Carbohydrate Polymers 111 (2014) 280–287

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Photoresponsive cellulose fibers by surface modification with multifunctional cellulose derivatives

Olga Grigoray[a], Holger Wondraczek[a], Elina Heikkilä[a], Pedro Fardim[a,b,*], Thomas Heinze[a,c]

[a] Laboratory of Fiber and Cellulose Technology, Åbo Akademi University, Porthansgatan 3, FI-20500 Åbo, Finland
[b] Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, Jeddah 21589, Saudi Arabia
[c] Center of Excellence for Polysaccharide Research, Institute of Organic Chemistry and Macromolecular Chemistry, Friedrich Schiller University of Jena, Humboldtstraße 10, 07743 Jena, Germany

ARTICLE INFO

Article history:
Received 11 August 2013
Received in revised form 4 December 2013
Accepted 22 April 2014
Available online 30 April 2014

Keywords:
Eucalyptus pulp fibers
Cationic cellulose derivatives
Photo-activity
Surface modification
ToF-SIMS
SPR

ABSTRACT

Eucalyptus bleached kraft pulp fibers were modified by adsorption of novel bio-based multifunctional cellulose derivatives in order to generate light responsive surfaces. The cellulose derivatives used were decorated with both cationic groups (degree of substitution, DS of 0.34) and photoactive groups (DS of 0.11 and 0.37). The adsorption was studied by UV–vis spectroscopy, surface plasmon resonance (SPR) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS). The adsorption isotherms followed the Freundlich model and it turned out that the main driving force for the adsorption was electrostatic interaction. Moreover, strong indications for hydrophobic interactions between the fibers and the derivatives and the derivatives themselves were found. ToF-SIMS imaging revealed an even distribution of the derivatives on the fiber surfaces. The modified fibers underwent fast photocrosslinking under UV-irradiation as demonstrated by light absorbance and fluorescence measurements. Thus, our results proved that the modified fibers exhibited light-responsive properties and can potentially be used for the manufacture of smart bio-based materials.

1. Introduction

Pulp fibers are intermediate products mainly used in the production of paper and paper boards (Freire, Silvestre, Gandini, & Neto, 2011). However, pulp fibers represent also an attractive substrate for the manufacturing of novel materials owing to their outstanding characteristics. They are relatively cheap, renewable, biodegradable, and can be recycled or converted to energy by combustion at the end of the life cycle of the product. Additionally, the fibers have good mechanical properties and relatively low density (Belgacem & Gandini, 2008; Freire et al., 2011; Ly et al., 2010).

Currently more than 180 million ton per year of pulp fibers (Sixta, 2006) are produced by well-established technologies like mechanical, chemo-mechanical and chemical pulping methods. The properties and the chemical composition (bulk and surface) of pulp fibers from the classical pulping techniques are very well-studied and vary significantly depending on the raw material and the way of the manufacturing. In order to utilize pulp fibers in new value added products, current research is focusing on the modification of their surfaces while keeping bulk properties such as morphology and native fiber wall structure (Grönqvist et al., 2006; Hedenberg & Gatenholm, 1995; Pan & Ragauskas, 2012). Biological (e.g. by enzymes, fungi), chemical (carboxylation, grafting) or plasma treatments and adsorption methods can be applied for this purpose (Gandini & Pasquini, 2012; Utsel, 2012).

From our point of view, the adsorption method appears to be the most promising tool among the techniques mentioned since it is water-based and can be easily combined with existing fiber line stages (Muguet, Pedrazzi, & Colodette, 2011). Traditionally, the research in fiber chemistry and technology has been mainly focusing on the improvement of mechanical, drainage and optical properties of pulp by adsorbing polysaccharides and polysaccharide-based polyelectrolytes for paper manufacture (Köhnke, Lund, Brelid, & Westman, 2010; Schönberg, Oskanen, Suurnäkki, Kettunen, & Buchert, 2001). In this regard, the application of underutilized biomass derived polysaccharides like hemicelluloses recently came into focus (Schwikal et al., 2011; Silva et al., 2011; Vega, Petzold-Welcke, Fardim, & Heinze, 2012).

* Corresponding author at: Laboratory of Fiber and Cellulose Technology, Åbo Akademi University, Porthansgatan 3, FI-20500 Åbo, Finland. Tel.: +358 504096424.
E-mail address: pfardim@abo.fi (P. Fardim).

http://dx.doi.org/10.1016/j.carbpol.2014.04.089
0144-8617/

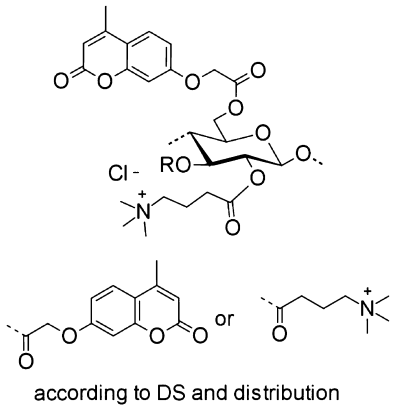

Fig. 1. Schematic presentation of the structure of the photoactive cationic cellulose derivative (PCCD).

Functional biopolymers with stimuli-responsive capabilities can be used for the modification of pulp in order to generate new fiber-based materials, whose properties could be triggered by an external stimulus. Multifunctional polysaccharide derivatives decorated with cationic and, in particular, light responsive substituents can be applied for this purpose. The light induced alterations, including isomerization, dissociation or crosslinking, of the photoactive substituents were described to cause changes in physical properties of the polymers itself or polymeric solutions (Irie, 1990; Wondraczek, Kotiaho, Fardim, & Heinze, 2010; Wondraczek, Pfeifer, & Heinze, 2011). Consequently, the possibility to control the properties of the interface of the fibers to which they are attached can be expected, and the properties of fiber-based materials and composites might be influenced.

The focus of the studies presented in this paper was to gain information about the interaction of pulp fibers and cellulose derivatives, which were decorated on one hand with cationic (3-carboxypropyl)trimethylammonium chloride ester moieties and on the other with hydrophobic (photoactive) 2-[(4-methyl-2-oxo-2H-chromen-7-yl)oxy]acetate substituents (Wondraczek, Pfeifer, & Heinze, 2012). In particular, the influence of the hydrophobic/hydrophilic balance of the derivatives on the adsorption behavior was investigated and a tentative hypothesis of the interaction of pulp fibers and such multifunctional cellulose derivatives was suggested. Moreover, the fiber surface composition and lateral distribution was evaluated by means of ToF-SIMS spectrometry and imaging.

2. Experimental

2.1. Materials

Eucalyptus air-dried unrefined bleached kraft pulp (bleaching sequence: A-ZD-EOP-D-Z-P brightness: 86% ISO) obtained from Botnia (Kaskö) was disintegrated according ISO 5263:1995(E). The disintegrated pulp was dewatered by centrifugation and the dry matter content according to ISO 638-1978 was determined to be approximately 30%. The total amount of anionic groups in the pulp was determined by the methylene blue sorption method (Fardim, Moreno, & Holmbom, 2005) to be 99 μmol/g. The amount of anionic groups on the fiber surfaces was analyzed by XPS measurements of the methylene blue treated pulps (Fardim et al., 2005). Deionized water was obtained from a Millipore Milli-Q system and possessed a conductivity of 0.05 μS. Photoactive cationic cellulose derivatives (PCCD-1 and PCCD-2, Fig. 1) were prepared as described (Wondraczek et al., 2012). Briefly, microcrystalline cellulose dissolved in *N*,*N*-dimethylacetamide (DMA)/LiCl was allowed to react with 2-[(4-methyl-2-oxo-2H-chromen-7-yl)oxy]acetic acid by the activation of the carboxylic acid with equimolar amounts of *N*,*N*-carbonyldiimidazole (CDI). Products with different degrees of substitution (DS) were obtained by the variation of the molar ratio of polymeric repeating unit to carboxylic acid and CDI. Subsequently, the photoactive cellulose esters dissolved in DMA were reacted with (3-carboxypropyl)trimethylammonium chloride in the presence of equimolar amounts of CDI. The final products were isolated by precipitation in acetone and washed with acetone and ethanol and further purified using dialysis against water through a cellulose membrane (Spectra/Porr; MWCO = 3500 g/mol) and subsequent lyophilization. Characterization of the PCCDs was done using NMR and IR spectroscopy and described elsewhere in detail (Wondraczek et al., 2012). The PCCD stock solutions were prepared by dissolving of PCCDs in 10^{-5} M sodium bicarbonate solution under stirring. All other chemicals were purchased from Sigma–Aldrich and used as obtained.

2.2. Methods

2.2.1. Adsorption experiments

2.2.1.1. The design of the adsorption experiments. The adsorption experiments were designed considering conditions during papermaking process. Thus, a pulp consistency of 0.6% and neutral or weakly acid media were chosen similar to the properties of suspensions fed to paper machines. Sodium bicarbonate solution was used as a buffer to control the pH and electrolyte concentration of the suspension, which are known to influence the adsorption of charged polymers. The concentration of sodium bicarbonate solution was based on a preliminary study that showed a better adsorption of the derivatives at low electrolyte concentration (10^{-5} M). Different amounts of the PCCDs were used to study their adsorption behavior onto the fiber surfaces, preferably, in the range of low dosages. The influence of the time and temperature on the adsorption was not in the focus of the paper.

2.2.1.2. Adsorption conditions. Dewatered pulp corresponding to 150 mg of oven-dry pulp was dispersed in 10^{-5} M sodium bicarbonate solution. Different volumes of the PCCDs stock solutions were added corresponding to polymer dosages of 0.5, 1.6, 3.2, 5.0, 7.0, or 10.0% (w/w, based on dry pulp), respectively. The final pulp consistency was adjusted to 0.6% and the slurries were stirred at 270 rpm for 17 h at room temperature. Subsequently, the pulp fibers were separated from the aqueous media using a self-designed sheet former, which consisted of a hollow cylinder with the inner diameter of 36 mm, 200 mesh screen, ceramic funnel and suction flask. The mesh was placed between the cylinder and the funnel in order to form even sheets. Finally, the pads obtained were pressed and dried according to SCAN-CM 11:95, yielding sheets with a grammage of about 148 g/m^2. All adsorption experiments were done shielded from light and the sheets were kept in the dark in order to avoid undesired photoreactions.

2.2.2. Quantification of the PCCDs adsorption onto the pulp fibers

The amount of the PCCDs in filtrates collected during the preparation of the sheets was quantified by UV–vis spectroscopy. For this purpose, the UV–vis spectra of the different PCCDs dissolved in aqueous sodium bicarbonate solution (10^{-5} M) were measured in the wavelength range of 200–400 nm. The concentration range applied was 0.01–0.07 g/l. Two calibration curves were obtained by plotting the absorbance at 320 nm against the concentration. Utilizing this calibration curves the concentrations of the PCCDs in the filtrates was determined from their absorption value at 320 nm. Subsequently, the amount of the cellulose derivatives adsorbed on the pulp fibers was calculated by subtracting the amount of the polymers in the filtrates from the amount added. A blank sample

was prepared without addition of pulp to evaluate the amount of PCCDs adsorbed on the used glassware.

2.2.3. Interactions of the PCCDs with model surfaces

The adsorption of the cellulose derivatives onto the modified sensors was measured by a SPR-Navi 200 instrument. All solutions used for the SPR measurements were filtered, degassed and centrifuged to prevent introduction of impurities and air into the instrument. Basic gold sensor plates were purchased from Bionavis and treated with 11-mercapto-undecanoic acid, 11-mercapto-1-undecanol or 1-dodecanethiol in order to obtain self-assembled monolayers (SAM) possessing anionic (SAM-COOH), hydrophilic (SAM-OH) and hydrophobic (SAM-CH_3) moieties (Kaya et al., 2009; Schwikal et al., 2011). The sensor slide containing the SAM was placed into the SPR flow cell and 10^{-5} M aqueous sodium bicarbonate solution was introduced in the instrument at 23 °C with a flow rate of 20 μl/min for at least 0.5 h until a stable baseline was obtained. Subsequently, the PCCD solution (0.2 g/l in 10^{-5} M aqueous sodium bicarbonate solution) was injected into the flow cell via a switch valve and allowed to run for 5 min at the same flow rate and temperature as described above. Finally, the system was rinsed with 10^{-5} M aqueous sodium bicarbonate solution to remove unbound polymer. Experiments were run at least four times and the reported values indicate the average ± standard deviation.

2.2.4. Surface analysis of the modified pulp fibers

The time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements were carried out using a Physical Eletronics ToF-SIMS TRIFT II instrument equipped with a primary ion beam of $^{69}Ga^+$ (liquid metal ion source) and an electron flood gun for charge compensation. The applied acceleration voltage was 25 kV, used in positive ion mode. A raster size of 200 μm × 200 μm was scanned for 8 min in parallel measurement, and one scanning was made using the raster size 100 μm × 100 μm. As a reference, the PCCD was analyzed after dissolution in water, dropping on an ash-free filter paper and air-drying. Both positive and negative spectra of the reference were investigated in order to identify the characteristic fragments in the surface mass spectrum.

2.2.5. Optical properties of the modified pulp fibers

Diffuse reflectance UV–vis spectra of the pulp sheets were measured with Shimadzu 2600 spectrophotometer equipped with an integrating sphere ISR-2600 Plus. Fluorescence of the pulp sheets was studied using a Perkin-Elmer LS50B spectrofluorometer.

2.2.6. Photocrosslinking

Photocrosslinking reaction was performed by Bluepoint 4 UV-source (Hönle AG, Munich, Germany) equipped with BP4 320–390 nm filter.

2.2.7. Mechanical properties of modified hand-sheets

For evaluation of mechanical properties, hand-sheets were prepared according to SCAN-CM 64:00 using a standard sheet former. Tensile strength of the hand-sheets was measured according to T 494 om-01 at 50% relative humidity and 23 °C. To investigate the effect of the crosslinking, the samples were irradiated from both-sides for 7 min before the measurements.

3. Results and discussions

3.1. Interaction of PCCDs with the pulp fibers

Multifunctional cellulose-based polyelectrolytes decorated with photoactive 2-[(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetate and cationic (3-carboxypropyl)trimethylammonium chloride ester moieties were applied for the modification of eucalyptus unrefined bleached kraft pulp (Fig. 1). The different photoactive cationic cellulose derivatives (PCCDs) possess a degree of substitution of cationic groups ($DS_N{}^+$) of 0.34 and photoactive groups (DS_{Photo}) of 0.11 (PCCD-1) and 0.37 (PCCD-2), respectively. Different amounts of aqueous PCCD solutions were added to aqueous pulp suspensions of equal concentration to study the adsorption behavior of the additives and to determine the feasible dosage in respect to relative adsorbed amount. The concentration of PCCD in solutions was determined before and after their contact with the pulp fibers by means of UV–vis spectroscopy and from the difference, the amounts of PCCDs adsorbed were calculated. As shown in Fig. 2a the sorption isotherms were obtained by plotting the amount of positive charge adsorbed per gram of pulp (based on dry weight) versus the amount of the charge in solution after the contact with the pulp fibers. The adsorption isotherms did not reach a saturation plateau, which means that a maximum adsorption capacity of the fibers was not achieved, and the amount of adsorbed cationic groups was much lower than the amount of the available anionic groups on the fiber surfaces (73 μmol/g).

The adsorption data of both PCCDs were treated in accordance with two classical adsorption models for liquid–solid interface, the Langmuir and Freundlich models described by Eqs. (1) and (2), respectively (Fardim et al., 2005).

$$\frac{C}{S} = \frac{1}{n_s \times K_L} + \frac{C}{n_s}, \tag{1}$$

where C is the equilibrium concentration of PCCDs in solution (μmol/L), S is the amount of PCCDs adsorbed at equilibrium (μmol/g), K_L is the Langmuir constant (L/μmol), and n_s is a monolayer sorption capacity at equilibrium (μmol/g). K_L and n_s can be estimated from the intercept and slope of the linear fit to the plot of C/S against C.

$$\log S = \log A + \frac{1}{n} \times \log C, \tag{2}$$

where A and n are the Freundlich constants related to adsorption capacity and adsorption intensity. A and n can be estimated in the same manner as described above for K_L and n_s of the Langmuir model.

Fig. 2c and d shows plots of C/S vs C and log S vs log C with fitted linear regressions. The comparison of the linear fits showed higher correlation coefficient R^2 for the Freundlich equation than for the Langmuir one for both PCCDs (Table 1). This indicates that the adsorption of the PCCDs is well described by the Freundlich model. The model refers to the adsorption onto a heterogeneous surface with different affinities of bonding sites. Also it assumes infinite adsorption with an increase of added dosage of the adsorbate and that the mechanism of adsorption involves both adsorbate-adsorbent and adsorbate-adsorbate interactions (Itodo, 2011).

The adsorption intensity (n) estimated from the Freundlich equation is higher than 2 (Table 1), indicating good adsorption characteristics of PCCDs with respect to cellulosic fibers (Tiwari, Gupta, Pandey, Singh, & Mishra, 2009). The slope $1/n$ (Table 1) was lower than unity implying favorable adsorption of PCCDs at low concentrations (Fig. 2b) (Guo & Gemeinhart, 2008). Moreover, it could be noticed that there was no significant difference in the adsorption capacity (A) of the fibers for the different PCCDs. This indicated that the adsorption was governed predominately by electrostatic interactions and that the hydrophobic groups had only minor influence.

3.2. Interaction of PCCDs with the model surfaces

For a better understanding of the adsorption phenomena described above the interaction of the PCCDs with different model

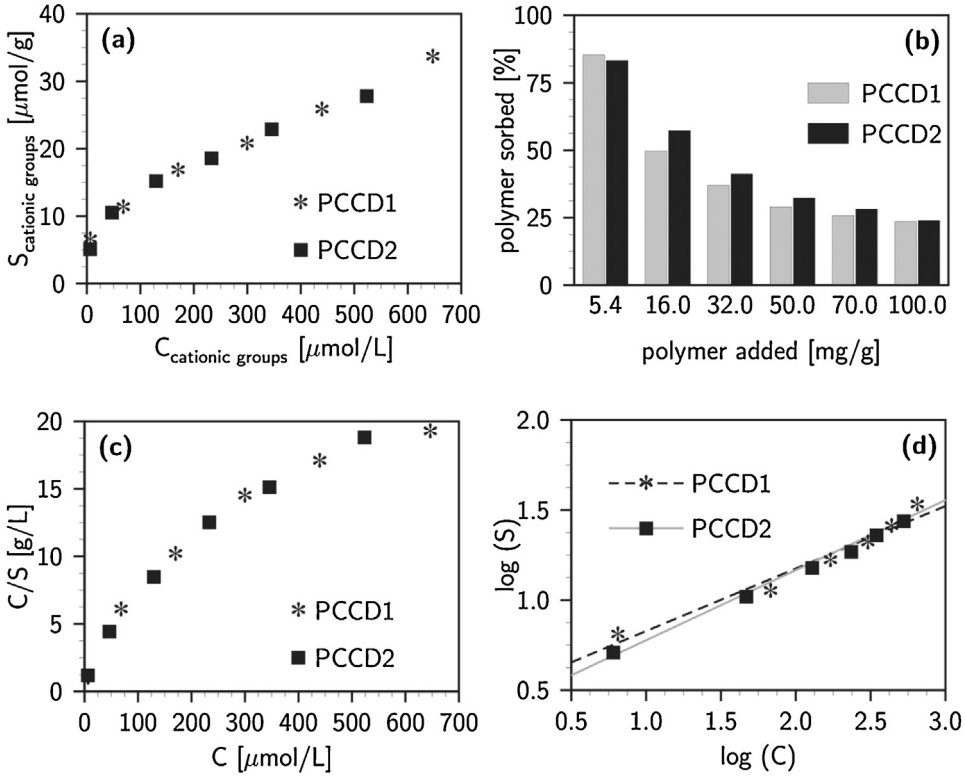

Fig. 2. (a) The photoactive cationic cellulose derivatives (PCCDs) adsorption isotherms onto the fibers. (b) Amount of the PCCDs adsorbed as the percentage of added amount. Linear representation of the isotherms according to Langmuir (c) and Freundlich (d) models. DS of cationic group is 0.34 and DS of photoactive group is 0.11 and 0.37 for PCCD-1 and PCCD-2, respectively.

surfaces was investigated by SPR measurements. For this purpose model surfaces, bearing anionic (SAM-COOH), hydrophilic (SAM-OH), or hydrophobic (SAM-CH_3) groups, were used instead of cellulose model surfaces in order to distinguish between the different driving forces of the adsorption of the PCCDs. As expected, a fast, strong and irreversible interaction occurs between the different cationic cellulose derivatives and the negatively charged SAM-COOH surface (Fig. 3a). In contrast, only a very weak interaction was found between the hydrophilic surface (SAM-OH) and the cellulose derivatives (Fig. 3c). In addition, it could be noticed that the cellulose derivatives were removed almost completely from the surface by washing with aqueous solution of sodium bicarbonate. All studied derivatives had certain affinity to the hydrophobic surface where they were attached irreversibly (Fig. 3b). The increase of the DS_{Photo} improved the adsorption, which could be explained by the enhanced hydrophobic interactions. It is worth to note that the adsorption plateau was reached much faster for the anionic surface than for the hydrophobic one. Summing up, it can be concluded that an addition of the photoactive groups facilitates the adsorption of the cationic derivatives, although the dominant driving force for adsorption is electrostatic interaction.

The SPR data were in agreement with the adsorption isotherms of the PCCDs on the fibers. As it was shown, the adsorption of the PCCDs onto the fibers could be explained by the Freundlich model, which considers energetically heterogeneous surface and adsorbate-adsorbate interaction resulting in creation of the layers on the surface. From the SPR measurements it is suggested that the adsorption takes place predominately on the negatively charged groups of the fibers followed by intermolecular interactions between the hydrophobic groups of the cellulose derivatives. Moreover, interactions between the hydrophobic groups of the fibers and the PCCDs could also be involved in the adsorption mechanism. Combining the findings from the different analytical approaches it is possible to draw a tentative hypothesis of the adsorption of the PCCDs on the fibers (Fig. 4).

3.3. The distribution of the PCCDs onto the fiber surfaces

The modified fibers were analyzed with ToF-SIMS in order to gain information about the surface distribution of the fiber modifying agents and surface chemical composition of the modified fibers. Fig. 5 shows the ToF-SIMS spectra of PCCD-1 as a reference and the fiber treated with this derivative. On the basis of the reference spectrum (Fig. 5b), several characteristic signals from secondary ions with m/z = 58, 159, 189, and 235 were assigned to ions originating from the cationic-(fragment $[C_3H_8N]^+$) and the photoactive

Table 1
Adsorption data of photoactive cationic cellulose derivatives (PCCDs) treated with Langmuir and Freundlich equations.

Derivative	Adsorption model						
	Langmuir			Freundlich			
	n_s	K_L	R^2	R^2	n	$1/n$	A
PCCD-1[a]	36.76	0.007	0.8980	0.9606	2.86	0.35	3.0
PCCD-2[a]	30.30	0.011	0.9478	0.9915	2.56	0.39	2.4

[a] DS of cationic group is 0.34 and DS of photoactive group is 0.11 and 0.37 for PCCD-1 and PCCD-2, respectively.

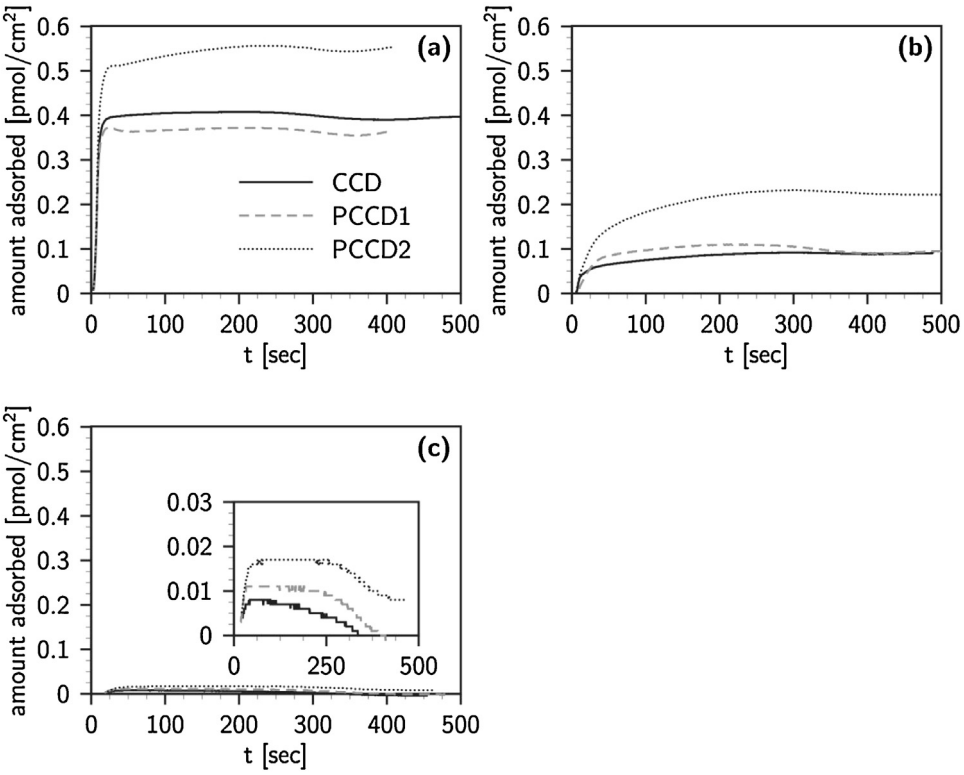

Fig. 3. Adsorption isotherms of cationic and photoactive cationic cellulose derivatives (CCD, PCCDs) onto SAM-COOH (a), SAM-CH_3 (b) and SAM-OH (c) surfaces. DS of cationic group is 0.34 and DS of photoactive group is 0.11 and 0.37 for PCCD-1 and PCCD-2, respectively. DS of cationic group is 0.29 for CCD.

substituent (fragments $[C_{10}H_7O_2]^+$, $[C_{11}H_9O_3]^+$ and $[C_{12}H_{11}O_5]^+$), respectively. In the surface mass spectra of the modified samples (Fig. 5a), these peaks had high intensity, which additionally proved adsorption of the cellulose derivatives onto the fiber surfaces. Accordingly, the mentioned peaks were not found in the previously published spectrum of the reference fiber sample (Neto et al., 2004). As shown in Fig. 6 the chemical imaging of the total secondary ions yields qualitatively the same image as the mapping of the characteristic fragments. Additionally, it could be noticed, that this effect was independent from the dosage of the PCCD applied. This clearly indicated a homogeneous surface distribution of the fiber modifying agents within the resolution of ToF-SIMS.

3.4. Optical properties of the modified fibers

Light absorption by modified and reference fibers were studied with UV–vis spectroscopy (Fig. 7). Unmodified fiber sheets showed two clear peaks at ca. 240 and 280 nm that originate from hexeneuronic acid groups and residual lignin, respectively (Liitia & Tamminen, 2007). The absorbance spectra of the modified pulps have an additional absorbance band with the maximum at around 320 nm arising from the $\pi\pi^*$ transition of the photoactive coumarin chromophor. A higher derivative dosage resulted in an increase of the peak intensity, thus the highest absorbance at 320 nm was reached at the highest dosage applied (10% (w/w), Fig. 7b).

In addition to light absorbance, coumarin-containing compounds possess natural fluorescence (Trenor, Shultz, Love, & Long, 2004). For fluorescence measurements the pulp sheets were irradiated with UV light at a wavelength of 320 nm corresponding to the absorption maximum of the derivatives. Reference pulp samples also show a natural fluorescence (Liukko, Tasapuro, & Liitia, 2007) that had considerably lower emission intensity at the applied excitation wavelength, compared to the samples containing the PCCDs (Fig. 7c). A maximum fluorescence intensity of the modified sample was found to be at around 380 nm.

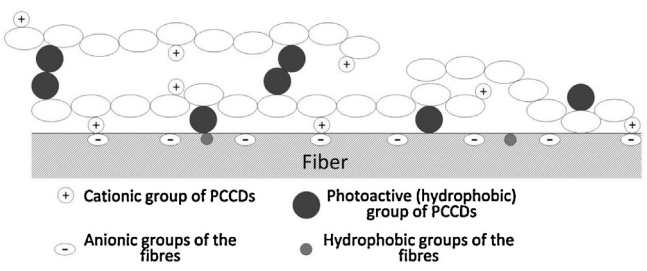

Fig. 4. A schematic illustration of the adsorption of the photoactive cationic cellulose derivative (PCCD) onto the pulp fibers.

3.5. Photocrosslinking, preliminary experiments

Previous studies revealed that polysaccharide derivatives bearing such photoactive groups are able to reversibly crosslink under UV light irradiation (Wondraczek et al., 2012). Fig. 8 shows changes in UV spectra measured from the fiber surfaces after it was exposed to the UV light. A decrease of absorbance at the wavelength in the vicinity of 320 nm could serve as an evidence of the crosslinking reaction which occurred via [2 + 2] cycloaddition of ethylene groups. The spectra also revealed that the reaction was fast and was completed within less than five minutes. Hence, the fluorescence of the modified fibers was drastically reduced (spectra not shown). Moreover, the intersection point of the spectra at 357 nm, the isosbestic point, indicates an uniform reaction, meaning that no degradation of the cellulose derivatives or formation of side products took place (Sauer, Hofkens, & Enderlein, 2011). The irradiation of the unmodified pulp fibers under similar conditions caused no changes in the UV spectra, which prove their stability under UV light.

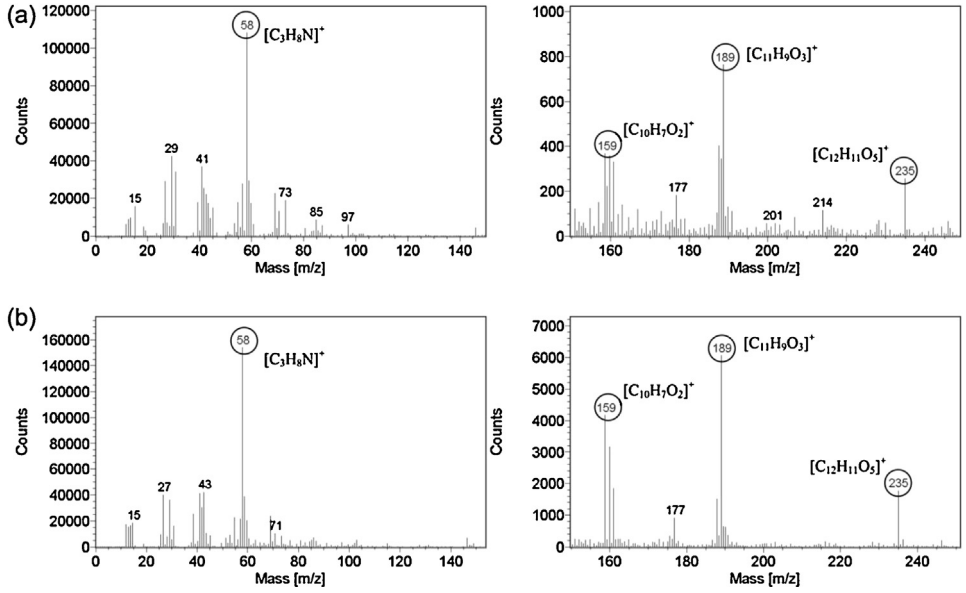

Fig. 5. ToF-SIMS spectrum m/z 0–250 of the pulp modified by photoactive cationic cellulose derivative (a) and the reference polymer (b).

As a preliminary study, a tensile index of the hand-sheets was measured. The tensile index refers to the strength and it is a crucial quality for the papers, which undergo direct tensile stress e.g. wrapping paper and paper bags (T 494 om-01). Also, printing paper grades should have high tensile strength to resist web breaking during printing and converting (T 494 om-01). The tensile index increased by 22% after the modification of pulp with PCCD-2 at the dosage of 3.2% (w/w, based on dry pulp). After irradiation of

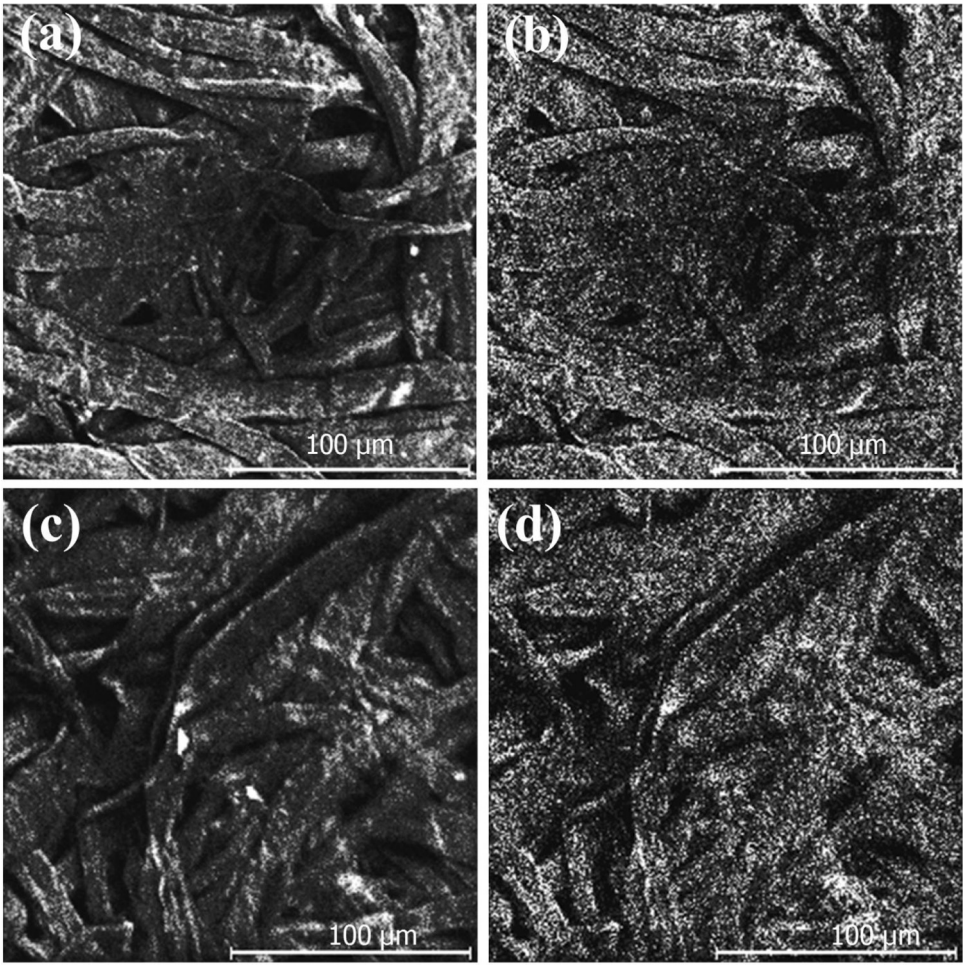

Fig. 6. ToF-SIMS images of bleached unrefined eucalyptus kraft pulp treated with photoactive cationic cellulose derivative (PCCD-1, DS_{Photo} of 0.11, DS_{Cat} of 0.34) of applied dosages 0.5% (w/w) (a and b) and 10.0% (w/w) (c, d). (a and c) and (b and d) total ion and characteristic ion images, respectively.

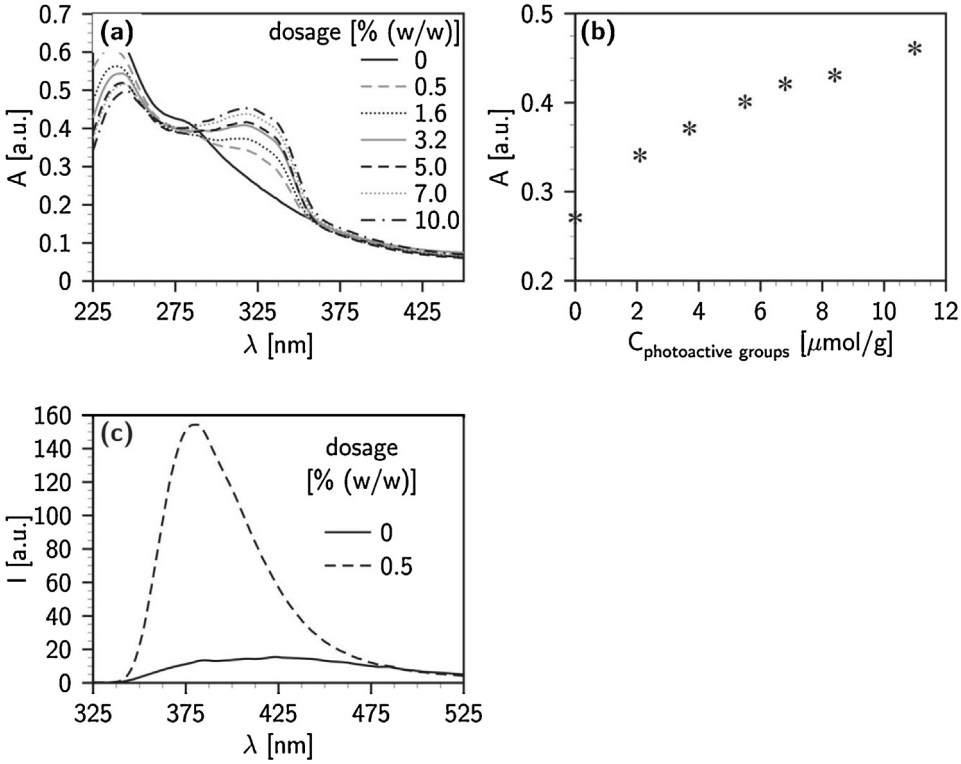

Fig. 7. (a) UV–vis spectra of the fibers modified by photoactive cationic cellulose derivative (PCCD-1, DS_{Photo} of 0.11, DS_{Cat} of 0.34) at dosages 0.5–10% (w/w). (b) Maximum absorbance of the fibers as a function of adsorbed amount of photoactive groups of the PCCD-1. (c) Fluorescence spectra of the reference and modified by PCCD-1 sample.

the modified sample, the tensile index increased by 39% compared with the modified sample and by 70% compared with the reference. The tensile index is directly related to the bonding ability of the fibers. Hence, the strength values showed that the modification and irradiation improved bonding between the fibers. It can be assumed that an addition of the flexible chains of the cellulose derivative increased the amount of the hydrophilic and hydrophobic groups available for interactions in the zones of fiber contact. The subsequent photocrosslinking led to a creation of covalent bonds between the pendant coumarin groups and thus the irradiated samples possessed better mechanical properties.

The photocontrol of the properties of the fiber interface (e.g. wetting) and directly related properties (e.g. fiber to fiber bonding) is currently under investigation and will be published elsewhere.

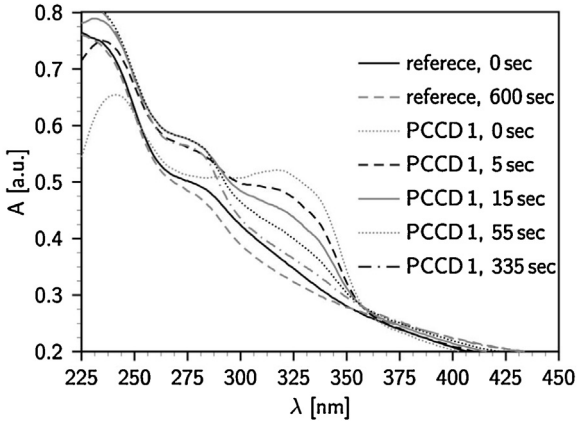

Fig. 8. UV–vis spectra of unmodified pulp fibers (reference) and the fibers modified by photoactive cationic cellulose derivative (PCCD-1, DS_{Photo} of 0.11, DS_{Cat} of 0.34, dosage of 3.2% (w/w)) recorded before and after irradiation with UV light.

4. Conclusions

Novel multifunctional cellulose derivatives decorated with both cationic and photoactive moieties were adsorbed onto the pulp fiber surfaces. Based on the results from UV–vis spectroscopy and SPR measurements, it was found that the electrostatic interaction was the main driving force of the adsorption of the derivatives onto the fibers. However, hydrophobic interactions between the fibers and the cellulose derivatives as well as between the cellulose derivatives themselves also contributed to the adsorption. The mechanism of the adsorption was well described by the Freundlich model. ToF-SIMS imaging showed that the derivatives were evenly distributed on the fiber surfaces independently of the dosage of the derivatives and DS of the photoactive group. UV light irradiation of the modified fibers triggered fast photocrosslinking of the attached photoactive groups resulting in changes of light absorption and fluorescence of the fibers. It can be suggested that the modified fibers bearing such photoactive groups have a great potential for application in novel bio-based light-responsive materials. Preliminary experiments on the photocontrol of the mechanical properties showed remarkable increase of the tensile index. Therefore a more detailed study on the photocontrol of these properties at the structural levels of single fibers and fiber network is currently under preparation and will be reported elsewhere.

Acknowledgements

Finnish Funding Agency for Technology and Innovation (Tekes) is acknowledged for funding. The authors are grateful to Professor Peter Mattjus from Åbo Akademi University for the access to the

SPR instrument and to Josefin Halin for her assistance with the SPR measurements. Annett Pfeifer and Cíntia Salomão Pinto Zarth are acknowledged for providing PCCDs and CCDs.

References

Belgacem, M. N., & Gandini, A. (2008). Surface modification of cellulose fibers. In M. N. Belgacem, & A. Gandini (Eds.), *Monomers, polymers and composites from renewable resources* (pp. 385–400). Amsterdam: Elsevier.

Fardim, P., Moreno, T., & Holmbom, B. (2005). Anionic groups on cellulosic fiber surfaces investigated by XPS, FTIR-ATR, and different sorption methods. *Journal of Colloid and Interface Science*, *290*, 383–391.

Freire, C. S. R., Silvestre, A. J. D., Gandini, A., & Pascoal Neto, C. (2011). New materials from cellulose fibers. A contribution to the implementation of the integrated biorefinery concept. *O PAPEL*, *72*, 91–96.

Gandini, A., & Pasquini, D. (2012). The impact of cellulose fiber surface modification on some physico-chemical properties of the ensuing papers. *Industrial Crops and Products*, *35*, 15–21.

Grönqvist, S., Rantanen, K., Alen, R., Mattinen, M. L., Buchert, J., & Viikari, L. (2006). Laccase-catalysed functionalisation of TMP with tyramine. *Holzforschung*, *60*, 503–508.

Guo, C., & Gemeinhart, R. A. (2008). Understanding the adsorption mechanism of chitosan onto poly(lactide-co-glycolide) particles. *European Journal of Pharmaceutics and Biopharmaceutics*, *70*, 597–604.

Hedenberg, P., & Gatenholm, P. (1995). Conversion of plastic/cellulose waste into composites. I. Model of the interphase. *Journal of Applied Polymer Science*, *56*, 641–651.

Irie, M. (1990). Properties and applications of photoresponsive polymers. *Pure and Applied Chemistry*, *62*, 1495–1502.

Itodo, A. U. (2011). Derived low cost biosorbent as water decolourizer. *Research Journal of Pharmaceutical, Biological and Chemical Sciences*, *2*, 693–700.

Kaya, A., Du, X., Liu, Z., Lu, J. W., Morris, J. R., Glasser, W. G., et al. (2009). Surface plasmon resonance studies of pullulan and pullulan cinnamate adsorption onto cellulose. *Biomacromolecules*, *10*, 2451–2459.

Köhnke, T., Lund, K., Brelid, H., & Westman, G. (2010). Kraft pulp hornification: A closer look at the preventive effect gained by glucuronoxylan adsorption. *Carbohydrate Polymers*, *81*, 226–233.

Liitia, T., & Tamminen, T. (2007). How to evaluate the kraft pulp brightness stability? In *3rd international colloquium on eucalyptus pulp* Brazil.

Liukko, S., Tasapuro, V., & Liitia, T. (2007). Fluorescence spectroscopy for chromophore studies on bleached kraft pulps. *Holzforschung*, *61*, 509–515.

Ly, E., Bras, H. B., Sadocco, J., Belgacem, P., Dufresne, M. N., & Thielemans, A. W. (2010). Surface functionalization of cellulose by grafting oligoether chains. *Materials Chemistry and Physics*, *120*, 438–445.

Muguet, M. C. S., Pedrazzi, C., & Colodette, J. L. (2011). Xylan deposition onto eucalypt pulp fibers during oxygen delignification. *Holzforschung*, *65*, 605–612.

Neto, C. P., Silvestre, A. J. D., Evtuguin, D. V., Freire, C. S. R., Pinto, P. C. R., & Santiago, A. S. (2004). Bulk and surface composition of ECF bleached hardwood kraft pulp fibres. *Nordic Pulp and Paper Research Journal*, *19*, 513–520.

Pan, S., & Ragauskas, A. J. (2012). Preparation of superabsorbent cellulosic hydrogels. *Carbohydrate Polymers*, *87*, 1410–1418.

Sauer, M., Hofkens, J., & Enderlein, J. (2011). *Handbook of fluorescence spectroscopy and imaging*. Wiley-VCH.

Schönberg, C., Oksanen, T., Suurnäkki, A., Kettunen, H., & Buchert, J. (2001). The importance of xylan for the strength properties of spruce kraft pulp fibers. *Holzforschung*, *55*, 639–644.

Schwikal, K., Heinze, T., Saake, B., Puls, J., Kaya, A., & Esker, A. R. (2011). Properties of spruce sulfite pulp and birch kraft pulp after sorption of cationic birch xylan. *Cellulose*, *18*, 727–737.

Silva, T. C. F., Lucian, J. L., Lucia, L. A., de Oliveira, R. C., Oliveira, F. N., & Silva, L. H. M. (2011). Adsorption of chemically modified xylans on eucalyptus pulp and its effect on the pulp physical properties. *Industrial and Engineering Chemistry Research*, *50*, 1138–1145.

Sixta, H. (2006). . *Handbook of pulp* (vol. 1) Winheim: Wiley-VCH., 9 pp.

Tiwari, S., Gupta, V. K., Pandey, P. C., Singh, H., & Mishra, P. K. (2009). Adsorption chemistry of oil-in-water emulsion from spent oil based cutting fluids using sawdust of *Mangifera indica*. *Journal of International Environmental Application & Science*, *4*, 99–107.

Trenor, S. R., Shultz, A. R., Love, B. J., & Long, T. E. (2004). Coumarins in polymers: From light harvesting to photo-cross-linkable tissue scaffolds. *Chemical Reviews*, *104*, 3059–3077.

Utsel, S. (2012). *Surface modification of cellulose-based materials for tailoring of interfacial interactions* (Doctoral thesis in pulp and paper chemistry and technology). Sweden: Stockholm.

Vega, B., Petzold-Welcke, K., Fardim, P., & Heinze, T. (2012). Studies on the fiber surfaces modified with xylan polyelectrolytes. *Carbohydrate Polymers*, *89*, 768–776.

Wondraczek, H., Kotiaho, A., Fardim, P., & Heinze, T. (2011). Photoactive polysaccharides. *Carbohydrate Polymers*, *83*, 1048–1061.

Wondraczek, H., Pfeifer, A., & Heinze, T. (2010). Synthetic photocrosslinkable polysaccharide sulfates. *European Polymer Journal*, *46*, 1688–1695.

Wondraczek, H., Pfeifer, A., & Heinze, T. (2012). Water soluble photoactive cellulose derivatives: Synthesis and characterization of mixed 2-[(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetic acid-(3-carboxypropyl)trimethylammonium chloride esters of cellulose. *Cellulose*, *19*, 1327–1335.