COST Action FP1405

Active and intelligent fibre-based packaging – innovation and market introduction

Novel bio-based materials for active and intelligent packaging

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EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

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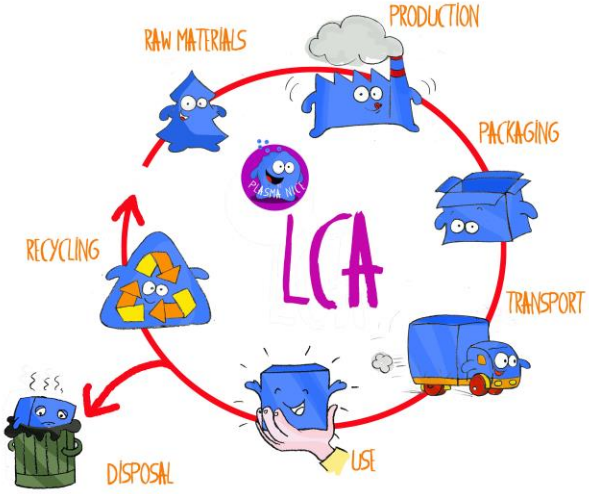
Introduction: Bioeconomy

- **Bioeconomy** is based on the shift from fossil to renewable raw materials to respond to the challenges of climate change, ecological scarcity and depletion of natural resources.

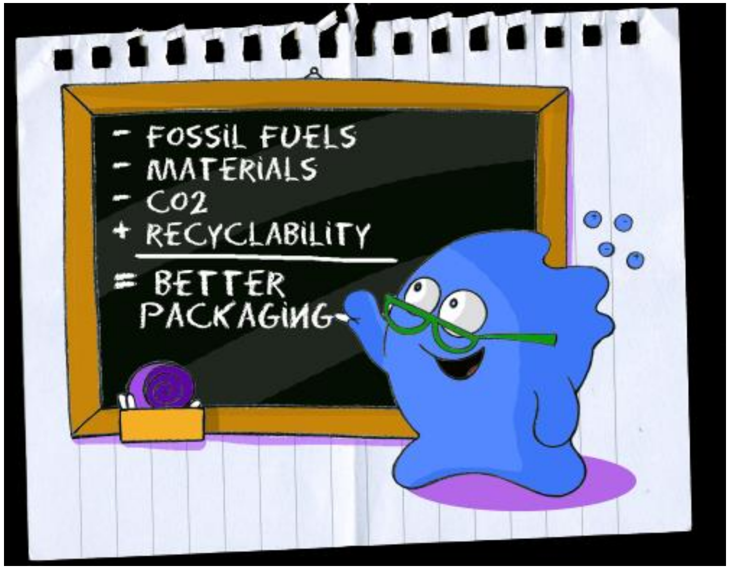
➢ It means production that utilises renewable raw materials and develops innovations and tecnologies based on that

- **Packaging** plays an important role i bioeconomy.



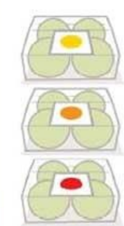
Introduction: Today's package development

- Packaging materials are usually multilayer structures
  - ➢ "Less is more" – optimisation of materials
  - ➢ Lighter packages save energy and environment
- Circular economy: biodegradability, compostability, environmentally friendly, recyclability, re-use….
  - ➢ Renewable alternatives for oil-based (non renewable) materials
- Demands for packaging industry (e.g.):
  - – Internet shopping is increasing
  - – Delivery chains are evolving
  - – Food losses should be prevented
  - – Product safety
  - ➢ Active and intelligent solutions

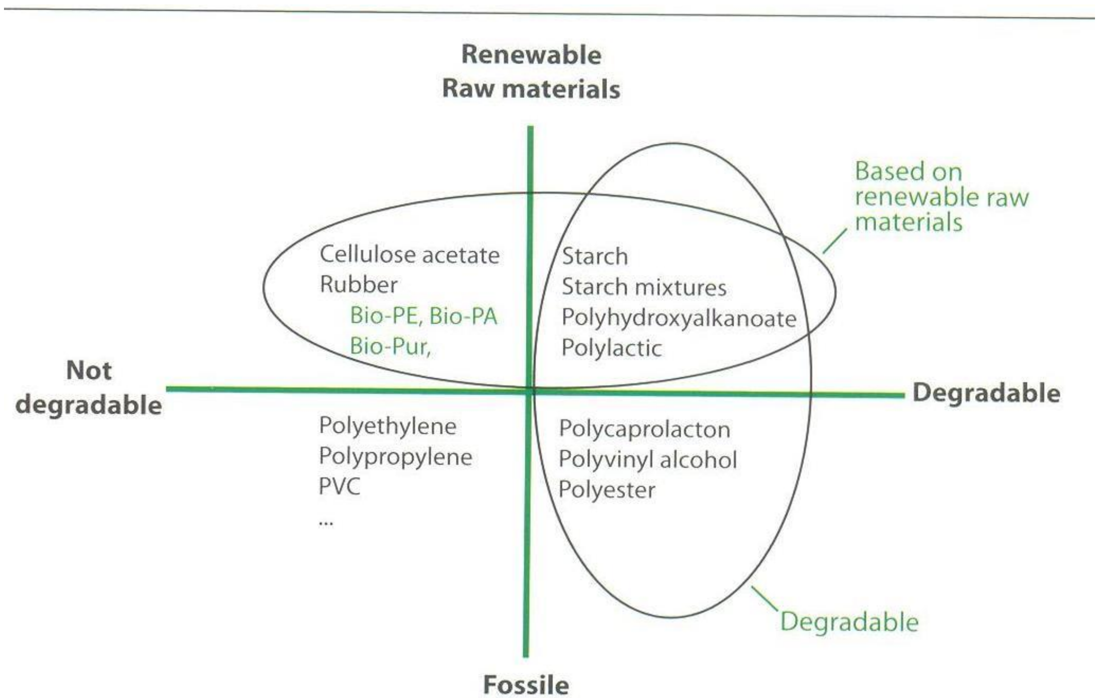


Introduction: A&I packaging

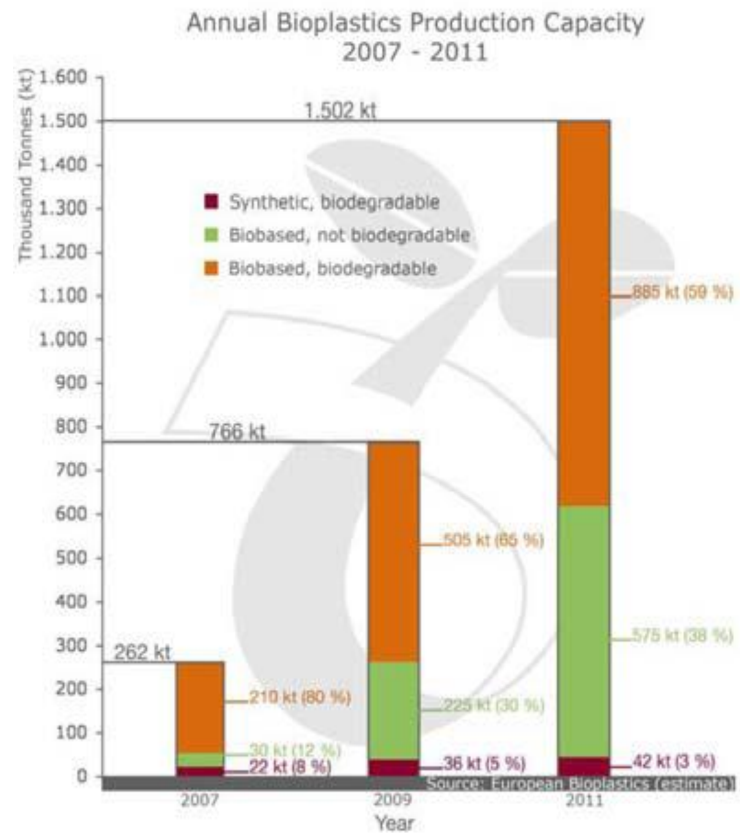
- Most of the current active or intelligent packaging solutions are plastic-based, so there is a clear demand for **renewable and sustainable solutions** to create new packaging materials and concepts.
- The use of **bio-based materials** in packaging decreases the dependence on fossil fuels. Wood based biomass that is available in a large scale offers attractive "green" polymers.
- Also biopolymers that are based on agricultural or other waste streams offer interesting alternatives for traditional oil-based polymers.



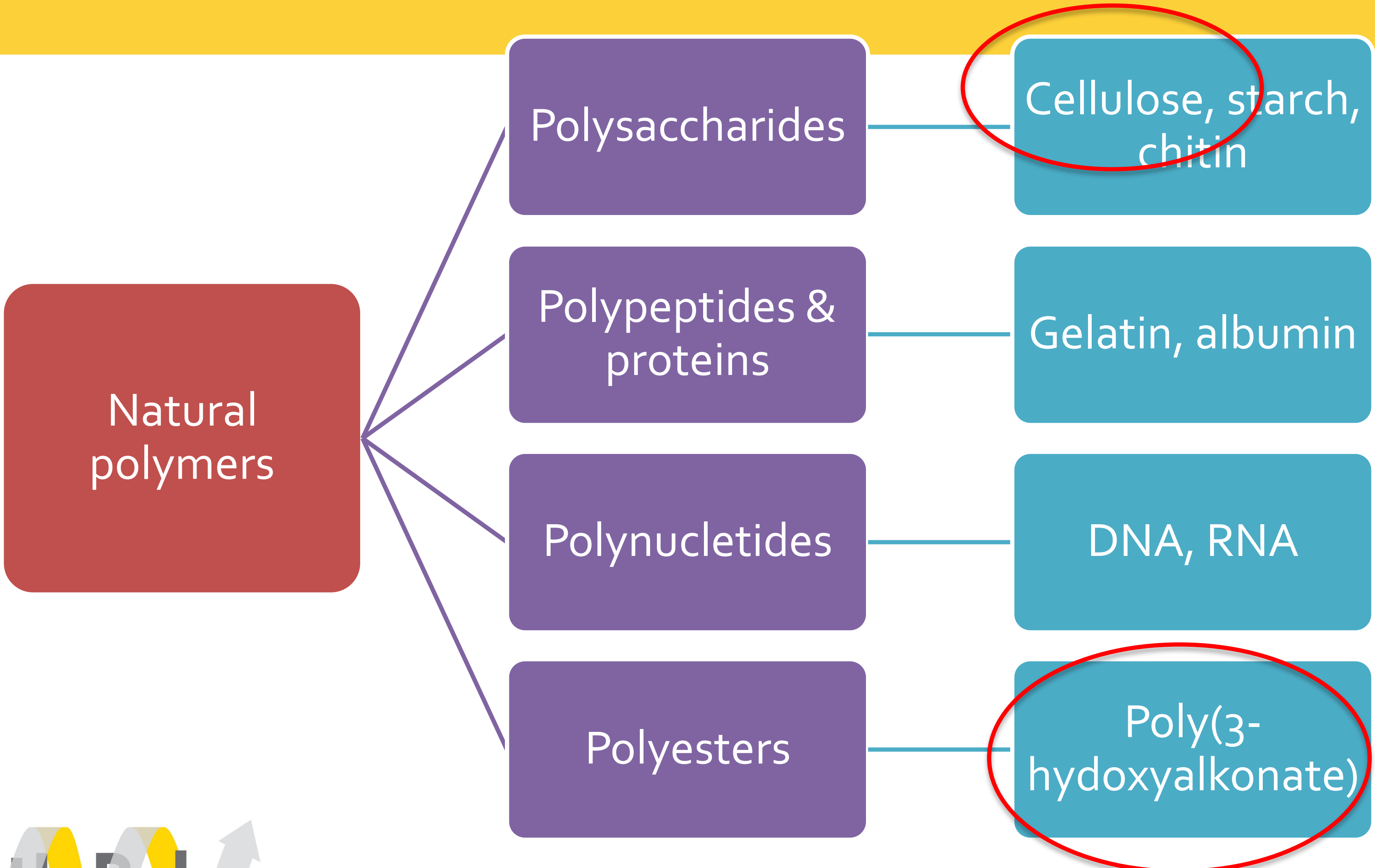
Classification of natural polymers based on raw materials



Source: Fachhochschule Hannover

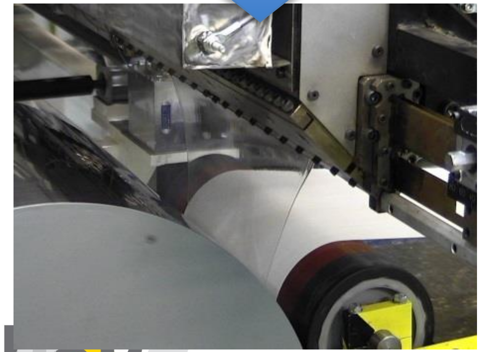


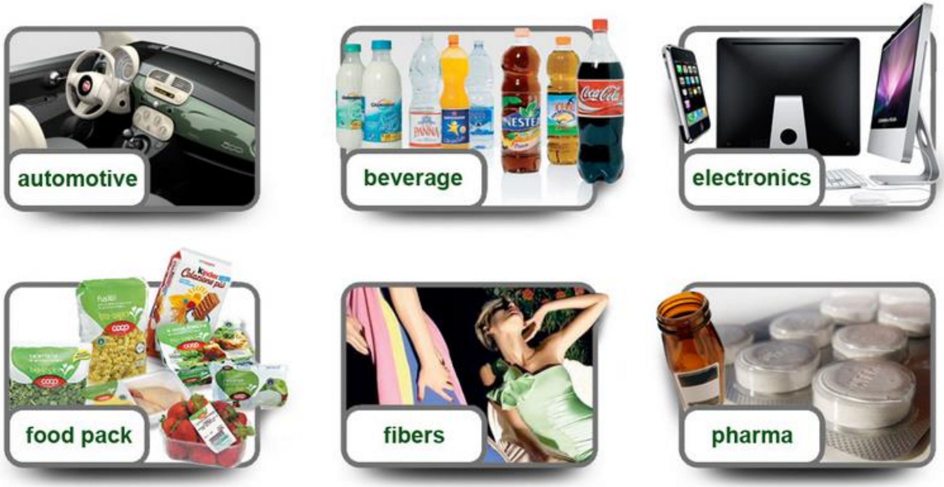
Classification of natural polymers based on structure



Bio-based materials for packages

- Wood-based materials like cellulose and other biopolymers provide new alternatives for packaging applications
- **Example: Biodegradable packaging material**
  - Paper or board + biopolymer (PHA) based on plant waste



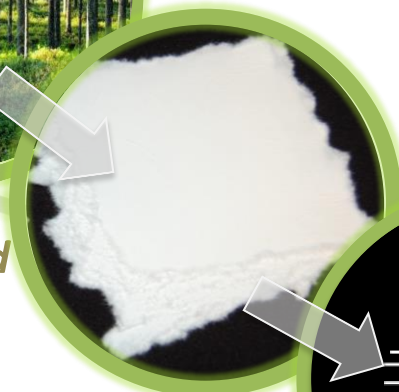


Ref. www.tut.fi, www.bio-on.it

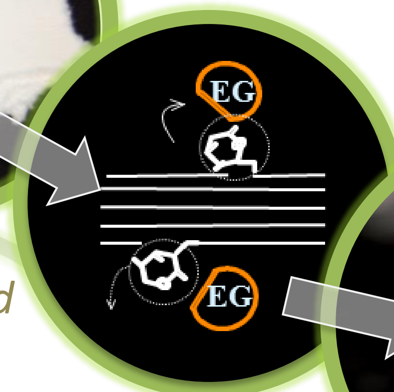
Preparation of cellulose and cellulose/lignin films

- **Biocelsol-process is an enzyme-catalysed water-based cellulose dissolution method without any hazardous chemicals.**
  - Dissolving pulp is pre-treated with cellulose-specific enzymes
    - Pre-treated cellulose is dissolved into water-based sodium zincate solvent through freezing-melting cycle
      - Films are formed with a lab scale hand coater and coagulated in mild sulfuric acid

Softwood



*Processed into **pulp***



Treated by enzymes

*Dissolved into **solvent***

*Coagulated into **Films***

Cellulose/lignin film

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Mechanical properties of cellulose film

Sample		Thickness, µm	Tenacity, MPa	Elongation at break, %	Ref.
Cellulose film (NaOH/ZnO)	**DRY**	**30 – 37**	**107**	**26.8**	**This work***
Cellophane	DRY	20-40	125	22	a
Experimental cellulose film (NaOH/urea)	DRY	70 ± 6	40	4	b
Experimental cellulose/starch, ionic liquid	DRY		32	96	c

*The thickness was measured according to ISO 4593:1999. The mechanical properties of the films was determined according to ISO 527-3:1998 by using Instron 5544 machine at institute of Chemical fibres, Poland

a) Navard (2012) The European Polysaccharide Network of Excellence (EPNOE), DOI 10.1007/978-3-7091-0421-7

b) Han, Yan, Chen, Li and Bangal (2011) Cellulose/graphite oxide composite films with improved mechanical properties over a wide range of temperature. Carbohydrate Polymers 83: 966-972.

c) Wu, Wang, Li, Li and Wang (2009) Green composite films' prepared from cellulose strach and lignin in room temperature ionic liquid. Bioresource Technology 100: 2569-2574

Oxygen permeability

Sample	Thickness, µm	OTR, ml m^{-2} day^{-1}	Ref.
Cellulose	**32 ± 2**	**8**	**This work**
Cellophane	21	3	a
MFC	21	17	b
Polyester	25	50 – 130	c
EVOH	25	3 – 5	c
Polyethylene LD	25	7800	c
Polyethylene HD	25	2600	c

References:

a) Kjellgren and Engström (2006) Influence of base paper on the barrier properties of chitosan-coated paper. Nordic Pulp Pap Res J 21(5):685–689. DOI 10.3183/NPPRJ-2006-21-05-p685-689

b) Syverud and Stenius (2009) Strength and barrier properties of MFC films. Cellulose 16:75-85. DOI 10.1007/s10570-008-9244-2

c) Parry (1993) Principles and applications of modified atmosphere packaging of foods. Chapman & Hall, Suffolk

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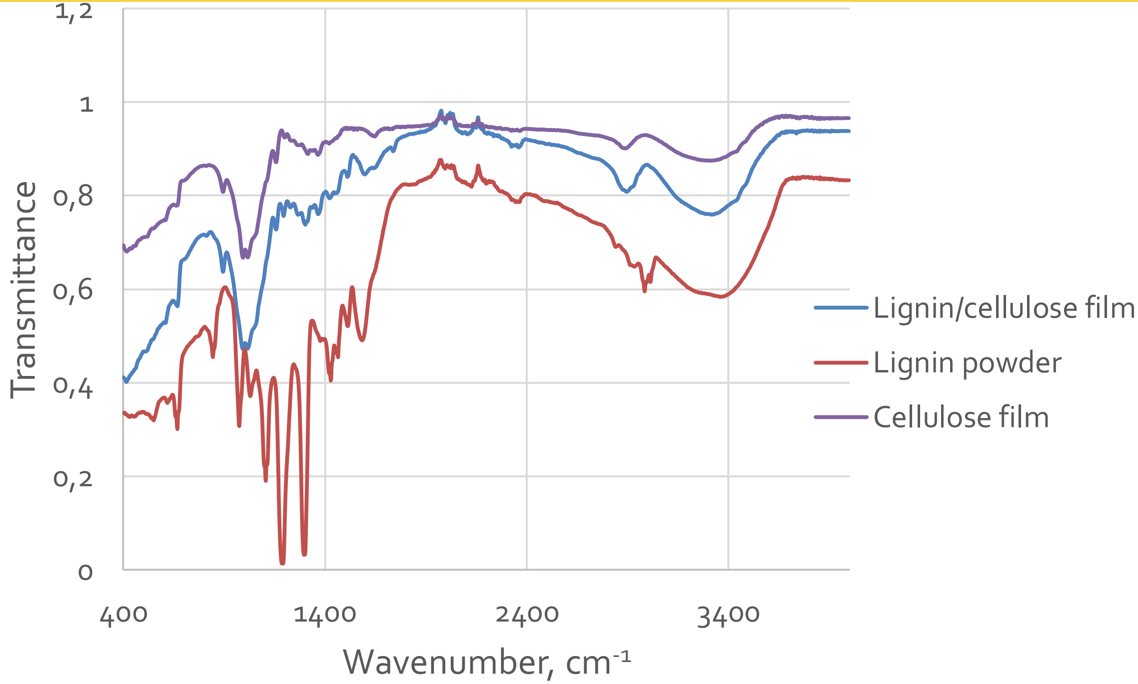
Chemical structure of cellulose and cellulose/lignin films



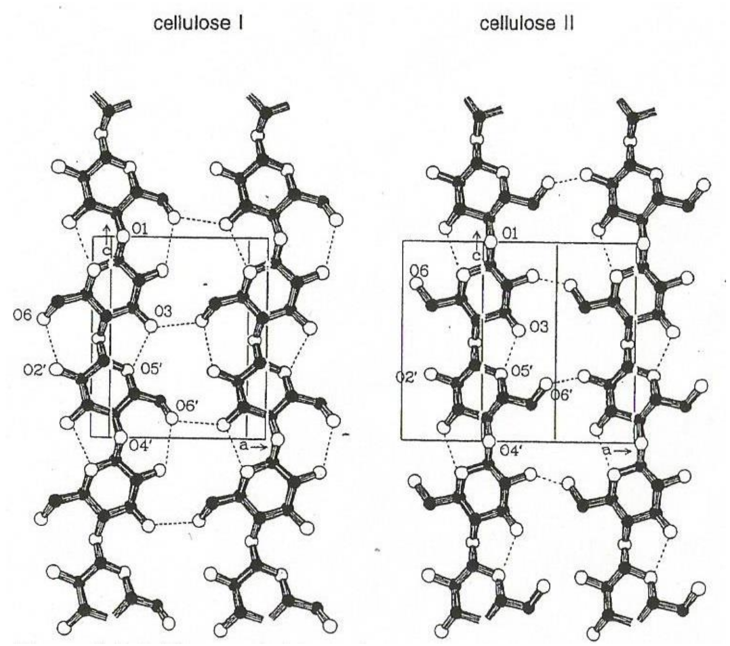
<u>The crystal structure of regenerated cellulose is Cellulose II</u>, the notable changes in FTIR spectrum occur at the wavelengths of 1430, 1160, 1111 and 897 cm^{-1}

The peaks of cellulose and lignin are overlapping, but phenolic hydroxyl groups of the lignin sample show characteristic peaks at the range of 1800 – 1300 nm that are seen in our sample in 1583, 1511 and 1428 cm^{-1} that are not seen in the cellulose sample.

Potential of cellulose as intelligent packaging

- Piezoelectricity is a fundamental property of cellulose
- Piezoelectricity is displayed by crystal structure lacking center symmetry
- The crystal structure of Cellulose II is monoclinic which is non-centrosymmetric

- **Inherent piezoelectricity of cellulose film may be used as a sensor and an actuator in intelligent packaging**



Klemm et al.(1998) *Comprehensive Cellulose Chemistry.* Weinheim: Wiley-VCH.

Potential of lignin as antioxidant in active packaging

- Lignin is the second most abundant natural polymer
- Complex chemical structure with aromatic rings, monomers are phenyl propanes
- Highly branched
- **Antioxidant activity** is based on polyphenolic structure

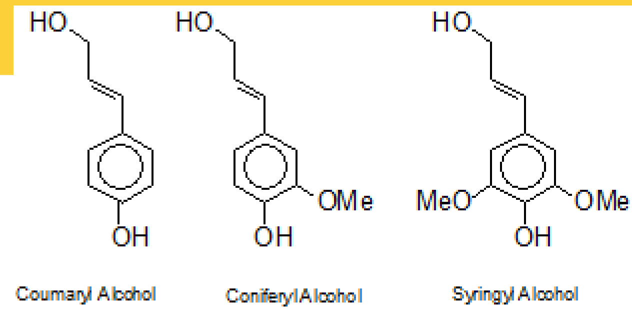
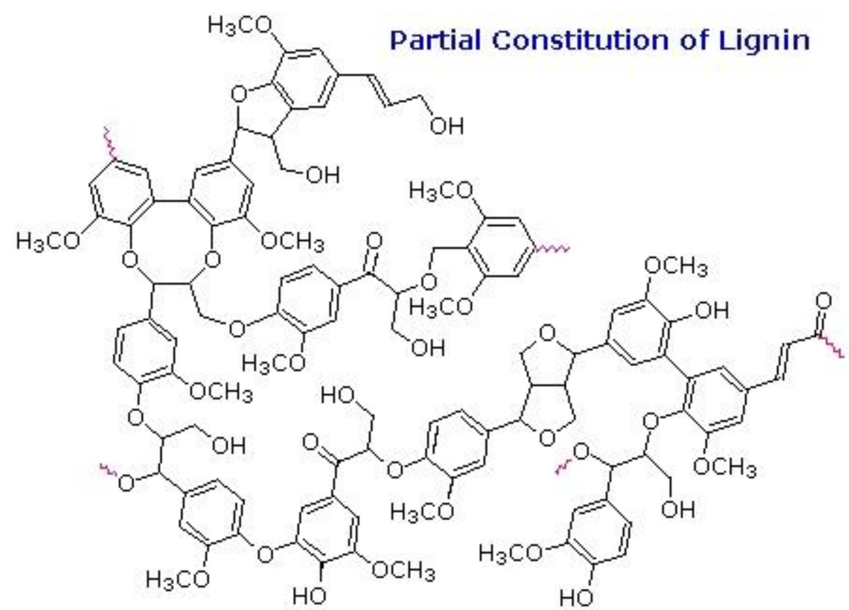


Figure 1: The three phenyl propane monomers in lignin

- Radical scavenging activity of lignin may be exploited in active packaging
- Lignin has shown also **antibacterial properties**



Challenges with biopolymers

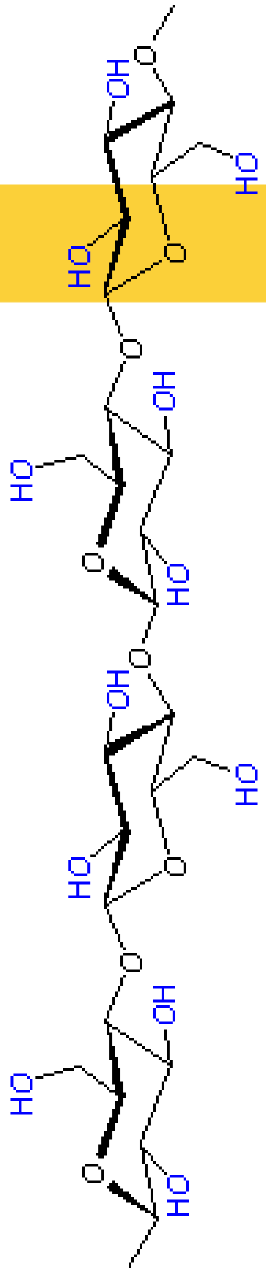
- Cellulose is a **hydrophilic** material -

It absorbs moisture also from air

- For example cellulose swell in contact with water

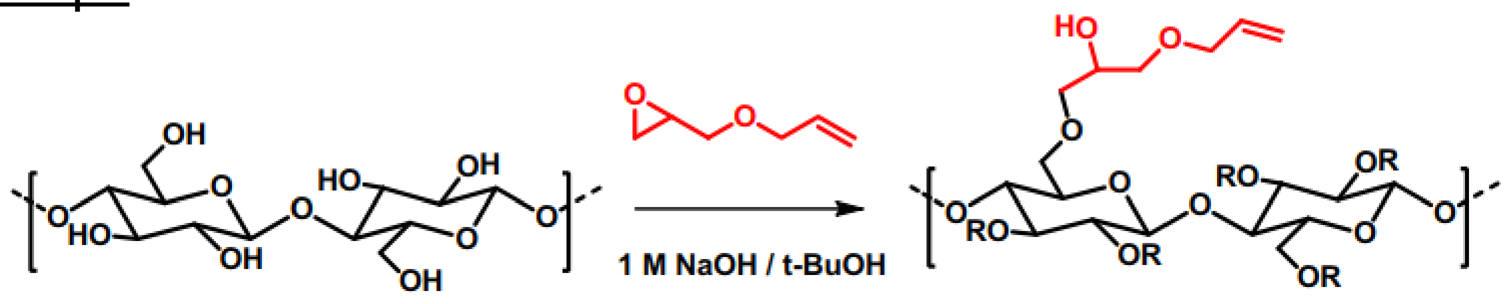
→The mechanical and barrier properties will weaken due to absorbed water

- Also some other biopolymers are moisture sensitive (like PLA), which restricts their use in certain applications



Chemical modification of cellulose

- **Dissolving pulp can be chemically modified** with allyl glycidyl ether to obtain 3-allyoxy-2-hydroxypropyl substituted cellulose
- The substituents have the reactive carbon double bonds, which makes it possible to further attach functional groups to the films



Synthesis of 3-allyloxy-2-hydroxypropyl A ether derivatives of cellulose. R=H or substituted with A groups

Ref. Vehviläinen, Kamppuri et al. (2015) Regeneration of fibres from alkaline solution containing enzyme-treated 3-allyloxy-2-hydroxypropyl substituted cellulose. Cellulose 22:2271-2282

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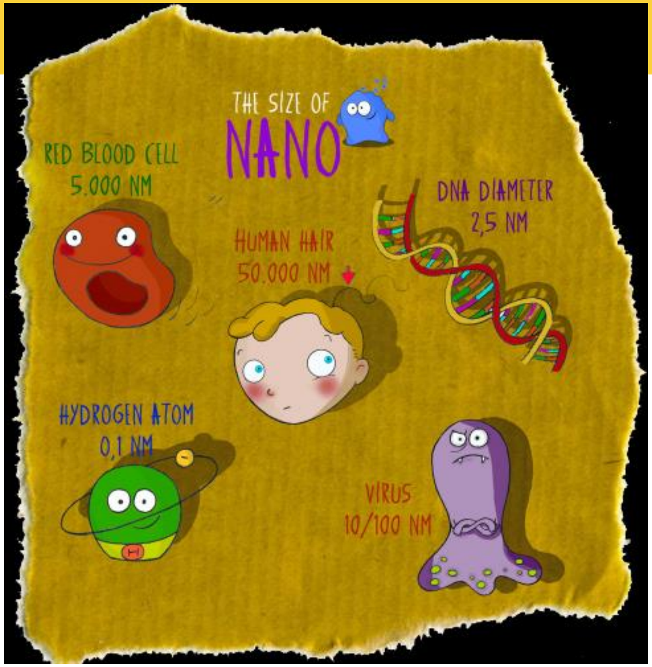
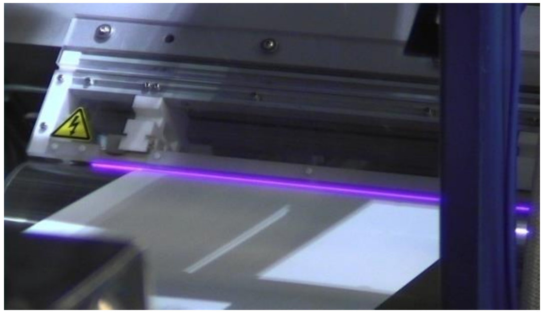
Nanotechnology for surface modification 1(2)

- Thin nanoscale coatings/layers
  (~ 10-100 nm)
  - Good barrier properties with very thin layers
  - Source reduction: Less material is needed
  - Replacement of materials like Al or oil-based polymers
- Several techniqures like ALD (Atomic Layer Deposition), PVD (Physical Vapour Deposition) and LFS (Liquid Flame Spray)



Ref. www.tut.fi/plasmanice



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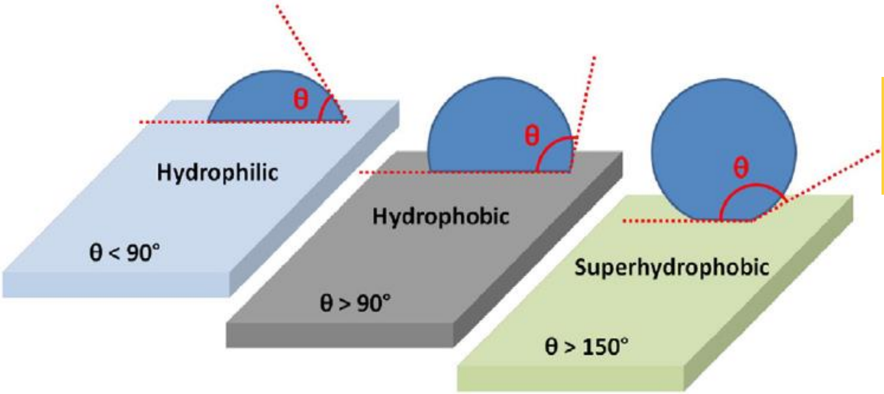
Nanotechnology for surface modification 2(2)



- Surface modification and generation of new functionalities
  - ➢ Repellency/Absorbency
  - ➢ Adhesion properties
  - ➢ Self-cleaning
  - ➢ Surface energy patterning
  - ➢ Adjusted wettability
  - ➢ Etc. etc.

Ref: Tuominen, M. et al 2013

Several applications:

- Packaging
- Textiles
- Printed electronics
- Flexible photovoltaics
- Microfluidics....


Ref: http://nanomend.eu/

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Conclusions

- Wood-based polymers and other biopolymers that are based on renewable raw materials offer interesting alternatives for packaging industry

➢ Packaging films and coatings for paper and board

➢ Renewable materials for A&I solutions

Ref.: Sitra, Heureka

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Thank you!

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Further information:

- www.tut.fi/mol
- www.tut.fi/plasmanice
- http://nanomend.eu/
- www.tut.fi/ROLLIPS
- http://www.actinpak.eu/
- www.uusipuu.fi