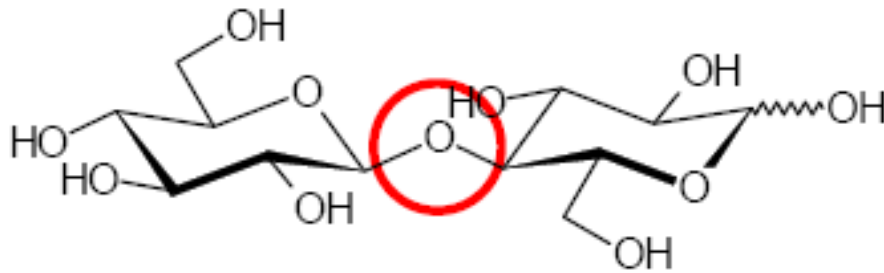


Cellulose chemistry

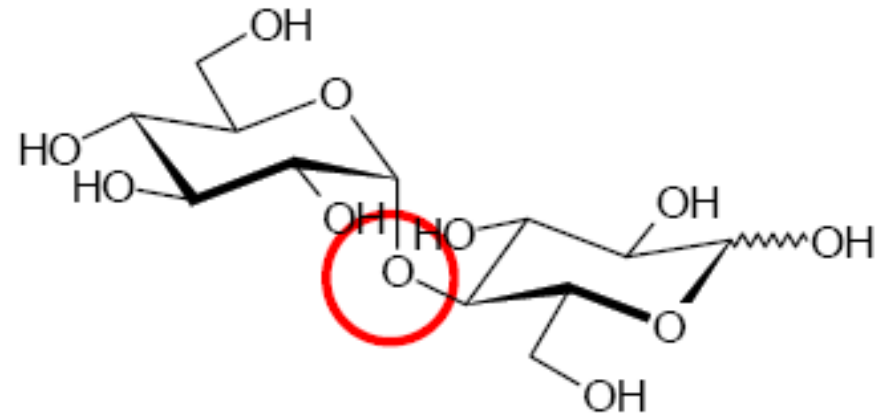


Cellulose chemistry

- The glycosidic bond

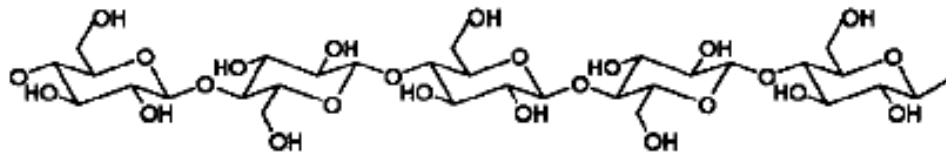


β -D-4-gucopyranosyl glucose
 β -D-Glcp-(1,4)-Glcp
cellobiose

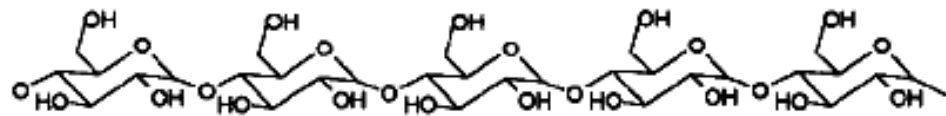


α -D-4-gucopyranosyl glucose
 α -D-Glcp-(1,4)-Glcp
maltobiose

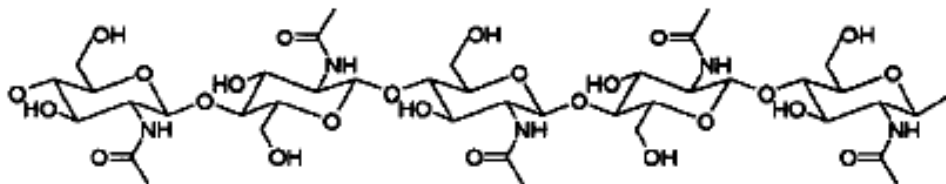
Cellulose chemistry



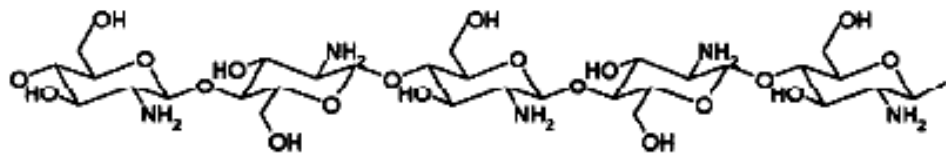
cellulose



amylose



chitin



chitosan

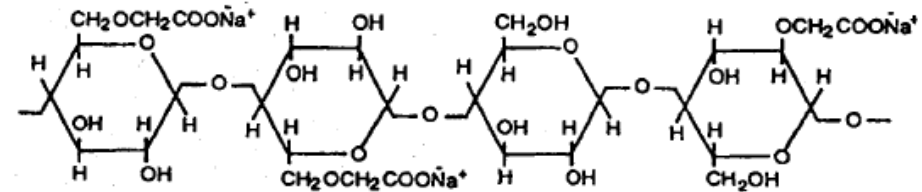


Figure 5.1 CMC with DS 0.75

Cellulose chemistry

Table 2.1.2. Content of carboxylic acid and carbonyl groups in some specimens of native cellulose (Schleicher and Lang, 1994)

Specimen	mmol of acid groups/kg	mmol of carbonyl groups/kg
Cotton linters	<10	–
Sulfite-dissolving pulp	20–30	7–20
Prehydrolyzed sulfate pulp	8–30	2–5
Paper pulp	20–300	–

Table 2.1.3. *DP* range of various cellulose materials

Material	Range of <i>DP</i>
Native cotton	up to 12000
Scoured and bleached cotton linters	800–1800
Wood pulp (dissolving pulp)	600–1200
Man-made cellulose filaments and fibers	250–500
Cellulose powders (prepared by partial hydrolysis and mechanical disintegration)	100–200

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D. Klemm, et al. (Eds.)
Wiley-VCH, Chichester, 1998

Supramolecular structure

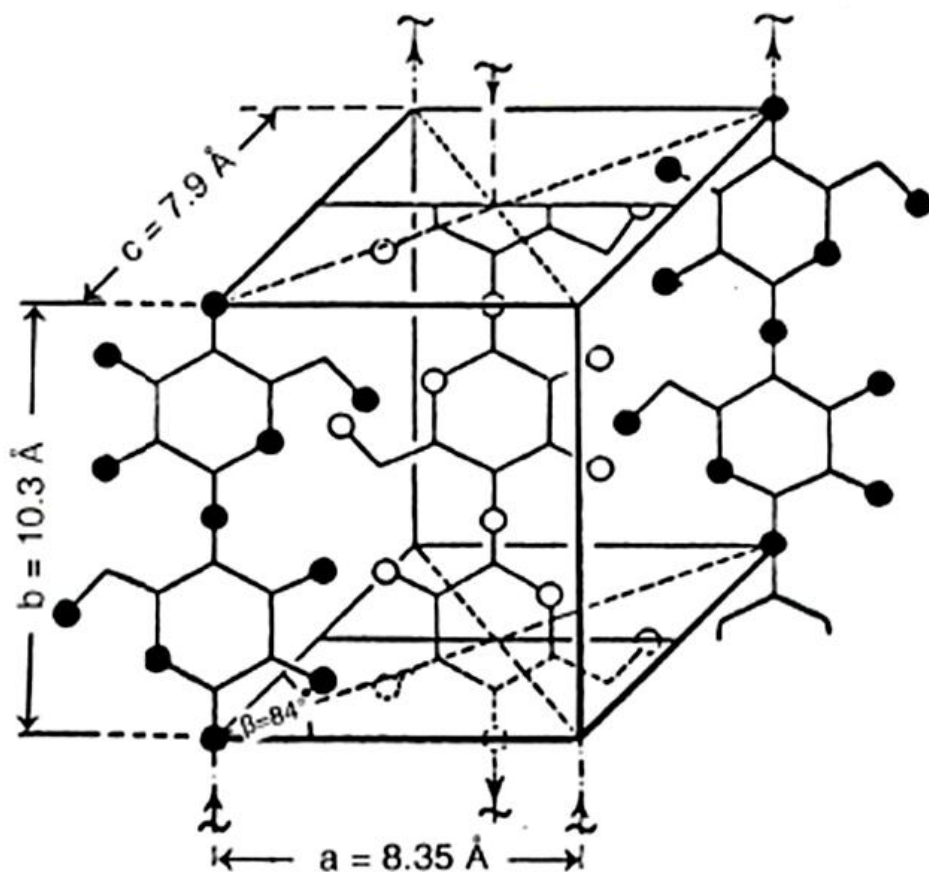


Figure 2.1.8. Unit cell of cellulose I according to the Meyer–Misch model.

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Wiley-VCH, Chichester, 1998

Cellulose Polymorphs

- Four polymorphs identified by X-ray diffraction
- Cellulose I
- Cellulose II
- Cellulose III
- Cellulose IV

Solid state ^{13}C -NMR

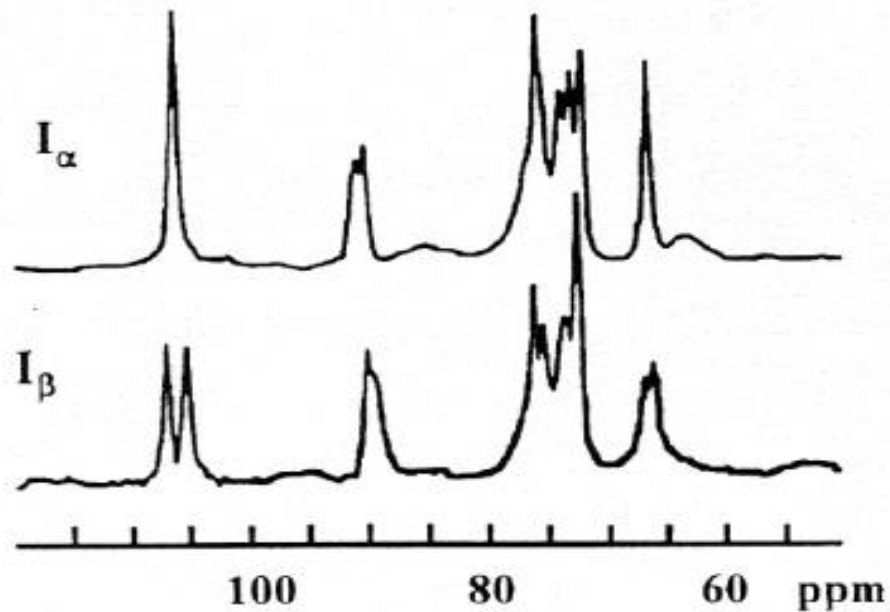


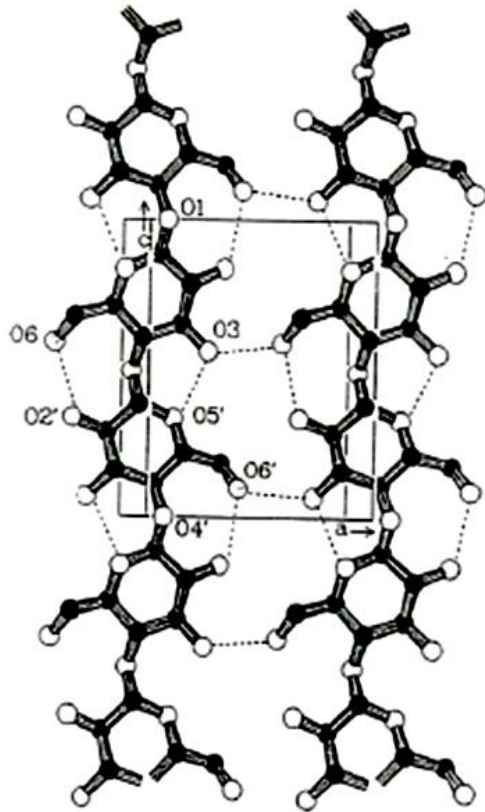
Figure I.6: NMR spectra of celluloses I_α and I_β . [Vanderhaart et al, 1984]

Facts about Cellulose I

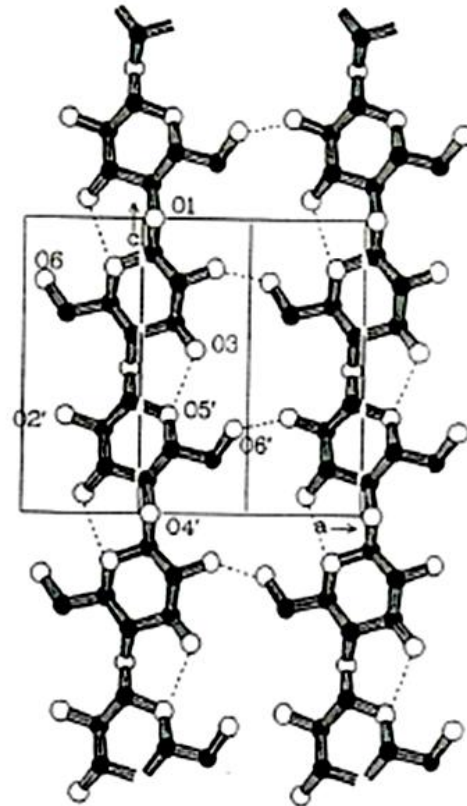
- Wood, cotton, shells of certain marine animals are : cellulose I β
- Primitive organisms, such as bacteria: Ia cellulose
- The crystalline phases Ia and I β are in various proportions depending of the origin of the cellulose
- Allomorph I β is thermodynamically more stable than Ia.
- Transformation of the Ia phase into I β is irreversible.

Cellulose II

cellulose I



cellulose II



Cellulose I, native cellulose

$C(3') - O(5')$

$C(2') - C(6')$

$C(6) - C(3')$

Cellulose II, regenerated cellulose

$C(5) - C(3')$

$C(2) - C(6')$

Figure 2.1.5. Most probable hydrogen bond patterns of cellulose allomorphs (Kroon-Batenburg et al., 1986).

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Cellulose II

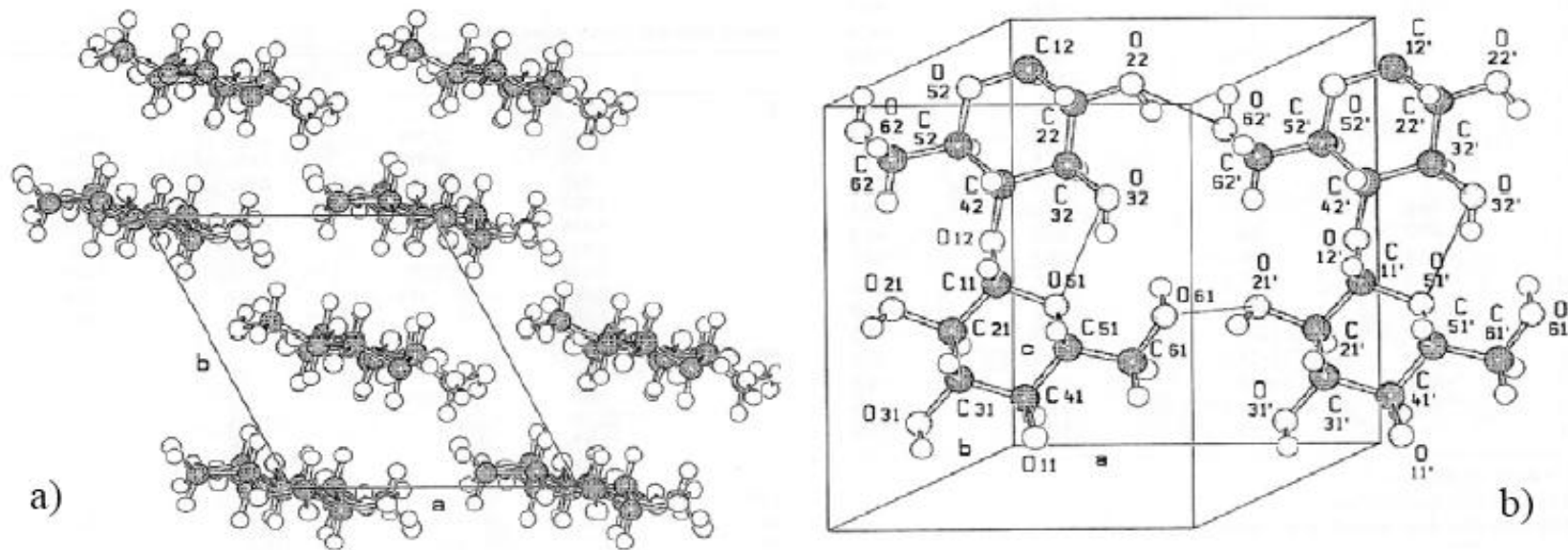


Figure I.9: Model of cellulose II: a) perpendicular projection to the (ab) plane and b) molecules in the crystallographic plane (010) [Zugenmaier, 2001]

XRD of Cellulose I and II

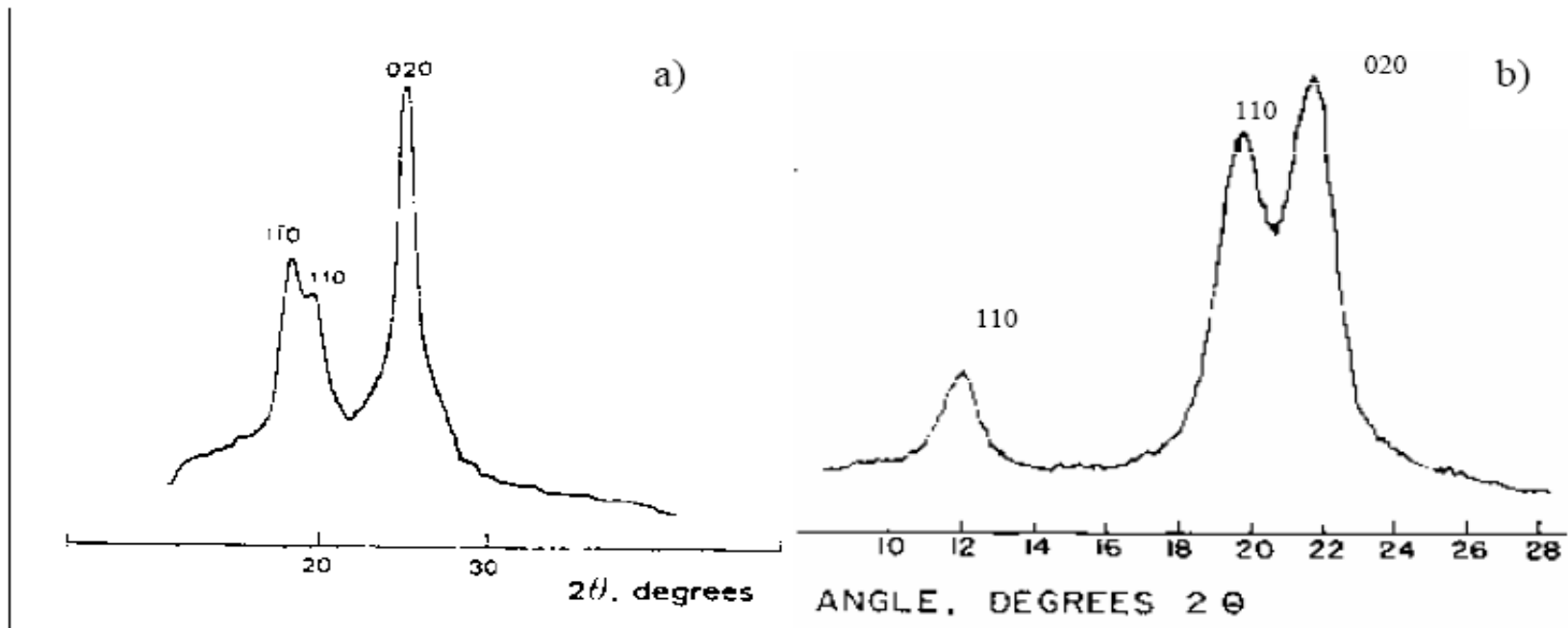


Figure I.11: X-ray diffractograms of two polymorphs of cellulose: a) cellulose I [Chanzy et al, 1983] and b) cellulose II [Nelson et al, 1964]

Facts about Cellulose I and II

- Polymorph II is energetically more stable than polymorph I. This is the reason why it is possible to convert cellulose I into cellulose II but not the contrary.
- The fibrillar arrangement of regenerated cellulose differs somewhat from the one of native cellulose, as arrangement in distinct layers does not exist.
- In the same way, the helicoidal structure, which exists in the cellular walls of native cellulose, does not exist in precipitated or regenerated cellulose fibres.

Cellulose III

- A treatment with ammonia or with certain amines as the ethylene diamine allows the preparation of cellulose III either from the cellulose I (which leads to cellulose III₁) or from the cellulose II (which leads to cellulose III₂).

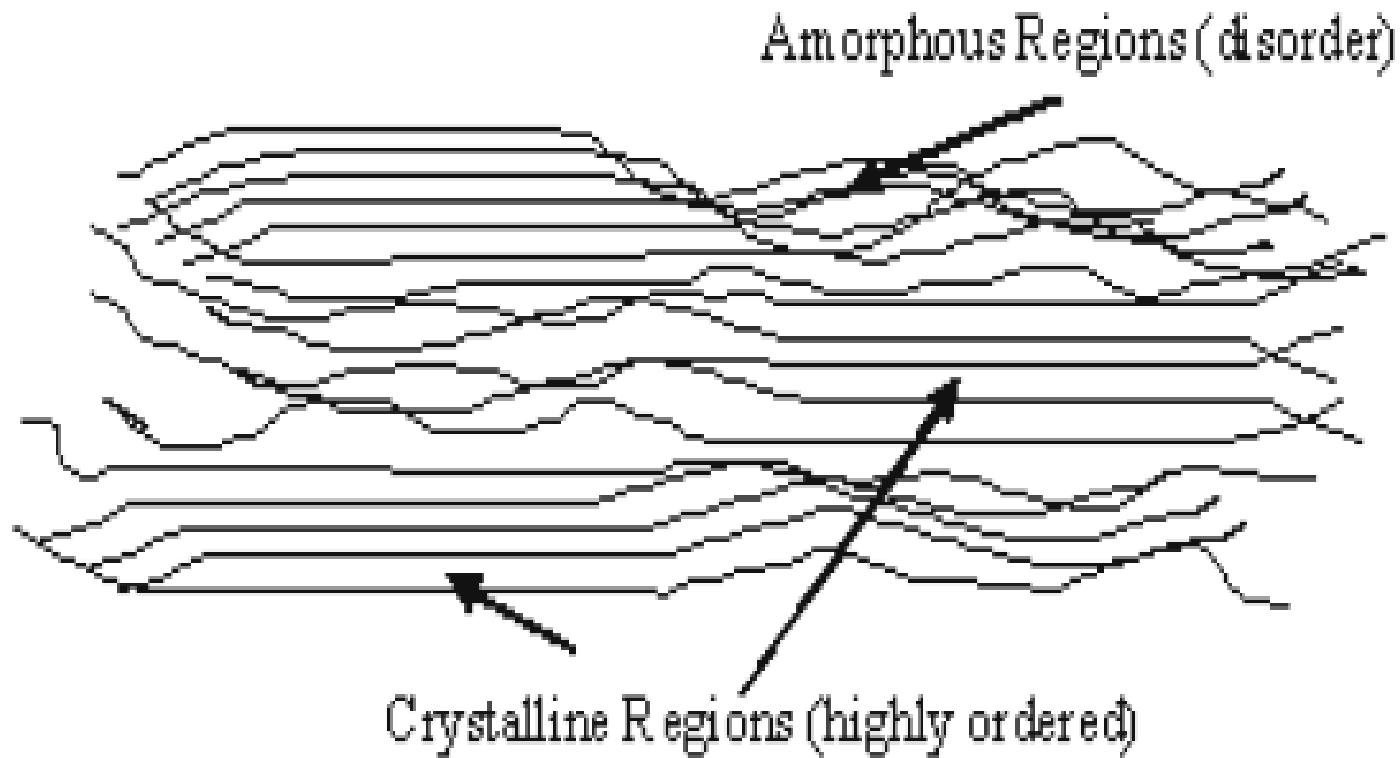
Cellulose IV

- Cellulose III, heated at high temperatures in glycerol, is transformed into cellulose IV. There are two forms: cellulose IV₁ and cellulose IV₂ obtained from cellulose III₁ and III₂, respectively.
- Cellulose IV is a disordered form of cellulose I, which explains why it can be found in X-ray diffractions for native cellulose of some plants.

Type	Unit (Å, °)					
	α	β	γ	a	b	c
I $_{\alpha}$	117	113	81	6.74	5.93	10.36
I $_{\beta}$	90	90	96.3	7.85	8.27	10.38
II merc.	90	90	117.1	8.10	9.05	10.31
III $_1$	90	90	122.4	10.25	7.78	10.34
IV $_1$	90	90	90	8.03	8.13	10.34
IV $_2$	90	90	90	7.99	8.10	10.34

Table I.3: Unit cell dimensions of cellulose polymorphs [Zugenmaier, 2001]

Cellulose microfibril



Supramolecular structure

Table 2.1.4. X-ray crystallinity \bar{x}_c of some cellulose materials (Fink and Walenta, 1994)

Sample	Comments	\bar{x}_c (%)
Cotton linters (scoured and bleached)	Samples of various origin	56–63
Sulfite dissolving pulp	Samples of various origin	50–56
Cellulose powder	Spruce sulfite pulp hydrolyzed	54
Sulfate pulp	Prehydrolyzed	46
Viscose rayon	Samples of various origin	27–40
Regenerated cellulose film	Samples of various origin	40–45
Experimental cellulose II filament	Filament spun from a solution of cellulose in <i>N</i> -methylmorpholine- <i>N</i> -oxide into water	42
Experimental cellulose II filament	Filament spun from trimethylsilyl cellulose solution into an acid bath	11

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Wiley-VCH, Chichester, 1998

Supramolecular structure

Table 2.1.6. Size and degree of disorder of crystallites of cellulose I and II (Fink and Walenta, 1994)

Sample	Allomorph	Average crystallite size		Area of cross section (nm ³)	Disorder parameter ^c $\sqrt{e^2}$
		Crystallite length (nm) ^a	Crystallite width (nm) ^b		
Valonia cellulose	I	–	8.9–10.1	–	0.01–0.02
Cotton linters	I	8.5–10.0	4.7–6.0	33–36	0.012–0.07
Sulfite dissolving pulp	I	7.5–9.7	4.1–4.7	16–21	–
Mercerized linters	II	–	5.9	–	0.027
Viscose rayon	II	–	4.2	–	0.032
Viscose staple	II	–	3.9	–	0.034

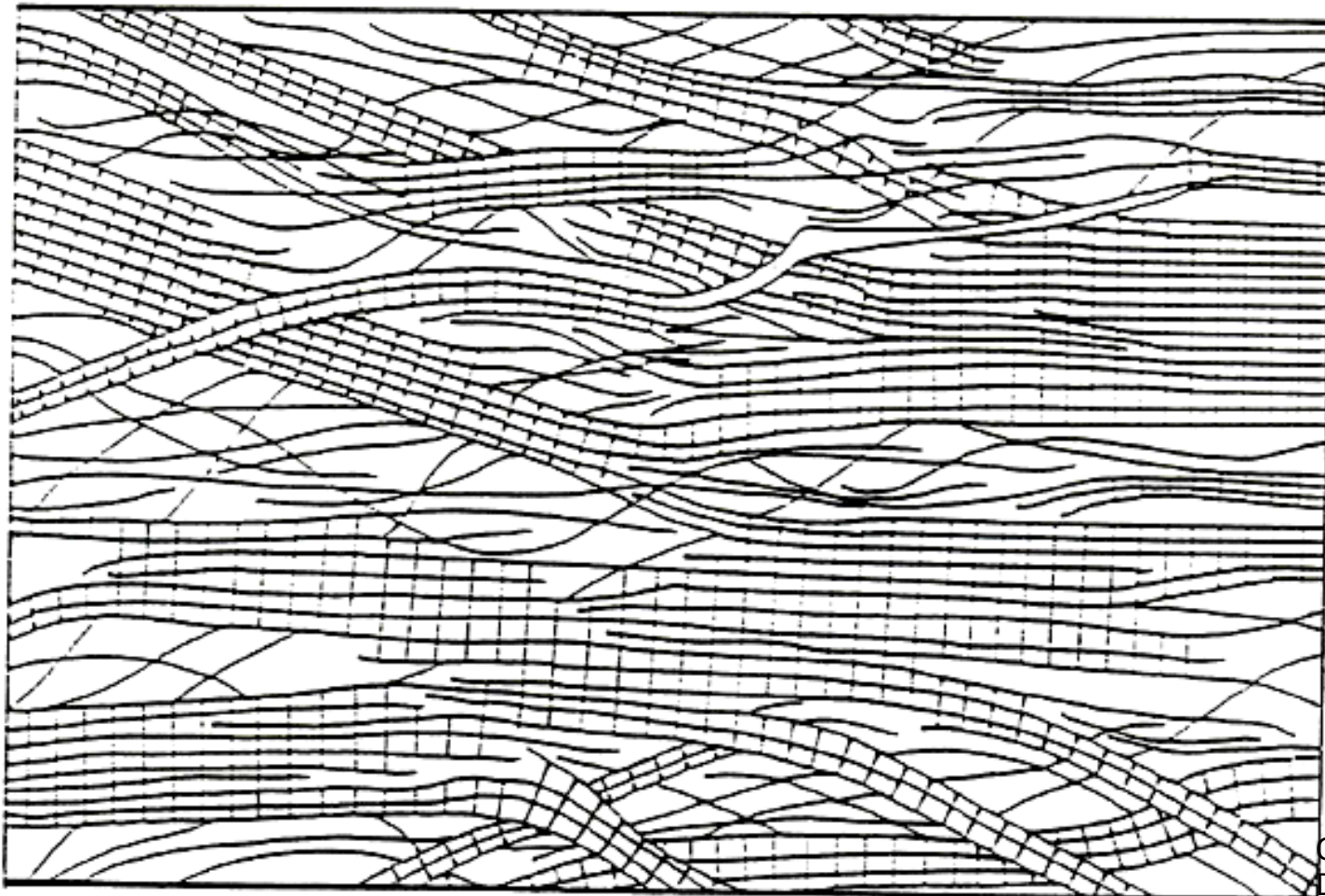
^aCrystallite length calculated from 040 WAXS peak.

^bCrystallite width calculated by Scherrer calculation (Klug and Alexander, 1974).

^cCalculated according to (Hofmann and Walenta, 1987).

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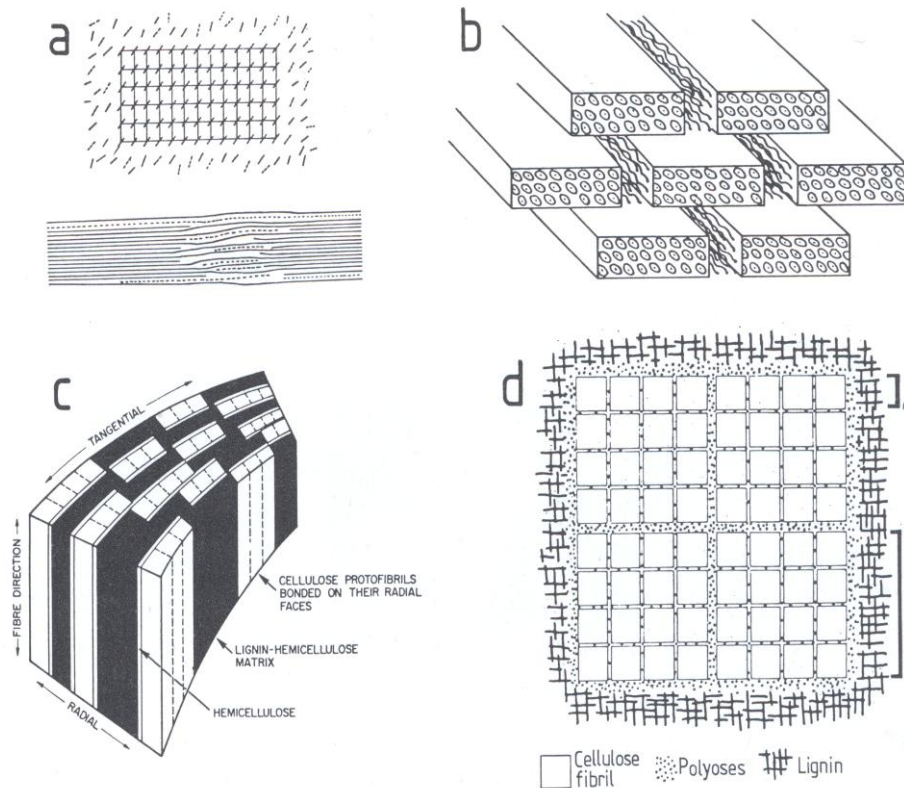
Supramolecular structure



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Figure 2.1.6. Fringed fibril model of cellulose supramolecular structure (Hearle, 1958).

Fibre Ultrastructure



Kolman/Côté (1984)

Elementary fibril (2 - 5 nm)
Microfibrils (10 - 30 nm)
Macrofibrils

Fig. 8-5. Models of the association of the cell wall components developed by various authors.
a) Preston (1962); b) Marchessault (1964); c) Kerr and Goring (1975); d) Fengel (1970).

Morphological structure

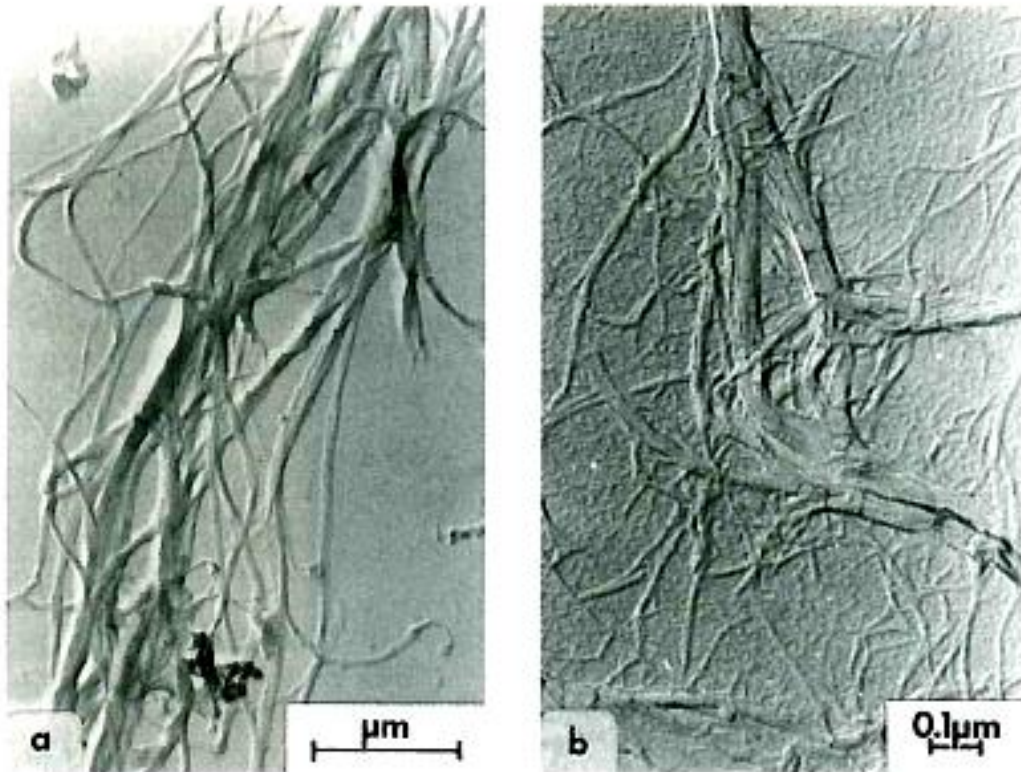


Figure 2.1.10. Isolated microfibrils of cellulose of different origin (a) cotton linters, (b) spruce sulfite pulp (Fink et al., 1990).

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Wiley-VCH, Chichester, 1998

Morphological structure

Table 2.1.7. Range of microfibril diameters of various cellulose samples (Fink et al, 1990)

Sample	Microfibril diameter (nm)
Bacterial cellulose	4–7
Cotton linters	7–9
Ramie	10–15
Dissolving pulp	10–30
Valonia cellulose	10–35

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Wiley-VCH, Chichester, 1998

Pore structure

Table 2.1.9. Voids in cellulose by mercury porosimetry (Quinn, 1963; Paul and Bartsch, 1972; Gröbe, 1989; Buschle-Diller et al., 1995)

Sample	Covered Pore size (nm)	Pore volume (cm ³ /g)	Porosity ^a (%)
Cotton	>800	0.087	–
	>150	0.045	6.6
Spruce sulfite pulp	8000–400000	0.072	17.3
Viscose rayon	1100–150	0.073	–
	>15	0.018	–
Viscose staple fiber	8000–400000	0.018	6.6

^aThe term 'porosity' denotes the total percentage of pores including the large ones (>1000 nm).

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Surface area

Table 2.1.11. Inner surface of cellulose fibers determined by water vapor sorption

Sample	Inner surface (m ² /g)	References
Spruce pulp ^a	1000 ^b	Stone and Scallan, 1967
Cotton	135	Krässig, 1993
Cotton flake	152	Brederick, 1989
Viscose cord rayon	292	Brederick, 1989
Viscose staple	292	Brederick, 1989
Microcrystalline cotton cellulose	135	Stone and Scallan, 1967
Microcrystalline cotton cellulose, mercerized	171	Stone and Scallan, 1967
'Amorphous' cellulose	434	Stone and Scallan, 1967

Table 2.1.10. Inner surface of some cellulose samples calculated from N₂ sorption
(Jacobasch, 1984)

^a Never dried.
^b Size-exclusion.

Sample	Pretreatment	Surface (m ² /g)
Spruce sulfite pulp	–	0.35
Spruce sulfite pulp	H ₂ O swollen, freeze-dried	5.3
Cotton	–	0.60–0.72
Viscose rayon staple	–	0.3–0.4

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Thermal properties of cellulose

Table 2.1.21. Thermal data on cellulose (according to Gröbe, 1989)

Glass transition temperature	230 °C
	230—245 °C
Specific heat	0.291 cal/g degree
cotton	
rayon	0.317
Thermal conductivity	ca. 5×10^{-4} cal/g cm degree
rayon staple	0.071 W/m degree
Coefficient of thermal expansion	
cotton linters	(-30—25°C): 4×10^{-4} degree ⁻¹
Heat of crystallization, extra purified, 100% crystallinity	25.3 ± 1.2 cal/g
Heat of transition Cell I → Cell II	38.1 kJ/kg
Heat of thermal transition at 120—140 °C	109—147 J/g

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Mechanical properties of cellulose

Table 2.1.17. Mechanical data of cellulose filaments and fibers of various origin
(Meredith, 1946)

Specimen	Initial Young's modulus (g/grex)	Breaking elongation (%)	Breaking strength (g/grex)	Work of rupture (toughness) (g cm/grex)
Cotton	50	7.3	3.1	0.10
Flax	183	3.0	5.5	0.08
Hemp	183	2.6	4.7	0.06
Jute	176	1.8	3.6	0.03
Ramie	149	3.7	6.0	0.11
Textile viscose	58	21	1.9	0.23
Stretched viscose	153	5.8	5.0	0.15
Acetate rayon	28	29	1.2	0.22
Silk	77	26	4.4	0.74
Nylon	27	26	4.8	0.77
Wool	25	38	1.3	0.32

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grex = international unit of fiber fineness

Cellulose reactivity

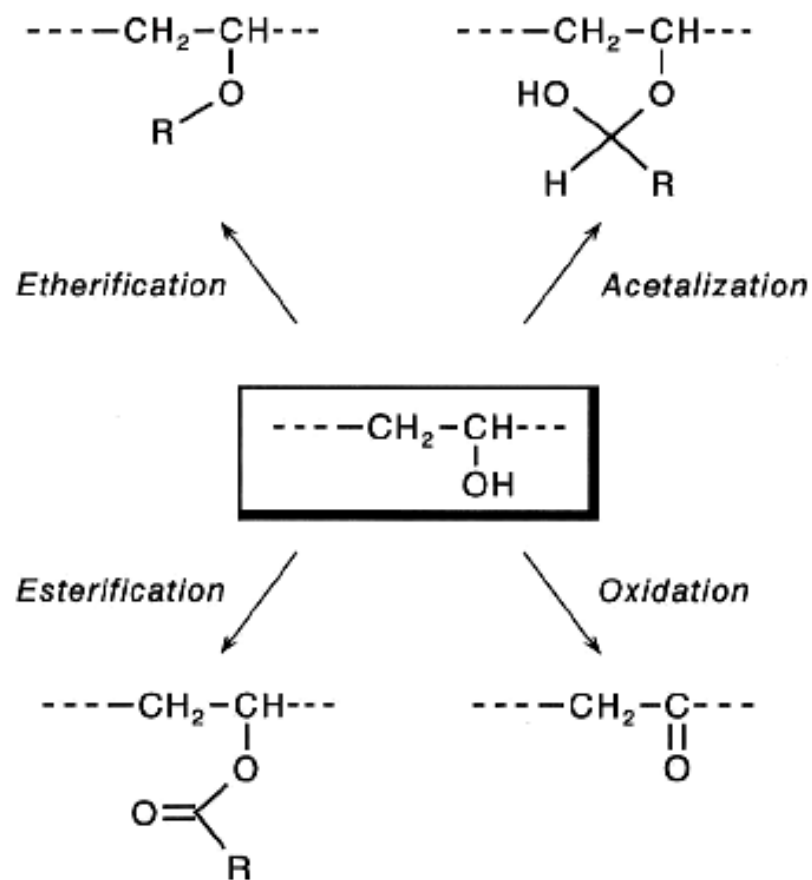
Cellulose activation

Table 2.4.1. Routes to cellulose activation

Spacing via intermolecular or covalent interaction ('chemical' methods)	Disordering of structure via energy input ('physical' methods)
Swelling in polar liquids like H ₂ O, NH ₃ , EtOH, DMSO	High-energy irradiation like electron beam irradiation; γ -ray irradiation
Inclusion of high boiling liquids like oligoethylene glycols	Heat treatment under defined conditions (120–180 °C, < 1 h)
Surface modification by surfactants	Mechanical disintegration by:
Transient formation of addition compounds with NaOH/H ₂ O (mercerization), R ₄ NOH/H ₂ O, NH ₃ or R-NH ₂ , N ₂ O ₄ /CH ₃ COOH, Br ₂ /H ₂ O	shredding conventional milling in a cutting or attrition mill ball milling vibration milling
Covalent derivatization to low <i>DS</i> by grafting with acrylonitrile, etherification with ethylene oxide	Sonication
Hydrolytic chain cleavage	

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Cellulose reactions



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Figure 2.4.1. Scheme of typical reactions of a hydroxy group in a polymer chain.

Cellulose reactions

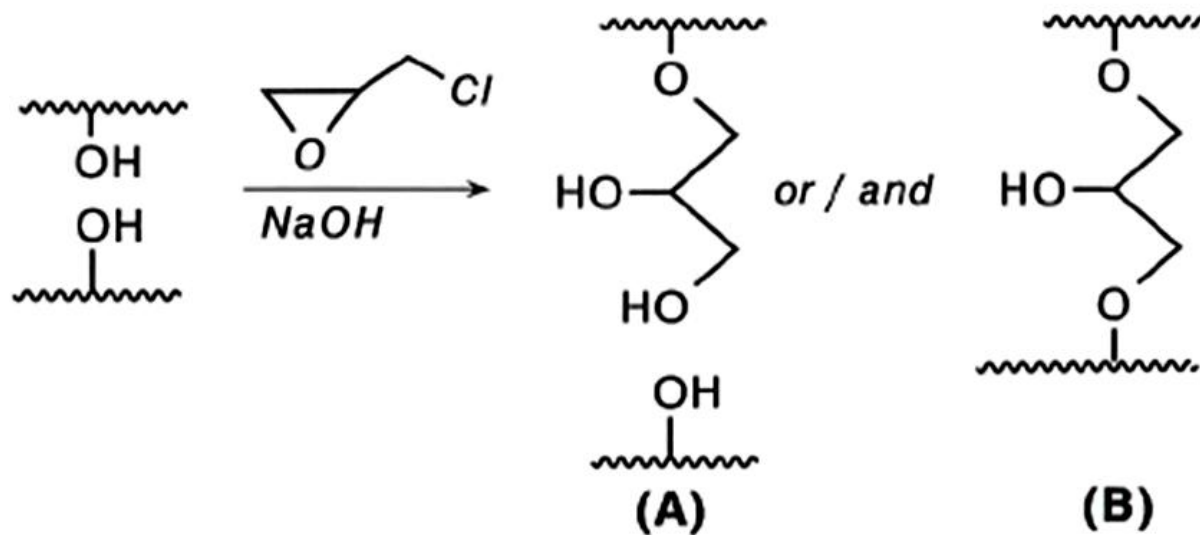


Figure 2.4.2. Mono- (A) and bifunctional (B) reaction of a crosslinking agent (epichlorohydrin) with hydroxy groups.

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Cellulose reactions

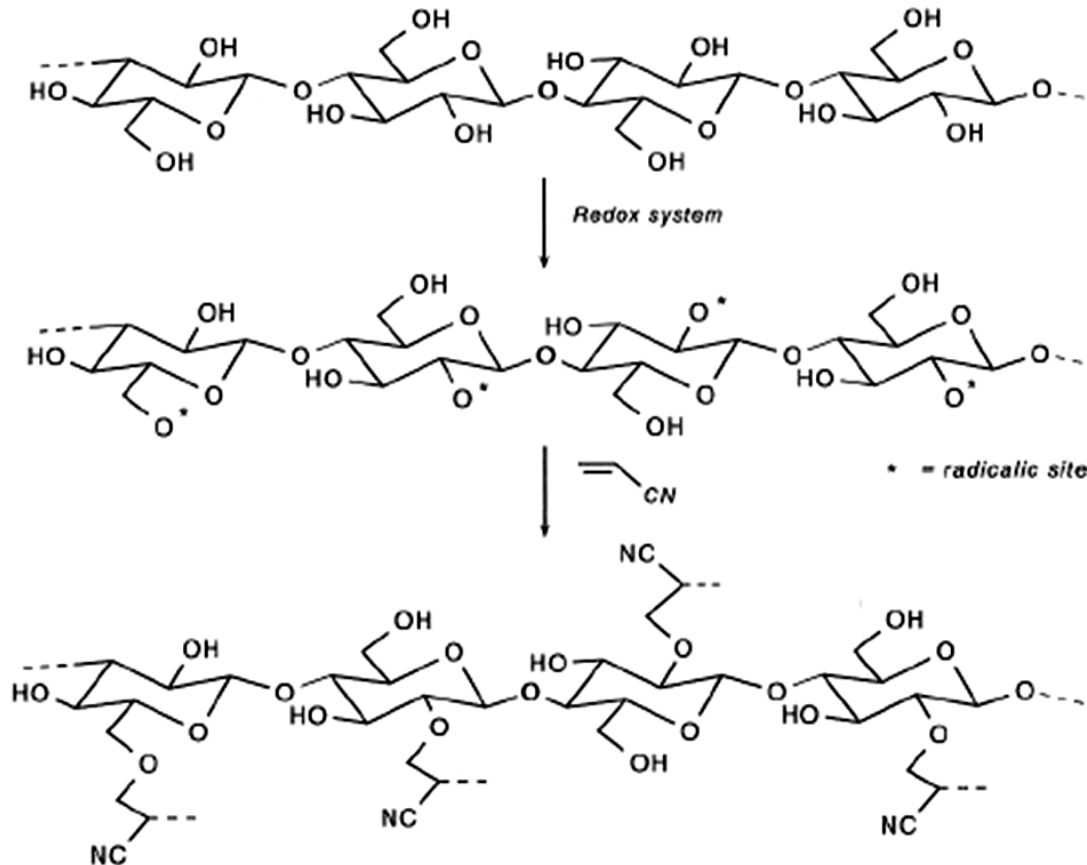


Figure 2.4.3. Scheme of cellulose grafting with acrylonitrile.

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Wiley-VCH, Chichester, 1998

Cellulose derivatives

Some cellulose derivatives of commercial or scientific relevance

extensive

Product	DS range	Areas of application
Nitrate ^a	2—3	Coatings, films, explosives
Acetate ^a	2—3	Films, fibres, cigarette filters
Xanthogenate ^a	0.2—0.6	Soluble intermediates (viscose process)
Sulfuric acid halfesters	0.2—2.8	Gel former, anticoagulant, polyelectrolyte complex component
Anionic cellulose phosphate		Cation exchanger
p-Toluene sulfonate	0.5—2.5	Reactive intermediate
Methyl ether ^a	1.5—2.0	Thickener, adhesive, dispersing agent
Ethyl ether ^a	1—2.5	Thickener, laquers, adhesives, tableting
Hydroxyethyl ether ^a	0.8—2.5	Thickener, binder, colloid stabilizer
Carboxymethyl ether ^a	0.5—1.0	Gel former, adhesives, viscosity enhancer, oil drilling
Cyanoethyl ether ^a	< 0.5; > 2	Rot proofing of textiles organo soluble derivative
Benzyl ether ^(a)	> 2	Melt processable plastics
Trialkylsilyl ether	1.5—3	Reactive intermediate
Triphenylmethyl ether	1 (in C-6)	Reactive intermediate

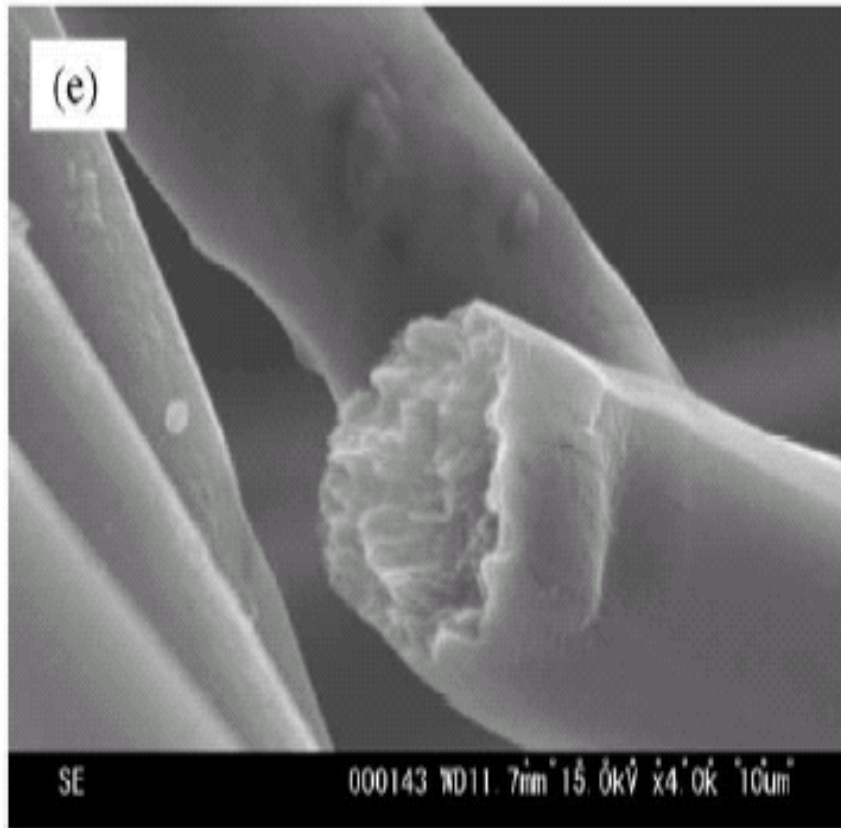
^a commercial product; ^(a) temporary commercial product

Cellulose Based Materials

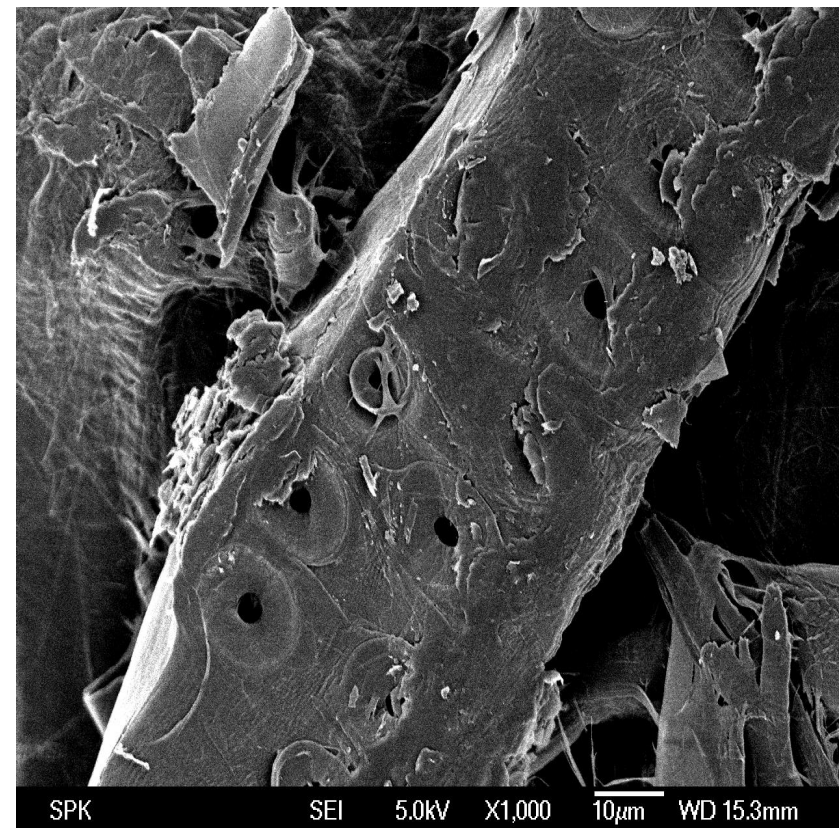
- Fibres
- Fibrills and nanorods
- Particles and beads

Cellulose Fibres

Regenerated fibres (Textiles)



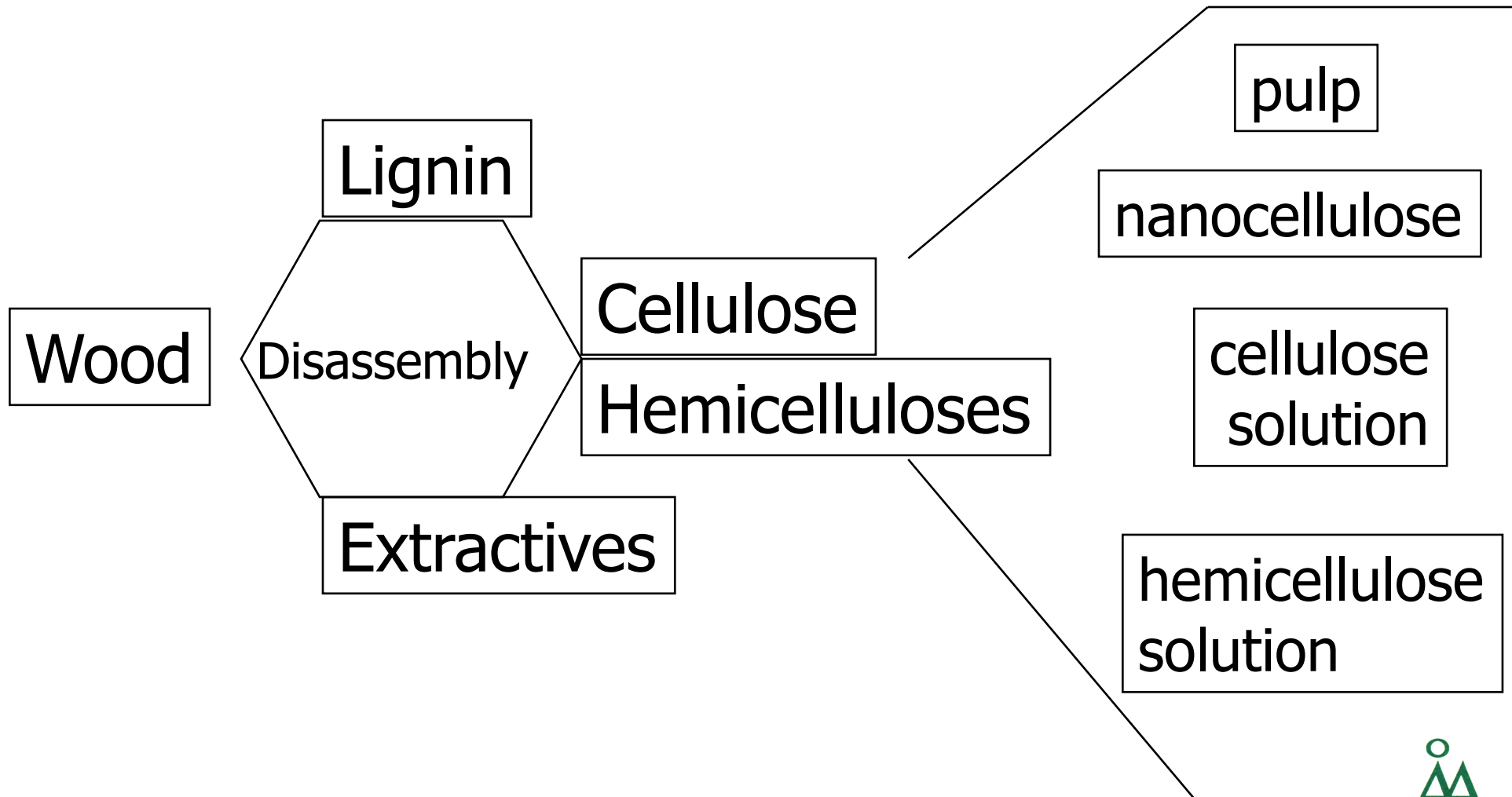
Wood fibres (Papermaking)



Zhang et al, Carbohydrate Polymers 59 2005, 173

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From wood to polysaccharides

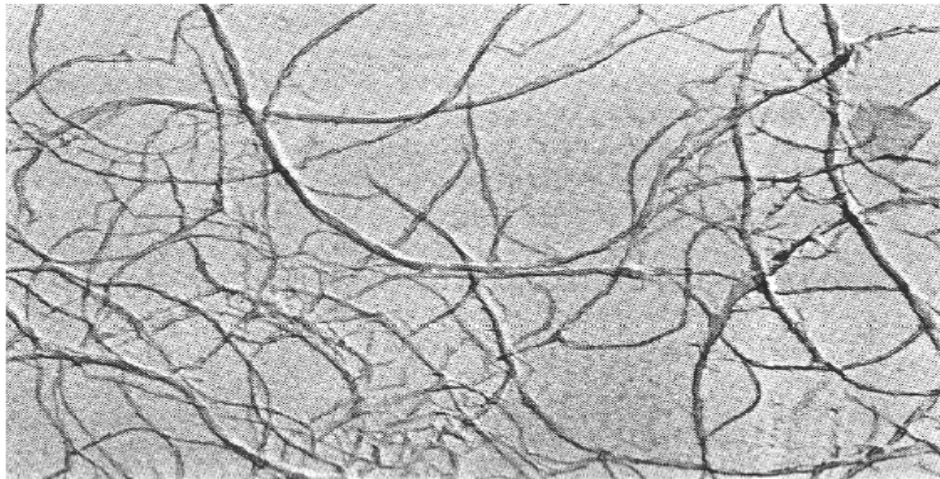


Disassembly of wood polysaccharides

Method	Products
Microfluidization of pulp	microfibrillar cellulose (nanocellulose)
Acid treatment of pulp	Cellulose nanorods
Chemical pulping (sulfate, pre-hydrolysis sulfate, sulfite)	Paper pulp, dissolving pulp, lignin
Organosolv pulping (ethanol, acetic acid, others)	Paper pulp, dissolving pulp, lignin
Ionic liquids (ILs)	Fractionation of wood components
Supercritical fluid extraction	Extraction, gasification, biofuels

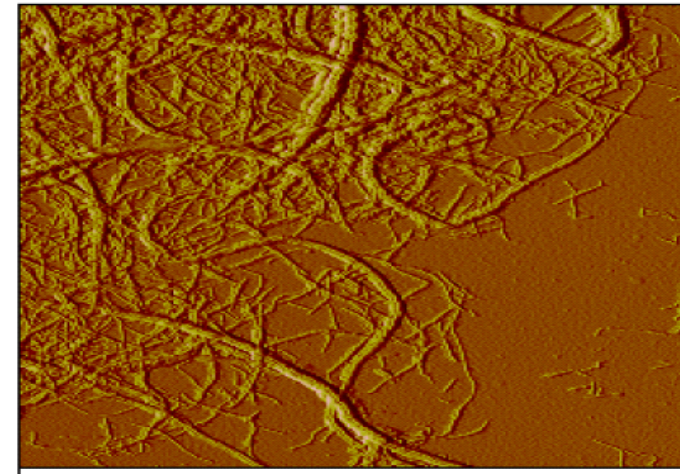
Microfibrillar cellulose (MFC)

SEM and AFM of MFC



SEM (40000x)

Lindström and Winter, 1988

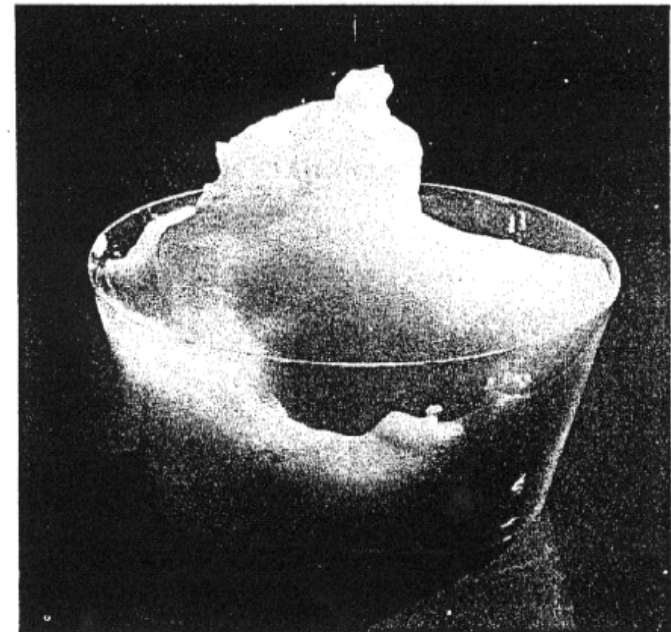
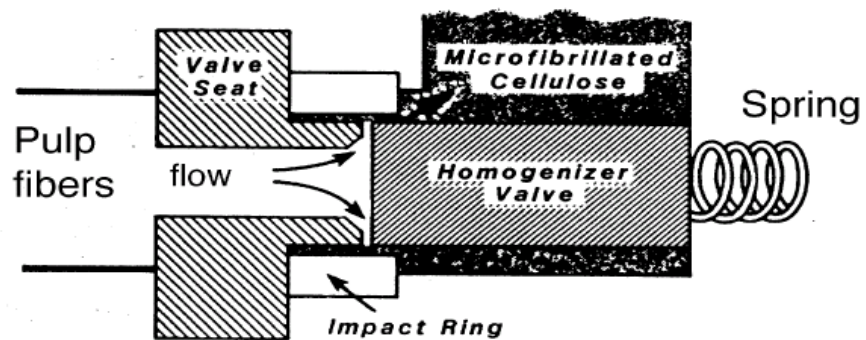


AFM

Notley, 2003

Preparation of MFC

Disintegration (homogenization)

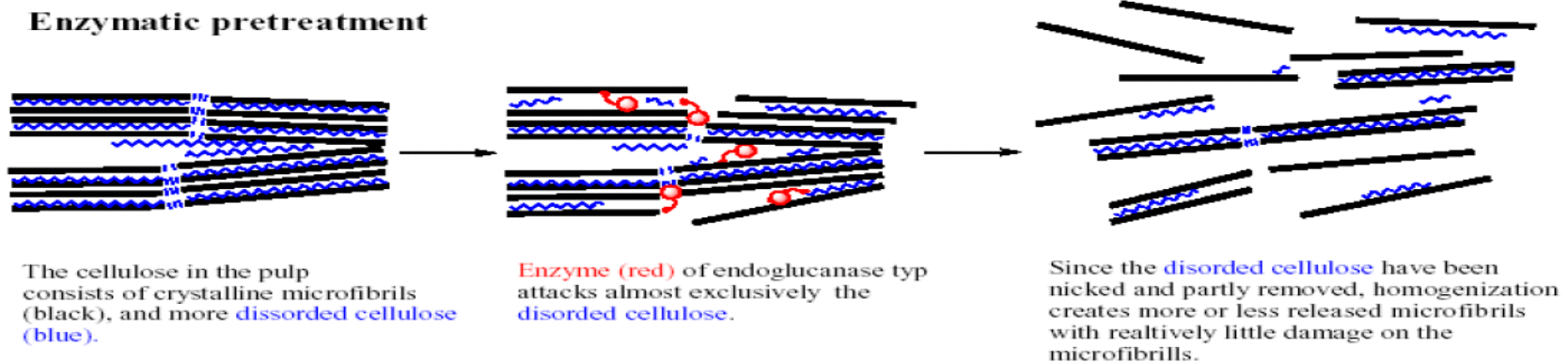


Microfibrillated Cellulose MFC

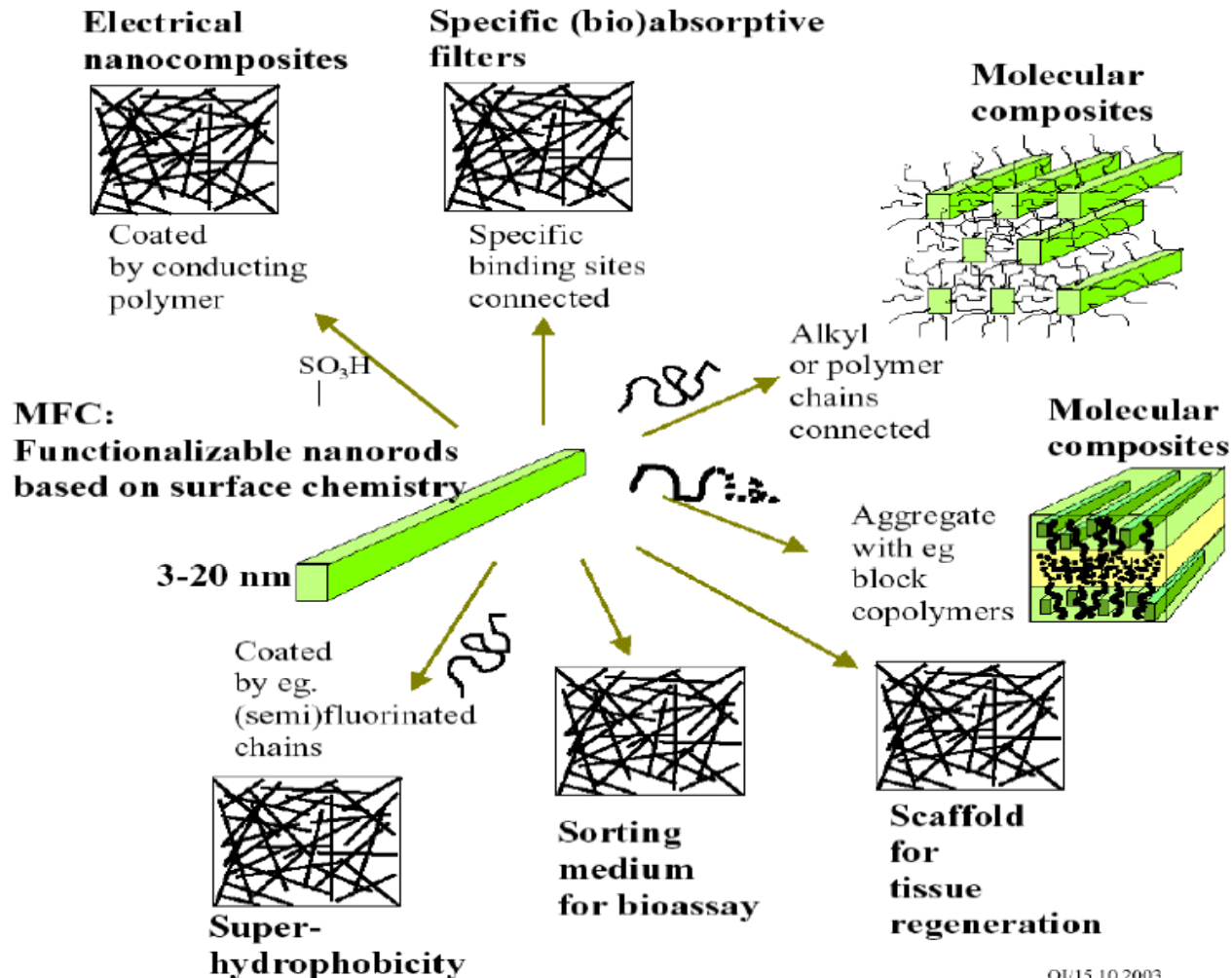
Turbak A F, Snyder F W and Sandberg K R
(1983): J. Appl. Polym. Science. Applied Pol.
Symp. 37

Pulp pre-treatment

Enzymatic Hydrolysis



Modification of MFCs



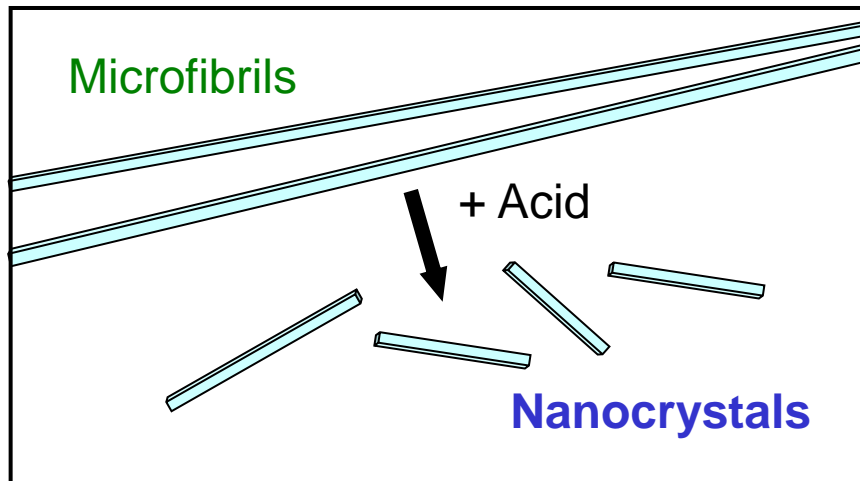
01/15.10.2003
draft

Some questions about MFCs

- Energy consumption in processing
- Usually produced to 2% dispersion in water
- Residual of hemicelluloses
- Surface modification/reactivity
- Balance between stabilization of dispersion/functionalisation

Cellulose nanorods (nanocrystals)

Pulp

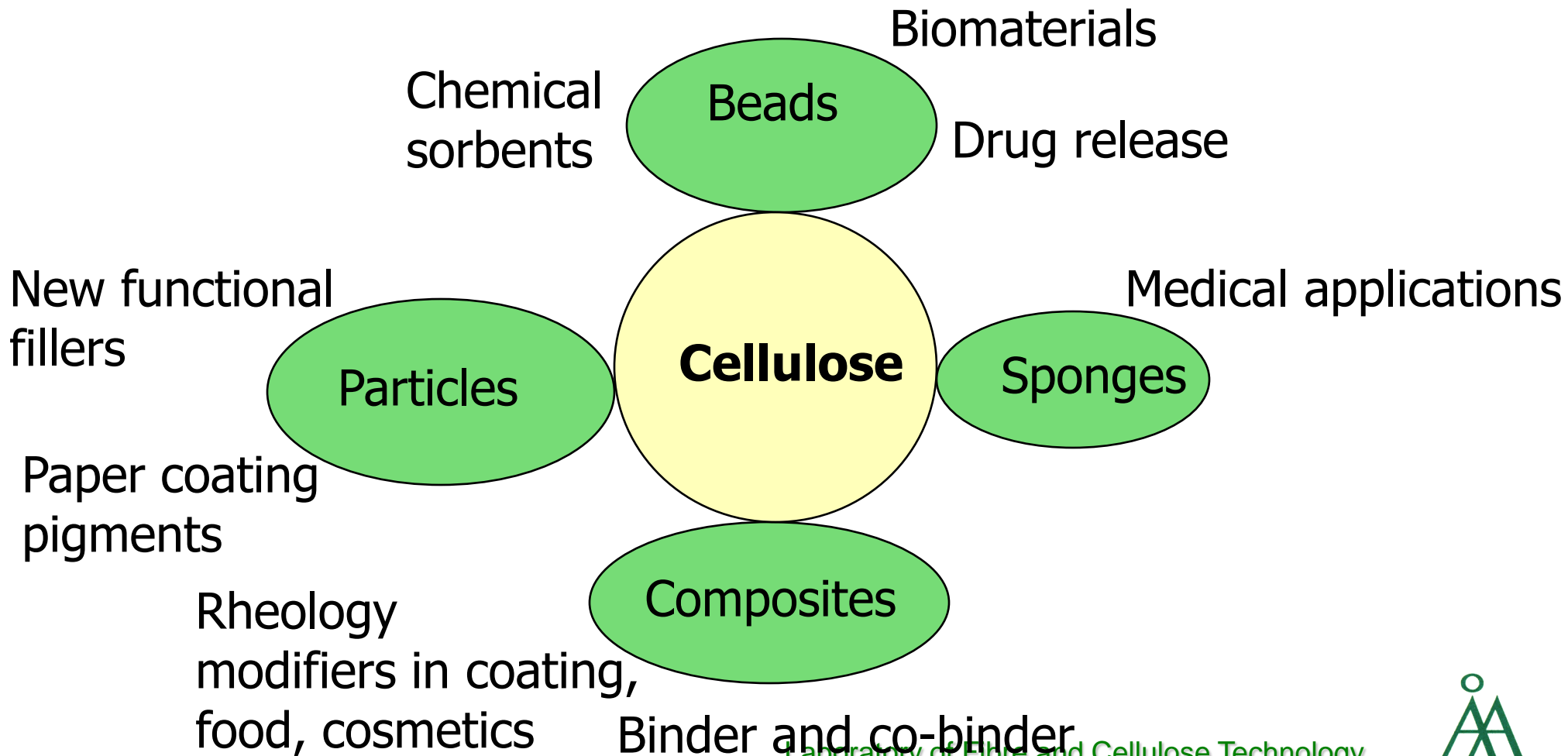


acid (HCl, H₂SO₄)
concentrations (65%)
temperature (40°C)
hydrolysis time (1 – 2 h)
acid-to-substrate ratio
(0.1 – 0.5 mol/g)

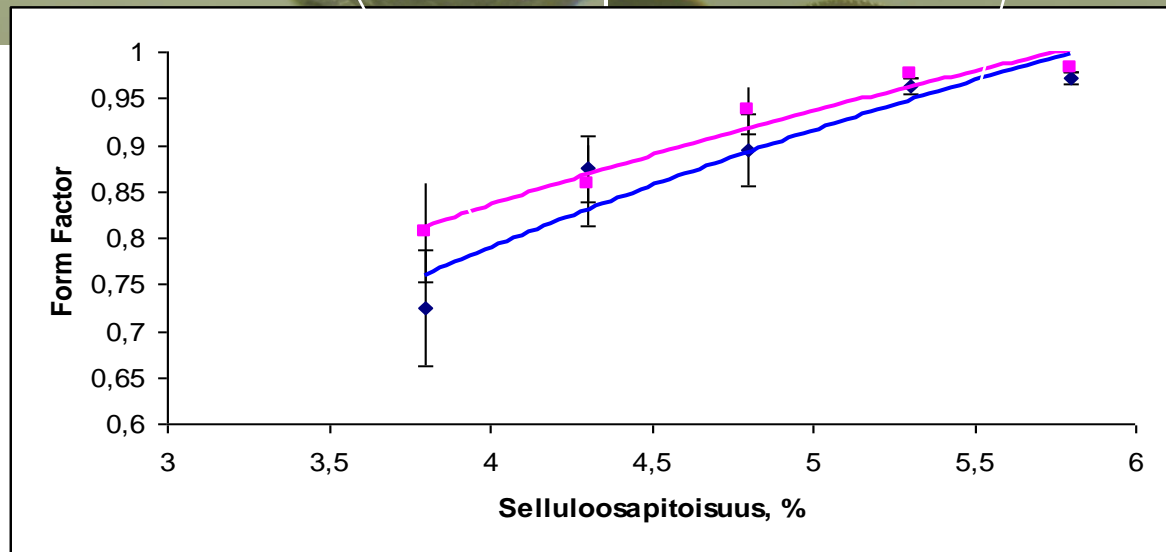
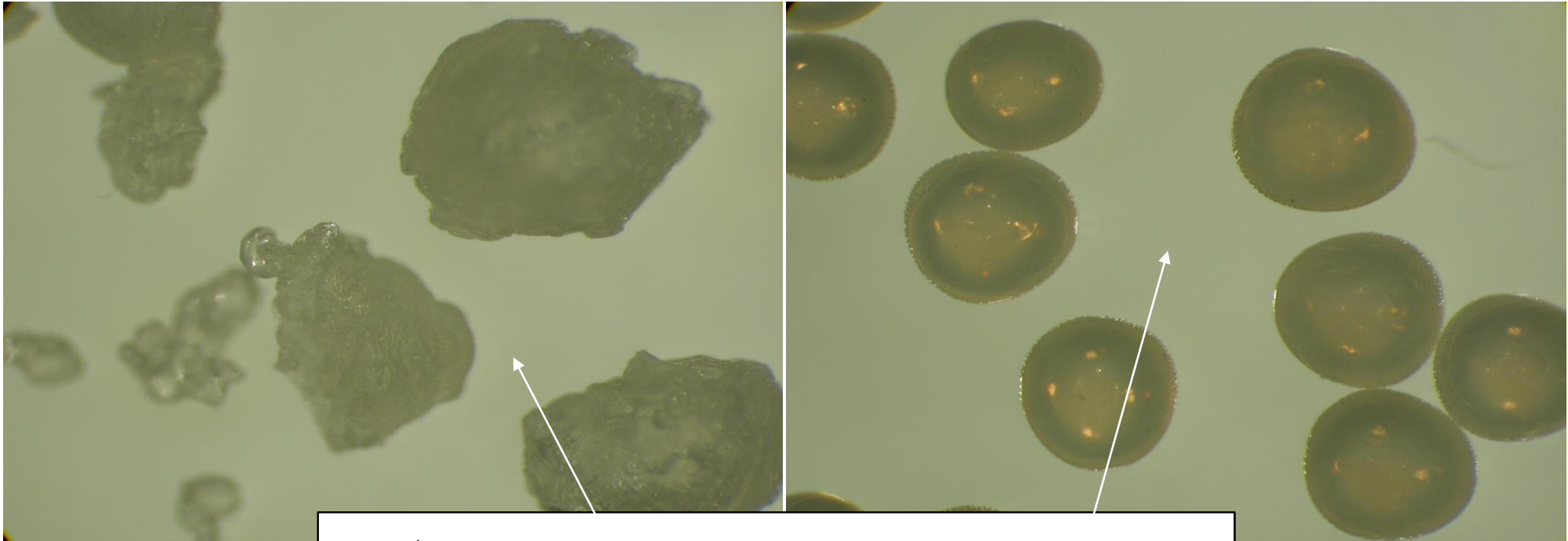
Some questions about cellulose nanocrystals

- Low yield
- Stabilization of nanocrystal dispersions
- Functionalisation of nanocrystals

Cellulose Materials

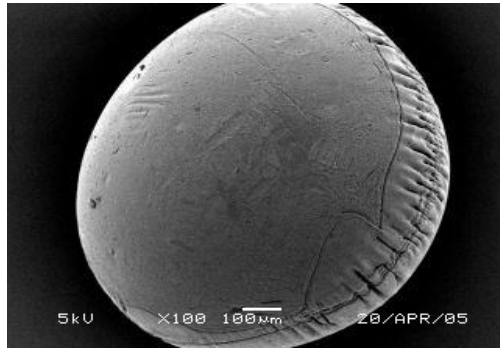


Form factor



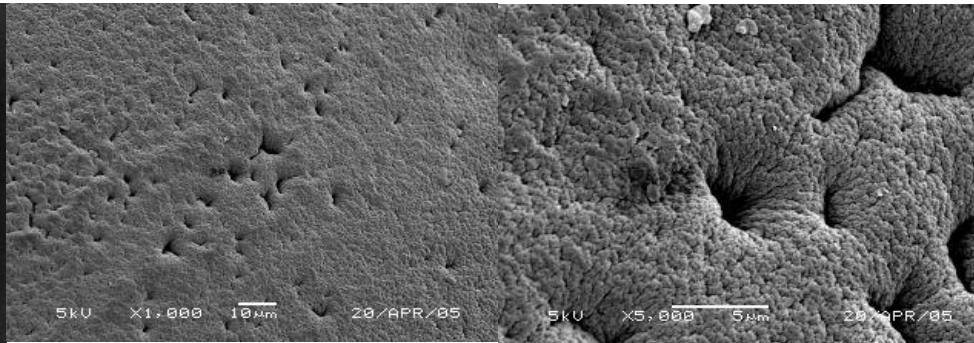
Beads of regenerated cellulose

x100



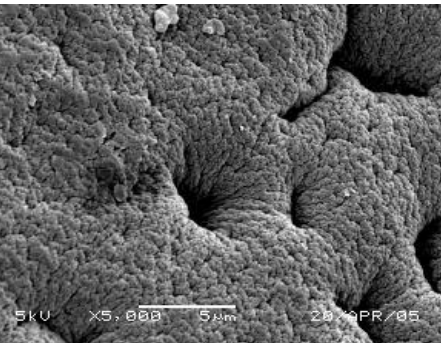
— 100 µm

x1000



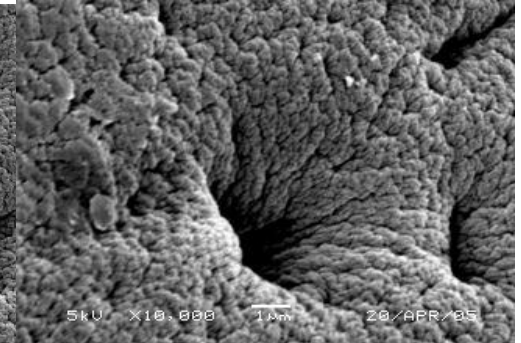
— 10 µm

x5000



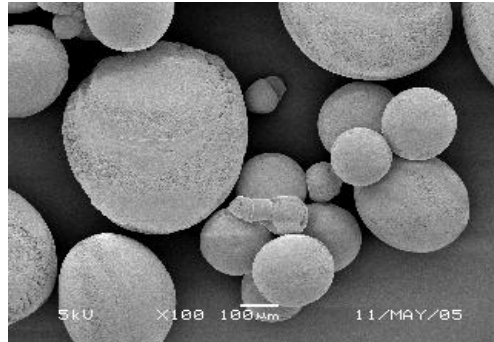
— 5 µm

x10000

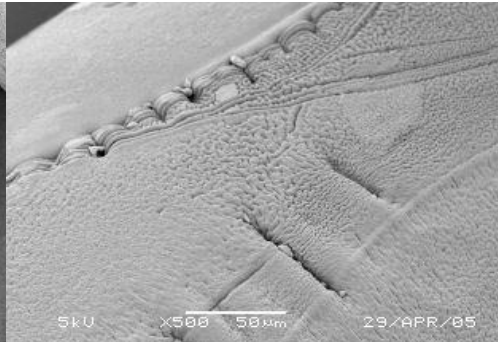


— 1 µm

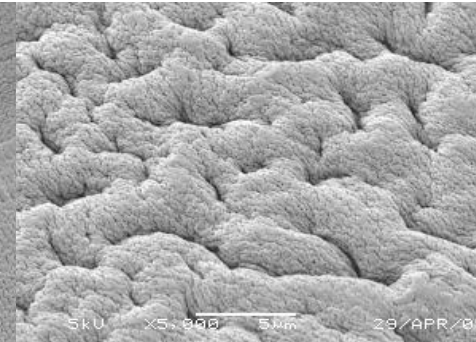
x100



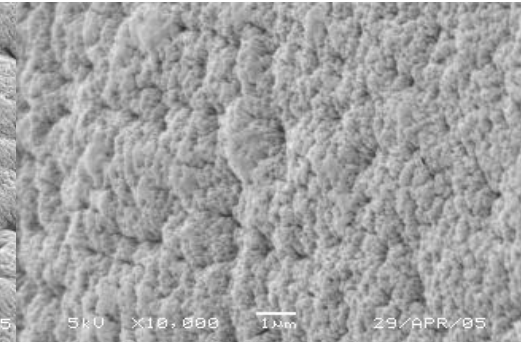
x500



x5000



x10000



Summary

- Cellulose can be modified using homogeneous or heterogeneous methods
- Cellulose derivatives have broad application areas
- Regenerated cellulose can be used as fibres, particles and sponges
- Cellulose fibrils have potential applications in several technological areas