



PULP AND PAPER
INSTITUTE, LJUBLJANA
Innovative Cellulose Products

Surface and chemical modifications of cellulose for food packaging applications

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The challenge

- How to control cellulose wettability/hydrophobicity with sustainable modification techniques based on renewable resources such as biopolymers and green chemistry.
- As the paper industry aims for high recyclability ratio for food packaging applications (self declared 90% by 2030 - 4evergreen alliance) these modifications need to ensure:
- Low LCA and energy consumption
- Full recyclability with minimal harmful processing chemicals in fibers, processing waters and production residues.

Current situation

- Previously the hydrophobization of cellulose with internal and surface sizing was aimed for processing improvements during papermaking as well targeted improvements of strength.
- But nowadays the focus is on barrier properties where surface sizing does not meet often the required water resistance of packaging materials.
- So it is a give and take situation:
- Cellulose can never be non permeable as classic fossil based polymers films without additional steps:
- Processing the cellulose to nanoscale and combine it with biopolymers
- Coat it - but you have to find the balance of the coating weight with biodegradation and recyclability
- Or chemically, physically or structurally modify it - what this presentation is about.

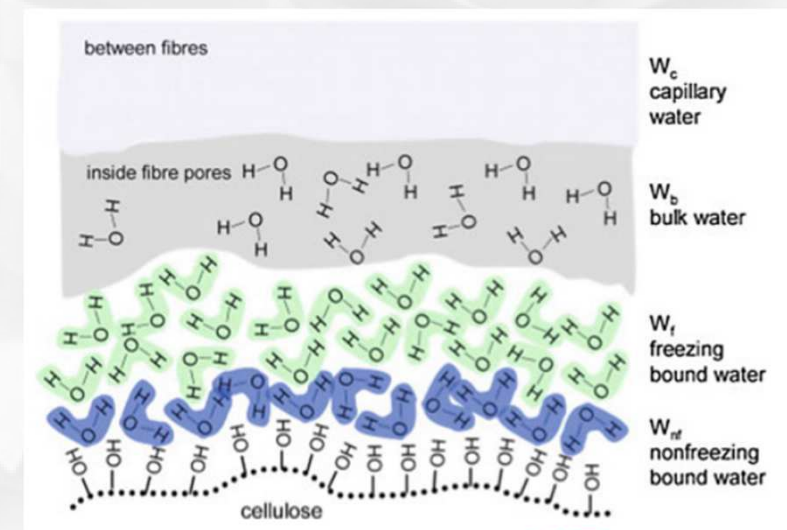
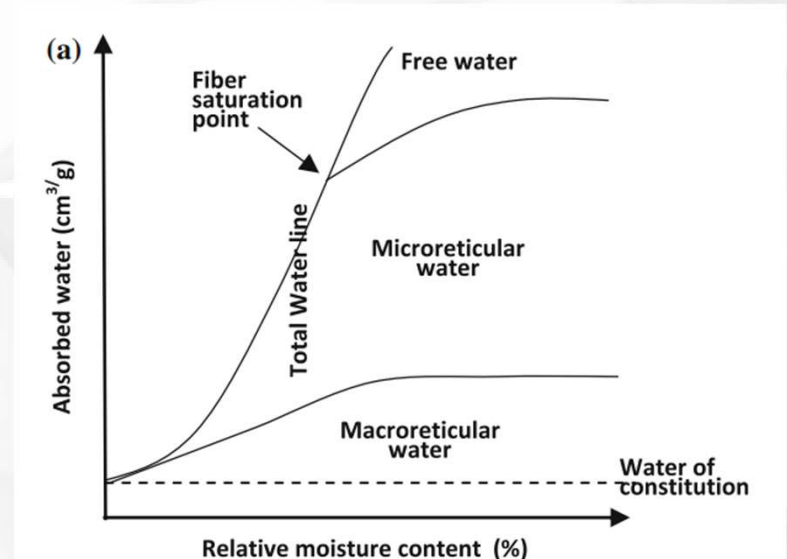
How barriers were achieved by now?

- The barrier properties and hydrophobicity of papers is nowadays mainly controlled by adding wax or fluorine derivatives.
- Waxed surfaces are difficult to glue and require additional corona or plasma treatment for preserving good printing properties,
- They tend to migrate during the drying process and form a continuous film holding the fibres together and reducing repulpability and bioegradation.



The cellulose - water tango

- The water transport into paper is generally based on a diffusion model, with following mechanisms:
- penetration in the capillaries of the sheet,
- surface diffusion along the capillary walls,
- diffusion through the fibres and
- vapour phase transport through the fibres.
- The dominating mechanism depends on the network structure, external pressure, time and hydrophobic fibre properties.



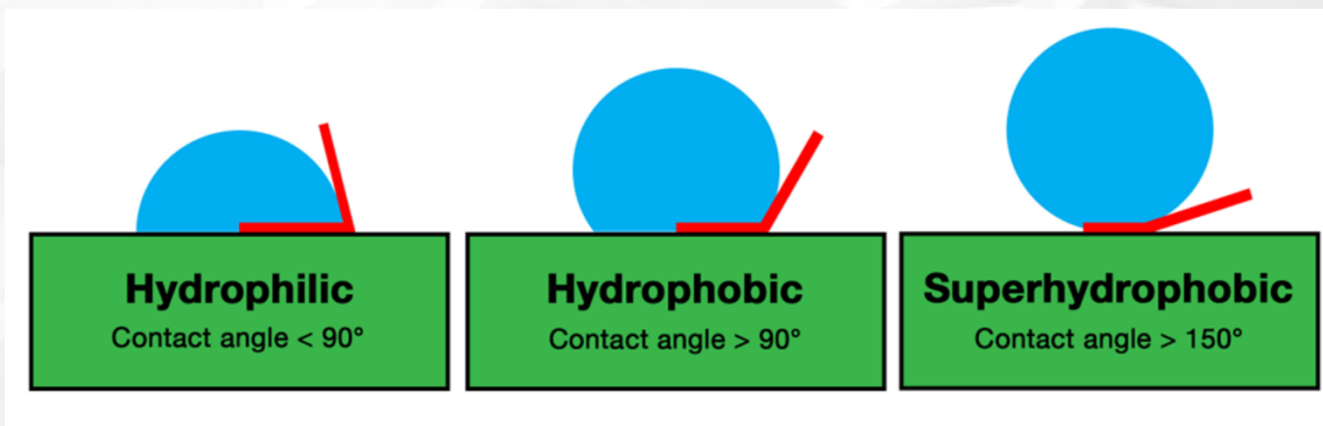
Water penetration into paper

- The water absorption in paper is dominated by penetration under capillary pressure, interfibre penetration and molecular diffusion.
- Therefore, the absorption mainly depends on the surface tension and capillary size of water in contact with the paper fibre.
- The degree of swelling depends on the amount of acidic groups in the carbohydrate fraction that enhance the interaction with water.
- As a result, the substitution of hydroxyl groups by hydrophobic groups, e.g. by acetylation decreases swelling

Nothing is ideal - paper surface and ideal case

- The wetting of fibrous and paper surfaces is complicated:
- Physical heterogeneities (e.g. surface roughness due to uneven fibres and porosity).
- Chemical heterogeneities (e.g. hydrophobic domains with variable size and concentration after internal sizing or coating).
- If we create external or internal barrier with coatings or sizing chemical and morphological heterogeneity of paper substrates further increases.
- This complex structure of cellulose fibres and papers often inhibit the use of common techniques for surface modification due to absorbance, swelling, inhomogeneity, porosity or thermal stability.

So for what are we aiming for?



- The contact angles of the usually used plastic materials:
- 72 to 102 for polyethylene, polypropylene, and polyethylene terephthalate.
- PLA and PHVB between 62-68.

Contact angle measurements

- Liquid drop on a solid surface – modifies its shape based on the interfacial tensions – creates material property of the system – contact angle.
- The measurement derived – can also be used for converting issues and to measure the use of plasma for example:

	Native	Corona	Flame	Helium Plasma	Argon Plasma
LDPE	103	75	77	75	76
PP	108	81	83	86	89

Contact angle measurements

- TAPPI T558, ASTM D5725



Contact angles of the paper components

	θ_0	$\theta_{15\text{ sec}}$	$\theta_{30\text{ sec}}$	θ_{ESEM}
α -cellulose	26	0	0	0
Cellophane	34	29	28	35
HWK	43	0	0	0
Holocellulose	56	0	0	0
TMP	73	30	25	70
Lignin	67	53	49	61
AKD	106	87	84	93
ASA + starch	77	76	75	—
Starch	43	42	42	—

Abbreviations: HWK = hardwood kraft pulp, TMP = thermo-mechanical pulp, AKD = alkyl ketene dimer, ASA = alkenyl acid anhydride.

(Liukkonen 1997)

So how we test how „good“ we are...

- The paper industry is mostly using the Cobb method – the amount of water absorbed into the surface by a sized (non-bibulous) paper, paperboard, and corrugated fibreboard paper or paperboard sample in a set period of time, usually 60 or 180 seconds (Cobb60 or Cobb180).
- Water absorbency is quoted in g/m²
- Standardized and easy
- Challenge is the dynamics and the „average“ sizing values
- There are also dynamical solutions – based on timescale measurement – but also miss some ad/absorption mechanics
- Or HST (Hercules Size Test) where Formic Acid ink to penetrate the product and the test is run according to TAPPI Test Method T530

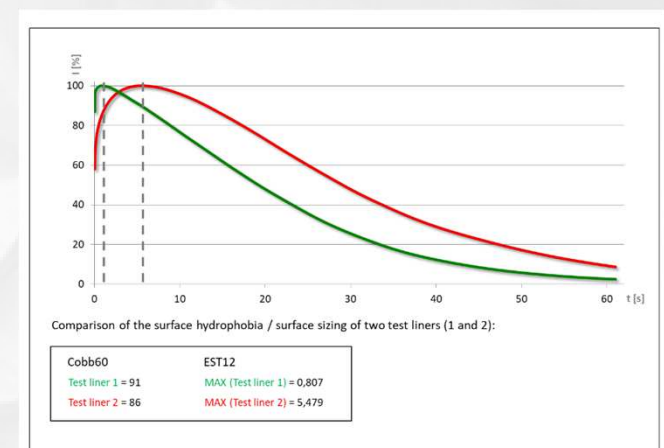
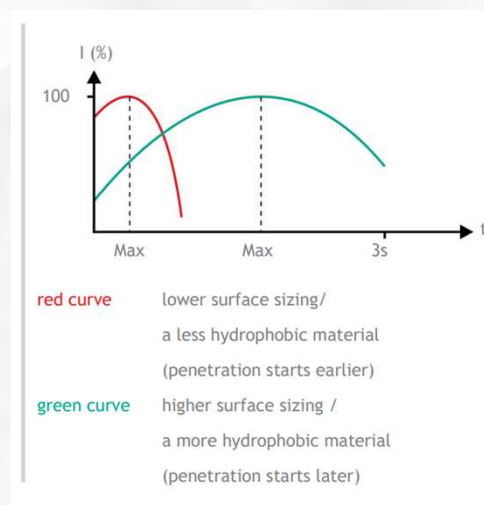


Ultrasound methods – for precise work

Ultrasound measurement of liquid penetration into paper and boards.

Not standardized – but specialized – with the aim of solving problems in converting (high speed dynamics)

Correlation with COBB but needs more knowledge about the processes.



So how to tackle the challenge?

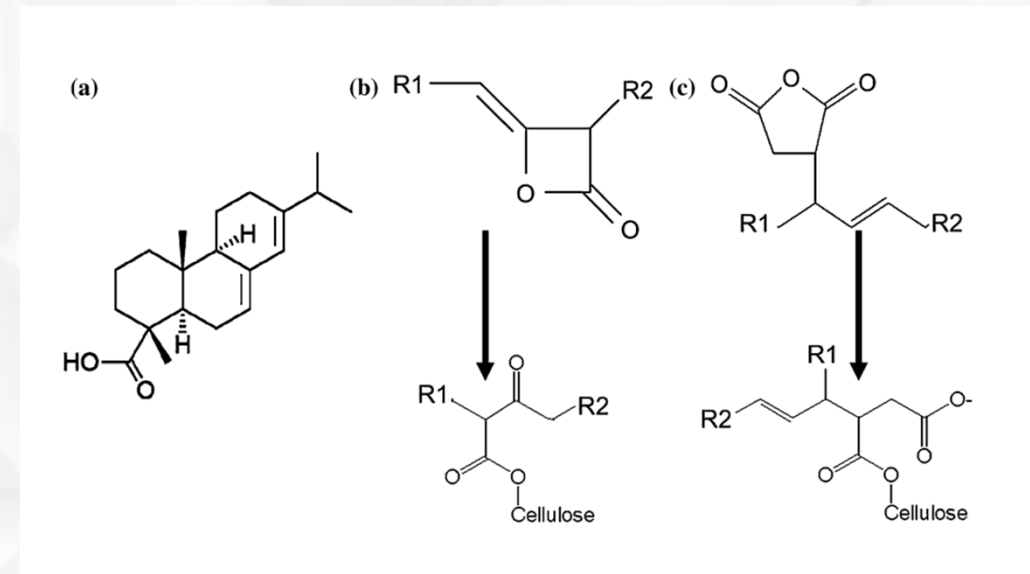
- Based on the general contact angle theory of Wenzel the surface hydrophobicity can be improved by:
- Reducing the surface energy, and
- Increasing the surface roughness of an initially hydrophobic surface, i.e. increasing the surface area on a microscopic scale.
- Or multifunctionalities of the paper chemicals.
- The strategy: Inhibit the adsorption of water vapor onto a package surface - more efficacious than later addressing the reduction of subsequent diffusion through the packaging (with nanofillers).

Hydrophobicity by paper sizing

- Papers are commonly protected against water by treating the pulp with hydrophobic agents
- The internal sizing is done by wet-end fibre modifications, using nonreactive agents or synthetic agents that chemically react with the cellulose hydroxyl groups to form stable ester linkages.
- For internal sizing, the dynamics of wetting are crucial as colloidal substances are first adsorbed onto the fibres and consequently wet the fibre surface under drying.

Traditional paper sizing for papermaking

- Rosin is usually added together with aluminium salts (acidic sizing)
- Alkene ketene dimer wax (AKD,
- Alkenyl succinic anhydride (ASA, neutral and alkaline sizing
- Different starches (chemically and enzymatically modified).



Classic surface sizing has additional effects

- AKD reduces the chances of machine breakdown
- Lesser difficulties in water recycling
- But drying method, time, temperature and raw material pH value needs to be controlled
- Better printability in some printing technologies

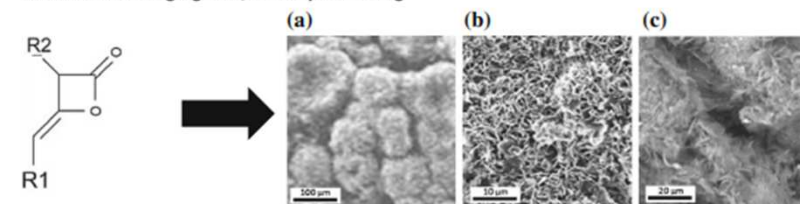
- ASA attains better operational capacity
- Preserves the dimensional stability of paper
- Reduces dust accumulation and protects from machine downtime.
- Also improves printing in some technologies.

Novel methods for traditional sizing

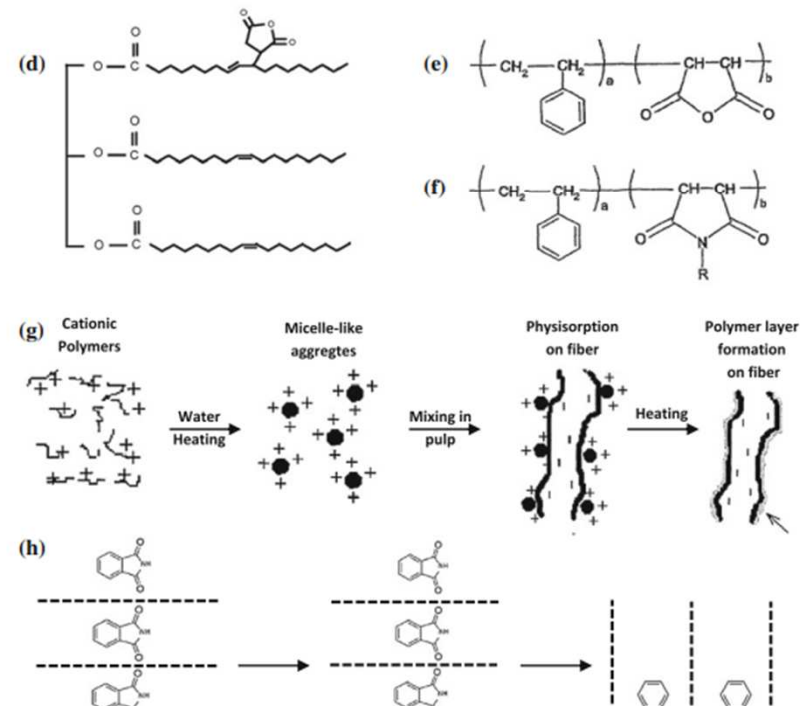
- Controlling the fractal growth of AKD crystals, a rough surface with contact angles of CA 174/109
- AKD deposition from a rapidly expanding supercritical carbon dioxide solution CA -173
- This tech-nique was also applied in combination of AKD with a crystallising wax from organic solvents.

INTERNAL SIZING

Traditional sizing agents, novel processing



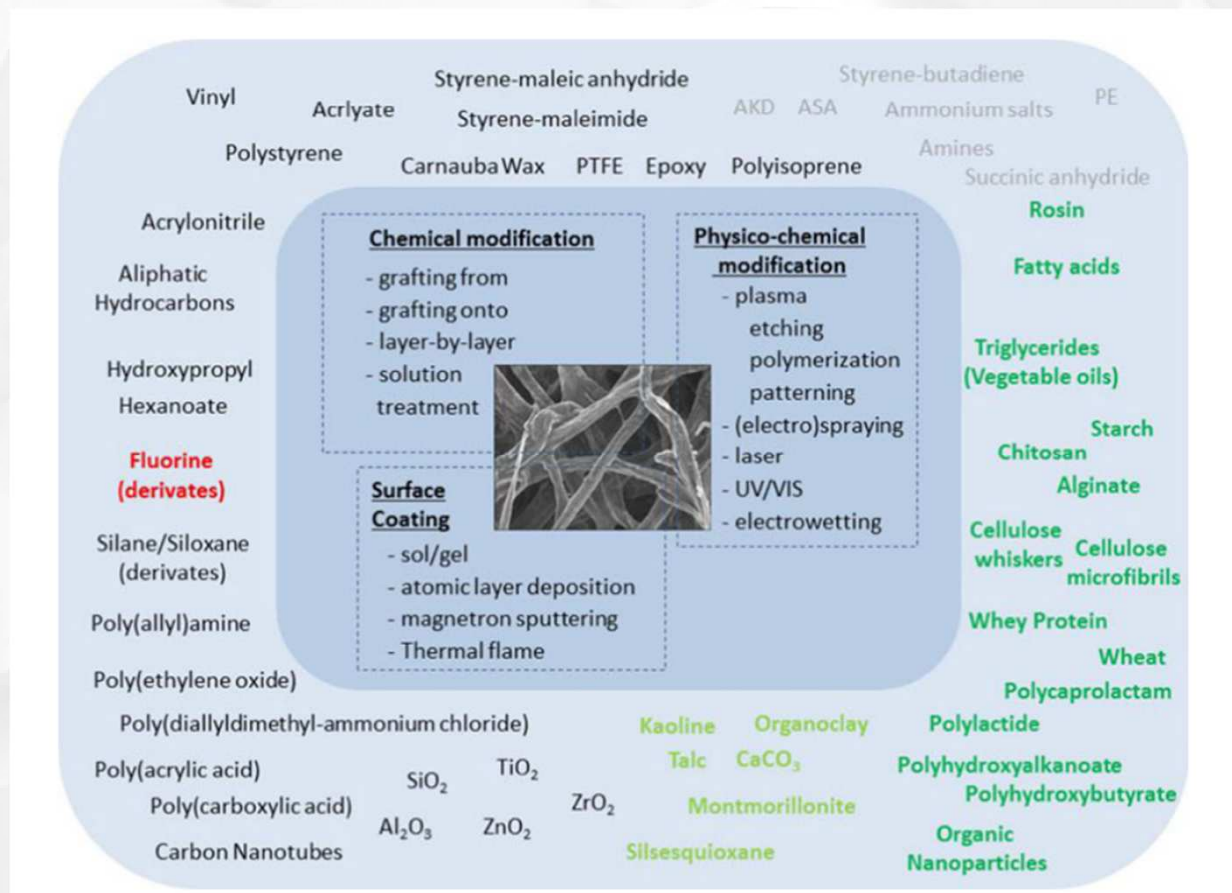
Novel sizing products



What surface sizing cannot do

- Provide any barrier to vapor, except as an indirect consequence of holding out size press starch or other water soluble polymers
- Affect the tendency of fibers in paper to change dimensions in response to humidity
- Provide any strength to paper that has become completely soaked with water
- So for food packaging with high barrier expectancy we need different ways of improving barrier properties and hydrophobicity.

Hydrophobicity by fibre surface engineering



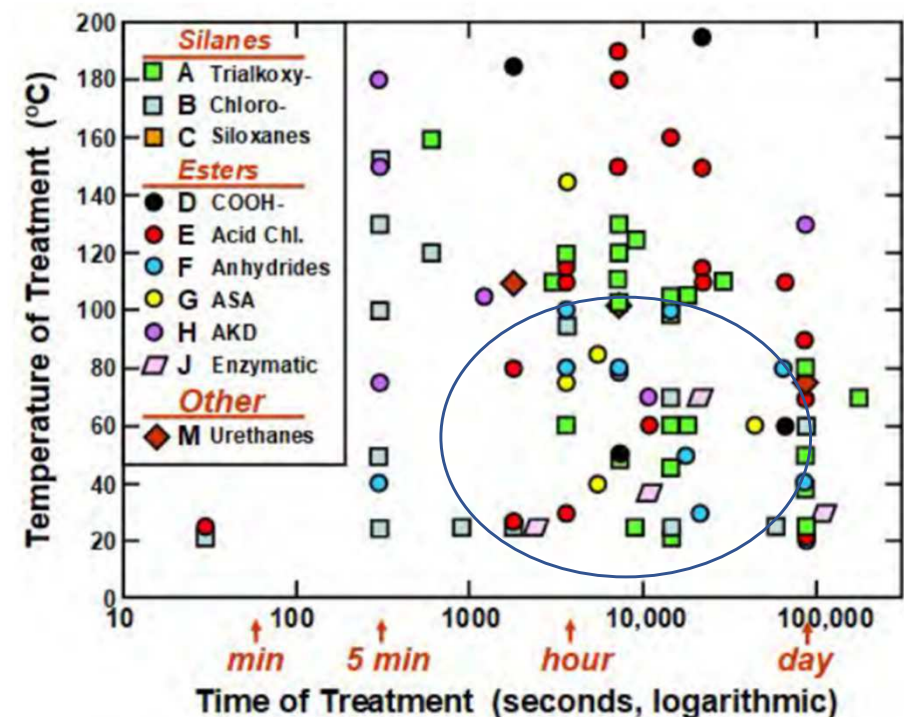
Physical
modification

Chemical
modification

Modification
with
polymers

All these solutions maybe work in the lab...

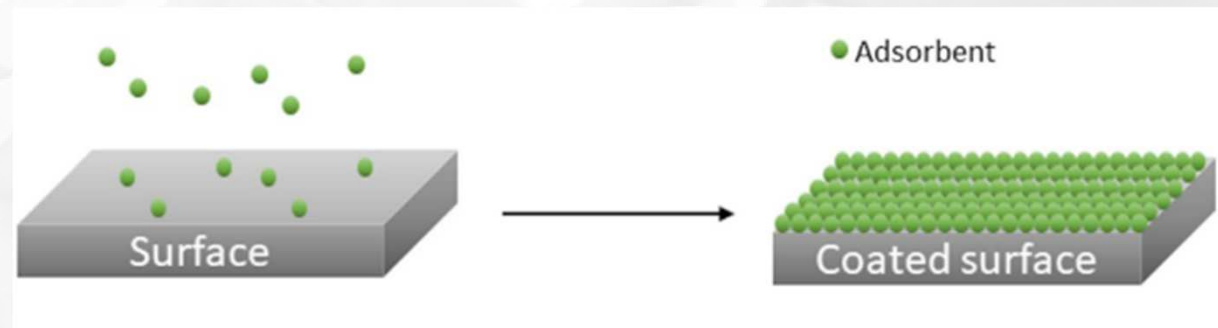
- But they have to be scalable
- With lower enviromental impact than surface sizing/lamination
- 100% recyclable with lower impact on all waste streams
- Minimum biodegradable.
- High temperature limitation
- Time on a contionuos web production.



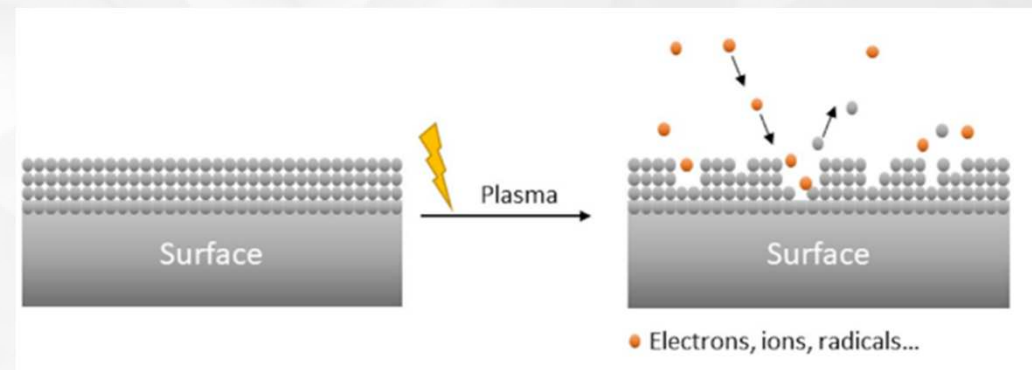
(Szlek, Reynold, Hube,
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Physical modifications

- Adsorption



- Plasma treatment



Adsorption

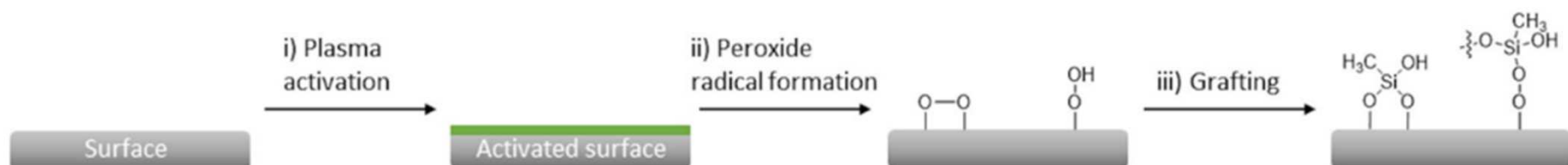
- This process relies on physical interactions between the adsorbed molecule and the cellulosic substrate, such as affinity between hydro-philic groups, the surface structure, electrostatic interactions, hydrogen bond formation or van der Waals interactions.
- For cellulose material modifications anionic surfactants are mostly used, followed by non-ionic and cationic surfactants.
- Cetyltrimethylammonium bromide (CTAB)
- Waxes
- Lignin

Plasma applications

- Plasma is used to physically and chemically modify surfaces.
- The ionised molecules present in the plasma state can increase the surface roughness by etching and/or activating the surfaces, enabling the graft-ing of molecules.
- Both etching and activation can modify the properties of the surfaces only and can be used to increase the hydrophobicity of the substrates.
- Etching increases the roughness of the substrates and is typically followed by coating with a hydrophobic compound of octafluorocyclobutane (c-C₄F₈), fluorocarbon (pentafluoroethane)
- Plasma-treated samples achieve very high contact

Plasma grafting

- In plasma, peroxide radicals are formed that initiate radical reactions that graft molecules to the activated surfaces.
- Often, these chain radical reactions result in the grafting of polymers.
- Already teste: Vinyltrimethoxysilane, γ -methacryloxypropyltrimet hoxysilane, CF₄, Carbon tetrafluoride, Butyric acid, Oleic acid

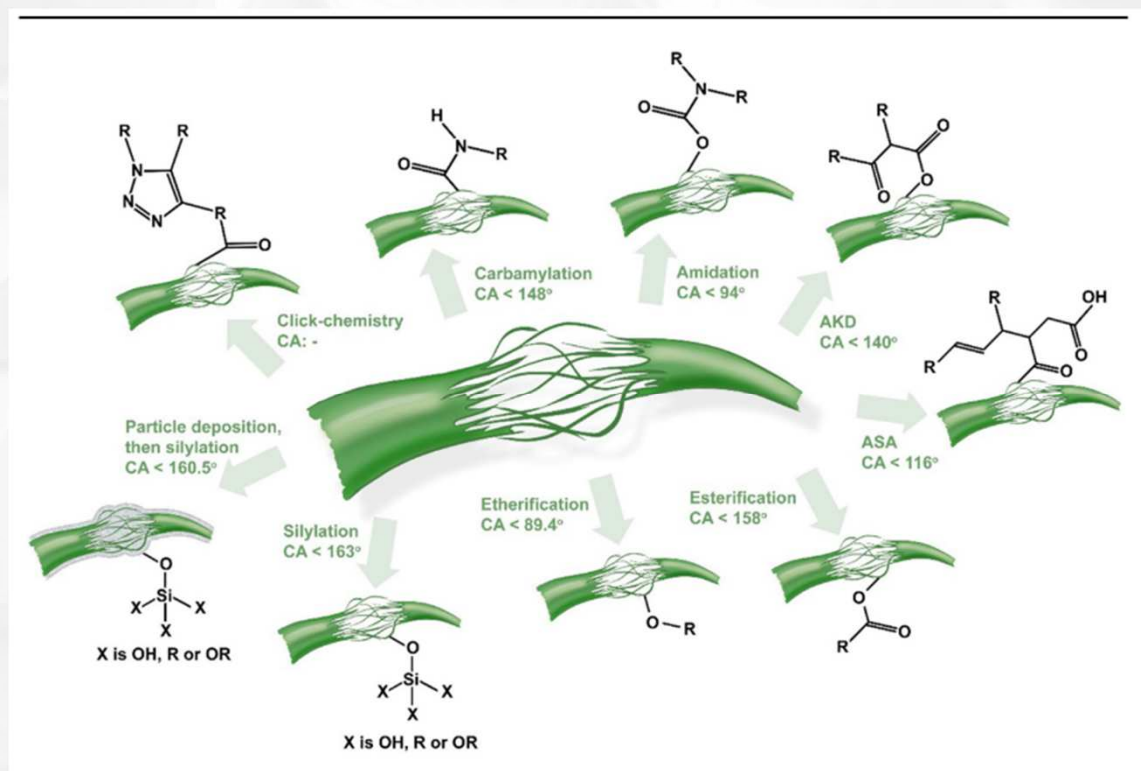


Possibility of use

- With regard to the implementation of adsorption and plasma techniques on an industrial scale, simple coating techniques (dip-coating, spraying, roll-coating etc.) are the most common coating approaches due to their simplicity and low cost.
- The implementation of plasma technology is still limited to certain sectors, such as the textile industry, where plasma has been used for decades.
- There are plasma installations in the food packaging industries (smaller width/are) but not in paper mills.
- Plasma treatment gives better hydrophobicity values

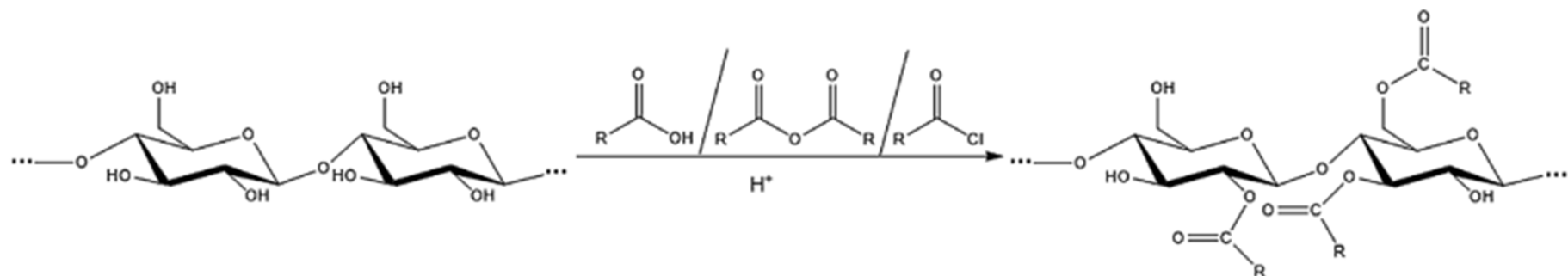
Chemical modifications

- Grafting of “short” molecules by a wide variety of reactions such as esterification, etherification, and silylation



Esterifications

- Esterification is one of the most used methods for cellulose hydrophobization via chemical modification.
- Esterification reactions occur between the hydroxyl groups of the cellulosic materials and either a carboxylic acid, an acid anhydride or an acyl chloride, introducing an ester group to the cellulose molecule.



Silylation

- Silylation is the reaction between nucleophilic groups such as alcohols, carboxylic acids and amines, with silyl groups (R_3Si-). Silylation is used to graft molecules to cellulose and its derivatives via covalent bonds
- The reaction requires the presence of water and involves three steps:
- hydrolysis of the silane molecules to the corresponding silanols (R_3Si-OH) in the presence of water,
- adsorption of the silanols onto cellulose surfaces by hydrogen bonding, and
- self-condensation of the silanols into a siloxane network and condensation of the siloxanes with cellulose by thermal treatment.
- Common hydrolyzable groups in silane molecules are $-Cl$, $-OR$, $-NMe_2$

Modifications with polymers

- Adsorption of polymers onto cellulosic materials is a non-covalent modification method driven by hydrogen bonding, van der Waals and electrostatic interactions, and the affinity between functional groups and surface structure
- Several methods can be used to coat surfaces with polymers, such as layer-by-layer deposition, dip-coating, and electro-spraying.
- These polymers can be amphiphilic copolymers, polyelectrolytes, or hyperbranched polymers.

Polymer applications

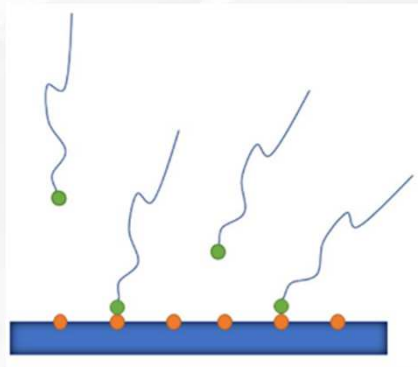
- In addition to grafting and adsorption of “short” molecules, grafting and adsorption of polymers are also techniques used to modify cellulosic materials.
- All these modifications with the polymers are mostly surface based.
- With regards to polymeric modifications, organic solvents are commonly used in both “grafting to” and “grafting from” approaches. Larger hydrophobic polymers used in the “grafting to” approach are not water-soluble, which is also true for most monomers used in the “grafting from” approach.

Adsorption of polymers

- TFEMA-st-DMAEMA, TFEMA-b-DMAEMA, PEO-PPO-PEO, Hyperbranched polyesters, hyperbranched, poly(urea-urethane), TiO₂ nanoparticles/PAA+FAS, PLL+wax, PAH/PAA PEO/PAA, PAH/PAA+wax, PLMA-PHEMA
- Contact angles mostly over 120°

Polymer grafting strategies

- In the “grafting to” approach, pre-synthesized polymer chains with reactive end-groups are attached to the cellulose substrates, allowing to characterize the polymers before grafting and control the properties of the resulting material.
- Low grafting densities due to the steric hindrance caused by the already grafted polymer chains, which prevents the diffusion of new chains towards the surface.



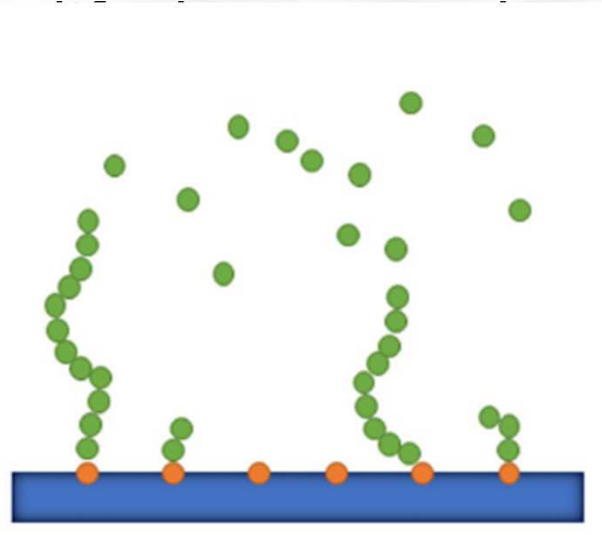
Some examples

Table 2 Overview of modifications of cellulosic materials by “grafting to”

Cellulose source	Type of cellulose	Polymer	Reaction type/covalent bond	Grafting yield (wt.%)	CA (°)
Avicel	CNC	PCL-diol	Azide alkyne cycloaddition/1,2,3-triazole		
	Microcrystalline cellulose (MCC)	PCL-diol	Azide alkyne cycloaddition/1,2,3-triazole		
		PLA, (PEG)	Azide alkyne cycloaddition/1,2,3-triazole		
Ramie fibers	CNC	PCL	Bimolecular addition/urethane bond		64,75
Cotton	CNC	PHBV	Esterification/ester bond		46–60
	CNC	PS, poly(<i>tert</i> -butyl acrylate)	Amidation reaction/amide bond	60–64	
	CNC	Polyether-polyurethane prepolymer	Bimolecular addition/urethane bond		
Bleached kraft pulp	Fibers	Maleated polypropylene	Esterification/ ester bond		
Cotton fabric	Fibers	PEG5000- <i>b</i> -P(MA- <i>co</i> -APM)- <i>b</i> -PHFA	Azide photolysis/ amine, amide bonds		155
BNC		P(APM- <i>co</i> -HFA)			138
		PLA- <i>co</i> -PGMA	Nucleophilic substitution/ ester bond		51–82
Jute fabric	Fibers	PBA	Free radical coupling (ether, alkane bonds)	2.34–2.98	125.1

Polymer grafting from

- In the “grafting from” approach, the polymer chains are grown at the surface of the sub- strate, using the hydroxyl groups directly as initiating sites or after activation.
- This method allows for high grafting densities, although the properties of the grafted polymer chains are not well defined and are



Grafting from approaches

- The polymerization methods can be divided into three main groups which are:
- ring-opening polymerization (ROP),
- free radical polymerization,
- controlled radical polymerization.

Source of cellulose	Type of cellulose	Monomer	Grafting yield (%)	Contact angle (°)
Whatman filter paper	Fibers	ϵ -CL	11	114
Cotton	MFC	ϵ -CL	16, 19, 21	
Oil palm mesocarp fibers	Fibers	ϵ -CL	78	
Ramie fibers	CNC	ϵ -CL		80
Lintier	CNC	ϵ -CL	85	
MCC	CNC	ϵ -CL	91.7–95.6	72.55–89.01
Ramie fibers	CNC	L-lactide		
Ramie fibers	CNC	D-lactide		
MCC	CNC	L-lactide		

Controlled radical polymerization

- Controlled radical polymerization allows the synthesis of polymers
- With defined architecture, composition and molecular weight distribution. Polymers with these characteristics are obtained using reagents that transfer the growing chains to a dormant state that is in equilibrium with the active species.
- Three types of controlled polymerization are used to graft polymers from cellulosic materials:
 - nitroxide-mediated polymerization (NMP),
 - atom transfer polymerization (ATRP), and
 - reversible addition-fragmentation chain-transfer polymerization (RAFT).

Other results

Source of cellulose	Type of cellulose	Initiator	Monomer	Grafting yield (%)	Grafting efficiency (%)	CA
Fully bleached spruce sulphite cellulose	MFC	CAN	GMA			
Bleached birch pulp	CNF	CAN	GMA	146–439	96–99	
			Ethyl acrylate	95–255	0–85	
			MMA	56–98	56–75	
			Butyl acrylate	177–392	83–89	
			2-hydroxyethyl methacrylate	19–37	18–64	
Cellulose powder		CAN	Ethyl acrylate		54.2–75.6	
Cotton filter	CNC	CAN	MMA	11		34.5
Cotton filter	CNC	CAN	4VP			34–47
<i>Hibiscus sabdariffa</i>	Fibers	KPS	MA	8.79–63.15		
<i>Hibiscus sabdariffa</i>	Fibers	KPS	MMA	5.47–50.93		
Cotton fiber	Fibers	KPS	MA	< 36.5		
			MMA	< 43.1		
			VAc	< 27.4		
MCC powder	CNC	KPS	Styrene			78
Bleached softwood kraft pulp	CNF	KPS	BA/styrene			149
Cellulose powder		Fenton	Vinyl acetate	0–12%	0–2.6	
Cellulose powder		Fenton	Ethyl acrylate	2.7–345.0	0.42–54.0	
<i>Abelmoschus manihot</i>	Fibers	Fenton	MMA	130		
Bleached eucalyptus pulp	CNF	Fenton	Methacrylic acid, maleic acid	130		

ATRP

Source of cellulose	Type of cellulose	Monomer	Grafting yield (%)	Contact angle (°)
Cotton wool	CNC	Styrene	8–22	
Filter paper	CNC	Styrene	68	
Filter paper	Fibers	MA		128, 133
Filter paper*	Fibers	MMA		109–112
		Styrene		132–137
		GMA		-
Filter paper*	Fibers	Lauryl acrylate		125, 135
		Octadecyl acrylate		134, 146
Poplar wood*	Wood	MMA	2.36–12.84	74–130
Filter paper	Fibers	GMA		154, 172
Cotton fabric		GMA		140.1–155, 163.7
Norway spruce*	Wood	TFEMA	Pyridine: 43.4 Dichloromethane: 42.9	
Filter paper	Fibers	NIPAAm		110
		GMA/NIPAAm		130
		4VP		pH 7 = 90–100 pH 9 = 125
		NiPAAm/4VP		115–120
	CNF	Styrene	12.7–46.2	85.1–98.7
BNC	BNC	MMA	59–887	134
		BA	110	116
		MMA/BA	616	

Additional radiation solutions

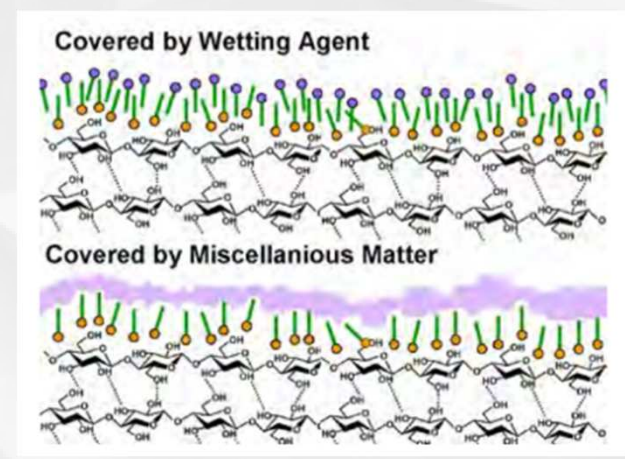
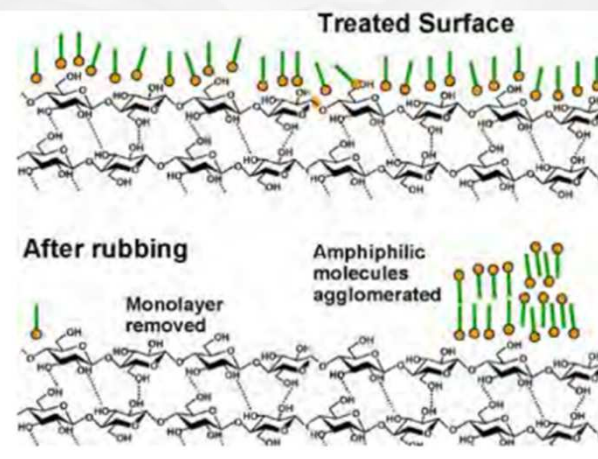
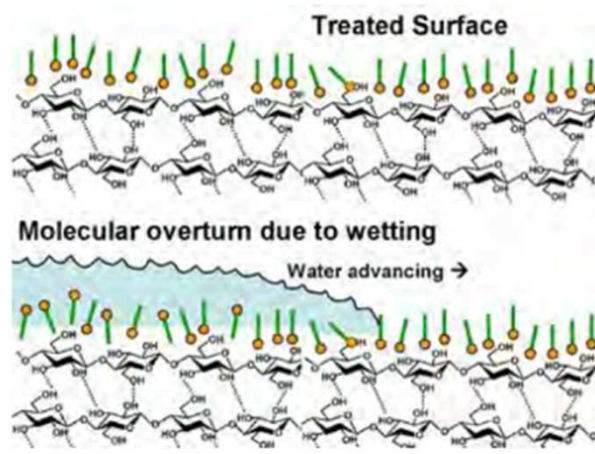
- Ultraviolet light
- Gamma radiation,
- and plasma.

Short overview of polymer solutions

- Amongst all the grafting techniques, radiation- induced polymerizations typically are more environmentally friendly, even though they offer little control on the polymerization process.
- Ring opening polymerization allows grafting of biodegradable polymers such as PLA and PCL,
- Radiation-induced modifications are the techniques with the highest potential for industrialization.
- Other grafted polymers on some cellulosic materials are just too niche due to high and complex production.

Critical points to solve

- Debonding of molecules comprising a hydrophobic monolayer - ester and amide bonds are subject to hydrolytic cleavage under ambient conditions.
- Such cleavage tends to be promoted by moisture, increased temperatures, and sufficiently strong acidic or basic conditions+enzymatic attack.
- Molecular overturn represents another potential mechanism by which a hydrophobic monolayer can become less effective with the passage of time.



Conclusion

- Silane chemistry, esters, and plasma treatments.
- The developments presented are not yet market ready as other protection technologies (coatings and films).
- Gap of knowledge on thin monolayer solutions which can be compromised during conversion or transport (durability, mechanical stresses).
- Time temperature challenge
- Plasma/vapour deposition solutions shift production of these solutions to converters less the paper mills (energy costs and investment).