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ISBN 978-952-12-3660-0 (printed version)  
ISBN 978-952-12-3661-7 (digital version)  
Painosalama Oy-Turku, Finland 2017

## Preface

This thesis is a summary of the work published in peer-reviewed journals (Papers I–IV). The work was done at the Laboratory of Fiber and Cellulose Technology (Åbo Akademi University, Finland) under supervision of Prof. Pedro Fardim (The head of the laboratory). A great part of the work was carried out in a close collaboration with a group of Prof. Thomas Heinze (Friedrich Schiller University Jena, Germany) and under his co-supervision.

- Paper I Grigoray, O., Järnström, J., Heikkilä, E., Fardim, P., Heinze, T. (2014). Modification of pine pulp during oxygen delignification by xylan self-assembly, *Carbohydrate Polymers*, 112, 308–315.
- Paper II Grigoray, O., Wondraczek, H., Heikkilä, E., Fardim, P., Heinze, T. (2014). Photoresponsive cellulose fibers by surface modification with multifunctional cellulose derivatives, *Carbohydrate Polymers*, 111, 280–287.
- Paper III Grigoray, O., Wondraczek, H., Daus, S., Kühnöl, K., Latifi, S. K., Saketi, P., Fardim, P., Kallio, P., Heinze, T. (2015). Photocontrol of mechanical properties of pulp fibers and fiber-to-fiber bonds via self-assembled polysaccharide derivatives, *Journal of Macromolecular Materials and Engineering*, 300 (3), 277–282.
- Paper IV Grigoray, O., Wondraczek, H., Pfeifer, A., Fardim, P., Heinze, T. (2017). Fluorescent multifunctional polysaccharides for sustainable supramolecular functionalization of fibers in water, *ACS Sustainable Chemistry & Engineering*, 5 (2), 1794–1803.

This work was mostly funded by Finnish Funding Agency for Technology and Innovation (Tekes). A financial support was also received from Åbo Akademi University as a scholarship and from Tekniikan edistämissäätiö (TES) as personal and incentive grants.

### *Contribution of the author to the papers*

*Paper I.* The author did preliminary study of HWX extraction and adsorption during an oxygen delignification stage, performed analyses of the extracted xylans except SEC, and wrote most of the manuscript.

*Paper II.* The author performed most of the experiments except ToF-SIMS, interpreted the results and prepared the manuscript.

*Paper III.* The author performed experiments except mechanical analyses of the samples, interpreted the results and prepared the manuscript.

*Paper IV.* The author performed most of the experiments and wrote most of the manuscript. The parts of the experiments related to synthesis of the derivatives and their characterization were done by co-authors and described by them in the manuscript.

### *Supporting work*

Vega, B., Grigoray, O., Gustafsson, J., Fardim, P. (2015). Advances in sugar-based polymers: xylan and its derivatives for surface modification of pulp fibres. In: Biomass sugars for non-fuel applications. Murzin D. and Simakova O. (Eds). Royal Society of Chemistry, pp. 134-158.

Fardim, P., Heinze, T., Wondraczek H., Grigoray, O. Polysaccharide derivatives as optical brightening agents. Patent application, WO2017162918 A1, September 28, 2017.

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## List of abbreviations, acronyms and symbols

Ara	Arabinose
CAX	Cold alkali extracted xylan
CCD	Cationic cellulose derivative
D	Chlorine dioxide bleaching stage
DMA	Dynamic mechanical analysis
DP	Degree of polymerization
DS <sub>Cat</sub>	Degree of substitution of cationic group
DS <sub>Photo</sub>	Degree of substitution of photoactive group
ECF	Elemental chlorine free
EOP	Hydrogen peroxide and oxygen reinforced alkaline extraction stage
FCCD	Fluorescent cationic cellulose derivative
FTIR-ATR	Fourier transform infrared - attenuated total reflectance spectroscopy
Gal	Galactose
GalA	Galacturonic acid
GC	Gas chromatography
Glc	Glucose
GlcA	Glucuronic acid
HexA	Hexenuronic acid
HPAEC-PAD	High performance anion exchange chromatography with pulsed amperometric detection
HWX	Hot water extracted xylan
Man	Mannose
MCCD	Multifunctional cationic cellulose derivative
MeGlcA	4-O-methyl- $\alpha$ -D-glucuronic acid
PCCD	Photoactive cationic cellulose derivative
PHWE	Pressurized hot water extraction
Py-GC-MS	Pyrolysis-gas chromatography-mass spectrometry
Rha	Rhamnose
SAM	Self-assembled monolayer
SEC	Size exclusion chromatography
SPR	Surface plasmon resonance
ToF-SIMS	Time-of-flight secondary ion mass spectrometry
UV-vis	Ultraviolet-visible
WRV	Water retention value
Xyl	Xylose

## Abstract

Pulp fibers are widely used in different types of everyday products. Even though the demand for newspaper and printing paper is declining, there is a clear growth in the consumption of such fiber-based products as specialty papers, packaging, tissue, and hygiene products. The growing concern about plastic pollution stimulates the development of bio-based technologies and biodegradable bio-based products. In light of the current situation, this work focused on the surface functionalization of pulp fibers to improve their properties as well as to introduce novel features. Such modification provides an opportunity to increase the value of the fibrous materials and broaden the application of pulp fibers.

Adsorption of biopolymers and their derivatives was chosen as a modification method that preserves the bulk structure of the fibers and that can be realized using facilities of the existing fiberlines of a pulp and paper mill. Two types of polysaccharides were used as surface modifying agents: extracted xylans and specially designed light-responsive derivatives of cellulose.

Xylans were extracted from birch wood and bleached birch kraft pulp using pressurized hot water and cold alkali extraction methods. The extracted xylans were considerably different from each other with respect to the appearance, chemical composition, and molar mass. The cold alkali extracted xylan (CAX) was much purer than the hot water extracted one (HWX). Both xylans were applied to pine kraft pulp fibers at dosages of 2 and 5% (pulp based) during an oxygen delignification stage. The addition of CAX had a positive effect on the selectivity of the process. Hand-sheets made of the oxygen delignified as well as further bleached and beaten CAX treated pulps had superior mechanical properties compared to the reference samples. In contrast, HWX, which contained higher amounts of the side groups and lignin impurities, showed worse performance than CAX. In particular, HWX had lower adsorption onto the pulp fibers and impeded the oxygen delignification process. Thus, these results demonstrated that CAX can be applied as a dry strengthening agent to improve mechanical properties of a final fiber product, and that the modification step of pulp can be executed in the oxygen delignification stage of the fiber production line.

Novel light-responsive multifunctional cationic cellulose derivatives (MCCDs) soluble in water were adsorbed onto bleached eucalyptus kraft

pulp in aqueous solutions to impart photoactive functionalities to the fibers. The studies covered the adsorption mechanism and the effect of the structure of MCCDs on the adsorption process. Applied coumarin-type MCCDs, namely mixed 2-[(4-methyl-2-oxo-2H-chromen-7-yl)oxy]acetic acid-(3-carboxypropyl)trimethylammonium chloride esters of cellulose, had an intrinsic ability to crosslink under UV light irradiation via cycloaddition reaction of the pendant photoactive moieties. The pulp fibers modified with this type MCCDs gained the photocrosslinking functionality of the derivatives. Hand-sheets made of such fibers and post-irradiated with UV light possessed a much stronger fiber network due to the formed covalent inter fiber bonds. In addition, stiffness of the individual functionalized fibers increased after the irradiation. Another group of MCCDs, namely mixed *N*-(3-propanoic acid)- and *N*-(4-butanoic acid)-1,8-naphthalimide-(3-carboxypropyl)trimethylammonium chloride esters of cellulose, endowed the fibers with fluorescence in the visible part of the spectrum. Under UV light exposure, fluorescence of the pulp fibers made them visually distinguishable from the reference fibers. Therefore, the fluorescent fibers can serve as an authenticity indicator when incorporated into the fibrous material, such as inner side of the packaging. Both types of the prepared light-responsive pulp fibers can be potentially used to design smart bio-based materials, *e.g.* in packaging, to increase its mechanical performance and to validate the packaging authenticity.

## Sammanfattning

Massafibrer används inom ett brett sortiment av vardagsprodukter. Fastän efterfrågan av tidningspapper och tryckpapper minskar, så ökar konsumtionen av sådana fiberbaserade produkter som specialpapper, förpackningar, mjukpapper och hygienprodukter. Den ökande oron om plastföroreningar stimulerar utvecklingen av teknologier för biobaserade och biodegraderbara produkter. I ljuset av det nuvarande läget fokuserar detta arbete på ytfunktionalisering av massafibrer för att förbättra deras egenskaper samt att introducera helt nya särdrag. Dylika modifieringar ger möjligheter att öka värdet av fibermaterialen och bredda tillämpningsområdet för massafibrerna.

Adsorption av biopolymerer och deras derivat valdes som modifieringsmetod eftersom den bevarar fibrernas bulkiga struktur och eftersom metoden kan appliceras på existerande fiberlinjer i massa- och pappersbruk. Två typer av polysackarider användes som ytmodifieringsmedel, nämligen extraherade xylaner och speicaldesignade cellulosaderivat som reagerar på ljus.

Xylaner extraherades från björkved och från blekt sulfatmassa av björk genom de två metoderna trycksatt hetvattenextraktion och kall alkaliextraktion. De två xylantyperna var betydligt olika varandra med avseende på utseende, kemisk sammansättning och molmassa. Kall alkaliextraherad xylan (CAX) var mycket renare än xylan extraherat med hetvatten (HWX). Båda xylanen applicerades med doseringarna 2 % och 5 % (baserat på torr massa) till sulfatmassa av tallfibrer i ett syrgasdelignifieringssteg. Tillsats av CAX hade en positiv effekt på processens selektivitet. Handark gjorda av syrgasdelignifierade fiber samt därefter blekta och malade fibrer, båda innehållande CAX, hade överlägsna mekaniska egenskaper jämfört med referensmaterialen. Däremot presterade HWX sämre än CAX, på grund av ett större innehåll av sidogrupper och ligninföroreningar. Särskilt adsorptionen av HWX på massafibrer var lägre och själva syrgasdelignifieringen försvårades. Dessa resultat demonstrerade sålunda att CAX kan appliceras som torrstyrkemedel för att förbättra de mekaniska egenskaperna av den slutliga fiberprodukten och att fibermassans modifieringssteg kan utföras i en fiberproduktionslinjes syrgasdelignifieringssteg.

Nya vattenlösliga multifunktionella katjoniska cellulosederivat (MCCD), som kan reagera på ljus, adsorberades i en vattenlösning på

blekt sulfatmassa av eukalyptus för att förse fotoaktivitet till fibrerna. Studierna omfattade adsorptionsmekanismen och effekten av MCCDs struktur på adsorptionsprocessen. De applicerade MCCD av kumarintyp (dvs. blandade 2-[(4-metyl-2-oxo-2H-kromen-7-yl)oxi]acetat-(3-karboxipropyl)trimetylammonium klorid estrar av cellulosa) hade en inneboende förmåga till tvärbinding vid bestrålning med UV-ljus. Tvärbindingen skedde via en cykloaddition reaktion mellan de utstående fotoaktiva grupperna. Massafibrerna som modifierades med denna typ av MCCD erhöll derivatens fototvärbindningsfunktionalitet. Handark av dylika fibrer, vilka bestrålades med UV-ljus ledde till ett mycket starkare fibernätverk tack vare de kovalenta bindningar som formades mellan fibrerna. Därtill ökade också de individuella fibrernas styvhet efter UV bestrålningen. En annan grupp av MCCD (blandade *N*-(3-propansyra)- och *N*-(4-butansyra)-1,8-naftalimid-(3 karboxipropyl)trimetylammonium klorid estrar av cellulosa) försåg fibrerna med fluorescens i den visuella delen av spektrumet. Under exponering med UV-ljus kunde de fluorescerande fibrerna med blotta ögat särskiljas från referensfibrerna. Följaktligen kan de fluorescerande fibrerna fungera som en äkthetsindikator när de integreras in till fibermaterialet, så som till den inre delen av en förpackning. Båda typer av preparerade massafibrer som reagerar på ljus kan potentiellt användas till att konstruera smarta bio-baserade material, t.ex. inom förpackningar, för att öka dess mekaniska prestanda och för att bekräfta förpackningens äkthet.

# 1 Introduction

Pulp fibers are extensively used in a variety of fiber-based products which have different functions, such as data transfer (printing and writing papers), value representation (paper money, security papers), load carrier (wrapping papers, paper bags, paperboard), liquid absorption (towels, napkins, diapers), among others. Among the reasons why fiber-based products are currently widely used are their environmental friendliness, availability, renewability and recyclability. In addition, growing competition in the pulp and paper sector stimulates the development of competitive and customer-oriented solutions.

## 1.1 Objective of the work

The aim of this work was to perform supramolecular functionalization of pulp fibers via adsorption of wood-based polysaccharides and their derivatives, and to study the effect of the functionalization on the properties of the fibrous materials. The long-term goal of this work was to make a contribution to the improvement of the properties of the existing fiber-based products and to the development of novel fiber-based materials using fiber modification as a tool that can be integrated into the fiber line processes.

In the first approach, two types of xylan were extracted from two raw materials, *viz.*, birch wood and bleached birch kraft pulp, and they were used to modify pine kraft pulp fibers during an oxygen delignification step.

In the second approach, novel MCCDs with photoactive functional groups were used as surface modifying agents to impart light-responsive functionalities to bleached eucalyptus kraft pulp fibers.

## 2 Background

### 2.1 Pulp fibers

Pulp fibers are isolated from plants using well-established technologies such as mechanical, chemimechanical, semichemical and chemical pulping methods (Sjöström, 1993). Properties and chemical composition of pulp fibers have been extensively studied, and they vary greatly depending on the raw materials and the manufacturing process (Sixta, 2006a). In Europe, pulp fibers are majorly produced from wood raw materials by chemical methods, among which kraft process is considerably dominant over another pulping method, sulfite process (Sjöström, 1993).

In softwoods (coniferous trees), fiber tracheids are the main cell type constituting 90–95% of the stem volume. In hardwoods (deciduous trees), there are two types of fibers, namely libriform and tracheids, which amount to 65 to 75% of the stem volume. Libriform fibers and tracheids are quite similar to each other, but the former have slit-like pits and the latter bordered pits. The dimensions of the fiber cells for softwoods and hardwoods are shown in Table 1. It is important to mention, that xylem of hardwood species also contains another type of cells, vessel elements, which are thin-walled tube-like prosenchyma cells with 0.2–0.6 mm length and 10–300  $\mu\text{m}$  width. These cells have numerous small bordered pits and perforated ends. Vessel elements are found in the amount of 20–30% of the stem volume of hardwoods. (Sjöström, 1993)

Table 1. Dimensions of most abundant cells of wood (Sjöström, 1993).

Cell type	Length, mm	Width, $\mu\text{m}$	Thickness, $\mu\text{m}$
Softwood fibers	1.4–6.0	20–50	2–8
Hardwood fibers	0.4–1.6	10–40	3–4

The fiber cell wall is made of concentric layers known as primary (P) and secondary (S) cell walls (Figure 1) (Sjöström, 1993). The latter is further divided into S1, S2 and S3 layers (Fengel and Wegener, 1984a; Sjöström, 1993). The skeleton of cell wall layers is composed of cellulosic fibrils surrounded by other structural components, heterogeneous branched polysaccharides, hemicelluloses, and aromatic crosslinked polymer, lignin (Sjöström, 1993). Cellulosic fibrils are formed by linear

cellulosic chains assembled together via hydrogen bonds into cellulose elementary, micro- and macrofibrils (Sjöström, 1993). Primary and secondary cell walls have a different distribution of the structural components and the orientation of the cellulosic fibrils (Figure 1) (Fengel and Wegener, 1984a; Sjöström, 1993). The primary cell wall is thin and contains a greater amount of lignin than other structural components (Alen, 2000). Contrarily, the second cell wall is thick, and holds the major part of the structural components found in the whole wall (Alen, 2000). Polysaccharides are the most abundant structural elements in this wall, with cellulose being predominant (Alen, 2000).

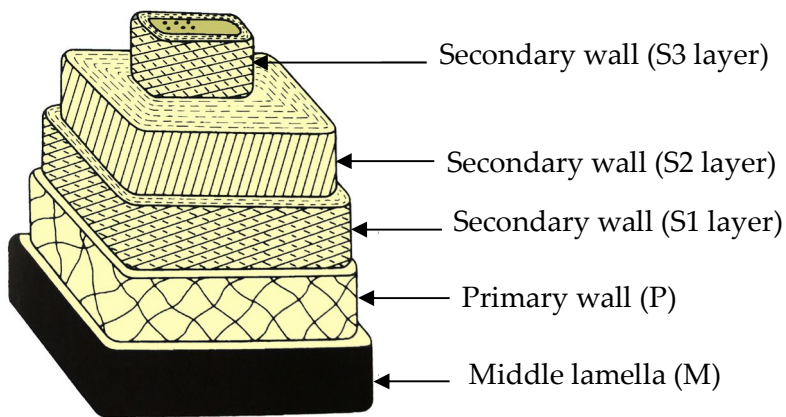


Figure 1. Fiber cell wall structure (Fengel and Wegener, 1984a).

When pulp fibers are isolated from wood by cooking and further purified by bleaching, different phenomena take place including removal of a considerable amount of lignin, dissolution and partial re-adsorption of hemicelluloses (Potthast, 2006; Sixta, 2006b). This has influence on the chemical composition of the fibers. They become rich in polysaccharides, specifically in cellulose (Table 2).



Table 2. Chemical composition of pine and birch wood and selected bleached kraft pulps (Neto et al., 2004; Normark et al., 2014; Sixta, 2006a, 2006c).

Component	Wood		ECF <sup>a</sup> bleached kraft pulps		
	Scots Pine ( <i>Pinus sylvestris</i> ) <sup>b</sup>	Birch ( <i>Betula pendula</i> )	Scots Pine ( <i>Pinus sylvestris</i> )	Birch ( <i>Betula pendula</i> )	Eucalyptus ( <i>Globulus</i> )
Carbohydrates, % <sup>c</sup>					
Glucose	42.0	39.7	84.7	76.1	82.9
Mannose	13.1	1.3	6.6	0.4	0.2
Galactose	2.7	1.0	0.2	0.0	0.3
Xylose	5.4	22.1	7.3	23.2	16.2
Arabinose	1.8	0.5	0.5	0.1	0.1
Rhamnose	-	0.3	-	0.2	0.3
Uronic acids	-	3.5	-	-	-
Acetyl groups	-	5.1	-	-	-
Lignin, %	28.8	23.3	-	0.33	0.33
Extractives, %	3.7	1.9	0.05	0.72	0.37
COOH groups, $\mu\text{mol/g}$	-	-	37	85	78

<sup>a</sup>ECF, elemental chlorine free bleaching;

<sup>b</sup>Original data presented as an average of mature heartwood and sapwood;

<sup>c</sup>Anhydrous.

## 2.2 Supramolecular functionalization of pulp fibers

Surface functionalization is a tool that enables modification of fiber surface properties along with preservation of the bulk properties such as relatively low density, high specific strength and stiffness (Dufresne, 2008). The aim of the modification is to improve performance of fiber-based materials as well as to broaden field of their applications (Belgacem and Gandini, 2008). Such modification can be done using biological (enzymes, fungi), chemical (carboxylation, grafting), physical adsorption and plasma treatment methods (Gandini and Pasquini, 2012).

Supramolecular functionalization of fibers by adsorption of polymers is a widely applied technique at industrial scale due to its simplicity and water-based reaction media. Various polymers, including polysaccharides as such or bearing functional groups, have been applied industrially (Krogerus, 2007; Marton, 1996) and also tested at a laboratory scale (Hedborg and Lindstrom, 1993; Horvath et al., 2008; Ishimaru and Lindström, 1984; Laine and Lindström, 2000; Schwikal et al., 2011; Vega et al., 2012; Wågberg and Odberg, 1989). This method proved to be effective in improving of the mechanical and drainage

properties of pulp for ensuing paper (Han et al., 2012; Krogerus, 2007; Marton, 1996; Ramírez et al., 2008; Schwikal et al., 2011). In addition, a broad range of various functional fibers can be prepared by this method opening new fields of application. For instance, Vega et al. (2016) demonstrated modification of pulp fibers by adsorption of cellulose derivatives containing reactive amino groups. Fibers prepared in a such way possessed enzyme binding functionality that made them potentially applicable as enzyme carriers (Vega et al., 2016). Adsorption of polymers with stimuli-responsive properties (Irie, 1990) can also be applied as a method to prepare pulp fibers, which properties can be controlled by external stimulus such as light, temperature and pH.

Together with the effect on the fiber properties, there are other positive aspects of such modification. Based on the target application, polymers used as surface modifying agents can be endowed with the variety of functionalities (Heinze et al., 2006; Heinze and Liebert, 2001). Since the adsorption is mainly designed and targeted to the surface of the fibers, relatively low dosages of the polymers are usually needed (Krogerus, 2007; Marton, 1996). At last, this method can provide additional market opportunity for biomass derived polysaccharides and their derivatives, which, in turn, would allow more efficient utilization of biomass.

#### *Kraft pulp fibers as a substrate for the surface modification*

Several parameters influence the adsorption of polymers onto pulp fibers. They include adsorption conditions, properties of the applied polymers and pulp fibers. (Ishimaru and Lindström, 1984; Laine and Lindström, 2000; Wågberg and Odberg, 1989)

Pulp fiber is a heterogeneous substrate that consists of cellulose, hemicelluloses, residual lignin and extractives. Bleached chemical pulps (Table 2) can be considered less heterogeneous substrate in comparison to unbleached pulps (Pinto et al., 2005) due to a much lower amount of residual lignin. As an example, surface composition of ECF bleached eucalyptus kraft pulp is comprised of 98% of carbohydrates, 2% of lignin and 5–7% of extractives (Neto et al., 2004). In contrast to the surface, a total (bulk) amount of lignin and extractives is much lower, ca. 0.3% and 0.2–0.4%, respectively (Laine et al., 1996; Neto et al., 2004).

Based on the chemical composition, kraft pulp fibers possess different adsorption sites or functional groups available for the interactions with applied polymers. In particular, the constituents of the pulp fiber contain

ionizable functional groups that originate from wood or they are formed during the fiber processing. These groups include carboxylic groups, hydroxyl groups of the polysaccharides and phenolic hydroxyl groups of lignin (Sjöström, 1989). Among those groups, carboxylic groups exist in an ionic form in neutral and slightly acidic conditions (Sjöström, 1989). According to (Fardim and Holmbom, 2005) carboxylic groups are present as 4-*O*-methyl- $\alpha$ -D-glucuronic acid (MeGlcA) groups of xylan originated from wood, and they are also produced during kraft cooking and bleaching, for example, saccharinic acid groups of polysaccharides and carboxylic groups of lignin (Fardim and Holmbom, 2005). Aliphatic and phenolic hydroxyl groups are generally deprotonated at alkaline conditions (Sjöström, 1989). Thus, the presence of various ionic groups implies that pulp fibers can be engaged in electrostatic interactions with surface modifying agents. In fact, dry strengthening agents used in papermaking bear cationic charge to facilitate interactions with pulp fibers (Marton, 1996). Contrarily, anionic polymers generally do not adsorb onto pulp fibers due to the repulsion forces (Laine & Lindström, 2000; Vega et al., 2012).

The constituents of pulp fibers can also be involved into the formation of hydrogen bonds (Sirviö, 2008). Generally, hydrogen bond is formed between electronegative atom and hydrogen atom covalently attached to another electronegative atom (Sirviö, 2008). In the case of pulp fibers and applied polymers, such combination could be an oxygen atom of one group and hydrogen of another hydroxyl group located in the vicinity, *i.e.* O $\cdots$ H-O (Sirviö, 2008). Ishimaru & Lindström (1984) studied the adsorption of non-ionic polymers onto different pulp fibers and concluded that for a group of polymers, including methyl cellulose and polygalactomannan, formation of hydrogen bonds with cellulose of the pulps played an important role in the adsorption onto unbleached and bleached kraft pulp fibers. It was also suggested that other types of polymers, such as polyvinyl alcohol, polyvinyl methyl ether and polyvinyl pyrrolidone, interacted with the fibers via formation of hydrogen bonds with the phenolic and/or catecholic groups of lignin (Ishimaru and Lindström, 1984).

Hydrophobic interactions between the pulp constituents and surface modifying agents also can contribute to the adsorption (Ishimaru and Lindström, 1984). Hydrophobic sites of the polysaccharides, *e.g.* axial C-H sites in glucopyranose rings in cellulose (Medronho et al., 2012) and

residual lignin (Ishimaru and Lindström, 1984), can be involved in these interactions.

It is known that several types of interactions can simultaneously occur between the applied polymers and the fibers. For instance, polyelectrolytes can be adsorbed to the pulp fibers via both electrostatic and non-electrostatic interactions (Wågberg, 2000).

Along with chemical composition and functional groups, porosity is another important characteristic of pulp fibers as the substrates for the adsorption (Wågberg, 2000). In aqueous solutions, pulp fibers swell, and partial separation of the fibrils of the fiber cell wall takes place (Alinec, 2002). As a result, pulp fiber cell wall contains small and large pores. According to Alinec (2002), the large cell wall pores between cellulose fibrils in swollen delignified pulp fibers have an average diameter of around 100 nm. The presence of large pores increases accessibility of the applied polymers to the interior of the fiber wall. Generally, the adsorption of the polymers with a high molar mass is restricted to the fiber surfaces, whereas polymers with a relatively low molar mass can penetrate into the fiber cell wall (Wågberg, 2000).

## **2.3 Hardwood xylan**

### **2.3.1 Xylan structure**

Xylan is the main hemicellulose of hardwoods and it constitutes 15–30% of the dry wood (Sjöström, 1993). Xylan backbone consists of xylose (Xylp) units linked by  $\beta$ -(1-4) glycosidic bonds (Figure 2) (Fengel and Wegener, 1984b; Sjöström, 1993). Degree of polymerization is in the range of 100–200 units (Fengel and Wegener, 1984b). Hydroxyl groups of xylan backbone are substituted with acetic acid group at C2, C3 or both at C2 and C3 positions (Fengel and Wegener, 1984b). The molar ratio of xylose units to acetyl groups varies from 1:0.5 to 1:0.6 (Fengel and Wegener, 1984b). MeGlcA is also attached to the xylan backbone. Each tenth unit of xylose carries one MeGlcA group at C2 position (Fengel and Wegener, 1984b).

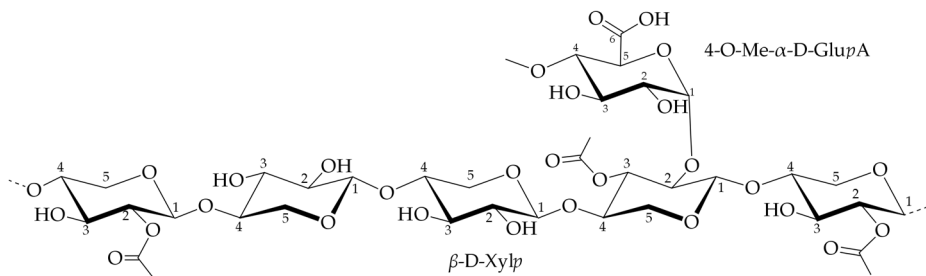


Figure 2. Structure of hardwood xylan (*O*-acetyl-4-*O*-methylglucuronoxylan) (Sjöström, 1993).

Moreover, rhamnose (*Rhap*) and galacturonic acid (*GalpU*) groups are found in small amounts in xylan. They are located before the reducing end group of xylan with the following sequence:  $\beta$ -D-Xylp-1 $\rightarrow$ 4- $\beta$ -D-Xylp-1 $\rightarrow$ 3- $\alpha$ -L-Rhap-1 $\rightarrow$ 2- $\alpha$ -D-GalpU-1 $\rightarrow$ 4- $\beta$ -D-Xyl. Arabinose is also present in xylan as non-reducing end group in quantity of about 2% based on xylan. (Fengel and Wegener, 1984b)

Owing to its side groups, xylan as a polymer soluble in aqueous solutions. However, xylan in raw material is linked to other substituents, which hinders its isolation. (Bobleter, 1994)

### 2.3.2 Xylan extraction by pressurized hot water (PHWE)

Treatment of wood chips by water or steam at elevated temperature, so-called prehydrolysis, is commonly applied in the production of dissolving grade pulps prior to kraft pulping to remove hemicelluloses (Lora and Wayman, 1978). The process temperature varies in the range of 160–180°C and treatment time is usually 30–180 min (Sixta, 2006b). After prehydrolysis, the extract is neutralized and combusted together with the dissolved material (Leschinsky et al., 2009).

In this work, PHWE is referred to the process that essentially is similar to prehydrolysis, but is used to extract hemicelluloses in a polymeric form. Therefore, the process is performed at milder conditions (Vega et al., 2012).

In the beginning of hot water extraction, the high temperature facilitates autodissociation of water and formation of greater amounts of hydronium ions ( $\text{H}_3\text{O}^+$ ) (Garrote et al., 1999). These ions serve as a catalyst of the hydrolysis reaction (Garrote et al., 1999). Ether and ester bonds of the main polymers of the wood are subjected to the hydrolysis (Bobleter, 1994). Deacetylation of hemicelluloses also takes place, and the

released acetic acid further contribute to the formation of the hydronium ions and lower the pH to 3–4 (Garrote et al., 1999).

Mainly hemicelluloses are subjected to the hydrolytic attack (Garrote et al., 1999). Cleavage of ether glycosidic bonds of hemicelluloses causes depolymerization and dissolution of hemicelluloses (Garrote et al., 1999). According to several researchers (Chen et al., 2010; Sjöström, 1993) hydrolysis of hemicelluloses (xylan) should be completed to a certain loss in a molar mass before hemicelluloses can be isolated from wood and dissolved. In addition, hemicelluloses are linked to lignin in so called lignin-carbohydrate complex (LCC) and to isolate hemicelluloses these linkages should be cleaved (Bobleter, 1994). However, LCC is also isolated during the process from the material (Chen et al., 2010; Tunc and Van Heiningen, 2008). Tunc & Van Heiningen (2008) suggested that isolated LCC can split into hemicelluloses and lignin in the extract.

During hot water treatment fragmentation of lignin with subsequent dissolution occurs through cleavage of aryl ether linkages (Leschinsky et al., 2009; Meshgini and Sarkanen, 1989). Dissolved lignin of a low molar mass remains soluble in the hydrolysates, while lignin of a higher molar mass condensates and precipitates (Leschinsky et al., 2009). The removal of lignin from raw material increases upon an increase in the process temperature (Borrega et al., 2011).

Cellulose is highly resistant towards hot water treatment (Bobleter, 1994; Garrote et al., 1999). In the case of hardwoods, little degradation of cellulose occurs below 230°C (Garrote et al., 1999). At mild conditions, hydrolysis causes reduction of cellulose degree of polymerization (DP) but the yield of the polymer stays unaffected (Testova, 2015).

Dissolved polymers and oligomers further degrade to monomers with the formation of different degradation products. For instance, furfural and hydroxymethylfurfural are produced by dehydration of pentoses and hexoses, respectively (Fengel and Wegener, 1984c). Moreover, as demonstrated by (Li et al., 2010), who monitored an amount of generated furfural at the temperature range of 150–210°C, the degradation of the monomers becomes more extensive at a higher temperature.

Hence, the yield and molar mass of the extracted hemicelluloses as well as the composition of the hydrolysates depends on the raw material and the extraction conditions. Extreme conditions, such as high temperature and extended extraction time, are undesirable for the extraction of hemicelluloses in a polymeric form with low amounts of impurities.

Recovery of hemicelluloses from the extracts can be performed by ultrafiltration (Al Manasrah et al., 2012) or precipitation with ethanol (Liu et al., 2011; Sixta et al., 2011; Vega et al., 2012).

### 2.3.3 Xylan extraction by cold alkali (CAE)

CAE along with hot alkali extraction method are traditionally applied to remove non-cellulosic compounds and to narrow a molar mass distribution of the dissolving grade pulps (Sixta, 2006d). CAE of pulps is usually performed at low temperature (20–40°C), high concentration of alkali (1–3 M) and 5–10% pulp consistency (Sixta, 2006d). The extraction occurs through swelling of the fibers and physical dissolution of the short-chain carbohydrates (Sixta, 2006d). The interaction of alkali and pulp is fast, and 5–10 min of the extraction process appears to be sufficient (Saukkonen et al., 2012; Sixta, 2006d). A further increase of the retention time has no effect on the yield of xylan extraction (Saukkonen et al., 2012; Sixta, 2006d). Recovery of xylan from the extracts can be done by precipitation with acid or by ultrafiltration (Sixta, 2006d).

Several research groups performed CAE to isolate birch xylan of pulps (Alekhina et al., 2014; Fuhrmann and Krogerus, 2009; Janzon et al., 2008). The extracted and recovered material from bleached birch kraft pulps was mainly composed of xylan, 95–99% (Alekhina et al., 2014; Fuhrmann and Krogerus, 2009; Janzon et al., 2008) which was still substituted with MeGlcA groups with the ratio 1.4–1.5:100 of MeGlcA:Xyl (Alekhina et al., 2014; Janzon et al., 2008). The absence of acetyl groups in the structure of the extracted xylan indicated deacetylation of the polymer that occurred due to severe conditions during pulping, bleaching and extractions (Alekhina et al., 2014; Janzon et al., 2008). The yield and weight average DP ( $DP_w$ ) of extracted xylan varied among the laboratories, probably due to differences in the extraction and recovery processes. So, that the reported values for xylan yield were 60–70% (Alekhina et al., 2014; Fuhrmann and Krogerus, 2009) and up to 98% (Janzon et al., 2008) based on the initial content of xylan in pulps, and the reported  $DP_w$  values were 89 (Alekhina et al., 2014; Janzon et al., 2008) and 197 (Fuhrmann and Krogerus, 2009). During carbohydrate analysis anhydroglucose, anhydromannose and anhydroarabinose were present in the extracted material with the amounts of less than 1% (Alekhina et al., 2014; Janzon et al., 2008). Lignin was not detected in the recovered material (Alekhina et al., 2014). Thus,

CAE allows isolation of pure deacetylated xylan with a relatively high molar mass and less substituted with MeGlcA side groups.

## 2.4 Light-responsive MCCDs

Light-responsive polymers contain in their structure chromophore groups, which are reactive towards the light (Irie, 1990). Under light exposure, electron transitions and photochemical reactions characteristic of the attached chromophore groups can become relevant for the polymers (Bretschneider, 2013; Wondraczek et al., 2012, 2011, 2010).

When a photon of light of a certain  $h\nu_A$  energy strikes the molecule, transition of the molecule takes place from its ground to the excited state of a higher energy (Figure 3). The excited molecule can release the acquired energy through non-radiative (internal conversion and intersystem crossing) and radiative (fluorescence, phosphorescence) photophysical processes. In addition, the excited molecule can also interact with other molecules, e.g. by direct energy or electron transfer as well as with the formation of excited complexes (excimers). (Berland, 2001; Lakowicz, 2006; Winnik, 1993)

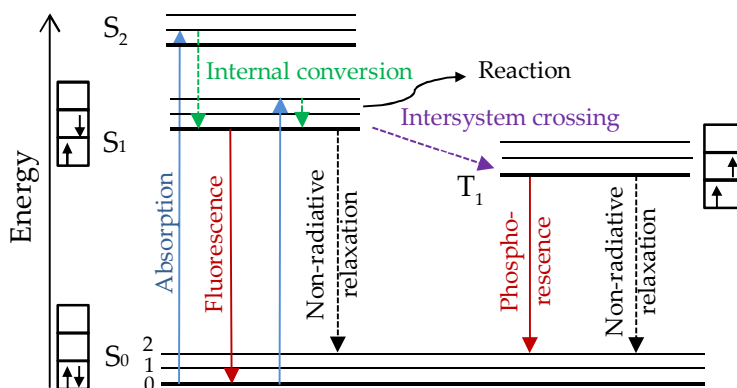


Figure 3. Jablonski diagram: electronic ( $S_0$ – $S_2$ ) and vibrational (0–2) transitions of an excited molecule by light.  $S_0$ ,  $S_1$  and  $S_2$  – a ground, first and second singlet electronic states;  $T_1$  – a triplet electronic state (Berland, 2001; Lakowicz, 2006).

The acquired energy can also induce different photochemical reactions such as isomerization, dissociation and crosslinking. In this case, the light absorption can cause changes in physical properties of the polymers such as viscosity, solubility, conductivity and, consequently, of



the materials to which they are attached. (Berland, 2001; Irie, 1990; Wondraczek et al., 2011, 2010)

#### 2.4.1 Cellulose as a raw material for MCCDs

Cellulose is the most abundant polysaccharide on Earth and can be found in all plants, *e.g.* wood contains 40–45% of cellulose on dry matter (Sjöström, 1993). Commercially, cellulose can be isolated from wood and cotton (Heinze and Liebert, 2001). With the former, prehydrolysis kraft pulping or sulfite pulping with subsequent bleaching are used (Sixta, 2006d).

Cellulose is a linear homopolysaccharide consisting of  $\beta$ -D glucopyranose units linked via 1–4 glycosidic bonds (Sjöström, 1993). DP of cellulose in wood is on average 10000 (Alen, 2000). Owing to the hydroxyl groups, cellulose macromolecules create inter and intra molecular hydrogen bonds and form microfibrils with amorphous and crystalline regions (Sjöström, 1993). Supramolecular structure and high DP make this polymer insoluble in most of the solvents (Sjöström, 1993).

Commercially, cellulose esters such as cellulose nitrate, xanthate, acetate, and cellulose ethers such as methyl, ethyl and carboxymethyl cellulose are produced by acylation and alkylation reactions in acidic and alkaline media, respectively (Sjöström, 1993). The reactions are performed under heterogeneous conditions, meaning that the polymer is not dissolved prior to the derivatization (Heinze et al., 2006; Sjöström, 1993). However, the homogeneous conditions are preferable in designing polysaccharides with specific functionalities due to better accessibility of the hydroxyl groups of cellulose. Reactivity of the hydroxyl groups also plays an important role in the derivatization reactions (Sjöström, 1993).

Recent studies demonstrated the possibility of the incorporation of several functional groups into the structure of bio-polymers using well established tools of polysaccharide chemistry (Bretschneider, 2013; Wondraczek et al., 2012, 2010). For instance, the cellulose derivatives can be designed in such a way that they bear one functional group, which is reactive towards the light, and another ionic functional group, which provides solubility of the derivatives in aqueous solutions (Wondraczek et al., 2012). The latter ionic group (cationic or anionic) can also facilitate interaction of the derivatives with the material bearing opposite charged groups. If applied as surface modifying agents, such light-responsive cellulose derivatives can endow the materials with light-responsive functionalities.

## 2.4.2 Synthesis of coumarin-type MCCDs

Coumarin and its derivatives can be considered good candidates for light-responsive functional groups of cellulose derivatives. In particular, under UV light exposure at 320 nm, depending on the light intensity, coumarin can possess fluorescence, phosphorescence or crosslink with the formation of dimers (Trenor et al., 2004).

Recently, Wondraczek, Pfeifer, & Heinze (2012) demonstrated a two-step homogeneous synthesis reaction for the making of cellulose derivatives with both pendant coumarin and cationic moieties (Figure 4). The groups are introduced in the first and in the second step, respectively. Prior to the first step, 2-[(4-methyl-2-oxo-2H-chromen-7-yl)oxy]acetic acid (**1**) was activated with a *N,N*-carbonyldiimidazole (CDI) coupling agent, and the produced imidazolide of the acid was used as an esterifying agent to obtain a coumarin-type cellulose derivative (**2**) (Figure 4). In the second step of the synthesis, the cellulose derivatives were allowed to react with imidazolide of a cationic carboxylic acid (**3**) to obtain coumarin-type cationic cellulose derivatives (**4**), namely mixed 2-[(4-methyl-2-oxo-2H-chromen-7-yl)oxy]acetic acid-(3-carboxypropyl)trimethylammonium chloride esters of cellulose.

The degree of substitution of photoactive ( $DS_{\text{Photo}}$ ) and cationic ( $DS_{\text{Cat}}$ ) moieties could be adjusted by varying the molar ratio of the carboxylic acid/CDI to anhydroglucose units of cellulose. For instance, the synthesized derivatives had  $DS_{\text{Photo}}$  of 0.05–0.37 and  $DS_{\text{Cat}}$  of 0.19–0.34 (Wondraczek et al., 2012). As the esterification was performed at mild conditions, the cellulose backbone was not degraded, which was concluded based on the fact that DP of cellulose was almost unchanged after the synthesis reaction (Wondraczek et al., 2012).

The obtained derivatives possessed photoactive functionalities intrinsic to coumarins, particularly, reverse photodimerization. Moreover, the derivatives were soluble in aqueous solutions. The solubility is an important property of the synthesized derivative that has direct influence on their final application. (Wondraczek et al., 2012)

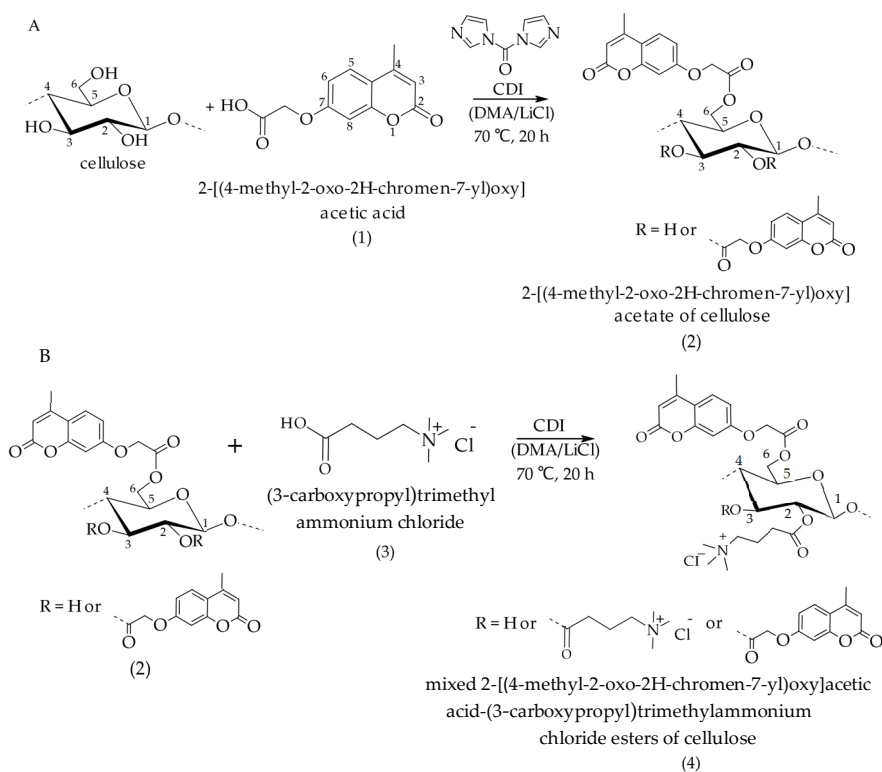


Figure 4. Synthesis of coumarin-type cationic cellulose derivatives (Wondraczek et al., 2012).

### 2.4.3 Synthesis of naphthalimide-type MCCDs

Naphthalimide-based fluorophores is another class of compounds that can be used to endow cellulose, or generally other materials, with light-responsive properties such as fluorescence. Similar to the coumarin compounds, the emission properties of naphthalimide and its derivatives are strongly dependent on the substituents (Jacquemin et al., 2010).

Bretschneider (2013) produced fluorescent naphthalimide-type MCCDs, namely mixed *N*-(3-propanoic acid)- and *N*-(4-butanoic acid)-1,8-naphthalimide-(3-carboxypropyl)trimethylammonium chloride esters of cellulose (7) (Figure 5). The two-step synthesis similar to the one used for coumarin-type MCCDs was applied to obtain such derivatives. The obtained naphthalimide cellulose derivatives had similar  $DS_{\text{Cat}}$  of 0.30–0.35 but differed in  $DS_{\text{Photo}}$ , with the maximum value of 0.2 in the case of the propanoic- and 0.3 for the butanoic-type cellulose derivatives. The solubility of the derivatives depended on the balance between  $DS_{\text{Cat}}$  and  $DS_{\text{Photo}}$ . So, that by increasing of  $DS_{\text{Photo}}$  to about 0.2 and at fixed  $DS_{\text{Cat}}$  of

0.3, propanoic naphthalimide cellulose esters became water insoluble.  
 Butanoic naphthalimide cellulose esters lost their solubility at 0.3 DS<sub>Photo</sub>.

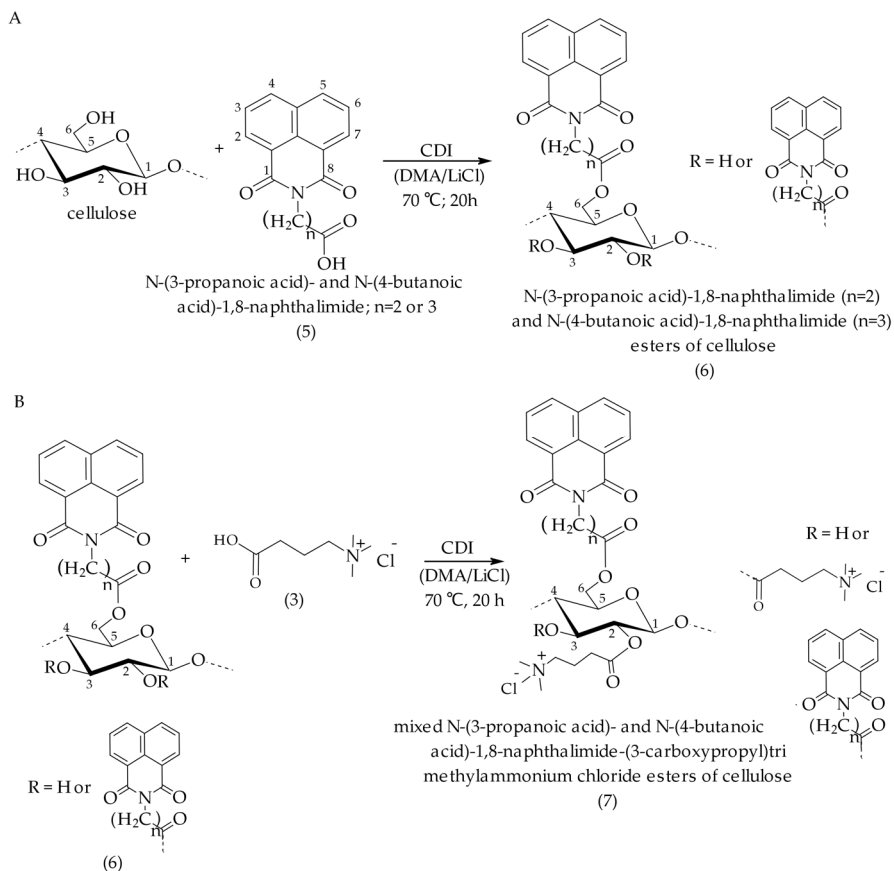


Figure 5. Synthesis of naphthalimide-type cationic cellulose derivatives (Bretschneider, 2013).

## 3 Experimental

### 3.1 Materials

#### 3.1.1 Raw materials

*Paper I.* Birch wood chips were obtained from UPM Kaukas mill (Lappeenranta, Finland), screened in the laboratory, and fractions with a thickness of 2–8 mm were used for PHWE of xylan. ECF bleached birch kraft pulp used for CAE of xylan and unbleached pine kraft pulp used for the fiber modification by xylan were collected from Metsä Fiber Oy's Rauma mill (Finland). The unbleached pulp was screened and simultaneously washed using Valmet TAP 3.3 screener with a screen basket of 0.15 mm aperture size.

*Papers II, III, IV.* Bleached eucalyptus kraft pulp was received from Metsä Fiber Oy (Kaskö, Finland). The air-dried pulp was disintegrated according to ISO 5263:1995 (E), centrifuged and stored in a cold room.

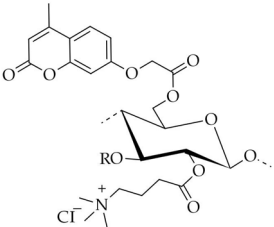
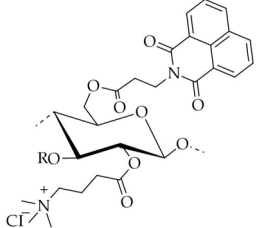
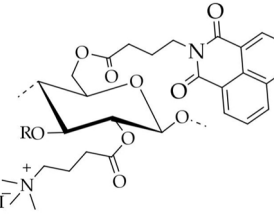
#### 3.1.2 Synthesized MCCDs

*Papers II-III.* Mixed 2-[(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetic acid-(3-carboxypropyl)trimethylammonium chloride esters of cellulose designated herein as PCCDs were synthesized and characterized by (Wondraczek et al., 2012), and described therein (see Section 2.4.2.)

*Paper IV.* Preparation and characterization of mixed *N*-(3-propanoic acid)- and *N*-(4-butanoic acid)-1,8-naphthalimide-(3-carboxypropyl)trimethylammonium chloride esters of cellulose designated herein as FCCD-1 and FCCD-2 are described elsewhere (Bretschneider, 2013; Grigoriy et al., 2017), see Section 2.4.3.

Both PCCDs and FCCDs were used as surface modifying agents for the eucalyptus pulps (Table 3).

Table 3. Description of MCCDs applied for the fiber modification.

Structure	Photoactive group type	Code	DS <sub>Photo</sub>	DS <sub>Cat</sub>
	2-[(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetic acid	PCCD-1	0.11	0.34
		PCCD-2	0.37	0.34
	N-(3-propanoic acid)-1,8-naphthalimide	FCCD-1	0.07	0.31
		FCCD-2a	0.11	0.32
	N-(4-butanoic acid)-1,8-naphthalimide	FCCD-2b	0.22	0.33

### 3.1.3 Other chemicals and materials

*Paper II.* Basic gold sensor plates were purchased from Bionavis and used in surface plasmon resonance (SPR) experiments for modelling of adsorptive surfaces. 11-mercapto-undecanoic acid, 11-mercapto-1-undecanol and 1-dodecanethiol were obtained from Sigma-Aldrich and used as self-assembled monolayers (SAM): SAM-COOH, SAM-OH and SAM-CH<sub>3</sub>, respectively.

*Papers I-IV.* Other chemicals and solvents were purchased from chemical companies and used without further treatment.

## 3.2 Methods

### 3.2.1 Extraction of xylans

#### *Isolation of xylan by PHWE*

*Paper I.* Screened birch wood chips were extracted in a 10 L rocking digester with distilled water at a liquid-to-wood ratio of 5:1. The heating rate was 2°C/min, and the extraction was carried out at 160°C for 10 min. After the extraction, the liquor was collected and evaporated at 42°C under vacuum. The precipitation of xylan was done by diluting the concentrated liquor with an 8-fold amount of ethanol (v/v) and keeping the beaker overnight in a cold room. The following day xylan was separated from the liquor by centrifugation and filtration, and it was washed with ethanol and freeze-dried. (Vega et al., 2012)

#### *Isolation of xylan by CAE*

*Paper I.* Air-dried bleached birch kraft pulp was torn into pieces and placed into a plastic bag. The isolation of xylan was done using 1 M solution of NaOH at 10 % (w/w) pulp consistency during 30 min at a room temperature. After the reaction, the pulp slurry was filtered and the liquor was neutralized with 1 M hydrochloric acid. The precipitated xylan was centrifuged, filtered, washed with ethanol and water, and freeze-dried. (Sixta, 2006d)

### 3.2.2 Modification of pine kraft pulp fibers during oxygen delignification by the extracted xylans

*Paper I.* Oxygen delignification of unbleached pine kraft pulp was carried out in a Quantum Mark IV (Akron, United States) reactor using the following conditions: consistency of 10%, temperature of 95°C, duration of 60 min, NaOH charge of 2% (dry pulp based), and oxygen pressure of 6 bar (Figure 6). The extracted xylans were dispersed in water and added to the reactor together with the NaOH solution. The dosages of the xylans were 2% and 5% (w/w). The delignified pulps were washed until neutral pH and clear filtrates.

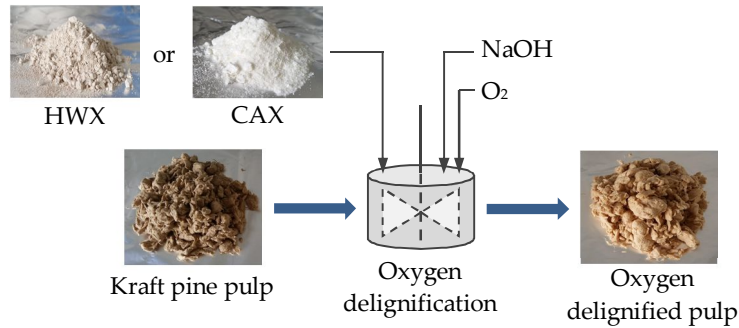


Figure 6. Modification of pine kraft pulp during oxygen delignification by adsorption of HWX and CAX.

### 3.2.3 Bleaching of the modified pine pulp fibers

*Paper I.* After oxygen delignification, the modified and reference pulps were bleached in a short bleaching sequence D<sub>0</sub>-EOP-D<sub>1</sub> (Table 4). The bleaching with chlorine dioxide (D<sub>0</sub>, D<sub>1</sub>) was carried out in plastic bags placed into a thermostatic bath. The oxygen and hydrogen peroxide reinforced alkaline extraction stage (EOP) was performed in the Quantum Mark IV reactor. The pulps were washed after each bleaching stage as described in section 3.2.2.

Table 4. Bleaching conditions (Gullichsen, 2000).

Parameters	D <sub>0</sub> <sup>a</sup>	EOP <sup>a</sup>	D <sub>1</sub> <sup>a</sup>
Consistency, %	6	8	8
Temperature, °C	60	80	75
pH	2-2.5	11	4.5-5
Reaction time, min	60	80	200
O <sub>2</sub> pressure, bar	-	2.8	-
NaOH, g/kg	-	20	-
ClO <sub>2</sub> , g/kg	5	-	8
H <sub>2</sub> O <sub>2</sub> , g/kg	-	6	-

<sup>a</sup>D, chlorine dioxide bleaching stage; EOP, hydrogen peroxide and oxygen reinforced alkaline extraction stage.

### 3.2.4 Beating of the bleached pine pulps

*Paper I.* The bleached modified and reference pulps were beaten using a valley beater as described in ISO 5264/1. The beating was conducted to achieve Schopper-Riegler number of 30–33 (SR, ISO 5267/1).



### 3.2.5 Modification of bleached eucalyptus kraft fibers by adsorption of MCCDs

#### *Adsorption of coumarin-type MCCDs*

*Paper II.* Wet pulp corresponding to 150 mg of dry weight was soaked in  $10^{-5}$  M sodium bicarbonate solution during 30 min in capped glass bottles. The pulp soaking and adsorption studies were performed at a room temperature and under 270 rpm agitation speed using a multipoint agitation plate (Figure 7). PCCD-1 and PCCD-2 (Table 3) were dissolved in  $10^{-5}$  M  $\text{NaHCO}_3$  solution to obtain 1 g/L stock solutions. Different volumes of the derivative solutions were added to the pulp suspension corresponding to 0.5, 1.6, 3.2, 5.0, 7.0 and 10% (pulp based) dosages. During the adsorption, the bottles were covered with foil to protect the samples from the light. The final concentration of the pulp suspension was 0.6% (w/w). The adsorption studies were done in duplicates during 17 hours at a room temperature. After the adsorption time elapsed, the pulp suspensions were filtered and used to prepare hand-sheets. The filtrates were collected and analyzed with a Shimadzu 2600 spectrophotometer (see Section 3.3.2).

In *Paper III*, the pulp fibers were modified by adsorption of PCCD-2 (Table 3) with the dosage of 3.2% (pulp based) as described above.

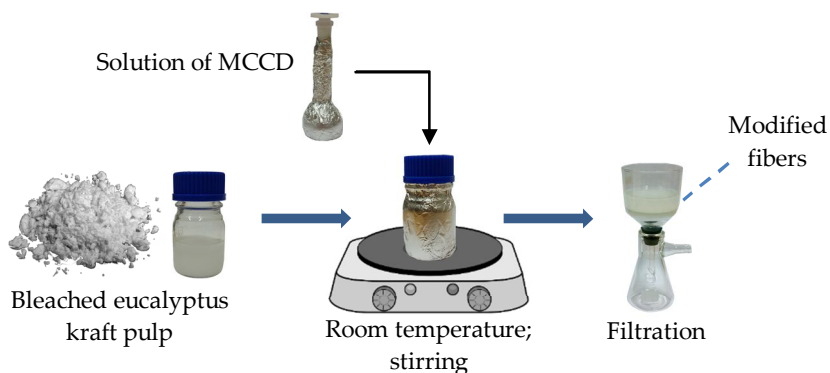


Figure 7. Modification of bleached eucalyptus kraft pulp fibers by adsorption of MCCDs.

#### *Paper IV. Adsorption of naphthalimide-type MCCDs*

Adsorption conditions were chosen similar to those described for *Papers II, III* with a few exceptions. The concentration of the stock solutions of the derivatives was 0.5 g/L. The dosages of the derivatives to

the pulp were varied in the range of 0.5–5% (w/w). In the end of the adsorption, the pulp suspensions were centrifuged at 3500 rpm for 5 min. The pulp samples were used to make hand-sheets and the filtrates were analyzed with a Perkin-Elmer LS50B spectrofluorometer (see Section 3.3.2).

### 3.2.6 Kinetic studies of the adsorption of MCCDs

*Paper IV.* The naphthalimide-type MCCDs were adsorbed onto the pulp fibers with the dosage of 2% (pulp based). The adsorption times varied from 10 min to 17 hours at  $25\pm 2^\circ\text{C}$ . Other conditions were the same as in the adsorption experiments (Section 3.2.5, *Paper IV*). After centrifugation, the filtrates were analyzed using a Shimadzu 2600 spectrophotometer.

### 3.2.7 Adsorption studies of MCCDs at different electrolyte concentrations

*Paper IV.* Sodium chloride used as an electrolyte was dissolved in deionized water to obtain solutions with concentrations of  $10^{-2}$ ,  $10^{-3}$ ,  $10^{-4}$  and  $10^{-5}$  M. The solutions had a pH of  $6.2\pm 0.1$ . These solutions were used to prepare solutions of naphthalimide-type MCCDs and adjust the consistency of the pulp suspensions. The dosage of the derivatives was always 2% based on pulp weight, and the adsorption time was 17 hours. Other conditions of the experiments were similar to the ones used in the kinetic studies (see Section 3.2.6).

To investigate desorption of the derivatives, the obtained after centrifugation modified fibers were again diluted with the corresponding NaCl solutions to the consistency of 1.5–2% (dry pulp based), shaken, centrifuged and the supernatants were analyzed.

### 3.2.8 Photocrosslinking of the fibers

Photocrosslinking of the fibers/fiber network was performed by a UV light using a Bluepoint 4 UV-source (Hönle AG, Munich, Germany) equipped with a BP4 320–390 nm filter.

*Paper II.* To study the photocrosslinking reaction as function of time, hand-sheets were made of the pulp fibers modified by adsorption of PCCD-1 at 3.2% dosage (pulp based, see section 3.2.5). The sheets were prepared using a self-designed sheet former. The irradiation of the air-dried sheets was done from one side.

*Paper III.* To study the photocrosslinking effect on the mechanical properties of the fibrous material, the pulp fibers were modified with PCCD-2 at 3.2% dosage (pulp based) and hand-sheets of 60 g/m<sup>2</sup> were made using a standard sheet former. 10<sup>-5</sup> M NaHCO<sub>3</sub> solution was used to fill the tower of the former. The prepared air-dried sheets were irradiated with the UV light at both sides for 7 min. To investigate the influence of the photocrosslinking on the properties of the single fibers, a dilute suspension of the modified fibers was irradiated for 8 min with shaking of the suspension each two minutes.

### 3.3 Analytical procedures

#### 3.3.1 Characterization of the extracted xylans

##### *Methanolysis and gas chromatography (GC)*

*Paper I.* Around 6 mg of HWX and 3 mg of CAX were weighted in pear-shaped flasks. Methanolysis was performed as described elsewhere (Sundberg et al., 1996). 0.1 mg/mL of resorcinol in methanol was used as an internal standard. The samples were analysed by GC with flame ionization detection (FID) with the following set-up: column J&W HP-1, 25 m × 0.200 mm (ID), film thickness 0.11 μm; the injector temperature 250°C, the split ratio 1:25; the temperature program of the oven 100°C, 1 min, 4°C/min, 170°C, 12°C/min, 300°C, 7 min. The temperature of the FID was 310°C. Hydrogen gas was used as a carrier.

##### *Fourier transform infrared - attenuated total reflectance spectroscopy (FTIR-ATR)*

*Paper I.* Infrared spectra of the xylans were obtained with a Thermo Scientific Nicolet iS50 FTIR spectrometer with an ATR module. The spectra were collected in a wavenumber range of 500–4000 cm<sup>-1</sup>, with the resolution of 4 cm<sup>-1</sup>, and number of scans of 32.

##### *Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS)*

*Paper I.* The presence of lignin impurities in the extracted xylans was evaluated via pyrolysis coupled with GC and mass spectrometry. The samples were pyrolyzed in a filament pulse resistance-heated pyrolyzer Pyrola 2000 (Pyrol AB, Lund, Sweden) connected to an HP 6890-5973 GC-quadrupole-MSD instrument (Hewlett-Packard, Palo Alto, CA). The

details of the analysis are described in (Smeds et al., 2012) with few adjustments. About 100 µg of the sample was placed on a Pt filament and one drop of acetone was added. After solvent evaporation, the probe was injected into the pyrolyser chamber. The pyrolysis of the samples was carried out during 2 s at 600°C, at a chamber temperature of 175°C. An assignment of the spectra was done with the help of mass spectral libraries of Wiley 275 and NIST 98, and the library developed by the Laboratory of Wood and Paper Chemistry, Åbo Akademi University.

### *Lignin determination*

*Paper I.* Lignin content in the crude xylans was measured according to TAPPI T 222 om-02 and TAPPI UM 250.

### *Size exclusion chromatography (SEC)*

*Paper I.* The molar masses of the xylans were determined employing JASCO SEC (Tokyo, Japan). The separation of the macromolecules was done using NOVEMA 3000 and NOVEMA 300 columns and the signal was collected with an RI detector (RI-930). Before the analysis, the xylans were dissolved in DMSO/LiBr at the concentration of 1 g/L. The conditions of the chromatography were the following: injection volume 100 µL, flow rate 0.5 mL/min, and temperature 65°C. DMSO/LiBr was used as an eluent. The results were processed with the help of software WinGPC (Polymer standard service, PSS Mainz, Germany). The calibration was carried out with pullulans.

### **3.3.2 Quantification of MCCDs adsorption onto the fibers**

*Papers II, IV.* Concentration of the derivatives in the filtrates after the adsorption was determined by measuring light absorption/emission spectra. Adsorption was estimated with the help of corresponding calibration curves prepared using aqueous solutions of MCCDs. The amounts of the adsorbed derivatives onto the fibers expressed as mg/g of pulp fibers and as percentage of the added amounts were calculated according to Equation 1 and Equation 2, respectively:

$$m_{ads} = \frac{(m_0 - C_t * V)}{m_f} \quad (1)$$

$$m_{ads} = \frac{(m_0 - C_t * V)}{m_0} * 100 \quad (2)$$

where,

$m_0$  – amount of added derivative, mg;  
 $m_f$  – amount of dry pulp fibers used for the experiment, mg;  
 $V$  – volume of liquid phase in the system, mL;  
 $C_t$  – concentration of the derivatives in the filtrate, mg/mL.

#### *Ultraviolet-visible (UV-vis) light absorption*

*Papers II-IV.* Concentrated solutions of MCCDs prepared for the adsorption studies (see 3.2.5, 3.2.6, 3.2.7) were diluted to 0.01–0.1 g/L concentrations with aqueous solutions of the corresponding ionic strength. UV-vis absorption spectra of the derivatives solutions were collected using a Shimadzu 2600 spectrophotometer.

#### *Emission of the light*

*Paper IV.* Fluorescence spectroscopy was performed with a Perkin-Elmer LS50B spectrofluorometer. Solutions of MCCDs with concentrations below 0.01 g/L were prepared in  $10^{-5}$  M solution of  $\text{NaHCO}_3$ . An excitation wavelength corresponded to the UV absorption maximum. The emission spectra were collected in the range of 350–600 nm, and a 350 nm cut-off filter was used during the measurements.

### **3.3.3 Interactions of MCCDs with model surfaces**

*Paper II.* Gold sensor plates were cleaned with a piranha solution and immersed for 24 hours into 1 mM solution of 11-mercapto-undecanoic acid or 11-mercapto-1-undecanol, or 1-dodecanethiol prepared in absolute ethanol to create self-assembled monolayers (SAM) representing anionic (SAM-COOH), hydrophilic (SAM-OH) or hydrophobic (SAM-CH<sub>3</sub>) surfaces, respectively (Kaya et al., 2009; Schwikal et al., 2011). Then, the model surfaces were inserted into a flow cell of an SPR-Navi 200 instrument to perform adsorption of the derivatives.  $10^{-5}$  M solution of  $\text{NaHCO}_3$  was run through the flow cell with a flow rate of 20  $\mu\text{L}/\text{min}$  at 23°C for at least 0.5 h to obtain a stable baseline. Subsequently, one of the cellulose derivative solutions with a concentration of 0.2 g/L was injected into the instrument, and it was allowed to run for 5 minutes. This step was followed by washing with the bicarbonate solution to remove unbound derivatives. For each polymer the measurements were done four times and the results were shown as an average curve.

### 3.3.4 Characterization of the reference and modified pulps

#### *Standard methods*

*Paper I.* Basic properties of pulps were determined using following standard procedures: kappa number (ISO 302-1981), hexeneuronic acid (HexA) content (T 282 pm-07) and intrinsic viscosity (ISO 5351/1-1981). A total amount of anionic groups of pulp fibers was determined according to (Fardim and Holmbom, 2003).

#### *Hydrolysis and liquid chromatography*

*Paper I.* Adsorption of the xylans onto the pulp fibers during an oxygen delignification stage and resistance of the adsorbed xylans towards bleaching and beating was evaluated via pulp hydrolysis and analysis of the hydrolysates with high performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD). Pulp samples were hydrolysed with 72% sulfuric acid according to (Sundberg et al., 2003). Autoclavation of the samples was done at 125 °C for 90 min. A barium hydroxide solution (0.1 M) was used for the sample neutralization. Sorbitol was added to the neutralized samples as an internal standard. Then, filtered samples were injected into the instrument. Different amounts of sugars (arabinose, glucose, xylose, mannose, rhamnose, and galactose) were dissolved in deionized water to prepare calibration solutions.

The instrument was used with the following set-up: Dionex ICS 5000 (Sunnyvale, United states) system, capillary PA20 CarboPac anion-exchange resin column (0.4 x 150 mm) run at 30°C, an eluent flow rate of 8 µL/min, and injection volume of the sample of 20 µL. Potassium hydroxide was used as the eluent. The concentration of the eluent was changed stepwise during the runs: 0–12 min 1 mM of KOH, 12–17 min 5 mM of KOH and 17–21 min 10 mM of KOH.

#### *Time-of-flight secondary ion mass spectrometry (ToF-SIMS)*

*Papers I, II.* Surface chemical composition of the pulp samples was analyzed using a Physical Electronics ToF-SIMS TRIFT II spectrometer. The surface of the samples (200x200 µm<sup>2</sup>) was bombarded by a primary ion beam of <sup>69</sup>Ga<sup>+</sup> (liquid metal ion source) to generate secondary ions. The applied acceleration voltage was 25 kV. An electron flood gun was used to compensate the charge of the surface. The mass spectra and

images were obtained based on signals of the positive secondary ions reached the detector. Assignment of the characteristic peaks for the xylans in the spectra of xylan-treated fibers was done according to literature (Fardim and Durán, 2003). To identify peaks in the spectra of PCCD-treated fibers, a drop of PCCD dissolved in water was placed on an ash-free filter paper, air-dried, and analyzed with the spectrometer.

### 3.3.5 Optical properties of the hand-sheets

*Papers I-IV.* Hand-sheets were made of pulp samples according to SCAN-CM 11:95.

*Papers II-IV.* A diffuse reflection of the light from the hand-sheets was collected with a Shimadzu 2600 spectrophotometer equipped with an integrating sphere ISR-2600 Plus.

*Papers I-IV.* An Elrepho spectrophotometer was used to measure brightness (ISO 2470) and whiteness (ISO 11475) of the hand-sheets. The equipment also allowed quantification of the fluorescence of the samples over the visible spectrum by subtracting the fluorescence obtained with and without a UV light component in the incident light (SCAN-G 5:03).

*Paper IV.* An image of single fibers fluorescing under the UV light was obtained using an Olympus BX60 fluorescence microscope coupled with a Nikon DS-Fi2 camera. The microscope set-up was as follows: excitation filter (330–385 nm), a dichroic mirror (400 nm) and a barrier emission filter (420 nm).

*Paper IV.* An image of the fluorescent logo of Åbo Akademi University was obtained under the light illumination using a UV black light bulb (15 W, 320–415 nm). The template with the logo of Åbo Akademi University was cut from the hand-sheet of the reference fibers, which then was placed on the top of a hand-sheet made of the modified fluorescent fibers.

### 3.3.6 Mechanical properties of the fibers and fiber networks

#### *Standard analyses*

*Papers I, III.* Mechanical properties of the pulps were determined using following standard procedures: tensile index (ISO 1924-2), and Z-directional tensile strength (ISO 15754) with a TIRA test system and 20 mm/min tensile velocity.

### *Dynamic mechanical analysis (DMA)*

*Paper III.* Viscoelastic properties of the pulp hand-sheets were studied with a dynamic mechanical analyser DMA/SDTA861e (Mettler Toledo). Prior to the analysis, the hand-sheets were conditioned at 30°C and 50% relative humidity in the instrument. Two different sets of the measurements were conducted. In the first set, the samples were subjected to displacement of varying amplitude (1–50  $\mu\text{m}$ ) at a constant frequency of applied stress (1 Hz). In the second set, the properties of the samples were measured at constant stress frequency of 10 Hz, and displacement amplitude of 4.5  $\mu\text{m}$  applied to the samples for 260 min. The relative humidity was varied according to the following sequence: 50%– 10%– 80% – 50%.

### *Flexibility of single fibers*

*Paper III.* A microrobotic platform for fiber manipulation and flexibility measurements was developed by the group of Prof. Kallio from Tampere University of Technology and was used to measure flexibility of single fibers. The fibers were taken from a drop of the suspension by two grippers and fixed between the grippers at two ends (Figure 8). The fibers were subjected to a constant deflection (3  $\mu\text{m}$ ) for a fixed period of time (5 sec) and the applied force was measured. The fibers underwent 10 loading cycles and 10 fibers were analyzed for each type of pulps. The flexibility of the single fiber was calculated from the deflection, the applied force required to bend the fiber and the length of the fibers (Saketi et al., 2010).

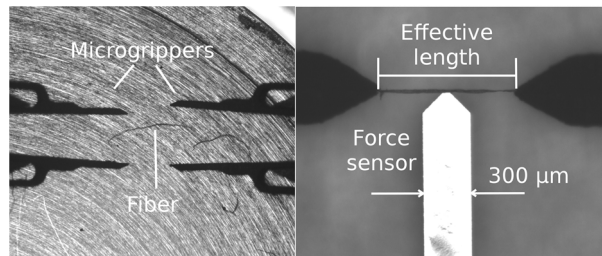


Figure 8. Flexibility analysis of pulp fibers with a microrobotic platform (Saketi et al., 2010).



## 4 Results and discussion

### 4.1 Modification of pine kraft pulp during oxygen delignification by the extracted xylans (Paper I)

#### 4.1.1 Characterization of the extracted xylans

Two types of xylan were used as dry strengthening agents. The first type of xylan, HWX, was isolated from birch wood by pressurized hot water and the second type of xylan (CAX) was extracted from bleached birch kraft pulp using cold alkali.

The results of methanolysis (Table 5) revealed that xylose in anhydrous form was the predominant hemicellulose unit in both polymers, however, its content was much larger in CAX. The amount of MeGlcA groups, as characteristic side group of hardwood xylan, in HWX was at least twice as much as in CAX. This was related to the cleavage of glycosidic bonds between the uronic acid groups and xylan backbone during kraft cooking (Sixta, 2006a). Besides, the uronic acid groups were partially converted to HexA after elimination of methanol during the cooking (Potthast, 2006). Furthermore, some of the uronic acid groups were removed during bleaching of pulp (Muguet et al., 2011; Potthast, 2006).

Table 5. Carbohydrate composition of the xylans by acid methanolysis and GC.

Sample	Anhydro-carbohydrate units <sup>a</sup> , % (w/w)								
	Ara	Xyl	Rha	Man	Glc	Gal	GlcA	Me-GlcA	GalA
HWX	0.12	51.01	0.88	4.38	3.12	3.04	0.16	3.41	1.42
CAX	0.12	79.35	0.08	0.03	0.02	0.04	0.00	1.55	0.00

<sup>a</sup>Ara, arabinose; Xyl, xylose; Rha, rhamnose; Man, mannose; Glc, glucose; Gal, galactose; GlcA, glucuronic acid; MeGlcA, 4-O-methylglucuronic acid; GalA, galacturonic acid.

Even though acetic acid groups are generally splitted off from xylan during PHWE (Sixta, 2006c), they were still present in HWX structure due to the mild conditions of the process. This conclusion was based on the FTIR-ATR spectrum of HWX (Figure 9) that showed several absorption bands originated from acetic acid groups of xylan. The bands were at 1732 cm<sup>-1</sup> due to C=O stretching vibration, 1375 cm<sup>-1</sup> due to CH<sub>3</sub> symmetrical deformation vibration and 1239 cm<sup>-1</sup> assigned to C-O-C

asymmetrical stretching vibration (Buslov et al., 2009; Socrates, 2004). On the other hand, these bands were absent in the spectrum of CAX, which lost acetic acid groups during pulping and pulp post-treatment (Alekhina et al., 2014; Janzon et al., 2008; Potthast, 2006).

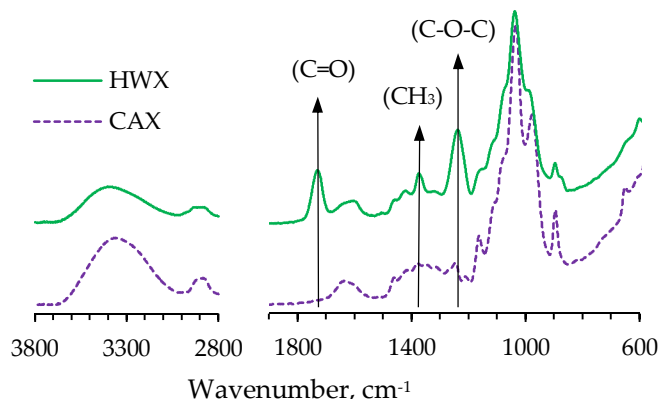


Figure 9. FTIR-ATR spectra of isolated HWX and CAX.

Another distinctive feature of HWX compared to CAX was its brownish color, which was related to the lignin impurities. A qualitative analysis of the xylans performed by Py-GC-MS revealed the presence of syringyl units of lignin in HWX. On the other hand, no lignin units were detected in CAX by this technique. Subsequent analysis of HWX using the standard procedures (TAPPI T 222 om-22 and TAPPI UM 250) revealed the lignin content of 4.8%.

A molar mass of HWX obtained by SEC showed two distinguished bands with the average molar mass ( $M_w$ ) of  $5.0 \times 10^3$  g/mol and  $6.5 \times 10^7$  g/mol. Considering impurities of lignin in HWX, it was proposed that the second peak with the higher average  $M_w$  could originate from lignin-carbohydrate complexes. In contrast, the chromatogram of CAX exhibited unimodal distribution with the average  $M_w$  of  $2.8 \times 10^4$  g/mol.

To sum up, the raw material and extraction method had direct influence on the structure of the isolated xylans. CAX appeared to be less substituted with the side groups, and it was much more pure than HWX owing to the harsh conditions during cooking, bleaching and alkali extraction.

### 4.1.2 Adsorption of the xylans during an oxygen delignification stage

The modification of pine kraft pulp with the xylans was performed during oxygen delignification. The dosages of the xylans were 2 and 5% based on the weight of oven-dried pulp.

The ratios of xylose-to-glucose in the oxygen delignified pulps (Figure 10) were compared to assess the adsorption of the polymers. The relative amount of xylose in the pulps treated with CAX during the delignification stage was higher compared to the reference delignified samples (Figure 10) strongly indicating the adsorption of the polymer. The pulps treated with CAX were more enriched in xylose and the ratio of xylose-to-glucose became higher upon the increase in the applied dosage. On the other hand, HWX had lower adsorption onto the pulp fibers as can be seen from the smaller difference in xylose-to-glucose ratios between the HWX treated oxygen delignified pulps and the reference one. The addition of the higher dosage of HWX did not result in any gain in the xylose-to-glucose ratio.

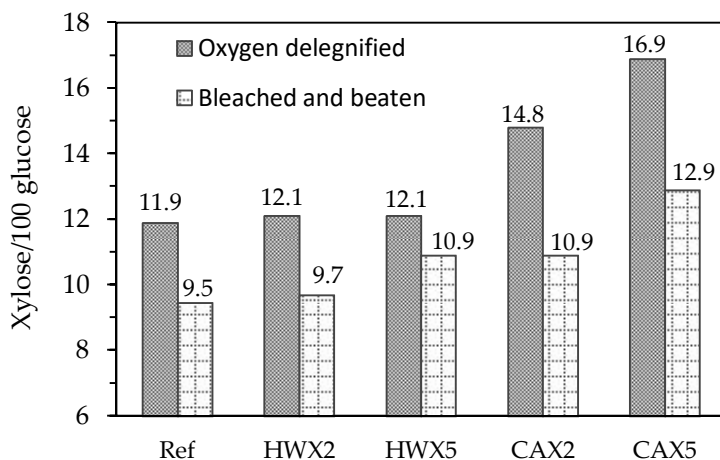


Figure 10. Ratios of carbohydrate units of the reference pulp and the pulps modified by HWX and CAX at the dosages of 2 and 5% (w/w) during an oxygen delignification stage. Error margins are within 5%.

The adsorption of CAX was more pronounced than of HWX owing to the difference in the chemical composition of the xylans. CAX was deacetylated and contained less amounts of glucuronic acid side groups, which facilitated the association of the xylan via intra and inter

molecular interactions of the chains and enhanced adsorption onto the fibers (Kabel et al., 2007; Linder et al., 2003). Also, a molecule with high molar mass as in the case of CAX loses less entropy on the adsorption and has more sites available for the interaction (Köhnke, 2010; Stenius, 2000).

#### **4.1.3 Effect of bleaching and beating on xylan retention**

Xylan was partially removed from the pulps during bleaching and beating stages (Figure 10). The loss in xylose-to-glucose ratio was larger for the CAX treated pulps with the highest initial amount of the adsorbed xylan. However, part of the adsorbed xylan retained as can be seen from the relative amount of xylose in the xylan treated pulps in comparison to the reference one. The pulps treated with 5% of CAX after the bleaching and beating exhibited the highest content of xylan.

#### **4.1.4 Surface characterization of the reference and modified fibers**

The surface composition of the bleached pulps before and after beating was characterized by ToF-SIMS. This technique determines the molar ratio of the components at the depth of up to 2 nm from the surface. In the spectra, the secondary ions with  $m/z$  of 115 and 133 were assigned to pentoses, namely xylose and arabinose (Fardim and Durán, 2003; Tokareva et al., 2011). In bleached pine kraft pulps, the amount of arabinose is rather low (Table 2). Therefore, these ions were formed mostly from xylose, *i.e.* xylan of the reference pulp and the adsorbed xylan. The secondary ions with  $m/z$  of 127 and 145 were attributed to hexoses originated from cellulose and mannan (Fardim and Durán, 2003; Tokareva et al., 2011). The ratio of the total ion counts of pentose-to-hexose (Figure 11) for the xylan treated bleached pulps was on average higher than for the reference bleached pulp. This was an additional proof that both HWX and CAX adsorbed onto the pulps during the oxygen delignification stage, and that the part of the adsorbed xylans survived the bleaching and remained on the fiber surface. In addition, the CAX treated pulps had a higher surface ratio of pentose-to-hexose than HWX treated pulps, which corroborate the findings of the HPAEC analyses of better adsorption of CAX in comparison to HWX. The ratio of pentose-to-hexose on the surface was independent of the added dosage of the

xylans. This could indicate that the xylans adsorbed deeper into the fiber wall through the pores (Köhnke et al., 2010; Liu et al., 2011).

Beating had an effect on the ratio of pentose-to-hexose of the pulp surfaces. However, based on the ratios one can conclude that the change was rather small.

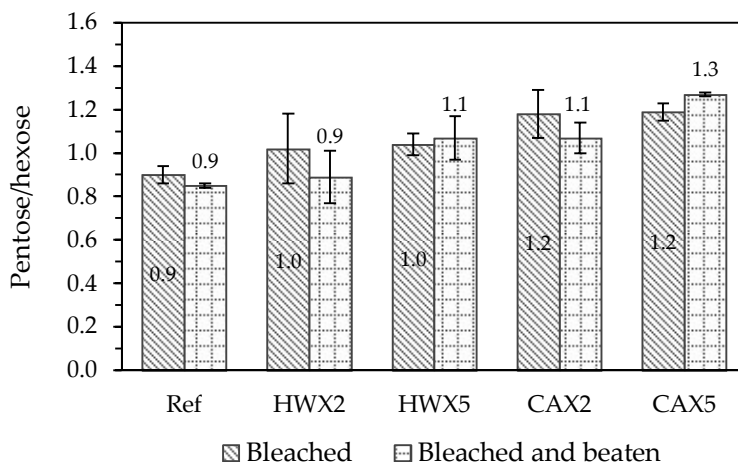


Figure 11. Ratio of pentose to hexose counts obtained by ToF-SIMS during surface characterization of the pulps: unmodified (Ref) and treated with 2 and 5% (w/w) of HWX and CAX during oxygen delignification.

#### 4.1.5 Effect of the added xylans on oxygen delignification

Addition of the xylans had an effect on the performance of the oxygen delignification stage (Figure 12A). The HWX treated pulps after oxygen delignification had a higher kappa number than the reference and CAX treated pulps. Kappa number is an indirect indicator of a lignin content, and accordingly it is higher for the pulps that contain more lignin. HexA groups also contribute to kappa number (Sixta, 2006e). However, HWX treated pulps had comparable or even lower amounts of HexA than the reference oxygen delignified pulp (Figure 13A). Therefore, the higher kappa number of HWX treated pulps was due to the higher lignin content. Moreover, HWX treated pulps had lower brightness (Figure 13C), which is an optical property related to the reflection of the light by the material (Jordan, 1996). Lignin as an aromatic polymer absorbs the light and generally has a negative effect on the brightness.

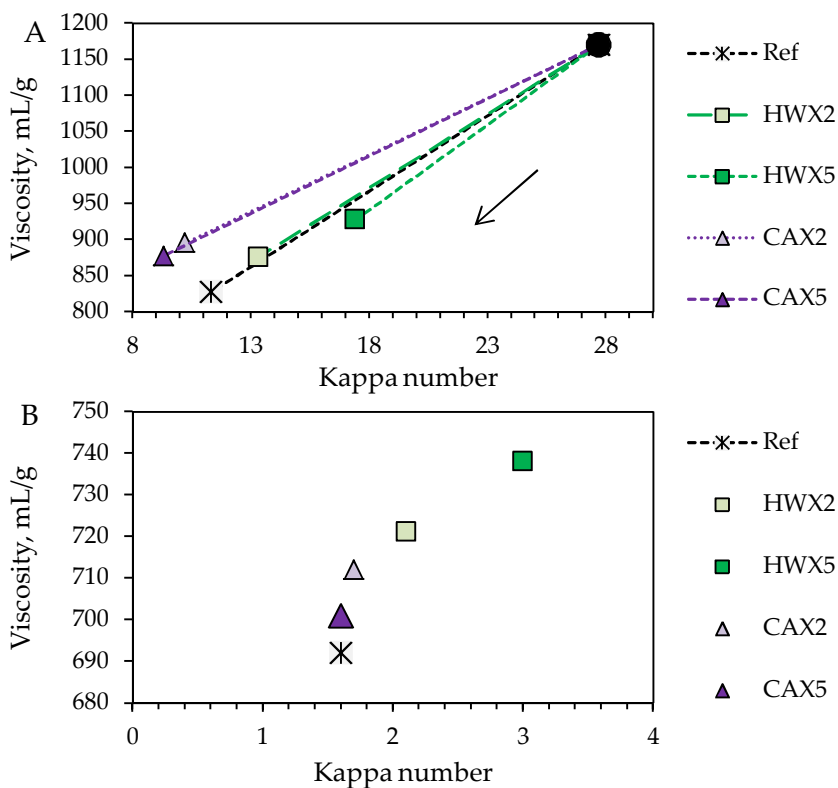


Figure 12. Kappa number and viscosity of the oxygen delignified (A) and bleached and beaten pulps (B). The pulps were modified by 2 and 5% (w/w) of HWX and CAX during an oxygen delignification stage.

The higher lignin content in the HWX treated oxygen delignified pulps could be related to the adsorption of lignin together with HWX. However, the increase in kappa number by 2 and 6 units for HWX2 and HWX5 treated pulps in comparison with the reference pulps was rather unlikely to happen only due to the presence of lignin impurities in the adsorbed xylan. Giving the fact that HWX contained around 5 % of lignin (xylan based) and the applied dosages of the xylan were 2 and 5 % (pulp based), the kappa number would have increased by around 0.7 and 1.7 units, respectively, if xylan had been adsorbed completely. This estimation was based on the assumption that 0.15 % of lignin corresponds to kappa number of 1 (Dang, 2007; Minor, 1996). Considering the actual magnitude of the kappa number increase and the partial adsorption of the xylan, the obtained results could be explained by a detrimental effect of HWX addition on the course of the oxygen delignification process. The added xylan contained uronic acids (Table 5)

as well as acetyl groups (Figure 9) that could consume the alkali. The charge of the alkali has a direct effect on both the delignification and the polysaccharide degradation (Potthast, 2006), and the lower alkali charge leads to the lower degree of delignification, *i.e.* higher kappa number, and lower cellulose degradation, *i.e.* higher viscosity (Potthast, 2006). Both these effects were observed when HWX was applied to the pulps, which implies that HWX impaired the delignification process.

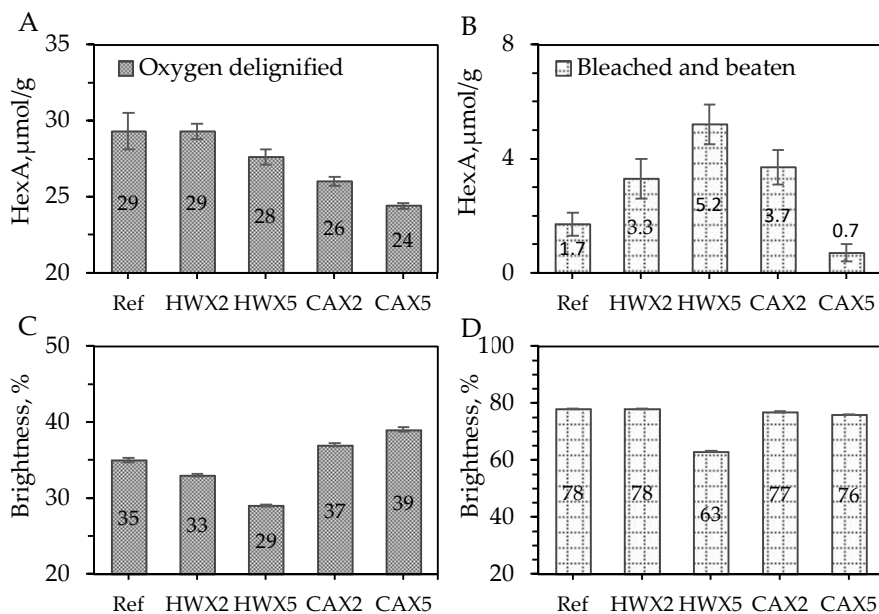


Figure 13. HexA content and brightness of the reference pulp and pulps modified during oxygen delignification by 2 and 5% (w/w) HWX and CAX.

In contrast, the addition of CAX had a positive effect on the results of oxygen delignification (Figure 12A). The CAX treated pulps had a higher viscosity and a lower kappa number than the reference pulp after the delignification stage. This means that the selectivity of the process was improved by the addition of CAX. This is in agreement with the earlier studies (Van Heiningen and Violette, 2003; Violette, 2003) that showed that the use of sugar-based polymers in an oxygen delignification stage improved the selectivity of the process. As was demonstrated, the polymers adsorbed on the pulp fibers protected cellulose from the degradation by shielding the cellulose from the radicals formed during the delignification process (Van Heiningen and Violette, 2003; Violette, 2003). Addition of CAX could exhibit a similar effect. Interestingly, the

kappa number for the CAX2 and CAX5 treated pulps was 1.1 and 2 units lower compared to the reference after the delignification stage. The same was observed for HexA content (Figure 13A). The magnitude of decrease in the HexA content for the CAX treated pulps was not enough to cause such a decrease in kappa number. 11.6  $\mu\text{mol/g}$  of HexA corresponds to 1 unit of kappa number (Li and Gellerstedt, 1997), which means that the kappa number would have additionally decreased by 0.3 and 0.4 units for CAX2 and CAX5 treated pulps after the delignification step. One could suggest that the decrease in both parameters was related to the higher yield of CAX treated pulps due to lower degradation of polysaccharides and adsorption of the xylan.

The bleaching of the pulps removed most of the lignin, which could be observed from the considerable drop in kappa number, and increased brightness (Figure 12B, Figure 13D). Degradation of polysaccharides also occurred during the bleaching as can be seen from the viscosity values (Figure 12B). The HWX treated pulps had a higher kappa number and viscosity due to the greater initial values for these pulps after the delignification stage. The brightness of the pulps was at the same level, except for HWX5 because of the higher lignin content (Figure 13D).

#### **4.1.6 Properties of the hand-sheets**

The addition of CAX at 5% dosage improved tensile index, tensile energy absorption and stretch of the oxygen delignified pulps (Figure 14). The values were higher on average by 24, 41 and 18% in comparison with the reference. The use of CAX at a lower dosage as well as the addition of HWX did not make any substantial improvement of the tested properties of the oxygen delignified pulps. However, oxygen delignified HWX5 and both CAX pulps after the subsequent bleaching and beating possessed superior mechanical properties than the corresponding reference one. Again, the pulps bearing CAX were stronger than the ones modified with HWX. In particular, bleached and beaten CAX5 pulp gained an increase in tensile index, tensile energy absorption and stretch by 23, 69 and 40%, respectively, in the relation to the corresponding reference pulp.



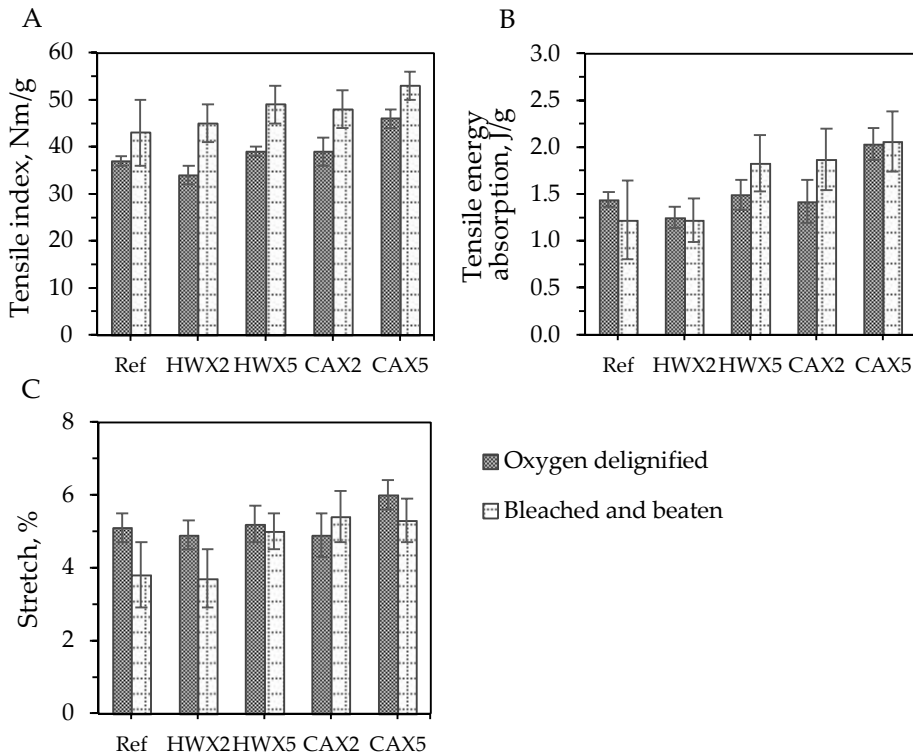


Figure 14. Mechanical properties of the reference pulp and pulps modified during oxygen delignification by 2 and 5% (w/w) HWX and CAX.

The better performance of CAX in the improvement of the pulp properties was related to the better adsorption and a higher purity of this xylan. A larger amount of the polymer on the fiber surfaces helped to create better contact between the fibers. The flexible chains of the polymer introduced more hydroxyl groups at fiber crossing areas creating additional hydrogen bonds between the fibers (Marton, 1996).

## 4.2 Photocrosslinkable pulp fibers via adsorption of coumarin-type MCCDs (Paper II)

Synthesized coumarin-type cationic cellulose derivatives have the ability to crosslink under UV light exposure (Wondraczek et al., 2012). This chapter of the thesis covers the study whether the derivatives as surface modifying agents can endow bleached eucalyptus kraft pulp fibers with photocrosslinking functionality and how this functionality can affect the performance of the fibers and fibrous materials.

Among the synthesized water soluble PCCDs (Wondraczek et al., 2012), two derivatives were selected for this study (Table 3). These derivatives possessed the highest  $DS_{cat}$ , the group that facilitates the solubility of the derivatives in aqueous solutions as well as potential interaction with the negatively charged substrate (fibers). In addition, the derivatives differed in the  $DS_{photo}$ , because, on the one hand, coumarin group is responsible for the photocrosslinking functionality, but, on the other hand, this bulky aromatic group could impair adsorption of the derivatives onto the fibers.

#### 4.2.1 Interaction of PCCDs with model surfaces

The purpose of this study was to find a type of interactions that could be involved in the adsorption of PCCDs. Three types of model surfaces were prepared containing hydroxyl, methyl and carboxyl functional groups available for the interactions to simulate hydroxyl, hydrophobic and carboxyl sites of a potential substrate (Kaya et al., 2009; Schwikal et al., 2011), *i.e.* the fibers (see Section 2.2). The experiment was performed in SPR instrument by running the flow of the derivatives solutions over the model surfaces with the following washing, and the results are depicted in Figure 15.

As shown in Figure 15A, the derivatives adsorbed rapidly and irreversibly on the anionic surfaces (SAM-COOH). This type of electrostatic interaction between the quaternary ammonium groups of the derivatives and carboxylic acid groups of the model surfaces by ion-exchange mechanism is characteristic of polyelectrolytes (Wågberg, 2000). In addition, the derivatives adsorbed irreversibly onto the hydrophobic surfaces (SAM-CH<sub>3</sub>, Figure 15B). Cationic cellulose derivative (CCD) could interact with the hydrophobic surfaces via axial C-H sites of the glucopyranose rings in the cellulose macromolecules (Medronho et al., 2012). In the case of PCCDs, coumarin functional groups could also be involved in the interaction with the surfaces. The absolute adsorbed amounts of the derivatives were larger and the adsorption plateau reached faster when the anionic surface was used as adsorbent in comparison to the hydrophobic one.

Contrarily, the adsorption of the derivatives onto the hydrophilic surfaces via hydrogen bonds was very weak and reversible, even for the CCD that did not contain the coumarin moieties (Figure 15C).

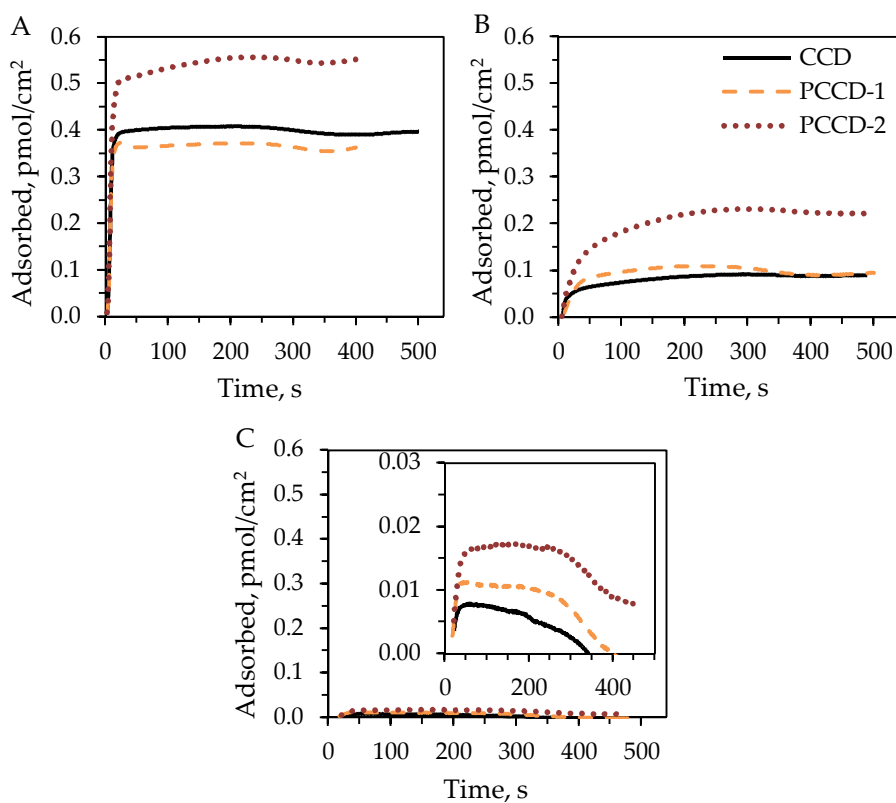


Figure 15. (A) Adsorption onto negatively charged (SAM-COOH), (B) hydrophobic (SAM-CH<sub>3</sub>) and (C) hydrophilic (SAM-OH) surfaces: CCD (DS<sub>Cat</sub> 0.29), PCCD-1 (DS<sub>Photo</sub> 0.11, DS<sub>Cat</sub> 0.34) and PCCD-2 (DS<sub>Photo</sub> 0.37, DS<sub>Cat</sub> 0.34). Washing was done after 5 min.

#### 4.2.2 Adsorption of PCCDs onto the pulp fibers

The modification of the fibers was done by adsorption of PCCDs onto the pulp fibers in an aqueous solution of NaHCO<sub>3</sub> 10<sup>-5</sup> M under agitation (Figure 7). The adsorption study was performed in the range of 0.5–10 % (dry pulp based) applied dosages of the derivatives. The adsorption isotherms had the same trend for both derivatives (Figure 16A) and showed the absence of a clear saturation plateau, meaning that more derivatives were adsorbed as larger amounts of the derivatives were added. However, the yield of the adsorption was higher at the lower applied dosages (Figure 16B).

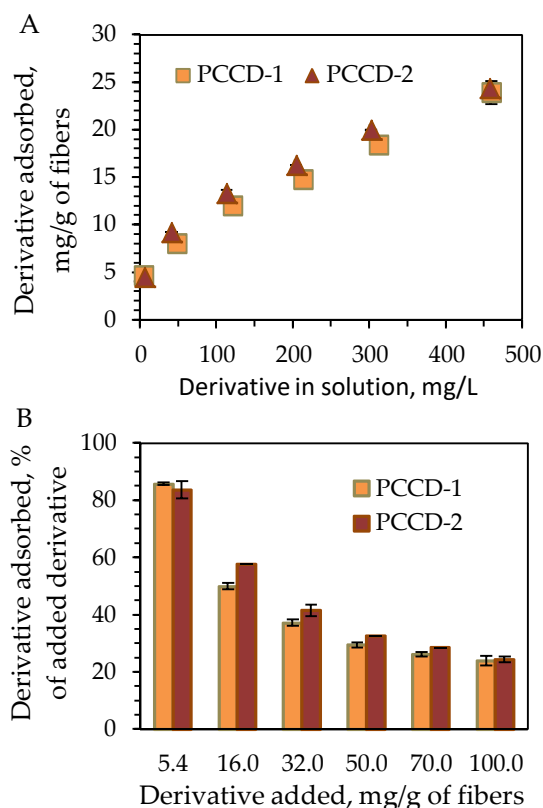


Figure 16. Isotherms (A) and the yield of the adsorption (B) of PCCD-1 ( $DS_{\text{Photo}} 0.11$ ,  $DS_{\text{Cat}} 0.34$ ) and PCCD-2 ( $DS_{\text{Photo}} 0.37$ ,  $DS_{\text{Cat}} 0.34$ ) onto the pulp fibers.

At 10 % dosage the amount of cationic groups adsorbed on the fibers was equal to  $34 \mu\text{mol/g}$  for PCCD-1 and  $28 \mu\text{mol/g}$  for PCCD-2. These values were much lower than the available amount of anionic groups of the fibers ( $89 \mu\text{mol/g}$ ) determined by the methylene blue sorption method (Fardim and Holmbom, 2003). Thus, PCCD-1 and PCCD-2 neutralized only 38 and 32 % of the fiber total charge. The reason for this could be limited accessibility of the fiber wall to the derivatives (Wågberg, 2000). In addition, anionic bonding sites could be sterically hidden by already adsorbed polymer chains.

As supported by SPR studies, hydrophobic interactions could be also involved in the adsorption of the derivatives onto the fibers.

Despite the difference in the  $DS_{\text{photo}}$ , the derivatives adsorbed to a similar extent on the fibers and, it could be concluded that the electrostatic interactions dominated in the adsorption process. It is also in agreement with SPR studies, which showed more pronounced affinity of PCCDs to negatively-charged surfaces. Figure 17 illustrates adsorption of the derivatives onto pulp fibers based on the described studies.

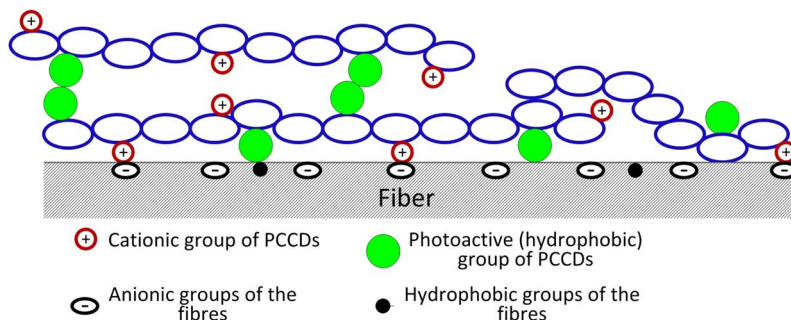


Figure 17. Schematic presentation of the adsorption of PCCDs onto pulp fibers.

#### 4.2.3 Distribution of the derivatives onto the fiber surfaces

ToF-SIMS was used as a tool to characterize surface composition of the fibers. In mass spectrum of PCCD (not shown), several peaks were tentatively assigned to the ion of the cationic group ( $m/z=58$ ; (Vega et al., 2012)) and the ions of the photoactive group ( $m/z=159$ ; 189; and 235) of the derivatives. The proposed fragmentation path is depicted in Figure 18. The ion  $C_{11}H_9O_3C(OH)_2^+$  with  $m/z=235$  was proposed based on the mass spectra of esters, whose fragmentation is accompanied by rearrangement of two hydrogen atoms and formation of protonated acid ion (Harrison and Jones, 1965; McLafferty, 1959).

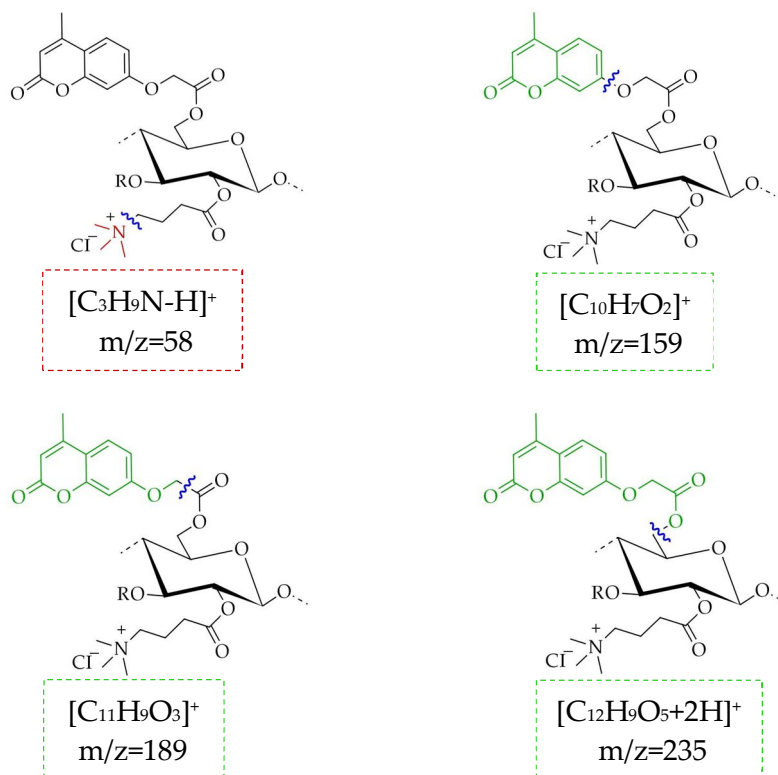


Figure 18. Proposed fragmentation of PCCD and corresponding m/z ratio of secondary ions by ToF-SIMS.

These characteristic peaks were found in the spectra of PCCD treated fibers and they had high intensity in relation to other peaks (Figure 19). On the other hand, these peaks were absent in the spectrum of the reference fibers (not shown).

Besides the spectra, images of the PCCD treated fiber surfaces were generated from the signals of the total ions and also from the signals of the characteristic ions (Figure 20). The presented images had the same pattern. Hence, it was proved that the derivatives were evenly distributed on the fiber surfaces within the resolution of ToF-SIMS.

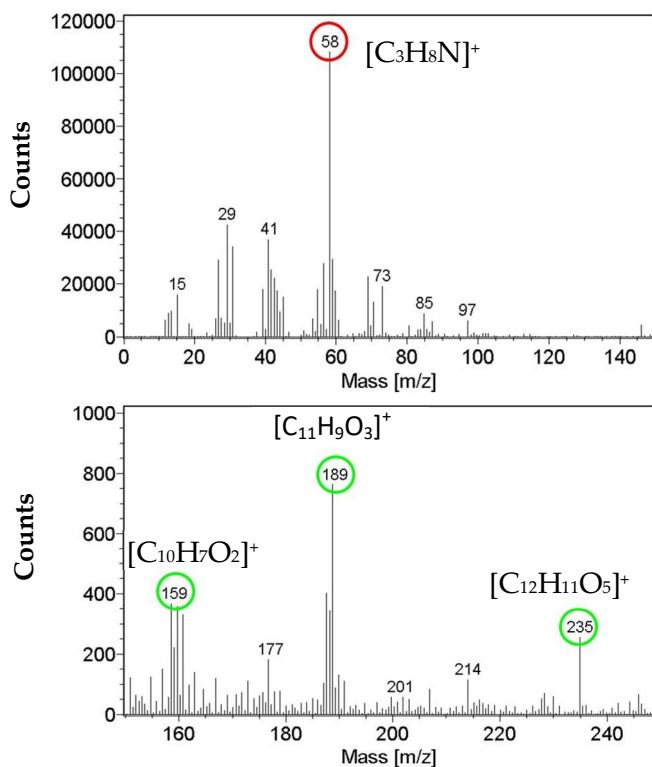


Figure 19. ToF-SIMS spectra of the PCCD-1 treated fibers ( $DS_{\text{Photo}}$  0.11,  $DS_{\text{Cat}}$  0.34) and proposed characteristic ions.

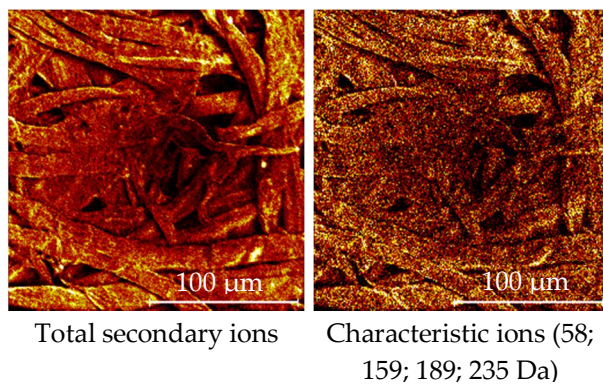


Figure 20. ToF-SIMS imaging of the pulp fibers modified by PCCD-1 ( $DS_{\text{Photo}}$  0.11,  $DS_{\text{Cat}}$  0.34; dosage of 0.5%, w/w).

## 4.3 Effect of light irradiation on the properties of photocrosslinkable fibers (Papers II, III).

### 4.3.1 Optical properties of the fibers (Paper II)

A UV light absorption spectrum of the reference pulp (Figure 21A) showed two absorption maxima at ca. 235 and 280 nm that were attributed to residual HexA and lignin (Liitiä and Tamminen, 2007). The spectra of the modified fibers had a prominent absorption band at longer wavelength with a maximum in the vicinity of 320 nm. This band is characteristic of the coumarin chromophore (Trenor et al., 2004) and was also found in the UV absorption spectra of aqueous solutions of PCCDs (Wondraczek et al., 2012). The absorption of the light at  $\lambda_{320}$  increased when more derivatives were adsorbed onto the fibers. Consequently,  $A_{320}$  was the highest for the 10% PCCD-1 treated fibers.

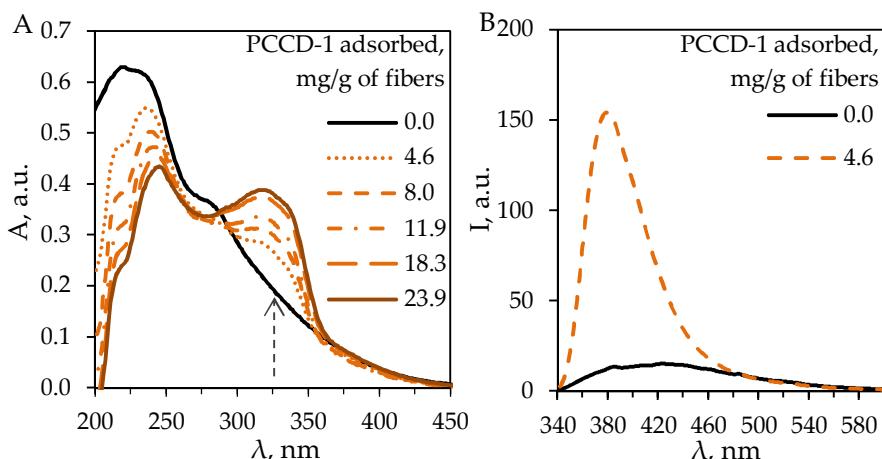


Figure 21. Light absorption (A) and emission (B) spectra of the unmodified and PCCD-1 ( $DS_{\text{Photo}}$  0.11,  $DS_{\text{Cat}}$  0.34) treated pulp sheets with corresponded applied dosages of 0.5, 1.6, 3.2, 7 and 10% (w/w).

Coumarin containing compounds possess fluorescence (Trenor et al., 2004). As a result of the modification, the PCCD treated fibers also gained fluorescence with the maximum of the emission at ca. 380 nm (Figure 21B). Since the excited molecules lost some energy as a result of vibrational relaxation process, the emission of the light occurred at longer wavelengths than that of the absorption (Berland, 2001). The modification of the fibers did not have any effect on brightness and



whiteness of the pulp sheets, and visually they looked as the unmodified fibers.

As was shown by Wondraczek et al. (2012), PCCDs dissolved in aqueous solutions have the ability to photocrosslink under UV light exposure via [2+2] cycloaddition reaction of ethylenic groups of the photoactive moieties.

The irradiation reaction of PCCD-1 treated fibers was done using a UV light source with the wavelength of 320–390 nm, and the kinetics of the reaction was monitored by the change in the characteristic absorption band ( $A_{320}$ ) in the UV spectrum of the modified fibers (Figure 22A). The photocrosslinking reaction was fast and most of the reaction was completed after 3 min (Figure 22B). Only slight changes in the spectrum of the reference pulp were observed after the irradiation which suggests that the irradiation did not have any significant impact on the reference fibers.

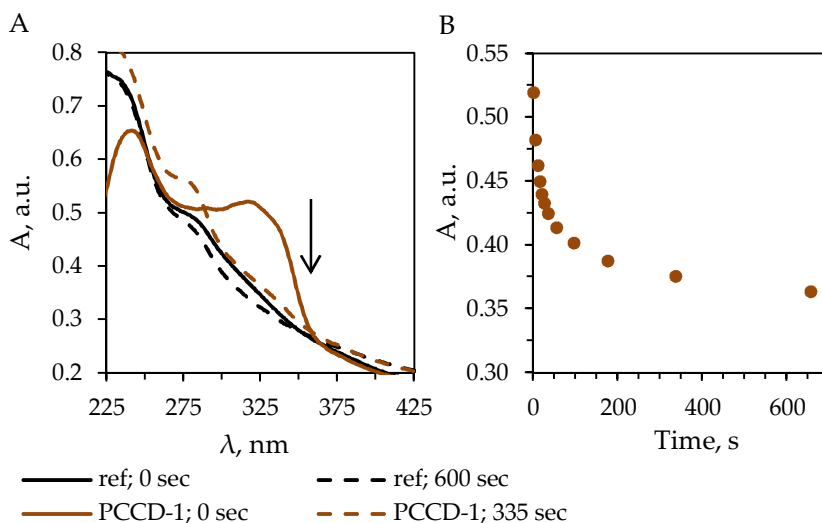


Figure 22. Photocrosslinking reaction of the reference and PCCD-1 treated fibers ( $DS_{\text{Photo}}$  0.11,  $DS_{\text{Cat}}$  0.34) with the dosage of 3.2% (w/w): UV-vis spectra (A) and  $A_{320}$  vs. UV light exposure time (B).

#### 4.3.2 Flexibility of the single fibers (Paper III)

The effect of the photocrosslinking reaction on the mechanical properties of the single fibers and the fiber network was studied for the PCCD-2 treated fibers due to the higher  $DS_{\text{Photo}}$  of the derivative in comparison to PCCD-1. In addition, the derivatives adsorbed onto the

fibers to a similar extent (Section 4.2.2). The applied dosage of the derivative was 3.2 % (w/w). The irradiation of the fibers was done in suspension to avoid hornification of the single fibers before irradiation due to drying of the fibers in air and also extra drying under the light exposure. Even though, from the UV spectra it was concluded that 5 min of irradiation time was sufficient, it was decided to extend the exposure time to 8 min.

Flexibility of the single fibers was tested using microrobotic platform (Saketi et al., 2010). After the modification of the fibers with the derivative, the flexibility of the fibers increased on the average by 58% (Figure 23). Irradiation of the modified fibers with the UV light resulted in the decrease in the fiber flexibility on the average by 60% in comparison to the reference fibers (Figure 23). The stiffening of the modified fibers after the irradiation happened due to the formation of the covalent bonds between the coumarin moieties of the derivative absorbed onto the fibrils of the fibers.

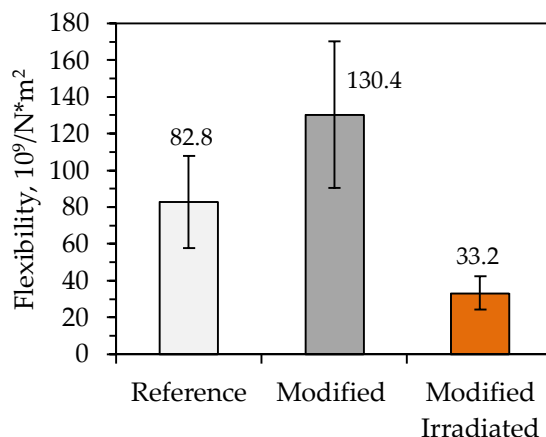


Figure 23. Flexibility of the reference and 3.2% PCCD-2 treated ( $DS_{\text{Photo}}$  0.37,  $DS_{\text{Cat}}$  0.34) fibers with following 8 min irradiation time.

### 4.3.3 Mechanical properties of the fiber network (Paper III)

The hand-sheets were prepared from the reference and PCCD-2 modified fibers. The UV light irradiation was done as post-treatment after the preparation and air-drying of the hand-sheets. The conditions for the irradiation were chosen experimentally by monitoring UV absorption spectra. Despite that 5 min of irradiation time appeared to be sufficient, it was decided to keep the sheets under light irradiation

during 7 min. From the UV spectra it was also found that the sheets had to be irradiated from the both sides. The prepared reference, PCCD-2 treated and PCCD-2 treated irradiated hand-sheets were tested for mechanical properties (strength) using DMA. In the first experimental set, the sheets underwent increasing oscillating displacement in a tensile mode under a fixed frequency, and the associated applied force was measured. The results showed that ultimate tensile strength of the reference fibers (0.72 N) increased by ca. 13% after the modification of the fibers with the derivative (0.81 N) and further by 68% after subsequent irradiation (1.3 N) based on the strength of the reference fibers (Figure 24A). Thus, the tensile strength at break was ca. 81% higher for the modified irradiated samples in comparison with the reference sample.

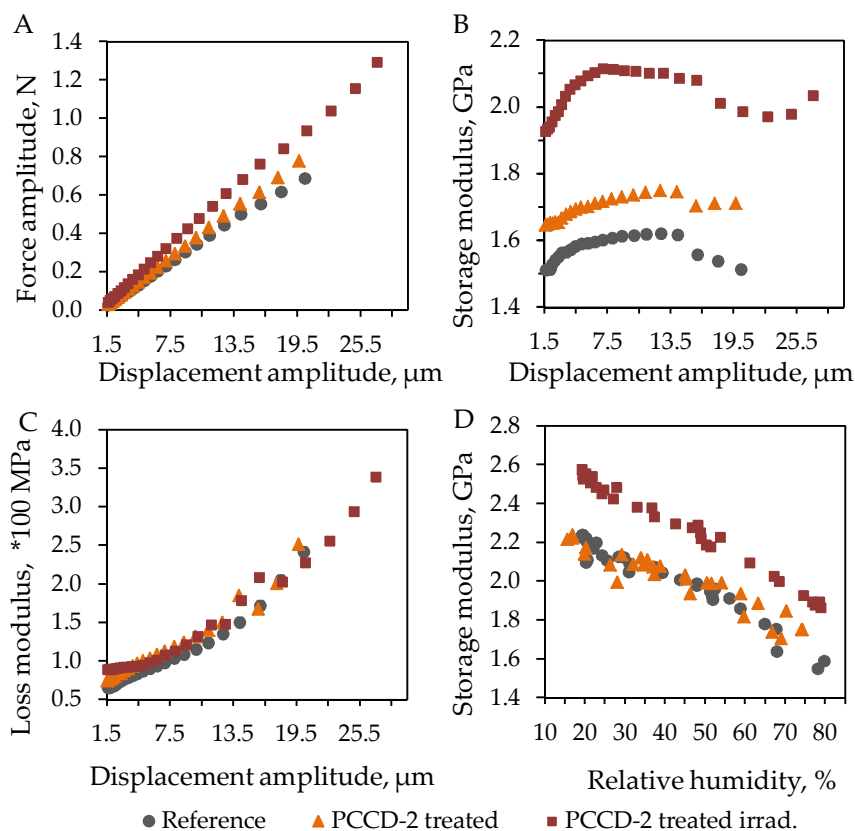


Figure 24. DMA of the sheets made of the reference and 3.2% PCCD-2 treated ( $DS_{\text{Photo}} 0.37$ ,  $DS_{\text{Cat}} 0.34$ ) fibers with following 7 min irradiation time (both sides).

The dynamic moduli of the sheets were calculated from the applied force and the resulting displacement amplitude. The storage (elastic) modulus of the samples increased initially upon the increase in the displacement amplitude (Figure 24B). This phenomenon was attributed to the strain hardening effect or restricted sample deformation caused by the dislocation or alignment of the fibers along the paper stripe after several loading cycles. This effect was more pronounced for the irradiated paper stripes made of the modified fibers. Comparison of the results at 10  $\mu\text{m}$  displacement amplitude showed that the modification increased the storage modulus by ca. 8%, whereas the modification with subsequent irradiation by 31% compared to the reference. The higher storage modulus is related to higher resistance of the materials to deformation, *i.e.* higher tensile stiffness, which is a crucial parameter, *e.g.* for paper converting.

Loss modulus, a parameter that is generally affected mainly by internal friction and molecular rearrangement, also became higher as the displacement amplitude increased, but the results did not exhibit significant differences between the samples (Figure 24C).

The increase of the ultimate strength and the higher storage modulus for the fiber network after the modification with PCCD-2 was related to dry strengthening effect promoted by the applied derivative. The cellulose derivative attached to the fiber surfaces improved the fiber bonding during the sheet formation (Marton, 1996). In the case of the modified irradiated fibers, the further remarkable increase of the tensile strength at break and the storage modulus were the result of the stiffening of the individual fibers and the formation of the new inter fiber bonding. The stiffening of the individual fibers led to the higher required force to bend the individual fibers and to cause displacement in the fiber network. As a result, the fiber network showed the higher storage modulus or in other words resistance to deformation. The additional bonding sites between the modified fibers were created by the formation of the covalent bonds between the derivatives adsorbed onto the fibers and located in the junction zones of the fibers during the photocrosslinking reaction (Figure 25). The later could be supported by the measurement of the storage modulus at varying relative humidity (Figure 24D). For all samples, the storage modulus decreased with the increase of the environment humidity. The reason for that was the partial disruption of the water sensitive hydrogen bonds between the fibers. However, the storage modulus of the modified irradiated samples was

higher than that for the other samples, confirming the presence of the covalent bonds.

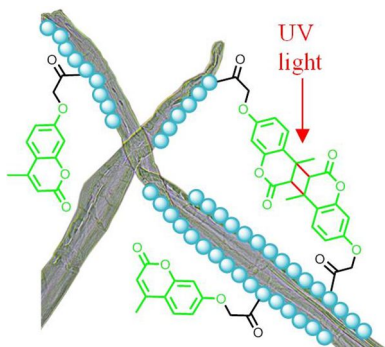


Figure 25. Drawing of photocrosslinking reaction and covalent bond formation between PCCDs adsorbed onto adjacent fibers.

Z-directional (*i.e.* in thickness direction) tensile test was another method that elucidated the effect of the fiber modification and the following photocrosslinking onto the fiber network. Most of the bond areas are roughly in plane with the surface (Bronkhorst and Bennett, 2002). Therefore, tests that pull the sheet apart in a thickness direction are designed to characterize internal fiber bonding strength (Bronkhorst and Bennett, 2002). In comparison with the reference samples, 42 % and 84 % extra force was required to break the sheets in Z direction made of PCCD-2 treated samples and PCCD-2 treated samples after subsequent irradiation (Figure 26).

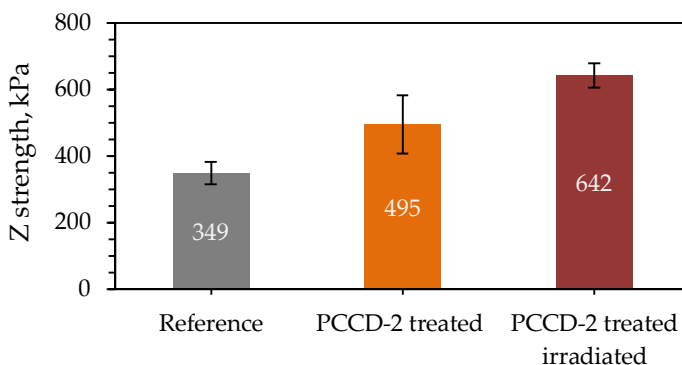


Figure 26. Z-directional tensile strength of the sheets made of the reference and 3.2% PCCD-2 treated ( $DS_{\text{Photo}}$  0.37,  $DS_{\text{Cat}}$  0.34) fibers with following 7 min irradiation time (both sides).

Thus, the fiber network was stronger for the sheets made of the modified fibers, and was further remarkably strengthened after the photocrosslinking reaction due to covalent bonds formation.

#### **4.4 Fluorescent pulp fibers via adsorption of naphthalimide-type MCCDs (Paper IV)**

Novel naphthalimide-type MCCDs were used to functionalize bleached eucalyptus kraft pulp to introduce fluorescent properties to the fibers (see Table 3, Figure 7). The derivatives differed in the length of the aliphatic chain connecting naphthalimide groups to the cellulose backbone (FCCD-1 and FCCD-2) as well as in the DS of naphthalimide group (FCCD-2a and FCCD-2b). These features of the naphthalimide functional group were expected to have the most effect on the optical properties of the fibers. Moreover, there were several other aspects that were taken into account during the selection of the derivatives. As was revealed in *Paper II*,  $DS_{\text{Cat}}$  of 0.3 was enough to provide a strong interaction of cellulose derivatives with the fibers. However, the solubility of the naphthalimide-type cellulose derivatives depended on the balance between  $DS_{\text{Cat}}$  and  $DS_{\text{Photo}}$ . Thus, by increasing  $DS_{\text{Photo}}$  to about 0.2 and at fixed  $DS_{\text{Cat}}$  of 0.3, propanoic naphthalimide cellulose esters became water insoluble. Butanoic naphthalimide cellulose esters lost their solubility at  $DS_{\text{Photo}}$  of 0.3.

##### **4.4.1 Optical properties of naphthalimide-type MCCDs**

Optical properties of the novel naphthalimide MCCDs were analyzed to evaluate the potential effect of FCCDs as modifying agents on the performance of the pulps fibers. In addition, the spectroscopic studies were used to calculate the adsorption of FCCDs onto the fibers.

Absorption spectra of FCCDs were similar to each other (Figure 27A) and showed several absorption maxima in the vicinity of 189, 215, 233, 295 and 343 nm. However, the polymers showed considerable differences in the emission spectra (Figure 27B) obtained upon excitation of the solutions by the light with  $\lambda_{340-344}$ . As can be seen, the spectra had a common band with a maximum at  $\lambda_{393-395}$  attributed to the naphthalimide monomer emission (Jones and Kumar, 2003). A clear difference between the spectra was found regarding another band that appeared in a blue-green part of the visible spectrum. Butanoic FCCD-2a exhibited second emission band with a maximum at 482 nm and FCCD-2b in the vicinity

of 495 nm. Contrarily, propanoic FCCD-1 did not have a clear second band in the range of studied concentrations ( $\leq 10$  mg/L).

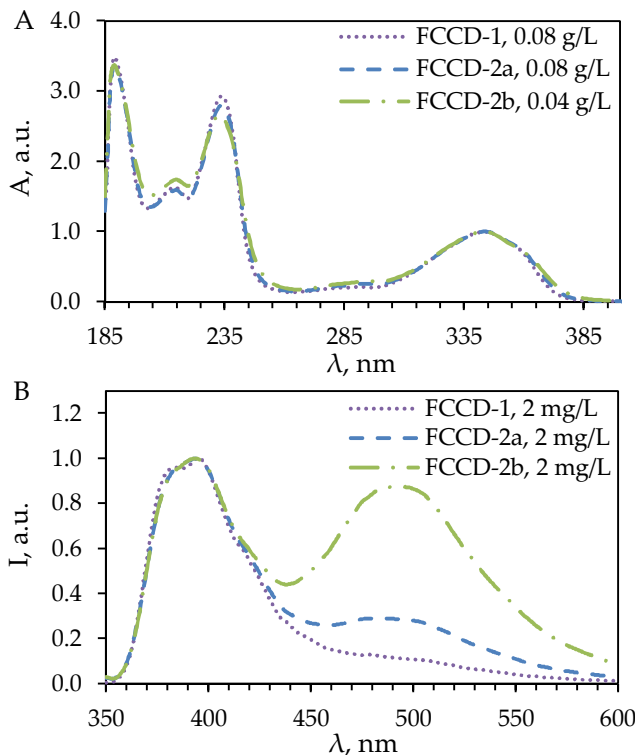


Figure 27. Normalized absorption (A) and fluorescence (B) spectra of FCCD-1 ( $DS_{\text{Photo}}$  0.07,  $DS_{\text{Cat}}$  0.31), FCCD-2a ( $DS_{\text{Photo}}$  0.11,  $DS_{\text{Cat}}$  0.32) and FCCD-2b ( $DS_{\text{Photo}}$  0.22,  $DS_{\text{Cat}}$  0.33) aqueous solutions. The spectra were normalized to  $\lambda_{343}$  and  $\lambda_{394}$ , respectively.

The second band in the emission spectra originated from excimers formed by the association of naphthalimide moieties (Ferreira et al., 2011). The ratio of emission maximum of excimer to one of the monomer ( $I_{\text{exc}}/I_{\text{mon}}$ ) was around 0.3 for FCCD-2a at solution concentrations of 2–10 mg/L and 0.9 for FCCD-2b at the solution concentration range of 0.8–5 mg/L. Within the studied range of the solution concentrations, the amount of fluorescent groups in the solutions was equal for both polymers because butanoic FCCD-2a had  $DS_{\text{Photo}}$  two times lower than FCCD-2b. Thus, the high intensity of the second emission band was related to association of the naphthalimide groups located on the same polymer chain.

#### 4.4.2 Effect of electrolyte concentration on the adsorption of FCCDs onto the pulp fibers

To gain insight into the interactions between FCCDs and the fibers, the adsorption was performed at different electrolyte concentrations in the suspension (Wågberg and Odberg, 1989).

Generally, higher amounts of FCCDs were adsorbed as the salt concentration increased in the system (Figure 28). As it was shown with similar type cellulose derivatives (PCCDs), such multifunctional cationic polyelectrolytes attach to the fibers primarily via electrostatic and additionally via hydrophobic interactions at electrolyte concentration of  $10^{-5}$  M (*Paper II*). Therefore, it was expected that the same interactions were involved in the adsorption of naphthalimide MCCDs onto the fibers at low ionic strength (Figure 28). High electrolyte concentration caused screening of the charge of the polyelectrolytes and fibers, which limited electrostatic interactions and increased the role of hydrophobic contribution in the adsorption (Wågberg, 2000). Among the groups participating in the hydrophobic interactions could be naphthalimide groups as well as axial C-H sites of the repeating units in the polysaccharide macromolecule (Medronho et al., 2012).

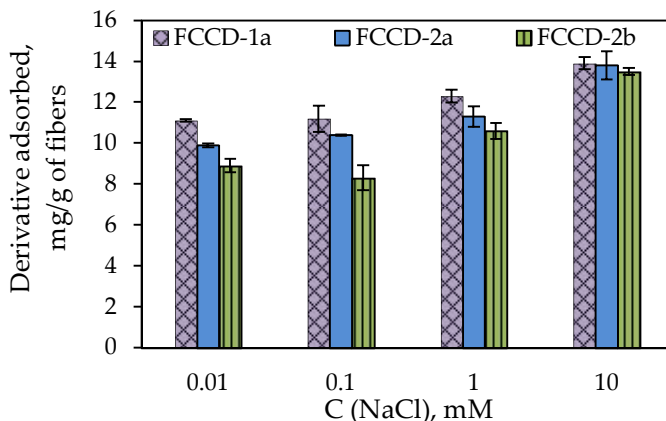


Figure 28. Adsorption onto the fibers as a function of salt concentration: propanoic naphthalimide FCCD-1 ( $DS_{\text{Photo}} 0.07$ ,  $DS_{\text{Cat}} 0.31$ ), butanoic naphthalimide FCCD-2a ( $DS_{\text{Photo}} 0.11$ ,  $DS_{\text{Cat}} 0.32$ ) and FCCD-2b ( $DS_{\text{Photo}} 0.22$ ,  $DS_{\text{Cat}} 0.33$ ).

Besides exerting an effect on the interaction between the derivatives and fibers, high salt concentration could decrease the repulsion between the macromolecules of the derivatives that positively influenced the



adsorption (Wågberg, 2000). It is worth mentioning that it was not possible to dissolve FCCDs at 0.1 M salt concentration due to strong intermolecular interactions and charge screening.

Desorption studies revealed strong interaction between the derivatives and the fibers independently of the adsorption conditions (ionic strength). It was determined that for all derivatives less than 5 % of the adsorbed amount was desorbed after resuspension of the modified fibers in the buffers. Moreover, these percentages could be attributed to the polymers entrapped with the solutions that were not completely removed with supernatants after centrifugation of the modified fibers.

Based on these studies, a buffer of  $10^{-5}$  M ionic strength was used for further experiments to assist ionic interactions.

#### 4.4.3 Kinetic studies of the adsorption for FCCDs onto the pulp fibers

The adsorption kinetics of the novel FCCDs onto the fibers was studied at different time intervals and a fixed dosage of the derivatives (2%, pulp based). As it is shown in Figure 29, the derivatives concentration in the suspensions steeply dropped during first 10 minutes, followed by a gradual decrease, and finally leveling out.

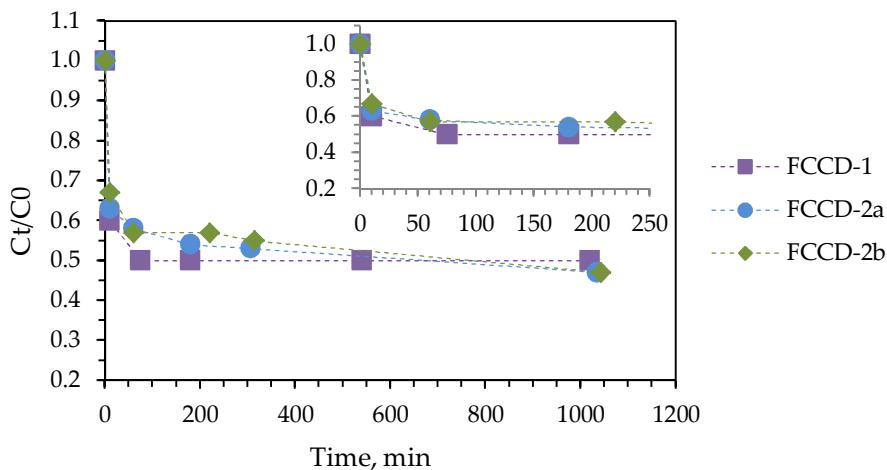


Figure 29. Kinetic studies of the adsorption onto the pulp fibers: propanoic naphthalimide FCCD-1 ( $DS_{Photo}$  0.07,  $DS_{Cat}$  0.31), butanoic naphthalimide FCCD-2a ( $DS_{Photo}$  0.11,  $DS_{Cat}$  0.32) and FCCD-2b ( $DS_{Photo}$  0.22,  $DS_{Cat}$  0.33).

To compare the efficiency of the adsorption for the studied time intervals, the adsorption rate of the derivatives was calculated as a ratio of  $\Delta$ adsorbed amount/ $\Delta$ time (%/min) and it was equaled to ca. 3-4 %/min during the first 10 minutes. This corresponded to 75, 70 and 62% (w/w) of the total adsorbed amounts of FCCD-1, FCCD-2a and FCCD-2b, respectively (Figure 30). During the rest time intervals the calculated adsorption rate was much slower. Hence, it is not necessary to extend the adsorption process.

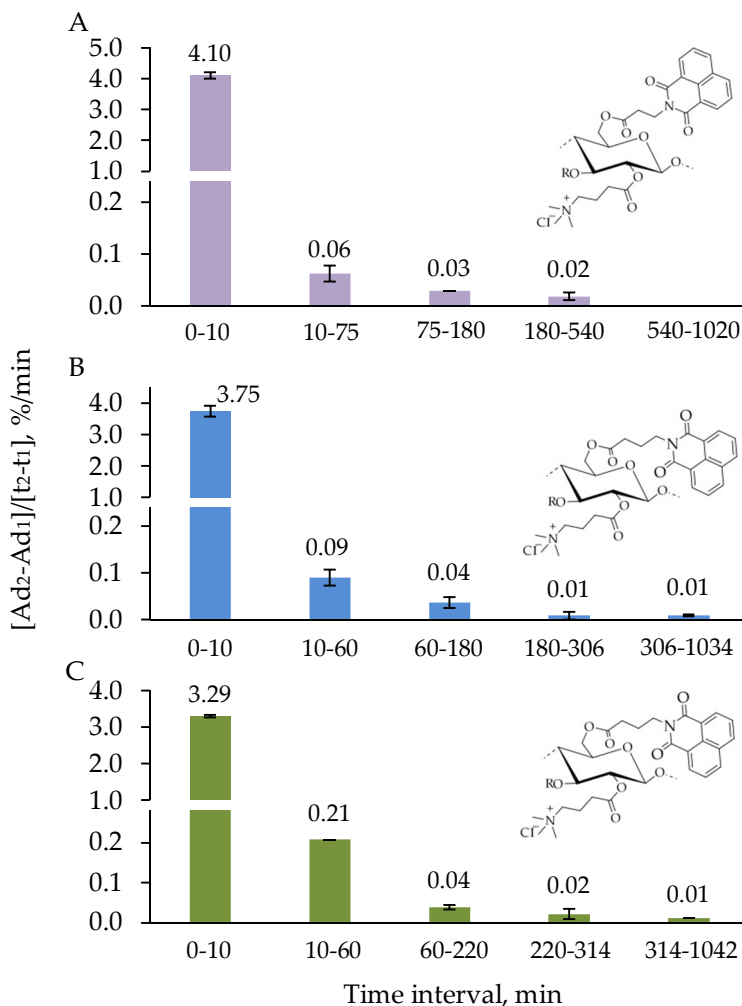


Figure 30. Rate of the derivatives adsorption onto the pulp fibers: FCCD-1 (A,  $DS_{Photo}$  0.07,  $DS_{Cat}$  0.31), FCCD-2a (B,  $DS_{Photo}$  0.11,  $DS_{Cat}$  0.32) and FCCD-2b (C,  $DS_{Photo}$  0.22,  $DS_{Cat}$  0.33).

The high initial adsorption rate could be explained by the high affinity of FCCDs to the fibers. It was supported by SPR studies (*Paper II*, Figure 15), that cellulose derivatives bearing both cationic groups and chromophore moieties interacted fast with the negatively charged as well as hydrophobic model surfaces. By the time, slowing down of the adsorption could be explained by steric and electrostatic repulsions between the adsorbed derivatives and the derivatives approaching the fiber surfaces.

#### 4.4.4 Adsorption isotherms for FCCDs onto the pulp fibers

Adsorption of the derivatives was also studied as a function of added dosages of the derivatives to find out the yield of the adsorption as well as to correlate these values with the optical performance of the fibers. Even though most of the adsorption happened fast, the derivatives were allowed to react with the fibers overnight. As Figure 31 depicts, the adsorption isotherm of butanoic derivatives had the same trend independent of the  $DS_{\text{Photo}}$ . FCCD-2a and FCCD-2b adsorbed onto the fibers at the same amounts and reached a saturation plateau. However, there was a clear difference between the adsorption isotherms of propanoic and butanoic naphthalimide cellulose derivatives. Adsorption of FCCD-1 was more pronounced in comparison to FCCD-2, specifically at higher applied dosages. It was suggested that FCCD-1 took more favorable conformation during the adsorption than FCCD-2a due to the shorter aliphatic chain.

Important to mention, that at the highest applied dosage of 5 % (pulp based), 24 and 14  $\mu\text{mol/g}$  of cationic moieties of FCCD-1 and FCCD-2 were adsorbed onto the fibers, which corresponded to 27 and 16% of the total fiber charge neutralization. For a comparison, PCCD-1 and PCCD-2 neutralized 21 and 19 % of the total fiber charge at the same applied dosage. Hence, FCCDs macromolecules were also not able to reach all charges of the fibers. As it was mentioned for PCCDs, one reason for that could be limited accessibility of FCCDs to the cell wall of the fibers (Wågberg and Hägglund, 2001). In addition, anionic groups of the fibers available for the interactions could be sterically blocked by the adsorbed chains of FCCDs.

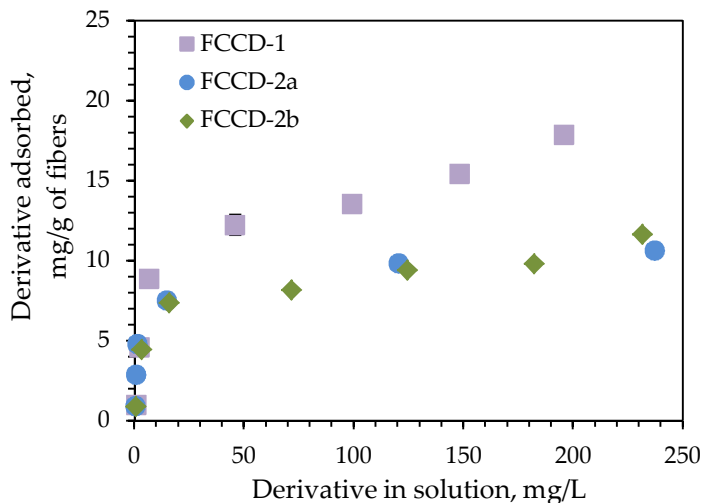


Figure 31. Adsorption isotherms of FCCDs onto the pulp fibers: propanoic naphthalimide FCCD-1 ( $DS_{Photo}$  0.07,  $DS_{Cat}$  0.31), butanoic naphthalimide FCCD-2a ( $DS_{Photo}$  0.11,  $DS_{Cat}$  0.32) and FCCD-2b ( $DS_{Photo}$  0.22,  $DS_{Cat}$  0.33).

Based on the adsorption isotherms it was concluded that the process was more efficient at lower applied dosages ( $\leq 1$  % pulp based, Figure 32).

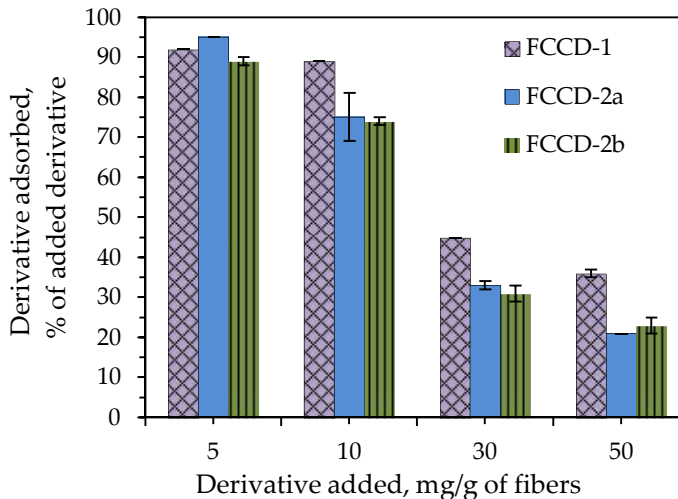


Figure 32. Yield of adsorption of FCCDs onto the pulp fibers as a function of the added dosage: propanoic naphthalimide FCCD-1 ( $DS_{Photo}$  0.07,  $DS_{Cat}$  0.31), butanoic naphthalimide FCCD-2a ( $DS_{Photo}$  0.11,  $DS_{Cat}$  0.32) and FCCD-2b ( $DS_{Photo}$  0.22,  $DS_{Cat}$  0.33).

#### 4.4.5 Optical properties of the fluorescent pulp fibers

Optical properties of the fibers such as light absorption and emission have a great influence on the perception of the fibrous materials and their final application. As it was shown in Section 4.4.1, the synthesized naphthalimide cellulose derivatives absorb UV light and re-emit it in the visible part of the light spectrum. This section is devoted to the analyses of the fibers treated with FCCDs to check whether the derivatives enabled the fibers with these properties and at the same time to investigate whether the adsorption affected the performance of the derivatives.

Figure 33 shows light absorption by the fibers in a form of hand-sheets. As can be seen, the FCCD-2b modified fibers had a broad absorption band with the maximum at 343 nm typical of naphthalimide (Jones and Kumar, 2003). The absorption intensity of this characteristic band increased as more derivative was attached to the fibers. In the case of FCCD-1 and FCCD-2a treated fibers, the absorption spectra had the same tendency and, therefore, are not shown.

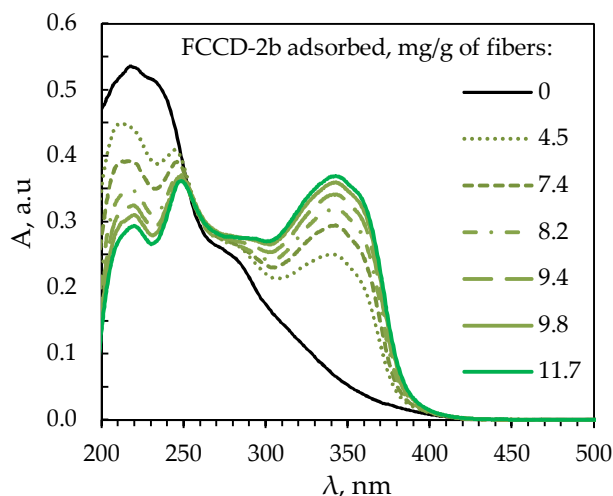


Figure 33. Absorption spectra of the fibers modified by butanoic naphthalimide FCCD-2b ( $DS_{\text{Photo}}$  0.22,  $DS_{\text{Cat}}$  0.33).

Figure 34 illustrates emission spectra of the fibers in a form of hand-sheets. The reference fibers exhibited a dim autofluorescence without a clear emission band (spectrum not shown). The emission spectra of the FCCD-1 and FCCD-2a modified fibers contained a clear band with the maximum at ca. 394 nm having a shoulder at longer wavelengths. The

intensity of this shoulder was higher for FCCD-2a treated fibers than for FCCD-1. The emission spectrum of the fibers modified by FCCD-2b looked more like two bands overlapping each other. A maximum of the first band was at ca. 398 nm. The maximum of the second emission band was hard to detect, but it can be assumed that it was in the wavelength range of  $410 \text{ nm} \leq \lambda \leq 454 \text{ nm}$ .

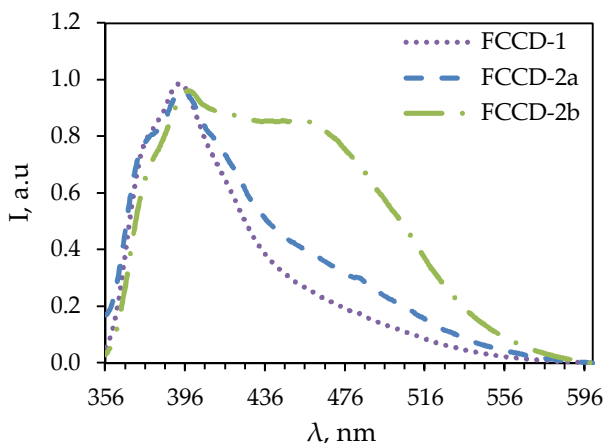


Figure 34. Emission spectra of the fibers treated with: 1% (w/w) propanoic naphthalimide FCCD-1 ( $DS_{\text{Photo}} 0.07$ ,  $DS_{\text{Cat}} 0.31$ ), 1% (w/w) butanoic naphthalimide FCCD-2a ( $DS_{\text{Photo}} 0.11$ ,  $DS_{\text{Cat}} 0.32$ ) and 0.5% (w/w) FCCD-2b ( $DS_{\text{Photo}} 0.22$ ,  $DS_{\text{Cat}} 0.33$ ).

Based on the spectroscopic studies of the derivatives in the solution, it was concluded that the origin of the second band in the blue-green spectral range was due to association of naphthalimide moieties and formation of excimers.

#### 4.4.6 The fluorescent pulp fibers as authenticity indicators

Visualization of the fluorescent single fibers was done by means of fluorescence microscope using FCCD-2b treated fibers. Two types of images were captured under a white light and UV light exposure of the fibers. In later case, the fibers were excited at 330–385 nm and the image was obtained by collecting the light at  $\lambda > 420 \text{ nm}$ . As depicted in Figure 35A, the modified fibers glowed under the UV light. Moreover, the derivative covered the fibers completely, because the same microstructural elements (pits) and fiber morphology were detected when the fluorescent image was compared to the one obtained under a white light (Figure 35B).

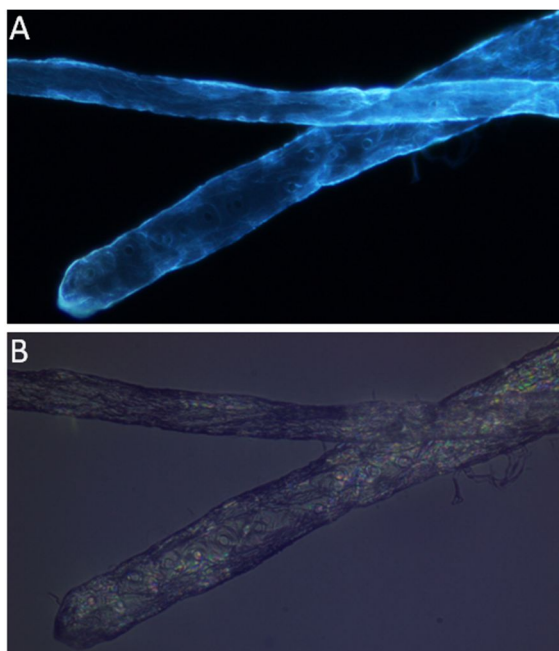

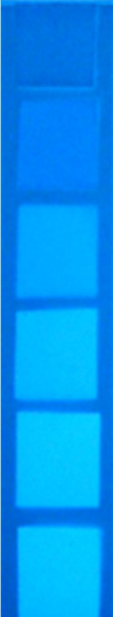




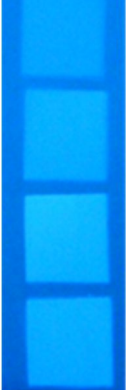





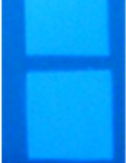




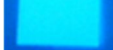


Figure 35. The pulp fibers modified by 2% (w/w) FCCD-2b ( $DS_{\text{Photo}} 0.22$ ,  $DS_{\text{Cat}} 0.33$ ): image obtained with epi-fluorescence microscope under UV light exposure (A) and white light (B).

Optical appearance of the hand-sheets made of the reference and modified fibers was evaluated under a black light (UV-A) that is used to detect counterfeiting (Table 6). At the dosage of  $\geq 0.5\%$  the modified fibers glowed efficiently to be distinguishable from the reference fibers by a naked eye. Under the black light, FCCD-2 treated fibers visually perceived whiter and with stronger intensity of the emission than FCCD-1 treated fibers.

Table 6. Optical appearance of the reference and modified fibers (quadrates) in contrast to the reference fibers (background) at different applied dosages.

Dosage, %	FCCD-1*		FCCD-2a*		FCCD-2b*	
	Sample	Photo groups adsorbed, $\mu\text{mol/g}$	Sample	Photo groups adsorbed, $\mu\text{mol/g}$	Sample	Photo groups adsorbed, $\mu\text{mol/g}$
0		0		0		0
0.1		0.3±0.0		0.4±0.0		0.7±0.0
0.5		1.4±0.0		2.2±0.0		3.6±0.0
1		2.7±0.0		3.4±0.3		5.9±0.1
3		4.1±0.0		4.4±0.2		7.5±0.5
5		5.4±0.2		4.8±0.1		9.4±0.8

\*FCCD-1 ( $DS_{\text{Photo}}$  0.07,  $DS_{\text{Cat}}$  0.31), FCCD-2a ( $DS_{\text{Photo}}$  0.11,  $DS_{\text{Cat}}$  0.32) and FCCD-2b ( $DS_{\text{Photo}}$  0.22,  $DS_{\text{Cat}}$  0.33).

The Elrepho spectrometer enables determination of fluorescence contribution to the whiteness of the materials. As Figure 36 shows, the fluorescent component of the whiteness was higher for FCCD-2 than for FCCD-1 treated fibers.

Such difference in the optical performance of the fibers was explained by the formation of the excimers that increase emission of the light in the blue-green visible part of the spectrum. Considering comparable adsorbed amounts of the photoactive groups for FCCD-1 and FCCD-2a treated fibers (Table 6), most probable, that greater length of the linker (aliphatic chain) between the cellulose backbone and the naphthalimide moieties promoted excimer formation and, therefore, a stronger light emission at longer wavelengths. This was in agreement with the spectroscopic studies of the derivatives in the solution (Figure 27B). In the case of FCCD-2b treated fibers, the emission was stronger due to



higher  $DS_{\text{Photo}}$  of the polymer compared to other applied polymers. In particular, as it was shown above (Figure 27B, Section 4.4.1) at  $DS_{\text{Photo}}$  0.22 corresponding to FCCD-2b the excimers could be formed by the naphthalimide groups located at the same polymer chain (intramolecular association). Moreover, higher concentration of the fluorescent moieties on the fibers could also facilitate excimer formation (intermolecular association).

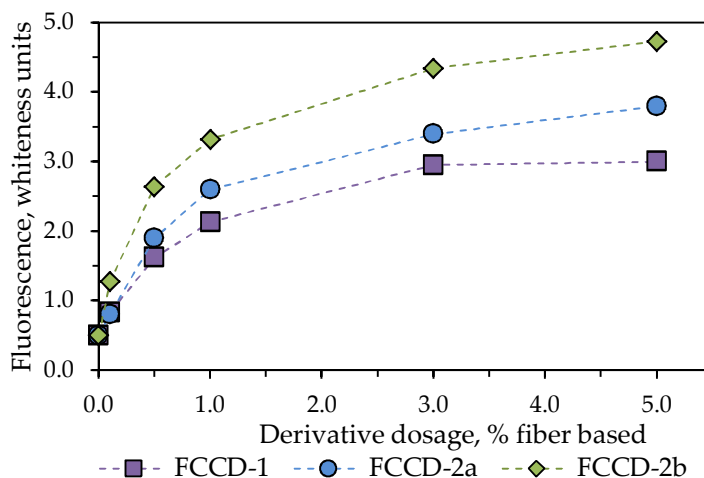
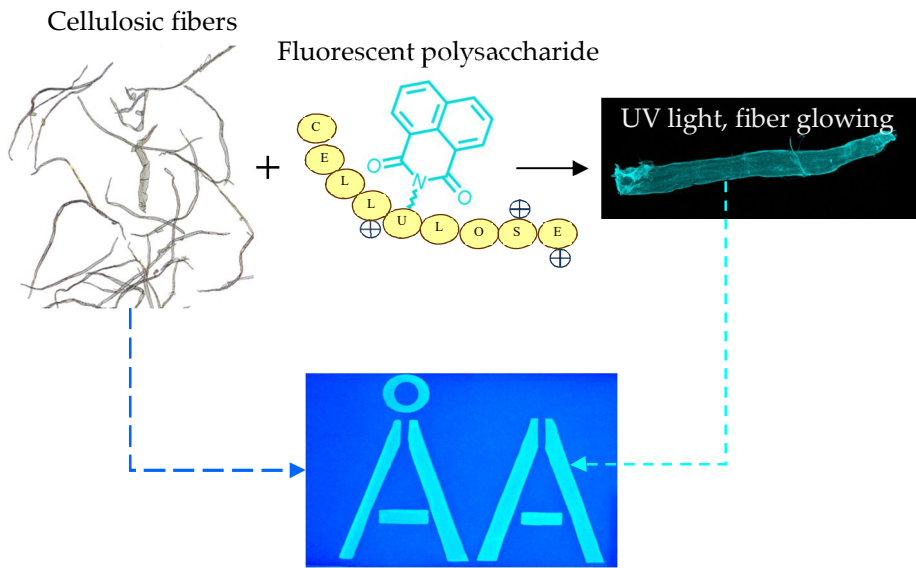


Figure 36. Fluorescence of the fibers as a difference in whiteness measured with and without a UV component in the incident light. Propanoic naphthalimide FCCD-1 ( $DS_{\text{Photo}}$  0.07,  $DS_{\text{Cat}}$  0.31), butanoic naphthalimide FCCD-2a ( $DS_{\text{Photo}}$  0.11,  $DS_{\text{Cat}}$  0.32) and FCCD-2b ( $DS_{\text{Photo}}$  0.22,  $DS_{\text{Cat}}$  0.33).

Finally, the modified fibers looked totally the same as the reference ones under a day light. Thus, the fluorescent fibers prepared in this study can be applied as security elements, *e.g.* in packaging to reveal counterfeiting (Figure 37).



The reference and fluorescent fibers under UV light

Figure 37. The prepared fluorescent pulp fibers as security elements for pulp-based materials.

## 5 Concluding remarks

The current work explored the supramolecular functionalization of pulp fibers as a tool for fiber engineering to enhance existing properties as well as to add new functionalities to the fiber-based materials. The general objective of the work was to apply biomass derived polymers, specifically polysaccharides, to modify pulp fibers using the existing stages of the fiberline processes.

The efforts of the first part of the work were made towards the functionalization of pine kraft pulp via adsorption of xylans performed directly during an oxygen delignification step. In the scope of the work, xylans were extracted from birch wood (HWX) and bleached birch kraft pulp (CAX) by means of hot water and cold alkali extraction methods, respectively. The characterization of the xylans showed that the source and the extraction method had a direct effect on the structure of the isolated polymers and, consequently, on their performance. In particular, HWX contained acetyl groups, a high amount of MeGlcA groups, and up to 5 wt% of lignin. The addition of HWX for fiber functionalization during the delignification stage deteriorated the process. In contrast, CAX with a much lower amount of MeGlcA groups and essentially free from the acetyl groups and lignin increased selectivity of the delignification stage. After the modification with CAX, the obtained pulps and the pulps after the following bleaching and beating had higher values of tensile index, tensile energy absorption, and stretch of the fiber network in relation to the corresponding reference pulps. Thus, the work showed that CAX can be potentially added in the course of oxygen delignification and used as a surface modifying agent with dual function viz as a protector of the pulp carbohydrates and as a dry strengthening agent.

The second part of the work was devoted to the design of light-responsive pulp fibers by supramolecular functionalization performed in aqueous solutions and at ambient conditions. The studies revealed that by adsorption of water soluble cationic cellulose derivatives with specific light-responsive functionalities, the properties of pulp fibers could be controlled by light. Particularly, bleached eucalyptus kraft fibers modified with coumarin-type cellulose derivatives gained photocrosslinking functionalities of the derivatives. Under UV light exposure, the fiber network made of such photocrosslinkable pulp became substantially stronger owing to the formation of covalent bonds

between the coumarin groups located on the adjacent fibers. When naphthalimide-type cellulose polyelectrolytes were used as surface modifying agents, the fibers were endowed with fluorescent functionalities that made the fibers distinguishable under UV light exposure. Such fluorescent fibers can be used as security fibers, *e.g.* to protect packaging from forgery. Thus, the performed work proved that new functionality can be added to pulp fibers by adsorption of wood-derived polysaccharide derivatives.

## 6 Acknowledgements

I would like to express my deepest sense of gratitude to my supervisor Prof. Pedro Fardim for the guidance throughout the work, support and patience. Thanks to Prof. Fardim, I had a chance to grow as a researcher and extend my knowledge in the field of fiber functionalization, pulp technology and biomass processing, to travel across Europe for different scientific courses, conferences and meetings, and to be a part of challenging but very interesting projects.

I would like to thank sincerely my co-supervisor Prof. Thomas Heinze (Friedrich Schiller University Jena, Germany) for the guidance throughout the work, discussions at the meetings and by emails, valuable comments to the manuscripts, and for providing collaboration with the group of “Center of Excellence for Polysaccharide Research”, Germany.

I am thankful to Holger Wondraczek who guided me as a PostDoc during a certain period and who is also a co-author of the most of my articles. Moreover, I am grateful to Dr. Wondraczek for sharing his knowledge regarding spectroscopic techniques.

I would like to express my appreciation to all co-authors of my articles: Stephan Daus, Pooya Saketi, Kourosh Latifi, Prof. Pasi Kallio, Elina Heikkilä, Joakim Järnström, Katrin Kühnöl, Annett Pfeifer. I wish to acknowledge Prof. Peter Mattijus and Josefin Halin for the access to SPR instrument and great assistance with the measurements; Leonore Bretschneider and Cintia Zarth for the synthesis of the derivatives that I used in my work.

I am also grateful to Soledad Peresin for giving me a possibility to collaborate with VTT and teaching me how to run QCM-D. This short collaboration was very inspiring for me and gave me a breath of fresh air.

Many thanks go to my current and former colleagues from the Laboratory of Fiber and Cellulose Technology for the cooperativeness, friendly atmosphere at work and for doing sport activities together. I would like to thank Jan Gustafsson for willingness to help in questions related to the laboratory, being supportive in grant applications and other practical questions as well as keeping us in mind for short coming projects. Agneta Hermansson and Marika Ginman are acknowledged for the help related to financial questions and for their supportive attitude towards the researchers.

Laboratory of Wood and Paper Chemistry, Laboratory of Physics and Laboratory of Paper Coating and Converting are acknowledged for the freely access to the instruments and provided help with the measurements. In this regard, many thanks go to Andrey Pranovich, Jarl Hemming, Kjell-Mikael Källman and Janni Kniivilä.

Separately, I would like to express my special thanks to Beatriz Vega for being a great colleague and my dear friend during all these years, for involving me in different scientific activities and for daily life talks.

I am immensely grateful to another my dear colleague and concurrently my beloved husband, Konstantin Gabov, for the scientific discussions and endless support, for being next to me during all these years.

Last but not least I would like to say huge thanks to all my friends and to my family! Your support and time that we spent together were very important and appreciated. Родители, все мои достижения благодаря вам!

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