Selluloosa-nanomateriaalit

- Nyt ja tulevaisuudessa

Sanna Siljander
Tomas Björkqvist

25.4.2019

Tampereen yliopisto

Kestävää kasvua ja työtä -ohjelma

Vipuvoimaa EU:lta 2014–2020

Euroopan unioni
Euroopan aluekehitysrahasto

Sisältö

Selluloosa-nanomateriaalit

- Rakenne
- Termit, laadut, standardit
- Ominaisuudet
- Fibrillointimenetelmät
- Tulevaisuuden näkymät
- Sovelluskohteet, haasteet
- Kaupalliset toimijat

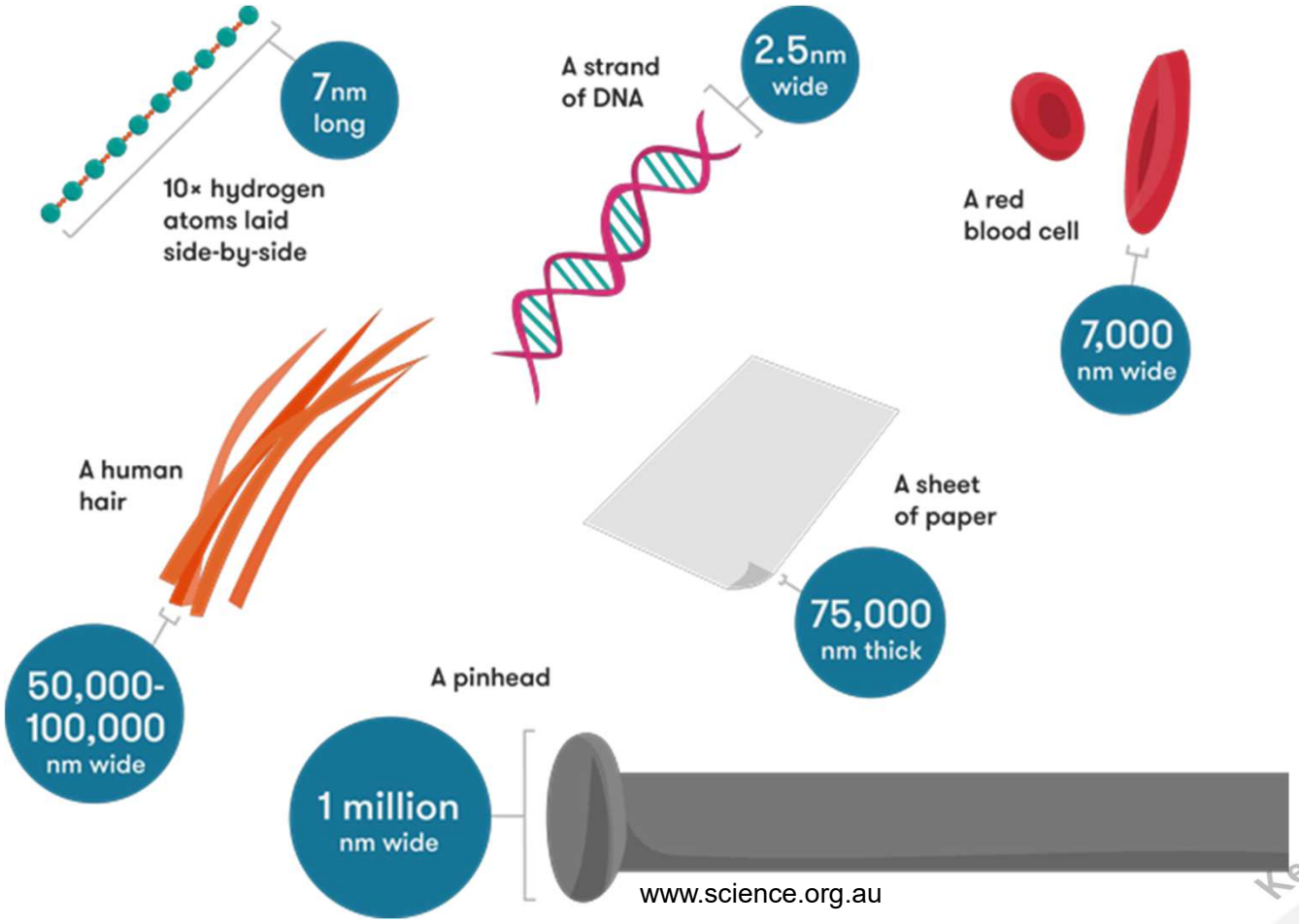
Mitä ovat nanomateriaalit?

- Nanomateriaalit ovat kemiallisia aineita tai materiaaleja, joiden hiukkaskoko on 1–100 nanometriä (nm) ainakin yhdessä suunnassa.

- Koska niiden spesifinen pinta-ala on suurempi tilavuuteen nähden, nanomateriaaleilla voi olla erilaisia ominaisuuksia verrattuna samaan materiaaliin, jolla ei ole nanoskaalan ominaisuuksia. Näin ollen nanomateriaalien fysikaalis-kemialliset ominaisuudet voivat olla erilaisia kuin massa-aineilla tai suuremmilla hiukkasilla.

- https://echa.europa.eu/fi/regulations/nanomaterials

Mitä ovat nanomateriaalit?



www.science.org.au

Ihmisen silmän erotuskyky
0,01 mm eli 10 µm

Kestävää kasvua ja työtä -ohjelma

Tampereen yliopisto

Vipuvoimaa EU:lta 2014–2020

Euroopan unioni
Euroopan aluekehitysrahasto

Selluloosa

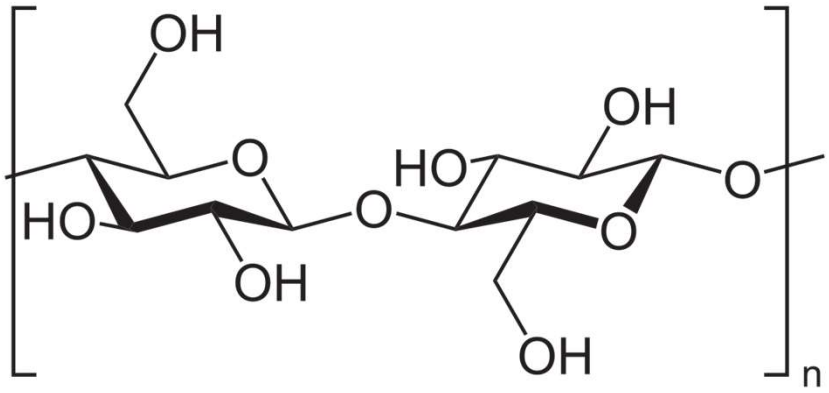
polysakkaridi, biomateriaali

Sanna Siljander

25.4.2019

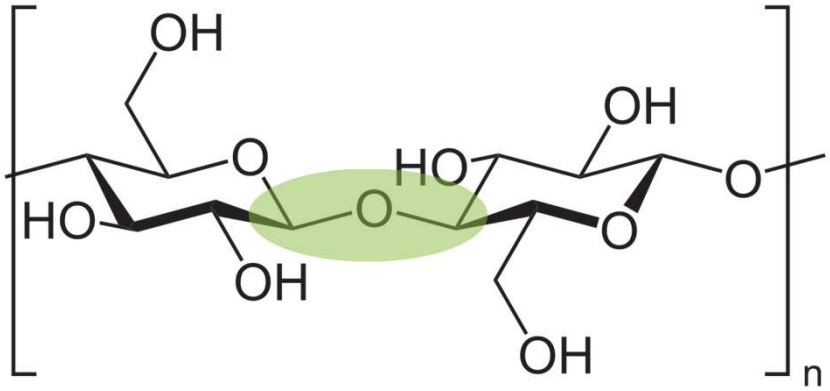
Rakenne

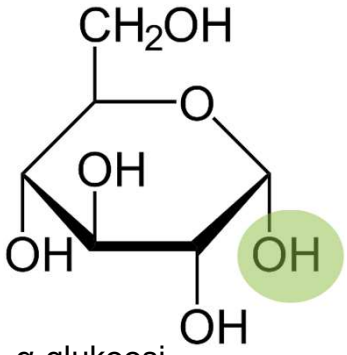
- Polysakkaridi
- Kasvien soluseinän pääkomponentti
- Selluloosa on hydrofiilistä mutta ei liukene veteen eikä orgaanisiin liuottimiin
- Selluloosa antaa kasvin soluseinälle sen lujuuden.



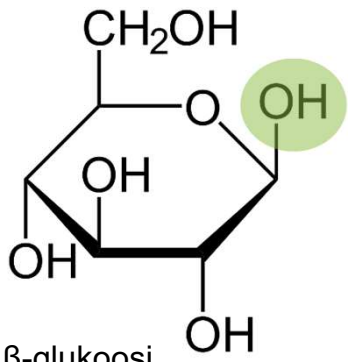
Rakenne

- Selluloosaketju muodostuu toisiinsa liittyneistä β-D-glukoosiyksiköistä, jotka ovat sitoutuneet toisiinsa (1→4) glukosidi sidoksin.
- Toinen glukoosiyksikkö kiertyy 180° ensimmäiseen nähden.
- Vahvat kovalenttiset sidokset





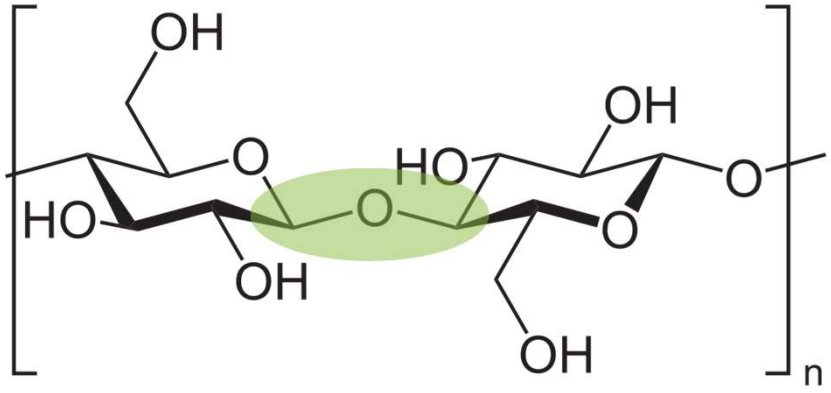
α-glukoosi



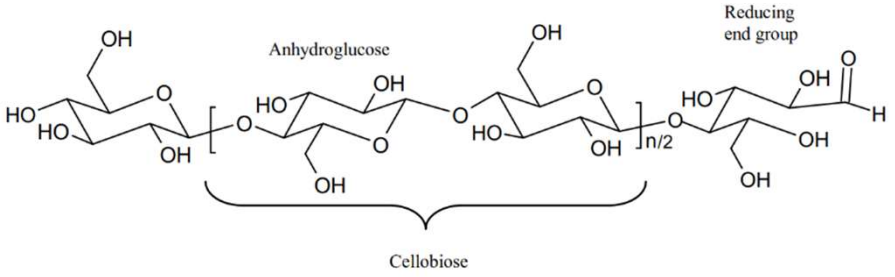
β-glukoosi

Rakenne

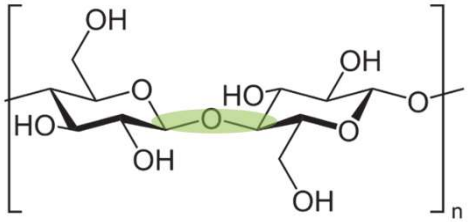
- Polysakkaridien avaruudellinen rakenne: identtinen kemiallinen rakenne $(C_6H_{10}O_5)_n$
  - (1→4) glukosidisidos voi suuntautua kahdella tavalla, muodostaen neljä erilaista sidosta.
    - Amyloosi
    - Selluloosa, lineaarinen
    - α-galaktaani
    - β-galaktaani



anhydroglukoosiyksikkö

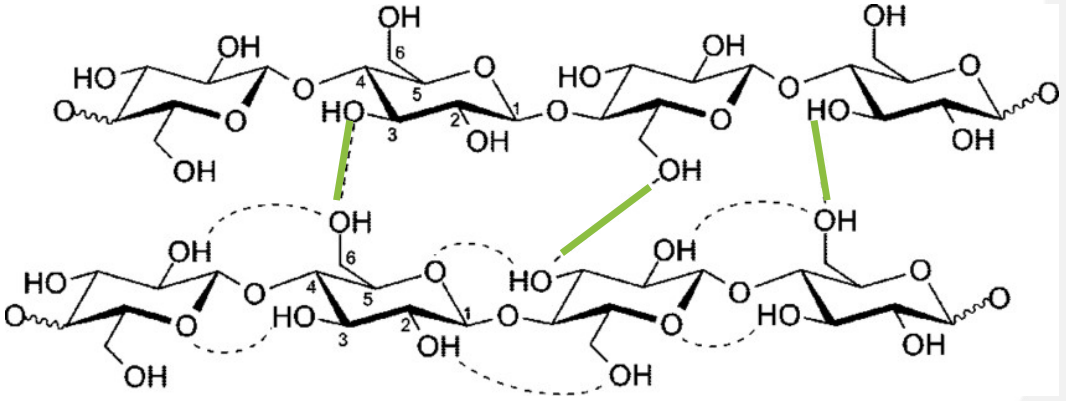


Rakenne



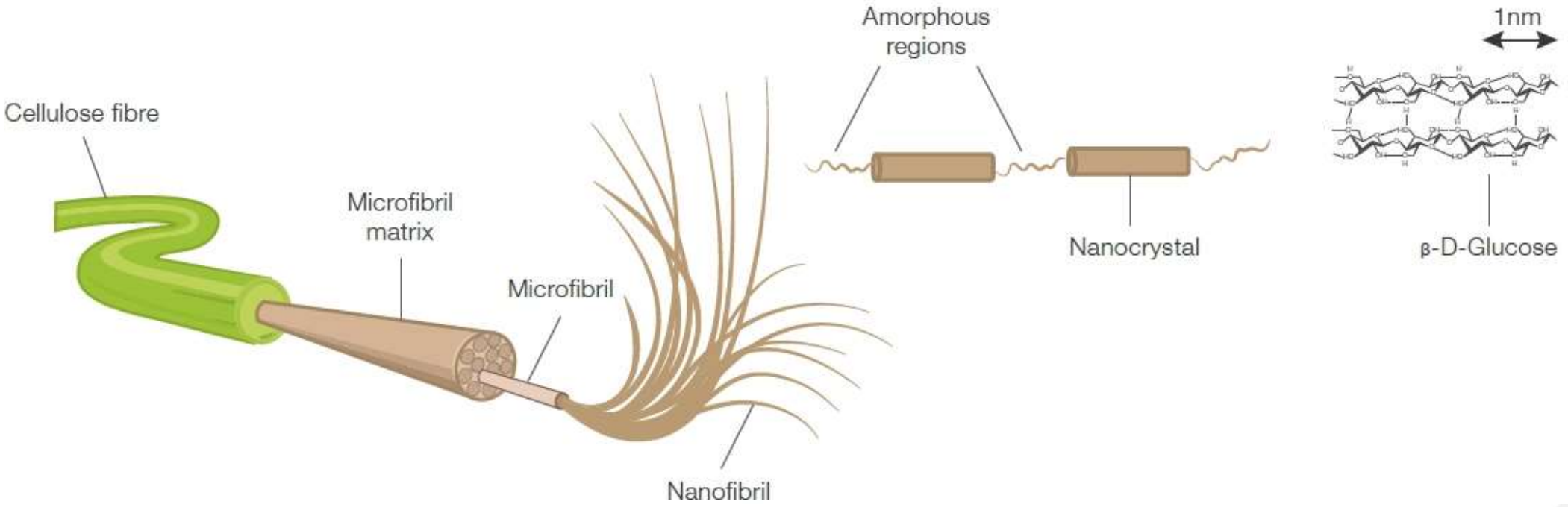
anhydroglukoosiyksikkö

- Puusta saatavan selluloosan polymeraatioaste on noin 10 000
  - Puuvilla 15 000
- Jokainen anhydroglukoosiyksikkö muodostaa
  - Ketjun sisäisiä vetysidoksia
  - Molekyyliketjujen välisen vetysidoksen

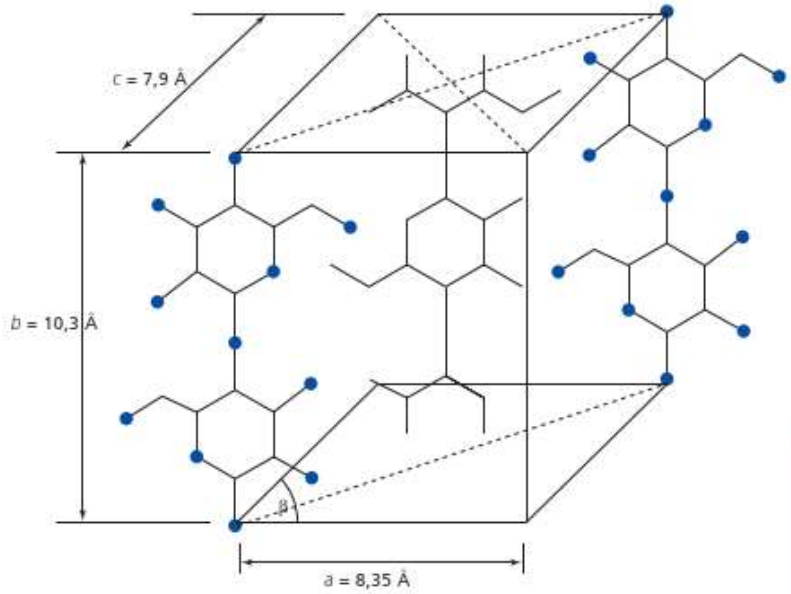


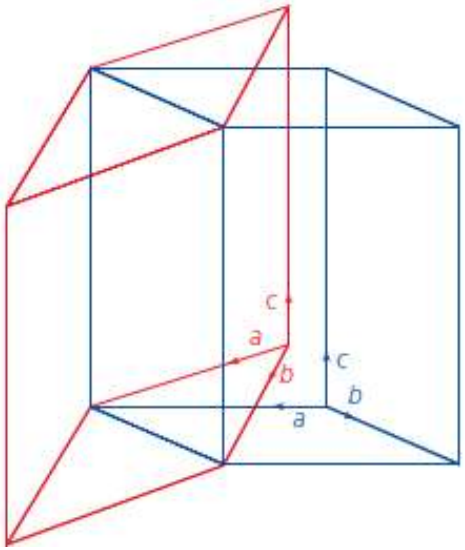
→ Taipumus muodostaa molekyylikimppuja:
alkeisfibrillit → mikrofibrillit

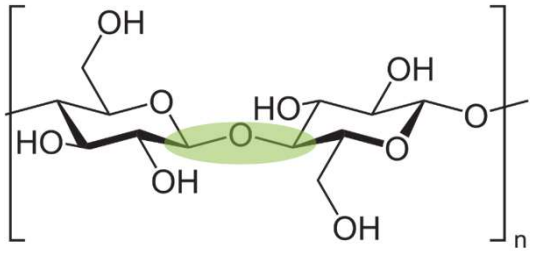
Rakenne



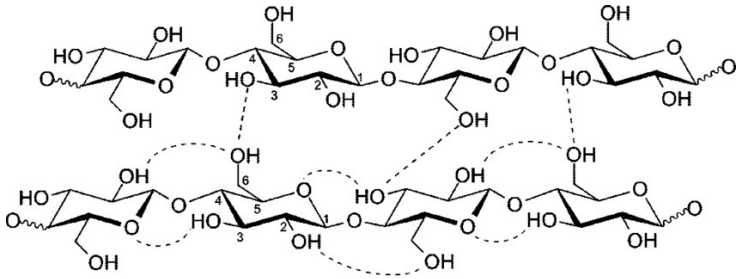
Rakenne





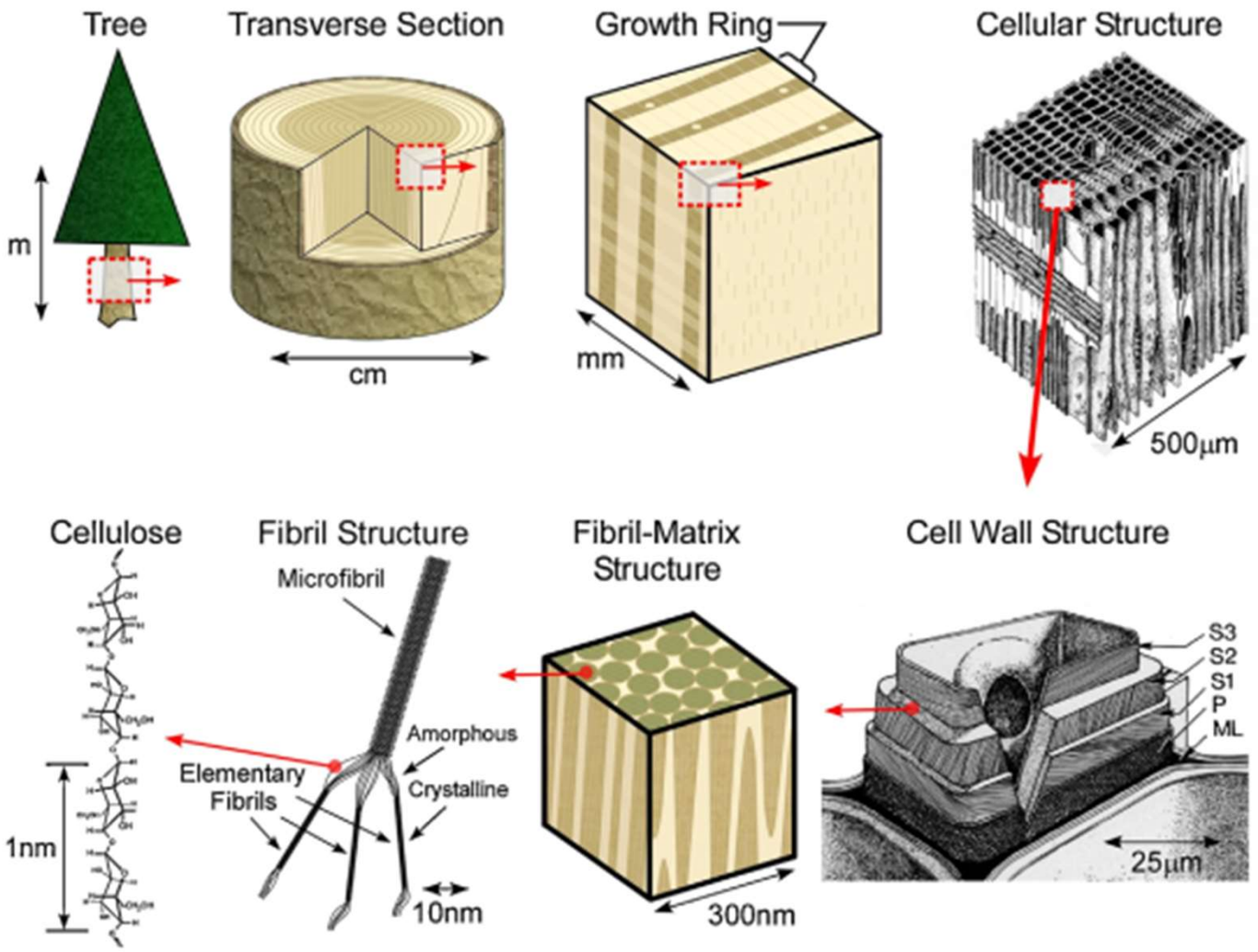


anhydroglukoosiyksikkö



Selluloosa Iα, triclinic (punainen)
Selluloosa Iβ, monoclinic (sininen)

Rakenne



Dufresne Alain, Materials Today, vol 16, 2013

Selluloosa-nanomateriaali laadut ja standardit

Sanna Siljander

25.4.2019

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Kestävää kasvua ja työtä -ohjelma

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Termit

Nanocellulose
Nanofibrillar cellulose
Cellulose nanofibrils
Cellulose nanofibres

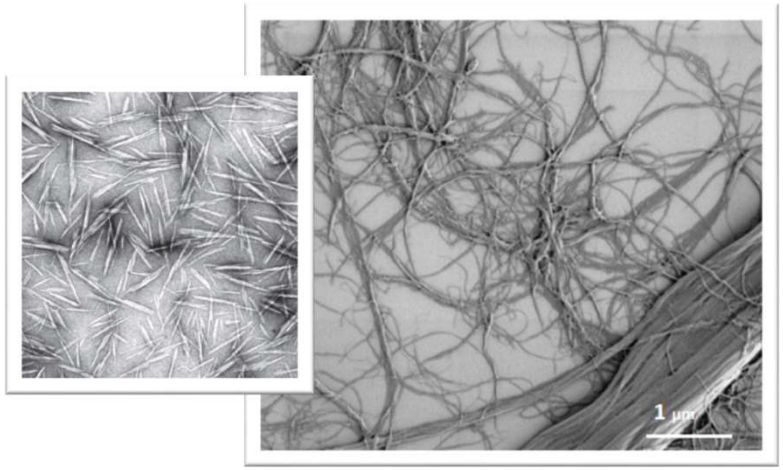
→ NC, NFC, CNF

Microfibrillar cellulose
Cellulose microfibres
Cellulose filaments

→ MFC, CMF

	Length	Diameter
CNC	50–500 nm	3–20 nm
CNF	0.5–2 µm	3–100 nm
MFC	0.5–10's µm	10–100 nm

Moon et al. 2011



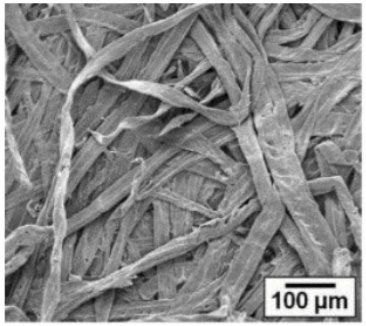
Cellulose nanocrystals, CNC, NCC, CNW

Rigid rods of crystalline cellulose

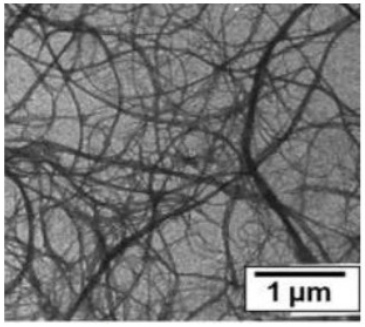
Bacterial cellulose, BC

A species of bacteria (acetobacteria xylinum) is able to produce pure cellulose microfibrils from sugars

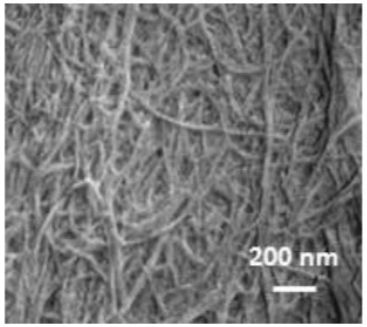
Selluloosa-nanomateriaalit



Pulp



Microfibrils
MFC Microfibrillated Cellulose
CF Cellulose Filaments



Nanofibrils
NFC Nanofibrillated Cellulose
CNF Cellulose Nanofibrils

Fiberlean.com

Source of cellulose	Lateral dimension	Preparation method
Mengkuang leaves (Pandanus tectorius)	5–25 nm	Acid hydrolysis
Banana rachis	10–60 nm	Acid hydrolysis
Sisal	20–80 nm	Acid hydrolysis
Kapok	20–70 nm	Acid hydrolysis
Pineapple leaf	50–150 nm	Acid hydrolysis
Coir	40–90 nm	Acid hydrolysis
Soft wood pulp	10–20 nm	High shear defibrillator
Cladophora sp. green algae	30–40 nm	Oxidation
Cotton linters	39 ± 7 nm	Acid hydrolysis
Pineapple leaf fibre	5–60 nm	Steam explosion acid hydrolysis
Microcrystalline cellulose	6.96 nm	Acid hydrolysis
Cellulose powder	20–50 nm	High-pressure homogenizer
Leaves licuri	5.7–61.6 nm	Acid hydrolysis
Kraft bagasse pulp	7.5–16.5 nm	Acid hydrolysis
Gluconacetobacter xylinus	128 nm	Bacterial synthesis
spruce and pine	5–10 nm	Acid hydrolysis
Rice straw	1.5–12.6 nm	High speed blender
Rice straw	1.4–8.5 nm	Acid hydrolysis
Rice straw	1.73 ± 0.56	TEMPO[a] oxidation
Bamboo fiber	10–30 nm	Alkali and acid hydrolysis
Rice straw	40–80 nm	Acid hydrolysis
Cotton lint	<50 nm	Acid and mechanical
Maize straw	15–25 nm	Acid hydrolysis
Pomelo Fruit Fibers	10–20 nm	Acid hydrolysis
Citrus waste	10 nm	Enzymatic hydrolysis

Mondal, Carbohydrate Polymers 163, 2017

Standardit

ISO 20477

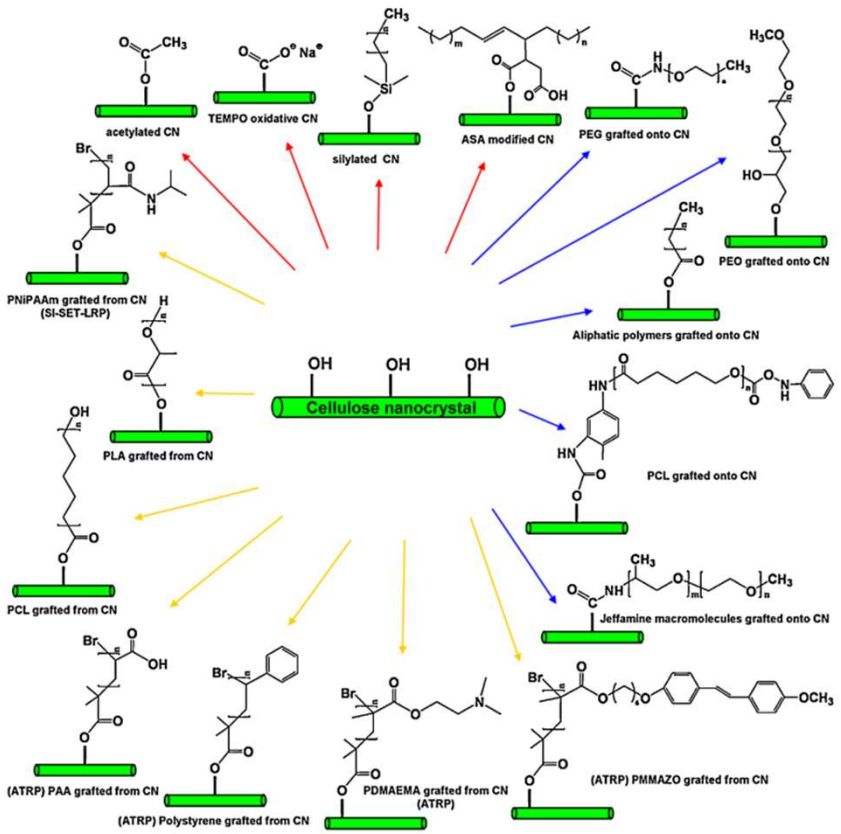
Nanotechnologies — Standard terms and their definition for cellulose nanomaterial

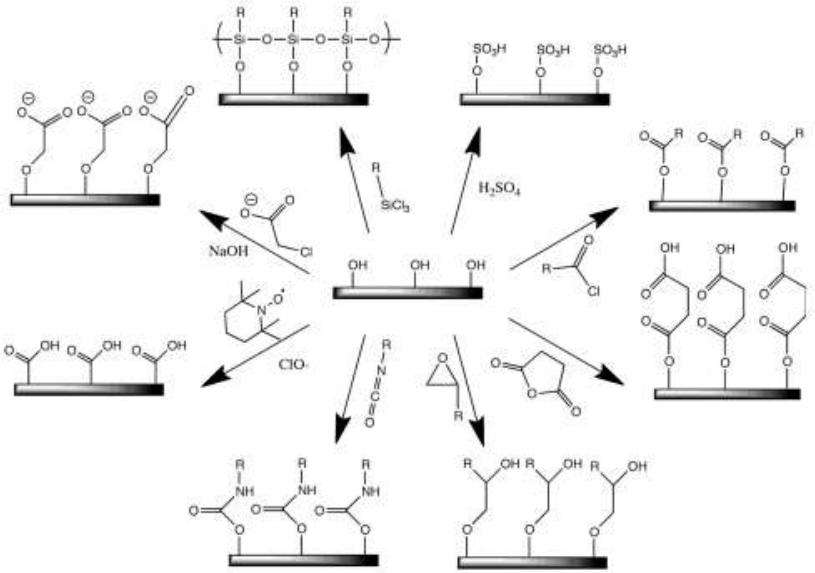
ISO/TC 229 – AWI TS 21346 : Characterization of individualized cellulose nanofibrils

Ominaisuudet – NFC, MFC

- Bio-based, sustainable, renewable
- Recyclable, biodegradable, biocompatible
- High strength and modulus
- High thermal stability
- Lightweight
- Non-toxic
- Thixotropic
- Optical transparency
- High water binding capability, absorbent
- High aspect ratio and high surface area
- Chemical functionality and modification
- Dimensional stability
- Barrier properties

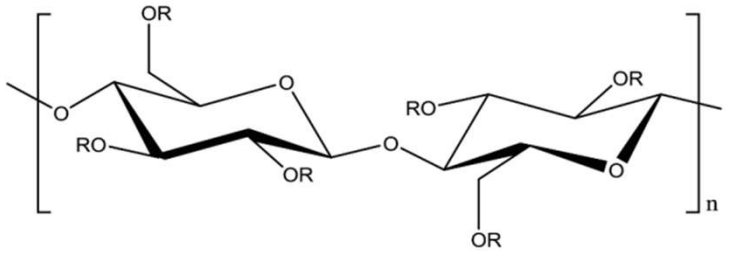
Ominaisuudet -





Dufresne Alain, Materials Today, vol 16, 2013

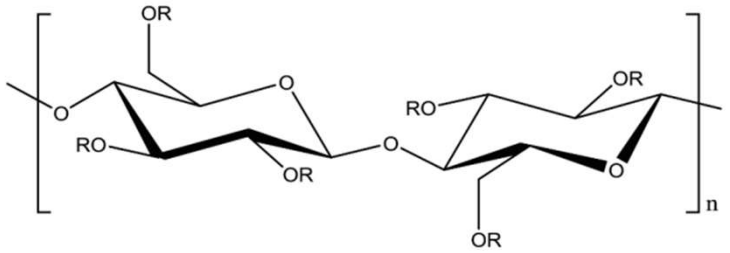
Selluloosajohdannaiset



- Ihmisen elimistö ei pysty pilkkomaan selluloosaketjua
  - Selluloosa luetaan kuuluvan ravintokuituihin
  - Selluloosa ja selluloosajohdannaiset ovat elintarvikkeissa sallittavia lisäaineita
  - Päivittäiselle käytölle ei ole asetettu ylärajaa (ADI)

- Käyttökohteet
  - Paakkuuntumisen estoaine
  - Täyteaine
  - Viskositeetin säätäjä

Selluloosajohdannaiset – E-koodit



- E460i, mikrokiteinen selluloosa
- E460ii, selluloosajauhe
- E461, metyyliselluloosa, R=H tai –CH3
- E462, etyyliselluloosa, R=H tai –CH2CH3
- E463, hydroksipropyyliselluloosa, R=H tai –CH2CH(OH)CH3
- E464, hydroksipropyylimetyyliselluloosa, R=H tai –CH3 tai -CH2CH(OH)CH3
- E465, etyylimetyyliselluloosa, R=H tai –CH2CH3
- E466, natriumkarboksimetyyliselluloosa R=H tai –CH2COONa tai -CH2COOH
- E469, entsymaattisesti hydrolysoitu karboksimetyyliselluloosa R=H tai –CH2COONa tai –CH2COOH

Selluloosa-nanomateriaalien valmistusmenetelmät

Sanna Siljander

25.4.2019

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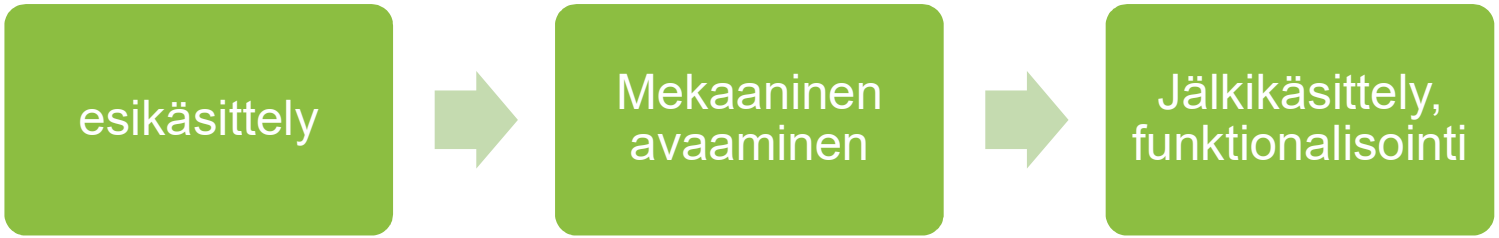
Vipuvoimaa EU:lta 2014–2020

Euroopan unioni
Euroopan aluekehitysrahasto

Historia

- Turbak, Snyder ja Sandberg vuonna 1977 kokeilivat maidon homogenisaattorin käyttöä 3% selluloosamassalle.
- ITT Rayonier laboratorio, Whippany, New Jersey, USA
- 11 patenttia koskien
  - MFC valmistusta
  - MFC käyttöä

Fibrillointimenetelmät

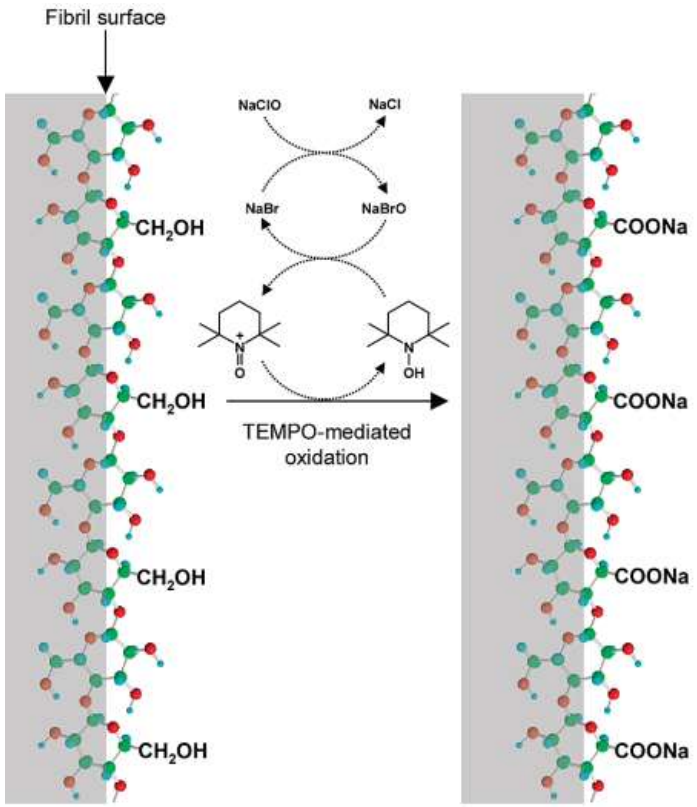


Energy consumption vary from 5580 kJ/kg to 78 800 kJ/kg
Meaning roughly 1500 kWh/ton to 20 000 kWh/ton

Fibrillointimenetelmät - Esikäsittelyt

More efficient operation, reduced energy comsumption and improved quality.

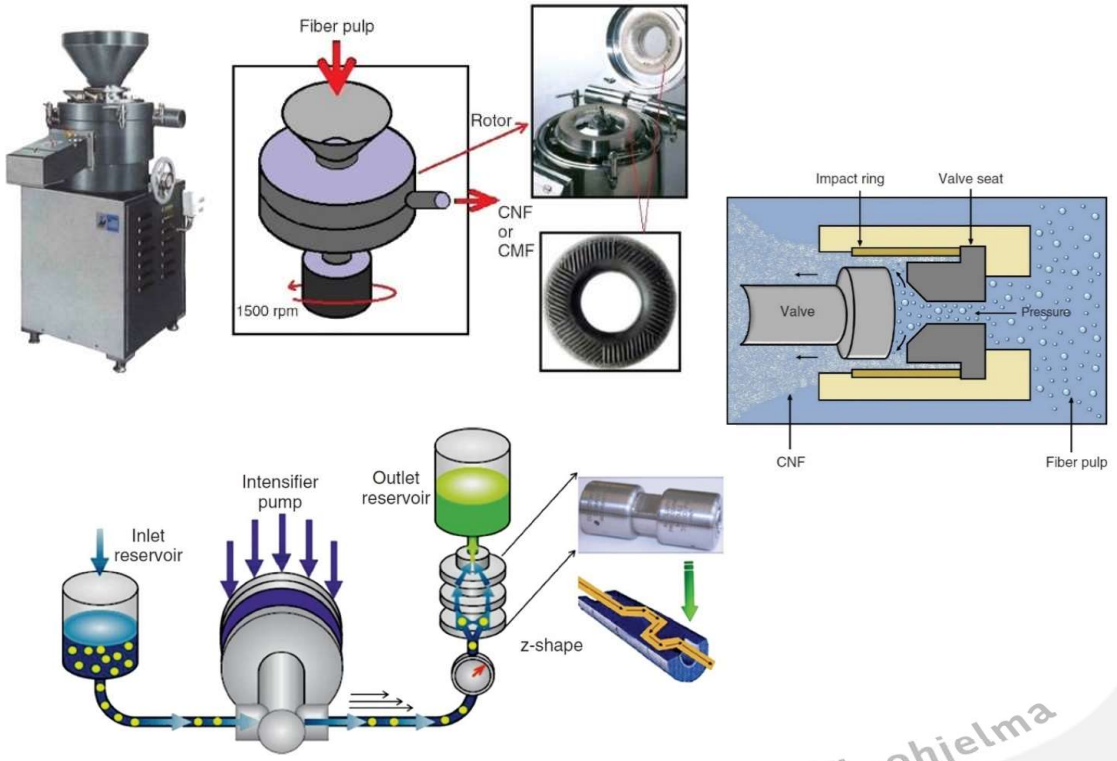
- TEMPO-mediated oxidation
  - Cellulose hydroxyl groups to carboxyl groups
  - TEMPO catalyst is toxic and difficult to recycle
- Periodate oxidation
- Enzymatic



Okita et al. Biomacromolecules 2010, 11, 1696

Fibrillointimenetelmät -mekaaninen

- High-Pressure homogenization
- Microfluidization
- High-intensity ultrasonication
- Grinding, microgrinding
- Cryocrushing
- Ball milling
- Steam explosion
- Dual water jet aqueous counter collision system



Kargarzadeh, H., Handbook of Nanocellulose and cellulose nanocomposites, 2017
Dufresne, A., Nanocellulose: From nature to high performance tailored materials, 2017
Phanthong, P., Nanocellulose: Extraction and application, 2018

Tulevaisuuden näkymät, sovelluskohteet ja haasteet

Tomas Björkqvist & Sanna Siljander

25.4.2019

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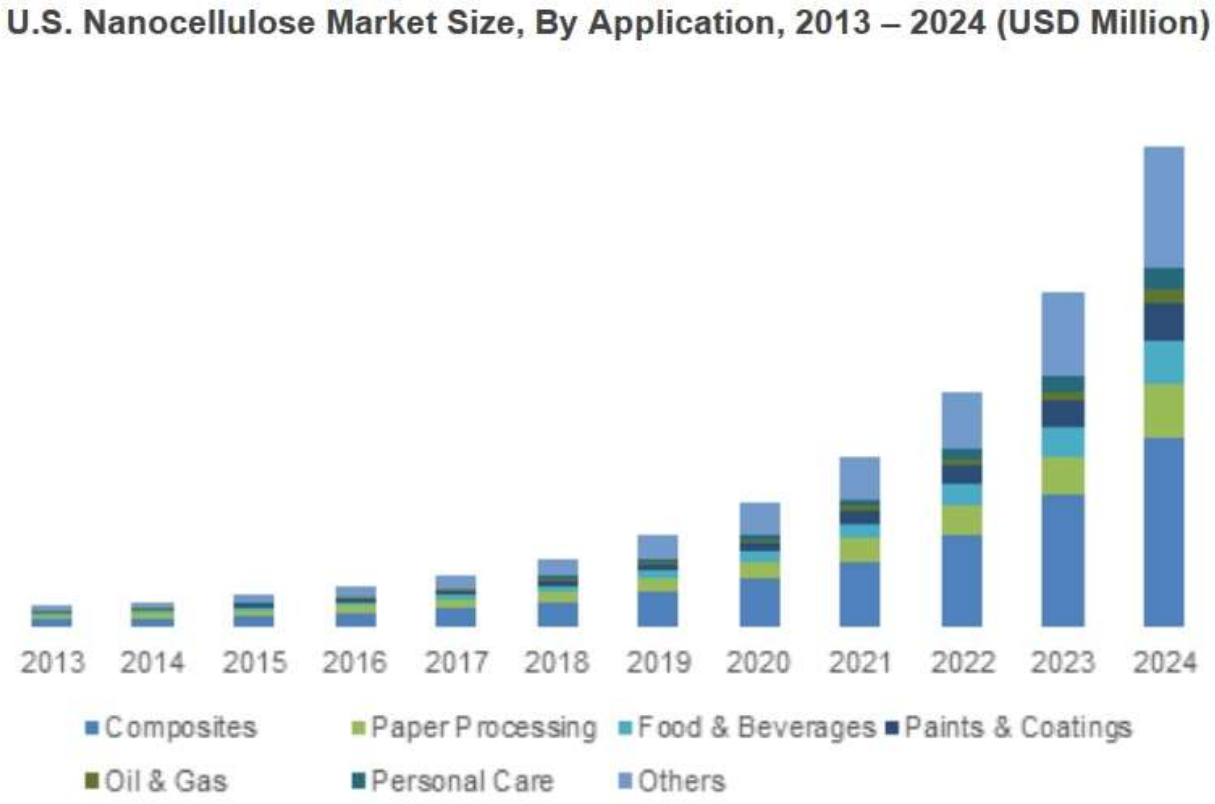
Tulevaisuuden näkymät

Nanocellulose market:

USD 1 billion by 2024

Nanofibrillated cellulose segment is said to gain the highest share of over

USD 540 million by 2024



https://www.gminsights.com/industry-analysis/nanocellulose-market

Kaupalliset toimijat

Kaupalliset toimijat

Producer	Process	Capacity	
Nippon Paper, Japan	TEMPO, carboxylated	560	
Turners Falls Paper, U.S.	Mechanical	520	*
University of Maine, U.S.	Mechanical	260	*
American Process, U.S.	SO_2 fractionation	130	*
CelluComp, U.K.	Chemical pre-treatment	100	
Chuetsu Pulp and Paper, Japan	Aqueous counter-collision	100	
Oji Paper, Japan	Phosphate esterification	40	
Sugino Machine, Japan	Mechanical	26	*
Seiko PMC, Japan	Modified hydrophobic	24	
VTT, Finland	Chemical, enzymatic	5	*
Tianjin Haojia Cellulose Co., Ltd., China	TEMPO, carboxylated	3	*
DKS Co. Ltd., Japan	TEMPO	1	
U.S. Forest Products Laboratory, United States	TEMPO, mechanical	<1	**
Daio Paper, Japan	N/A	Pilot	
ICAR-CIRCOT, India	Chemical, microbial	Pilot	
InoFib, France	Chemical pre-treatment	Pilot	
Luleå University of Technology, Sweden	Mechanical	Pilot	
Nanovin, Iran	N/A	Pilot	
U. of Kyoto (RISH), Japan	Modified hydrophobic	Pilot	
UPM, Finland	N/A	Pilot	

Capacity 2017
(metric tons/year, dry basis)

Sovelluskohteet

www.nipponpapergroup.com

Tulevaisuuden näkymät → Haasteet

Haasteet:

- Saatavuus
- Termistö
- Hinta
  - Suuri energian kulutus
- Alhainen kuiva-ainepitoisuus

Turvallisuus

Tukes:

https://tukes.fi/kemikaalit/nanomateriaalit

Työterveyslaitos

http://www.ttl.fi/partner/nanoturvallisuuskeskus/

EUR-Lex

https://eur-lex.europa.eu

ECHA

https://echa.europa.eu/fi/regulations/nanomaterials

EUON

https://euon.echa.europa.eu/fi/

Nano safety cluster

https://www.nanosafetycluster.eu

Kaupalliset toimijat - Sappi

https://www.sappi.com/nanocellulose

- A substitute for metal materials such as high-tech spun fibers, for example in vehicle manufacture
- Antimicrobial films and water absorbent pads in medical applications
- Electronic displays
- In sensors that could help monitor structures like bridges to detect stresses
- Food packaging material that prevents oxygen entry and spoiling
- A flavor carrier, suspension stabilizer and thickener in food
- A thickener in industrial applications
- As aerogel to mop up oil spills
- As an additive to improve the mechanical properties of rubber, latex, thermosetting resins, soya protein and starch-based matrices.

Kaupalliset toimijat - Borregaard

https://www.exilva.com/

- Adhesive and sealant systems
- Paint and coating systems
- Agricultural chemical products
- Cosmetics and personal care
- Liquid laundry and household products
- Cementitious systems

- For barrier air and gas barrier properties, Exilva can be extremely efficient. Our experience is that you will find abilities to improve your barriers at dosages of 1-5 g/m^2.

Kaupalliset toimijat – University of Maine

https://umaine.edu/pdc/

CNF/CMF	UMaine Cellulose Nanofibrils	Unit Size	Lead Time	Number of Units	Cost per Unit $USD	Cost - $USD S/H will be added
1	Standard Slurry, 3% Solids	**1 pound** 5-gallon pail	**1-2 Days**		$50	
2	Standard Slurry, ~15% solids	**1 pound** 1-gallon pail	**2-3 Days**		$75	
3	Standard Slurry, Freeze-dried	**1/4 pound** bag	**2-3 Days**		$200	
4	High fines slurry, 3% solids	**1 pound** 5-gallon pail	**Made to Order**		$75	
5	CNF Slurry – bulk volume	55-gallon barrel	**Please Call**			

Kaupalliset toimijat - Nanografi

Several application areas including foods, cosmetics, pharmaceuticals, paints, drilling muds, paper additives and paperboard barriers, medical products, etc

Wide: 10-20 nm, Length: 2-3 µm, Dry powder

30 €/5 grams
49 €/25 grams
128 €/100 grams
466 €/500 grams
794 €/1000 grams

Kaupalliset toimijat – Cellulose lab

https://www.celluloselab.com/

2019 Cellulose Lab Nanocellulose Products Price

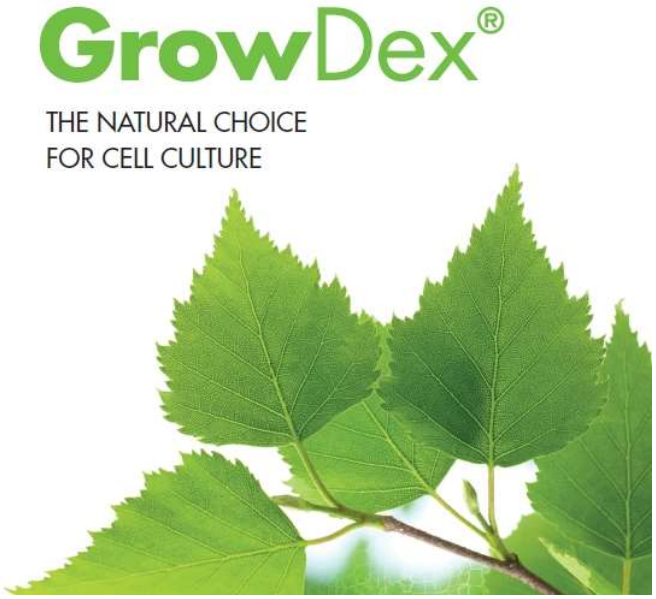
www.CelluloseLab.com

Product Series	Cellulose Lab Catalog Number	Product	Diamension, Surface group	Form	Small Package Order		Large Package Order		Extra Large Order
					Size (oven-dry weight basis)	Cost, USD per gram (oven-dry weight)	Size (oven-dry weight basis)	Cost, USD per gram (oven-dry weight)	
	CNF-Slurry-SMC	Cellulose Nanofibrils, prepared by supermass colloider	Width: nominal width 30-80 nm; Length: up to several hundred micron Surace Group: Hydroxyl Hydrophilic	1-3% solids in water	1 g — 500 g	$2.00	501 g —5 kg	$1.75	
	CNF-Slurry-HPH	Cellulose Nanofibrils, prepared by high pressure homogenizer	Width: 10-60 nm; Length: 800-3000 nm Surface Group: Hydroxyl Hydrophilic	1-2% solids in water	1 g — 500 g	$4.00	501 g —5 kg	$3.50	
	CNF-FD	Cellulose Nanofibrils Freeze-dried	Width: nominal width 30-80 nm; Length: up to several hundred micron Surace Group: Hydroxyl Hydrophilic	Dry	1 g — 200 g	$6.00	201 g — 2 kg	$5.50	
	CNF-CM-Slurry	Carboxymethylated Cellulose Nanofibrils	Width: 10-13 nm; Length: 1000-3000 nm Surface Group: Carboxymethyl Hydrophilic	0.5% - 5% solids in water	1 g — 60 g	$15.00	61 g — 1 kg	$12.00	
	CNF-CM-FD-P	Carboxymethylated Cellulose Nanofibrils, Freeze-dried, Pulp material	Width: 10-13 nm; Length: 1000-3000 nm Surface Group: Carboxymethyl Hydrophilic	Dry	1 g — 60 g	$15.00	61 g — 1 kg	$12.00	

Kaupalliset toimijat - UPM

https://www.upmbiomedicals.com/for-life-science/growdex

UPM's GrowDex® is the natural solution for cell culture - a bio-friendly hydrogel created from the Birch tree. GrowDex is a ready to use hydrogel that mimics the extracellular matrix (ECM), supporting cell growth and differentiation with consistent results.



GrowDex® 2.5 ml syringe View more » Catalogue code: 100103002	2.5 ml	In stock	€120.00
GrowDex® 5 ml syringe View more » Catalogue code: 100103005	5 ml	In stock	€160.00
GrowDex® 5 ml syringe + GrowDase™ combo pack View more » Catalogue code: 100103905	7.5 ml	In stock	€300.00
GrowDex® 10 ml syringe View more » Catalogue code: 100103010	10 ml	In stock	€290.00
GrowDex® 3 x 5 ml syringe multipack View more » Catalogue code: 100103305	15 ml	In stock	€430.00

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Kiitos!

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25.4.2019

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