

INTERACTION BETWEEN WATER-SOLUBLE POLYSACCHARIDES AND NATIVE NANOFIBRILLAR CELLULOSE THIN FILMS

Paula Eronen,^a Karoliina Junka,^a Janne Laine,^a and Monika Österberg^{a,*}

The objective of this work was to compare the adsorption of different polysaccharides and cellulose derivatives on cellulose nanofibril films. Cellulose films having the native cellulose I structure were prepared from hardwood kraft pulp by extensive mechanical disintegration. Further fractionation enabled the preparation of reproducible, nanometer-scale thickness films. Systematic comparison by Quartz Crystal Microbalance with Dissipation (QCM-D) showed that various industrially available galactomannans have almost as good affinity to cellulose surface as xyloglucan and that most of the polysaccharides attach irreversibly to cellulose nanofibrils at low pH (4.5) and intermediate ionic strength (10 mM). SPR results support the QCM-D findings. Atomic Force Microscopy (AFM) imaging and Digital Pulsed Force Mode (DPFM) measurements further confirmed that a uniform non-aggregated layer of polysaccharides was formed that changed the properties of the NFC film.

Keywords: Nanofibrillar cellulose; Polysaccharides; QCM-D; AFM; SPR

Contact information: a: Department of Forest Products Technology, School of Chemical Technology, Aalto University P. O. Box 16300, FIN- 00076 AALTO, FINLAND * Corresponding author: monika.osterberg@aalto.fi

INTRODUCTION

The search for new, renewable biobased materials for various applications has made cellulose an attractive raw-material beyond the traditional processes of paper and board manufacture. Combined with the emerging nanotechnology, the preparation of new sustainable functional materials is one possible area where wood can be used (Klemm et al. 2005; Eichhorn et al. 2010). To produce nanocellulose, the natural composite structure of cellulose fibres has to be disintegrated. Numerous chemical ways for achieving this are known, such as acid hydrolysis, which yields short and rigid structural elements (Azizi Samir et al. 2005) or oxidation catalyzed by TEMPO, retaining the fibrillar structure (Bragd et al. 2004; Saito et al. 2006). Fibrils can also be separated physically, by means of intense mechanical shearing of pulp, a method first described by Turbak et al. (1983). The method has been further developed by adding either a chemical modification step in the grinder operation (Abe et al. 2007) or combining an enzymatic pre-treatment step and disintegration in high-pressure operated fluidizer (Pääkkö et al. 2007), to name a few. The resulting suspension is known as microfibrillated cellulose (MFC) or as more extensively separated, nanofibrillated cellulose (NFC) (Hubbe et al. 2008). NFC have been shown to have application potential in strong nanopaper (Henriksson et al. 2008; Nogi et al. 2009), as paper strength additive (Ahola et al. 2008a; Taipale et al. 2010), or a

promising barrier material (Syverud and Stenius 2009; Aulin et al. 2010). NFC could also be utilized as a reinforcing component in new types of composite materials, such as flexible, transparent displays due to its thermal stability (Siró and Plackett 2010). In addition, nanofibrillar ultrathin cellulose films retain the chemical composition of cellulose fibres and therefore can be applied as a representative surface in high-precision interaction studies (Ahola et al. 2008b).

The hydrophilicity and tendency for extensive intermolecular bonding between cellulose molecules that is responsible for the high strength and stiffness properties of native cellulose fibers often reduces the compatibility with other materials needed in high-end applications. The same is true also for NFC, and thus there is a need for compatibilizing modifications of the cellulose nanofibrils (Klemm et al. 2005). However, extensive chemical modifications can weaken the interactions between cellulose fibrils and thus impair the mechanical properties of the nanofibrils. A more preserving treatment, suggested by Teeri et al. (2007) involves coating of the cellulose fibrils with material having natural affinity towards cellulose, mimicking rather than unfolding the original plant cell-wall structure. The attached structure could then be further modified to enhance the compatibility with other materials while preserving the cellulose fibrils in their more natural state.

Renewable and commercially available water-soluble polymers are also gaining more attention (Ebringerová 2005; Hansen and Plackett 2008). Fundamental interactions of numerous polysaccharides with cellulose kraft fibers (Laleg and Pikulik 1991; Laine et al. 2000; Hannuksela et al. 2002; Christiernin et al. 2003; Westbye et al. 2006; Ren et al. 2009) have been studied, making the basic interactions well known but rather divergent depending on the precise chemical and morphological structures of the polysaccharides and the fibres used in the study. The main interaction between cellulose and polysaccharides has been suggested to be hydrogen bonding of unsubstituted chain regions. They are both formed via (1→4)-glycosidic bond joined monosaccharide units (Ishimaru and Lindström 1984; Sjöström 1993). However, it has also been suggested that cellulose as an amphiphilic molecule could have hydrophobic interactions (Lindman et al. 2010). As bleached kraft pulp, even without special treatments, bears an anionic net charge due to carboxylic groups (Lindström 1989), it also enables electrostatic interactions with charged polysaccharides.

In this paper the adsorption of readily available water-soluble polysaccharides or cellulose derivatives to nanofibrillar cellulose is studied. The goal is to compare how the properties of the used polysaccharides, namely basic chemical composition and molecular weight, affect the interactions and surface properties. Since polysaccharides can be further functionalized, for example by the established XET (xyloglucan endo-transglycosylase)-technique (Zhou et al. 2007) or by click-chemistry (Liebert et al. 2006), they are interesting components for NFC modification to build new high-performance materials from renewable resources. Another purpose of this work is to compare the adsorption of polysaccharides on nanocellulose with the previous studies obtained with fibres. Although the crystal structure and chemical composition stay relatively unchanged (Ahola et al. 2008b; Aulin et al. 2009), the substantially larger specific surface area and absence of pores distinguish the fibrils from fibers and can have an effect on interactions. High-precision adsorption techniques were applied, revealing differences in polysac-

charide attachment. In addition, the morphology of the adsorbed layer was characterized, indicating softening of the film.

EXPERIMENTAL

Materials

Nanofibrillar cellulose

The nanofibrillar cellulose (NFC) was obtained from The Finnish Centre for Nanocellulosic Technologies. Never-dried bleached kraft birch pulp from a Finnish pulp mill was used as starting material. The pulp was washed into its sodium form according to Swerin et al. (1990), and further treated by numerous passes (~30) through a high-pressure fluidizer (Microfluidics, M-110Y) to disintegrate the fiber structure into fibrils. The carbohydrate composition of the resulting gel (approx. dry matter content 1.6 m-%) was 72.8% glucose, 25.6% xylose, and 1.4% mannose. Charge of the pulp used as starting material was determined by conductometric titration (Katz et al. 1984) to be about 65 $\mu\text{eq/g}$. The zeta potential of the fibril supernatant used for NFC film formation was estimated to be -2 mV from zeta-potential measurements (Coulter Delsa 440, Coulter Corporation, Miami FL, USA) at pH 4.5 and 5mM NaCl, where the pH was adjusted with HCl.

Polysaccharides

All polysaccharides were commercially available products. They were diluted to a set concentration of 100 mg/L in 10 mM sodium-acetate-acetic acid buffer with the pH adjusted to 4.5 from daily prepared stock solutions. Sodium acetate and acetic acid used to prepare the buffer solution were of analytical grade. Ultrapure MilliQ-water filtered through Millipore Synergy UV unit (Millipore S.A.S, Molsheim, France) was used for all dilutions. Xyloglucan (XG), supplied by Megazyme, was from Tamarind seed and had the sugar constitution of 35% xylose, 45% glucose, 16% galactose, and 4% arabinose, as specified by the manufacturer. XG was dissolved by rigorous mixing into hot MilliQ-water and stirred for at least 4 hours for good dissolution. Xylan (Xyl) extracted from birch wood was obtained from Fluka (Fluka 95588) with a reported xylose content of 99%. Carboxymethyl cellulose (CMC, grade BW, NaCMC content 73%, DS 0.52) was a kind donation from CP Kelco. Guar gum (GG) from gum plant seeds (G4129), locust bean gum (LBG) from ceratonia siliqua seeds (G0753), chitosan (low molecular weight, 448869), and methyl cellulose (MC) (M7140) were all supplied by Sigma-Aldrich. Both LBG and GG were of technical grade, and contained about 25% insoluble matter, which was removed from overnight stirred samples by centrifugation (10 kG, 20 °C, 30 min). To know the precise concentration, the dry weight of the gum solution was determined, and the sample was diluted accordingly. To dissolve chitosan 1 w-% strong acetic acid was added, and for MC cold water under strong initial agitation was used until a clear solution was obtained.

Methods

Polysaccharide degradation and molecular weight determination

Acid hydrolysis according to Cheng et al. (2002) was adopted to decrease the molecular weight (*MW*) of the GG sample to study the effect of *MW* on adsorption. The procedure was repeated two times for GG to ensure proper degradation. The molecular weights of all polysaccharide samples were estimated by the Mark-Houwink equation (1),

$$[\eta] = KM^a \quad (1)$$

where $[\eta]$ is the intrinsic viscosity, M the molecular weight, and K and a are the Mark-Houwink parameters.

The intrinsic viscosity was measured by capillary viscometer (Schott Geräte AVS 350, Hofheim, Germany) at $25.0 \text{ }^\circ\text{C} \pm 0.05 \text{ }^\circ\text{C}$. Approximately 15 mL of the sample was injected into the capillary (diameter 0.63 mm). The viscosity of the solutions was measured three times and at least in three different concentrations. The parameters were taken from previously determined literature values (references are collected in Table 1). More details can be found in (Cheng et al. 2002; Picout and Ross-Murphy 2007).

To confirm the results obtained from viscosity measurements, especially for the acid-hydrolysed sample, selected samples were also characterized with high performance size exclusion chromatography (HPSEC) combined with refractive index, light scattering, and viscometric detectors in water-based eluent system according to parameters described by Pitkänen et al. (2009).

NFC substrate preparation

A procedure developed by Ahola et al. (2008b) was followed with a slight modification related to cationic anchoring polymer. NFC ultrathin films were prepared on either silica coated QCM-D (QSX303, Q-Sense AB, Västra Frölunda, Sweden) or gold coated SPR (Biacore SIA Au-kit, GE Healthcare, Uppsala, Sweden) sensors. The silica or gold coated sensors were rinsed with ultrapure water and further cleaned in a UV-ozonator (Bioforce Nanosciences, Ames, IA, USA). 1g/L polyethylene imine solution (PEI, Polysciences Inc., *MW* 50-100 000, charge density 15meq/g) was either self-assembled (15 min) or spincoated (1 min, 3000 rpm) on the sensors as an anchoring layer. The NFC gel was diluted to 1.67 g/L, treated with ultrasound microtip (25 % amplitude, 10 min, Branson Sonifier S-450 D, Branson Corp., Danbury, CT) and centrifuged (10 000 G, 45 min, 24 °C, Optima L-90 K ultracentrifuge, Beckman Coulter Inc., Brea, CA). The supernatant (1.25 g/L) was spincoated (1 min, 3000 rpm) immediately on the PEI-covered substrate. The prepared fibril substrates were stabilized in the aqueous electrolyte solutions overnight. The average root mean square roughness was around 3 to 4 nm, and the thickness was about 5 to 8 nm for all the prepared substrates as determined from the atomic force microscopy (AFM) images.

Quartz Crystal Microbalance with Dissipation (QCM-D)

The main method used to monitor the adsorption of polysaccharides on cellulose model film was QCM-D, as described more in detail in Rodahl et al. (1995). It measures the change in frequency and dissipation at a fundamental resonance frequency (f) and its

overtone. The adsorbed mass per unit surface is proportional to the decrease or increase in the resonance frequency according to the Sauerbrey (1959) equation (2),

$$\Delta m = -\frac{C\Delta f}{n}, \quad (2)$$

where C is the device sensitivity constant and n is the overtone number.

The simultaneously measured dissipation (D) factor gives information related to the frictional losses due to the viscoelastic properties of the adsorbed layer. The dissipation energy increases as a function of adsorption if viscoelastic layers are formed when adsorbing the polysaccharide on the cellulose model film. The dissipation factor is defined in equation 3:

$$D = \frac{E_{diss}}{2\pi E_{stored}}, \quad (3)$$

where E_{diss} is the dissipated energy during one oscillation and E_{stored} is the total energy stored in the oscillation system.

The QCM-D measurements were performed with the E4 instrument (Q-Sense AB, Västra Frölunda, Sweden) with controlled flow. The diluted samples (concentration 100 mg/l) were pumped at constant rate of 0.1 mL/min through the measurement chambers. The polysaccharide solutions were added after first acquiring a stable baseline with buffer solution. The fundamental resonance frequency was 5 MHz, and the overtones 15, 25, 35, 45, 55, and 65 MHz were recorded. Results are shown and calculated from the 3rd overtones. At a minimum, all experiments were duplicated on separate days using freshly prepared solutions. Representative results are displayed.

For swollen gel-like films the Sauerbrey equation has been found to underestimate the adsorbed amount. Another model, developed by Johannsmann et al. (1992) gives more accurate estimate of the true sensed mass for viscous films,

$$\hat{m}^* = m^0 \left(1 + \hat{J}(f) \frac{\rho f^2 d^2}{3} \right) \quad (4)$$

where \hat{m}^* is the equivalent mass, ρ is the density of the fluid, d is the thickness of the film, $\hat{J}(f)$ the complex shear assumed independent of frequency, and m^0 is the true sensed mass. The latter is obtained from the intercept of a plot taking the equivalent mass as the function of frequency squared (Naderi and Claesson 2006).

The adsorption curves were also analyzed using a Voigt-based model provided by Q-Tools data analysis program based on calculations from Voinova et al. (1999). Similar parameters as used by Liu et al. (2011) were applied in the fitting for shear viscosity (η_f), elastic shear modulus (μ_f) and thickness (h_f). The layer densities of different polysaccharides were estimated to be 1100 kg/m³ for comparable results, and overtones 3, 5, and 7 (15, 25, and 35 MHz) were used in modeling.

Surface Plasmon Resonance (SPR)

Selected polysaccharides were also characterized with surface plasmon resonance (SPR) to estimate the adsorbed amount without the coupled water. The method was suggested by Kretschmann (1971) and further developed by Liedberg et al. (1993). In this work a Biacore 1000 instrument (GE Healthcare, Uppsala, Sweden) was used. Experimental conditions were the same as in QCM-D experiments except for a filtering step through 0.22 μm Millipore filters before injection and a degassing step of water used for buffer solution preparation. Nanofibrillated cellulose surfaces were prepared carefully on gold-layer SiAu-sensors on top of a spincoated PEI-layer. The chip was assembled according to instructions provided by manufacturer and stored in a cold-room overnight. The films were equilibrated by running the buffer through for 2 h. After that, 300 μL of polysaccharide solution was injected. The flow rate was 5 $\mu\text{L}/\text{min}$, and T was 25 $^{\circ}\text{C}$. The results were y-transformed to convert the baseline to 0 response units prior to sample injection. The measurements were repeated twice. The constant for transforming the raw SPR-data into mass was calculated with Equation 5 obtained by relating de Feijter's equation (de Feijter et al. 1978) of the change of the refractive index, into change of the SPR angle,

$$m_{\text{SPR}} = \frac{\pi d_f}{A \cdot 180 \cdot 10^4} \frac{dn}{dc} \Delta RU \quad (5)$$

where d_f is the thickness (here it was estimated from QCM-D modeling or literature), dn/dc the refractive index increment value (Table 1), ΔRU the change in response units at the end of the experiment after rinsing, and the constant A is calculated according to:

$$A = \frac{1}{n_1 \cos \theta_f} \sqrt{\left(\frac{\epsilon_m}{\epsilon_m + n_f^2} \right)^3} \approx 1.35 \quad (6)$$

where n_1 is the refractive index of the medium (glass ~ 1.7), ϵ_m is the dielectric constant of metal (gold) $\approx -19.9 + 1.45i$ at 720 nm wavelength (Zheng et al. 2010), θ_f is the angle of incidence of light after the film formation (60), and n_f is the refractive index of such film (1.33).

Atomic Force Microscopy (AFM)-imaging

AFM images were recorded from the QCM-D crystals after polysaccharide adsorption using digital pulsed force mode (DPFM) in air with a WITec alpha 300R instrument (WITec GmbH, Ulm, Germany). The main advantage of using this imaging mode is that in addition to normal topographical images, also information about e.g. adhesion and stiffness can be simultaneously acquired. The cantilevers were Arrow FM (NanoWorld AG, Switzerland) with nominal spring constant of 2.8 N/m. The imaging size was 10x10 μm^2 . More information about DPFM-measurements can be found from Schmidt et al. (2005). The amplitude set point was ~ 0.2 V, and f 1000 Hz.

RESULTS AND DISCUSSION

Polysaccharide Characterization

Water-soluble polysaccharides are commercially available in varying molecular weights. In this work, some of them were tested. Of the neutral polymers, xyloglucan (XG) adsorption on nanofibrillar cellulose has been studied in the past (Ahola et al. 2008c), and it was chosen as a reference to compare other neutral polysaccharides, such as different galactomannans and methyl cellulose. The galactomannans were chosen because they are cheap and available in larger quantities compared to XG. Also a few charged polysaccharides were included in the comparison. Anionic carboxymethyl cellulose (CMC) is able to attach on cellulose under elevated electrolyte conditions (Laine et al. 2000) and contains carboxyl groups that opens up possibilities for surface chemical modification. Chitosan, a cationic and antibacterial biopolymer, has shown potential in biocompatible applications (Lundin et al. 2010) and has strong interaction with cellulose (Nordgren et al. 2009).

Guar gum was degraded to smaller *MW* by acid hydrolysis to be able to distinguish between the effect of chemical structure and size on the adsorption. In Table 1 the *MW* estimations of samples are presented, determined from the intrinsic viscosity of the samples. In addition, HPSEC measurements were carried out to verify the accuracy of the intrinsic viscosity measurements. The high polydispersity of the degraded sample and reduced solubility somewhat affected the results. The results obtained with the two methods are only rough estimations, but for the purpose of this study they give an indication of the polysaccharide size range. In addition, for the GG sample where the role of *MW* was more thoroughly investigated, SEC analysis gives more detailed *MW* information.

Table 1. Polysaccharide Abbreviations and Properties

Polysaccharide	Abbr.	Reference for Mark-Houwink parameters	dn/dc (ml/g)	M_v visc. (kDa)	M_w SEC (kDa)	PDI * (SEC) (M_w/M_n)	R_g (nm)
Neutral							
Xyloglucan	XG	(Picout et al. 2003)	0.146 **	190			
Guar gum	GG	(Cheng et al. 2002)	0.135 •	2110	2040	1.2	114
Locust bean gum	LBG	(Cheng et al. 2002)		1960	1060	1.2	93
Guar gum hydr.	GG _{deg}	(Cheng et al. 2002)		250	460	11.8	66
Methyl cellulose	MC	(Hirrien et al. 1996)		20			
Anionic							
Xylan	XYL	(Ebringerová and Heinze 2000)		9			
Carboxy-methylcellulose	CMC	(Stelzer and Klug 1980)		370			
Cationic							
Chitosan	CHI	(Mao et al. 2004)	0.181 ○	230			
* the ratio of weight and number average molecular weights (M_w and M_n , respectively)							
** obtained from Picout et al. 2003							
• obtained from Robinson et al. 1982							
○ obtained from Harding 2005							

Adsorption of Polysaccharides on Nanofibrillar Cellulose Film

QCM-D experiments at constant pH and electrolyte concentration (pH 4.5, 10 mM) were performed, and the results are presented in Figs. 1 and 2. The acetic acid-sodium acetate buffer was chosen to keep the charge of the cellulose model film low in order to minimize the swelling of the cellulose film. The measurements were continued until an apparent plateau value was reached, however not for longer than 2 hours. The cell was rinsed with buffer solution after completed adsorption to verify the irreversibility of the adsorption. Figure 1 presents a comparison of adsorption during the first 18 minutes for the polysaccharides with molecular weights approximately 200 to 250 kDa, but different backbone and charge properties. The adsorbed amounts are estimations calculated by the Sauerbrey equation (Eq. 2), shown as a function of time (Fig 1a). Also the Johannsmann estimations (Eq. 4) are presented as open symbols, yielding slightly higher adsorbed amounts. The corresponding energy dissipation values are presented in Fig. 1b as a function of time. XG had the fastest attachment rate and highest adsorbed amount in the initial stage of adsorption. Neutral, degraded GG and anionically charged CMC showed similar change in dissipation, but the adsorbed mass in comparison was higher for GG. Likewise, the smaller slope in $\Delta m/t$ plot compared to XG and GG_{deg} indicated slower adsorption. Although the CMC attachment was not as strong compared to neutral polysaccharides, the anionic CMC still adsorbed irreversibly at low pH in contrast to pH 8, where adsorbed CMC was removed during rinsing (Ahola et al. 2008c). At low pH the carboxylic groups on CMC and on cellulose are partly protonated facilitating adsorption (Laine et al. 2000). However, the relatively higher ΔD vs. Δm -values indicate that CMC has more hydrated water-containing structure than the other polysaccharides due to the charged groups. Chitosan, being clearly cationic at pH 4.5, adsorbed fast, but since the polysaccharide adsorbed in a flat conformation and very low amount of chitosan was needed for charge neutralization, the detected adsorbed mass was very low. The adsorbed mass estimations at the end of the experiment before rinsing are included in Table 2 together with percentage of mass removed during rinsing.

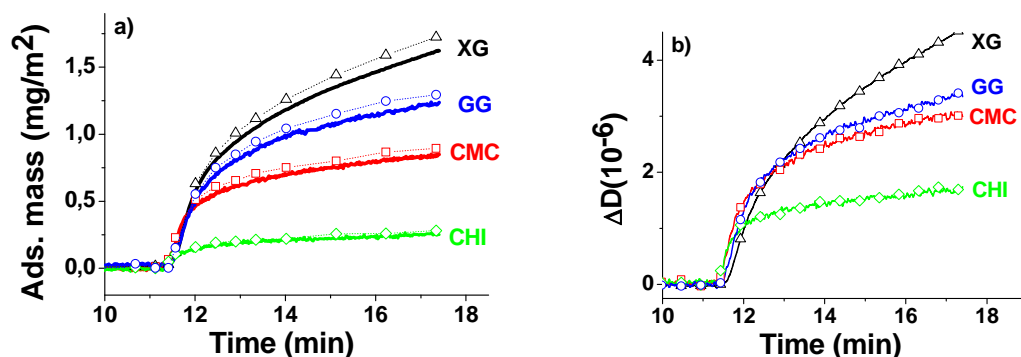


Fig. 1. Change in the adsorbed mass calculated from the 3rd overtone frequency (Hz) values and dissipation (10^{-6}) as the function of time on selected polysaccharides with approximately similar molecular weight (200-250 kDa). The dashed line and open symbols in a) represent the adsorbed amounts calculated at selected points by applying the Johannsmann's equation, and the solid lines correspond to values using the Sauerbrey equation.

In Fig. 2 the change in dissipation as a function of change in frequency omitting the time as a variable is shown. From these D - f -curves, differences in the adsorption behavior and layer structure of polysaccharides can be seen. The results are divided into neutral, high MW (Fig. 2a), and charged and low molecular weight polysaccharides (Fig 2b). All the water-soluble polysaccharides had rather similar adsorption profiles on a mechanically disintegrated nanofibrillar cellulose surface, especially the neutral ones. For XG, the strong initial attachment continued, resulting in rather high adsorbed amount with relatively lower increase in dissipation compared to other studied polysaccharides. This is attributed mainly to the resemblance of the β -(1 \rightarrow 4) linked glucan backbones facilitating close contact and consequent formation of hydrogen bonds (Zhou et al. 2007). The interaction has been observed with different types of cellulosic materials (e.g. Mishima et al. 2003 and Lima et al. 2003). Likewise, the affinity of high molecular weight galactomannans to cellulosic fibres has previously been established (Rojas and Neuman 1999; Lindström et al. 2005). The similarity in the backbone stereochemistry is also suggested to be the driving force behind adsorption on cellulose of galactomannans (Gruenhut 1953). In contrast to XG, their adsorption to cellulose nanofibrils from industrial raw materials however has previously not been studied. The adsorbed amounts (including the bound water) were very similar for the neutral polysaccharides. The adsorbed layer of GG and LBG gums seemed to have, however, slightly more extended conformation compared to XG, as seen from the steeper D - f slope (Fig. 2A). The comparison of high molecular weight GG and LBG does not show significant differences; slightly stronger affinity for LBG was observed. As LBG has higher mannose to galactose ratio compared to GG (Whitney et al. 1998; Picout et al. 2002), it can result in formation of more coiled polysaccharide dispersion via mannose-mannose interactions. However, as the persistence length and radius of gyration values for galactomannans regardless of side group substitution pattern (3-5 nm) and XG (4-6 nm) are very similar (Picout et al. 2002, 2003), the similar adsorption tendencies are not surprising. The relatively high ΔD -values indicate that, in contrast to many cationic polyelectrolytes, the galactomannans have a dispersing effect on the cellulose fibrils instead of compressing the swollen film upon adsorption.

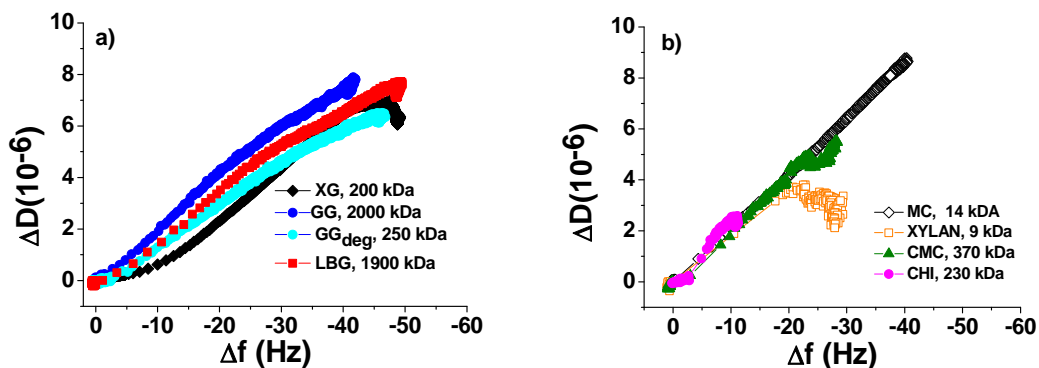


Fig. 2. Change of dissipation value as a function of frequency change. In a) the neutral and in b) the charged and small MW polysaccharides are shown.

The dispersing action of galactomannans, was already seen with GG for pulp fibres (Swanson 1950), and with XG on NFC substrates (Ahola et al. 2008c) and is essential in many applications, e.g for paper strength. The observed adsorption of the readily available GG and LBG suggest that they could be used as starting material for fibril modification while retaining the unique properties of the cellulose fibrils.

The effect of *MW* on adsorption was further investigated by decreasing the high initial molecular weight of GG. Results (Fig. 2a) showed a decrease in the GG_{deg} *D-f* slope, which indicates a small reduction in the hydrolyzed GG_{deg} layer structure. The adsorbed mass of GG increased after hydrolysis, but not significantly (Table 2). This correlates well with results obtained with bleached softwood kraft fibres (Hannuksela et al. 2002), where the structure (galactose to mannose ratio) affected adsorption more than the molecular weight. However, comparison between adsorption studies between nanofibril substrates and bulk fibre suspensions is not entirely straightforward. In pulp suspensions, different accessibility due to presence of pores and more three-dimensional network structure are present, unlike the case of planar nanofibril substrates used in QCM-D. The high polydispersity of GG_{deg} suggests that high *MW* portions of GG still remain, which may preferentially adsorb in competition with the smaller molecules (Fleer et al. 1993). This can explain why drastic difference in the *D-f* plot was not observed for GG samples.

Figure 2b) presents a similar change in dissipation (ΔD) versus change in frequency (Δf)-curves for cellulose derivative methylcellulose (MC), cationic chitosan, and negatively charged xylan from wood. MC, as biocompatible methyl ether derivative of cellulose, preferentially adsorbs on pure cellulose (Ishimaru and Lindström 1984). The attachment of MC also on NFC substrate that also contains hemicelluloses was of the same order compared to other neutral polysaccharides. The steeper slope of the *D-f* curve, however, indicates a more extended conformation of the adsorbed layer. Taking into account the significantly smaller *MW* of MC compared to the other polysaccharides, the steep slope indicates weaker affinity. The higher persistence length (14-17 nm) compared to other polysaccharides (Patel et al. 2008) could be behind this behavior. The lowest adsorbed amount was observed for chitosan, although strong, non-electrostatic origin interactions between chitosan and cellulose have been shown to exist (Laleg and Pikulik 1991, Nordgren et al. 2009). Besides backbone induced co-crystallization, also covalent bonds between primary amino groups in chitosan and aldehyde groups of cellulose can promote the interaction (Li et al. 2004; Lindström et al. 2005). The effect of pH with chitosan interactions is a governing factor. Under the chosen experimental conditions (pH 4.5, 10 mM ionic strength) chitosan is fully charged, and the adsorption was of electrostatical origin. The adsorption was fast and leveled off quickly, indicating strong interaction, which is in accordance to previous QCM-D observations (Myllytie et al. 2009). Due to its cationic charge chitosan has an extended conformation in solution compared to the neutral polysaccharides and adsorbs in a thin layer, quickly (over)compensating the charge of the NFC. Xylan had very similar *D-f* curve as previously observed on a regenerated Langmuir-Schaefer (LS) cellulose surface (Tammelin et al. 2009). Also, the low charge of cellulose (zeta-potential -2mV) and neutral segment binding of xylan could be reasons for the observed adsorption.

The adsorption of differently structured polysaccharides was surprisingly similar on NFC substrates. Therefore it was decided to study the adsorbed layers in detail by viscoelastic modeling by using the QCM-D-software (QTools). The hydrodynamic thickness, shear viscosity, and elastic shear modulus of the water containing polysaccharide layers were estimated (Table 2). Only the thin chitosan layer was unsuitable for this estimation. For the other polysaccharides, the fittings were relatively successful. However, instead of absolute values of these modeled parameters, they are more appropriate for relative comparison of values between different polysaccharides. The estimations showed that most of the adsorbed polysaccharide layers had rather similar aqueous thickness, close to 10 nm. The highest layer thickness was estimated for MC, suggesting formation of an extended layer of the stiff polymer chains. The hydrodynamic layer thickness for the GG_{deg} was only slightly reduced in accordance with the small decrease observed in *D-f* plots, as discussed previously. The estimated values for xylan and CMC layer are of the same order compared to previous publications by Tammelin et al. (2009), and Liu et al. (2011), respectively, despite the differences in cellulose substrates. Thus neither cellulose supramolecular structure nor hemicelluloses present in the NFC film affected the adsorption of anionic polysaccharides.

Table 2. Comparison of Layer Properties for Polysaccharides Adsorbed on Films

Poly-saccharide	h_f (nm)	$\eta_f (10^{-3})$ (N·s·m ⁻²)	$\mu_f (10^5)$ (N·m ⁻²)	Ads. amount QCM (Eq.4) mg/m ²	Detached in rinsing (%)	Ads. amount SPR (Eq.5) mg/m ²	Water content [%]
XG	11.5	2.2	1.4	3.0	<1	0.29	90
GG	11	1.7	1.0	2.6	1		
LBG	12	2.0	1.1	3.1	<1		
GG _{deg}	10	1.9	1.1	2.9	<1	0.26	91
MC	34	1.2	0.1	2.5	6		
CMC	8	1.7	1.2	1.7	2		
XYL	5	1.5	5	1.8	6		
CHI	-	-	-	0.7	3	0.08	88

Dry Mass of Adsorbed Polysaccharides in SPR Analysis

The effect of coupled water in hydrated polysaccharide layers was further evaluated for selected samples using SPR. This method is common in biochemical studies (Green et al. 2000) but has rather recently found use in cellulosic research (Hedin et al. 2007; Ahola et al. 2008c; Kaya et al. 2009). Three polysaccharides chosen were XG, GG_{deg}, and CHI. GG_{deg} is a commercially interesting alternative for XG to use as a basis for modifications of NFC, and CHI, due to the cationic charge different interaction with cellulose. Experimental conditions were kept as close as possible to those in the QCM-D-measurements. Figure 3 shows the detected change in SPR angle represented as ΔRU -values as the function of time. The low adsorbed amount of chitosan compared to the other polysaccharides observed using QCM-D was verified. XG showed high level of adsorption, but quite surprisingly, the rate of adsorption was not as clearly faster as it was in the QCM-D experiments. In comparison, the attachment of degraded GG to NFC was very fast and almost on a similar level to that of XG.

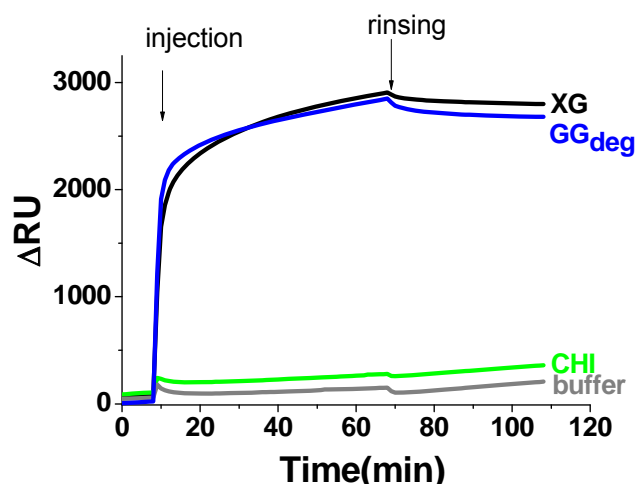


Fig. 3. The adsorption profiles shown as change in the response unit for SPR measurements as the function of time for different polysaccharides. Buffer indicates the injection of pH 4.5, 10 mM sodium acetate-acetic acid solution and the characteristic profile caused by the injection.

The SPR results after rinsing were calculated with Eq. 5, using the hydrodynamic thickness values estimated by QCM-D modeling (Table 2) for XG and GG_{deg}. For CHI, an estimation of 3 nm was used based on layer-by-layer assembly of chitosan with-cellulose nanowhiskers (de Mesquita et al. 2010). As already noted, the QCM-D measures also the water bound to the attached hydrophilic polysaccharides, whereas SPR should be able to distinguish the dry polymer. The adsorbed mass estimations were many times lower when calculated by SPR, which was expected based on previous results (Ahola et al. 2008c, Liu et al. 2011). The water content was very high, in the range of 90% for polysaccharides. Although the experimental conditions were kept as similar as possible in QCM-D and SPR experiments, the differences in the experimental set-up, e.g. flow rate could influence the comparability. The SPR experiments showed that the adsorbed polysaccharide layer is highly water swollen, even in the case of cationic chitosan. The observed extensive adsorption and dispersing effect of the natural polysaccharides on NFC suggests strong natural affinity but also that due to their hydrogen bonding ability the polysaccharides do not interfere with the bonding of water, and thus the fibrillar network stays swollen. Although hydrogen bonds between cellulose and the polysaccharides are very important in dry state, hydrogen bonds to water are probably more important in aqueous state (Lindman et al. 2010).

Morphology of Adsorbed Layer – AFM Imaging

All QCM-D crystals of the polysaccharides adsorbed on nanocellulose films were dried and at least one of the parallel sensors was imaged with AFM. All the films looked essentially similar, before and after measurements, without any large aggregates. This is in contrast to previous experiments where slight aggregation has been observed (Tammelin et al. 2009). This showed that all polysaccharides had been fully soluble during adsorption experiments. To further probe the influence of the polysaccharide layer on the properties of the NFC film, the DPFM-mode was used to investigate relative changes in film stiffness and adhesion properties. Figure 4 illustrates the results from these comparative measurements. The topographic images look very similar, as do the

stiffness values, but the adhesion between silicon nitride tip and film surface was clearly lower after polysaccharide adsorption. The difference shown by DPFM-AFM measurements illustrates that although usually not directly visible in AFM-imaging; the polysaccharides do attach irreversibly onto the NFC substrates and alter the surface properties even after drying of the substrate. Direct modification of cellulose is either challenging to perform or detrimental for the e.g. mechanical properties. Therefore, first attaching a polysaccharide, which in turn can be modified, could offer an alternative approach. However, more research is still needed.

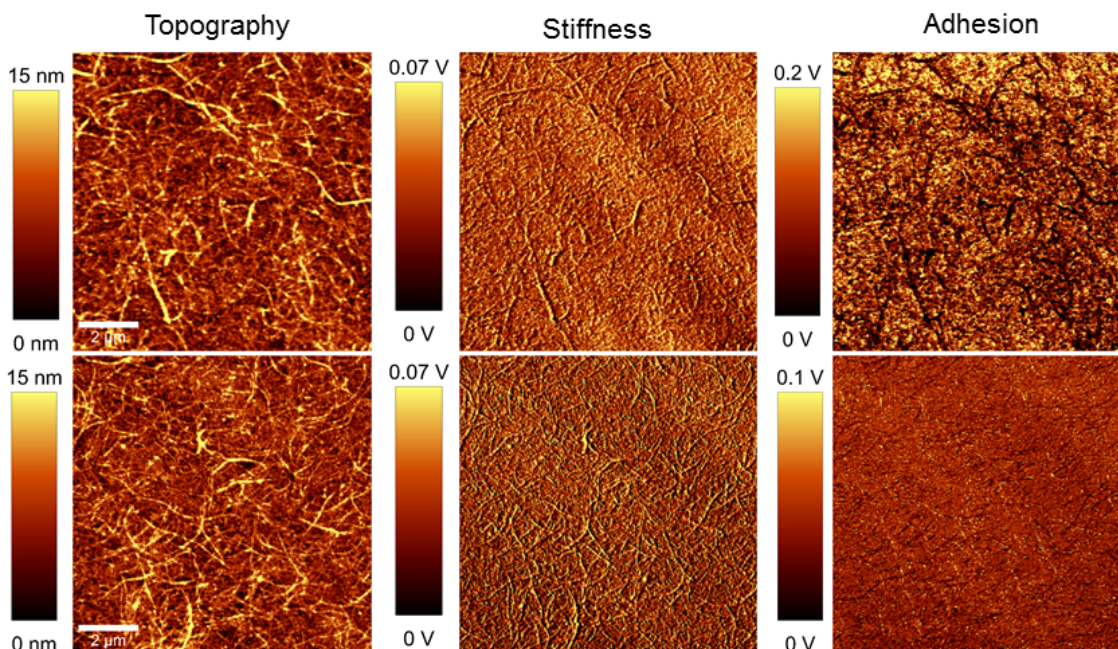


Fig. 4. DPFM-mode AFM images of reference NFC substrate (upper row) and LBG-covered NFC substrate. The uniform reduction in adhesive forces verifies that fibrils are well covered by a uniform polysaccharide layer.

CONCLUSIONS

1. All water soluble polysaccharides tested adsorbed irreversibly on thin nanofibrillar cellulose films prepared from unmodified bleached birch kraft pulp.
2. The polysaccharide molecular structure and presence of charges affects the polysaccharide adsorption more than solely molecular weight.
3. Xyloglucan and galactomannans adsorbed the most and formed water-rich dispersive layers on NFC.
4. AFM-imaging verified that thin, fully covering layers of unaggregated polysaccharides were formed. This layer affected the interaction properties of the NFC. The adsorbed polysaccharides can easily be further used for surface modification of the NFC.

ACKNOWLEDGMENTS

M. Sc. Tuija Teerinen from VTT Biotechnology, Finland is gratefully acknowledged for the performing the SPR-runs and providing fruitful discussions. Prof. Maija Tenkanen is thanked for providing the HPLC-characterization in Helsinki University, Department of Applied Chemistry and Microbiology. Ms. Ritva Kivelä and Ms. Aila Rahkola from Aalto University are thanked for their help with characterization of samples. Funding for this work was received from Naseva-project supported by Finnish Technology Development Center (TEKES) and industrial partners.

REFERENCES CITED

- Abe, K., Iwamoto S., and Yano, H. (2007). "Obtaining cellulose nanofibers with a uniform width of 15 nm from wood," *Biomacromol.* 8(10), 3276-3278.
- Ahola, S., Österberg, M., and Laine, J. (2008a). "Cellulose nanofibrils—adsorption with poly(amideamine) epichlorohydrin studied by QCM-D and application as a paper strength additive," *Cellulose* 15(2), 303-314.
- Ahola, S., Salmi, J., Johansson, L.-S., Laine, J., and Österberg, M. (2008b). "Model films from native cellulose nanofibrils. Preparation, swelling, and surface interactions," *Biomacromol.* 9(4), 1273-1282.
- Ahola, S., Myllytie, P., Österberg, M., Teerinen, T., and Laine, J. (2008c). "Effect of polymer adsorption on cellulose nanofibril water binding capacity and aggregation," *BioResources* 3(4), 1315-1328.
- Aulin, C., Ahola, S., Josefsson, P., Nishino, T., Hirose, Y., Österberg, M., and Wågberg, L. (2009). "Nanoscale cellulose films with different crystallinities and mesostructures – Their surface properties and interaction with water," *Langmuir* 25(13), 7675-7685.
- Aulin, C., Gällstedt, M., and Lindström, T. (2010). "Oxygen and oil barrier properties of microfibrillated cellulose films and coatings," *Cellulose* 17(3), 559-574.
- Azizi Samir, M. A. S., Alloin, F., and Dufresne, A. (2005). "Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field," *Biomacromol.* 6(2), 612-626.
- Bragd, P., van Bekkum, H., and Besemer, A. C. (2004). "TEMPO-mediated oxidation of polysaccharides: Survey of methods and applications," *Top. Catal.* 27(1), 49-66.
- Cheng, Y., Brown, K. M., and Prud'homme, R. K. (2002). "Preparation and characterization of molecular weight fractions of guar galactomannans using acid and enzymatic hydrolysis," *Int. J. Biol. Macromol.* 31(1-3), 29-35.
- Christiernin, M., Henriksson, G., Lindström, M. E., Brumer, H., Teeri, T. T., Laine, J., and Lindström, T. (2003). "The effects of xyloglucan on the properties of paper made from bleached kraft pulp," *Nordic Pulp Pap. Res. J.* 18(2), 182-187.
- de Feijter, J. A., Benjamins, J., and Veer, F. A. (1978). "Ellipsometry as a tool to study the adsorption behaviour of synthetic and biopolymers at the air-water interface," *Biopolymers* 17(7), 1759-1772.

- de Mesquita, J. P., Donnici, C. L., and Pereira, F. V. (2010). "Biobased nanocomposites from layer-by-layer assembly of cellulose nanowhiskers with chitosan," *Biomacromol.* 11(2), 473-480.
- Ebringerová, A., and Heinze, T. (2000). "Xylan and xylan derivatives - biopolymers with valuable properties, 1. Naturally occurring xylnans structures, isolation procedures and properties," *Macromol. Rapid Commun.* 21(9), 542-556.
- Ebringerová, A. (2005). "Structural diversity and application potential of hemicelluloses," *Macromol. Symp.* 232(1), 1-12.
- Eichhorn, S., Dufresne, A., Aranguren M., Marcovich, N., Capadona, J., Rowan, S., Weder, C., Thielemans, W., Roman, M., Renneckar, S., Gindl, W., Veigel, S., Keckes, J., Yano, H., Abe, K., Nogi, M., Nakagaito, A., Mangalam, A., Simonsen, J., Benight, A., Bismarck, A., Berglund, L., and Peijs, T. (2010). "Review: Current international research into cellulose nanofibres and nanocomposites," *J. Mater. Sci.* 45(1), 1-33.
- Fleer, G. J., Cohen Stuart, M. A., Scheutjens, J. M. H. M., Cosgrove, T., and Vincent, B. (1993). *Polymers at interface*. Cambridge, Chapman & Hall, University Press.
- Green, R. J., Frazier, R. A., Shakesheff, K.M., Davies, M. C., Roberts, C. J., and Tendler, S. J. B. (2000). "Surface plasmon resonance analysis of dynamic biological interactions with biomaterials," *Biomaterials* 21(18), 1823-1835.
- Gruenhut, N. S. (1953). "Mannangalactan gums-the mechanism of retention by paper fibers," *Tappi* 36, 297-301.
- Harding, S.E. (2005). "Analysis of polysaccharides by ultracentrifugation. Size, conformation and interactions in solution." *Adv. Polym. Sci* 186 (Polysaccharides I), 211-254.
- Hannuksela, T., Tenkanen, M., and Holmbom, B. (2002). "Sorption of dissolved galactoglucomannans and galactomannans to bleached kraft pulp," *Cellulose* 9(3), 251-261.
- Hansen, N. M. L., and Plackett, D. (2008). "Sustainable films and coatings from hemicelluloses: A review," *Biomacromol.* 9(6), 1493-1505.
- Hedin, J., Löfroth J.-E., and Nydén, M. (2007). "Adsorption behavior and cross-linking of EHEC and HM-EHEC at hydrophilic and hydrophobic modified surfaces monitored by SPR and QCM-D," *Langmuir* 23(11), 6148-6155.
- Henriksson, M., Berglund, L. A., Isaksson, P., Lindström, T., and Nishino, T. (2008). "Cellulose nanopaper structures of high toughness," *Biomacromol.* 9(6), 1579-1585.
- Hirrien, M., Desbrières, J., and Rinaudo, M. (1996). "Physical properties of methylcelluloses in relation with the conditions for cellulose modification," *Carbohyd.Polym.* 31(4), 243-252.
- Hubbe, M. A., Rojas, O. J., Lucia, L.A., and Sain, M. (2008). "Cellulosic nanocomposites: A review," *BioResources* 3(3), 929-980.
- Ishimaru, Y., and Lindström, T. (1984). "Adsorption of water-soluble, nonionic polymers onto cellulosic fibers," *J. Appl. Polym. Sci.* 29(5), 1675-1691.
- Johannsmann, D., Mathauer, K., Wegner, G., and Knoll, W. (1992). "Viscoelastic properties of thin films probed with a quartz-crystal resonator," *Phys.Rev. B.* 46(12), 7808-7815.

- Katz, S., Beatson, R. P., and Scallan, A. M. (1984). "The determination of strong and weak acidic groups in sulfite pulp," *Svensk Papperstidn.* 87(6), R48-R53.
- Kaya, A., Du, X., Liu, Z., Lu, J. W., Morris, J., Glasser, W. G., Heinze, T., and Esker, A. R. (2009). "Surface plasmon resonance studies of pullulan and pullulan cinnamate adsorption onto cellulose," *Biomacromol.* 10(9), 2451-2459.
- Klemm, D., Heublein, B., Fink, H.-P., and Bohn, A. (2005). "Cellulose: Fascinating biopolymer and sustainable raw material," *Angew. Chem. Int. Ed.* 44(22), 3358-3393.
- Kretschmann, E. (1971). "Determination of the optical constants of metals by excitation of surface plasmons," *Zeitschrift für Physik* 241(4), 313-324.
- Laine, J., Lindström, T., Glad-Nordmark, G., and Risinger, G. (2000). "Studies on topochemical modification of cellulosic fibres. Part 1. Chemical conditions for the attachment of carboxymethyl cellulose onto fibres," *Nordic Pulp Pap. Res. J.* 15(5), 520-526.
- Laleg, M., and Pikulik, I. I. (1991). "Wet-web strength increase by chitosan." *Nordic Pulp Pap. Res. J.* 6(3), 99-103.
- Li, H., Du, Y., and Xu, Y. (2004). "Adsorption and complexation of chitosan wet-end additives in papermaking systems," *J. Appl. Polym. Sci.* 91(4), 2642-2648.
- Liu, Z., Choi, H., Gatenholm, P., and Esker, A.R. (2011). "Quartz crystal microbalance with dissipation monitoring and surface plasmon resonance studies of carboxymethyl cellulose adsorption onto regenerated cellulose surfaces," *Langmuir* 27, 8718-8728.
- Liebert, T., Hänsch, C., and Heinze, T. (2006). "Click chemistry with polysaccharides," *Macromol. Rapid Commun.* 27(3), 208-213.
- Liedberg, B., Lundström, I., and Stenberg, E. (1993). "Principles of biosensing with an extended coupling matrix and surface plasmon resonance," *Sens. Actuators B*, 11(1-3), 63-72.
- Lima, D. U., Oliveira, R. C., and Buckeridge, M. S. (2003). "Seed storage hemicelluloses as wet-end additives in papermaking," *Carbohydr. Polym.* 52(4), 367-373.
- Lindman, B., Karlström, G., and Stigsson, L. (2010). "On the mechanism of dissolution of cellulose," *J. Mol. Liq.* 156, 76-81.
- Lindström, T. (1989). "Some fundamental chemical aspects on paper forming," In: *Fundamentals of Papermaking*, C. F. Baker and V. W. Punton, (eds.), Mech. Eng. Pub. Ltd., London, 311-412.
- Lindström, T., Wågberg, L., and Larsson, T. (2005). "On the nature of joint strength in paper - A review of dry and wet strength resins used in paper manufacturing," *Advances in Paper Science and Technology: 13th Fundamental Research Symposium*, Pulp and Paper Fundamental Research Society, Bury, 457-562.
- Lundin, M., Blomberg, E., and Tilton, R.D. (2010). "Polymer dynamics in layer-by-layer assemblies of chitosan and heparin." *Langmuir* 24(8), 3242-3251.
- Mao, S., Shuai, X., Unger, F., Simon, M., Bi, D., and Kissel, T. (2004). "The depolymerization of chitosan: Effects on physicochemical and biological properties," *Int. J. Pharm.* 281(1-2), 45-54.
- Mishima, T., Hisamatsu, M., York, W.S., Teranishi, K., and Yamada, T. (1998). "Adhesion of beta-glucans to cellulose," *Carbohydr. Res.* 308(3-4), 389-395.
- Myllytie, P., Salmi, J., and Laine, J. (2009). "The influence of pH on the adsorption and interaction of chitosan with cellulose," *BioResources* 4(4), 1647-1662.

- Naderi, A., and Claesson, P. (2006). "Adsorption properties of polyelectrolyte-surfactant complexes on hydrophobic surfaces studied by QCM-D," *Langmuir* 22(18), 7639-7645.
- Nogi, M., Iwamoto, S., Nakagaito A. N., and Yano, H. (2009). "Optically transparent nanofiber paper," *Adv. Mat.* 21(16), 1595-1598.
- Nordgren, N., Eronen, P., Österberg, M., Laine, J., and Rutland, M. W. (2009). "Mediation of the nanotribological properties of cellulose by chitosan adsorption," *Biomacromol.* 10(3), 645-650.
- Patel, T. R., Morris, G. A., Garcia de la Torre, J., Ortega, A., Mischnick, P., and Harding, S. E. (2008). "Molecular flexibility of methylcelluloses of differing degree of substitution by combined sedimentation and viscosity analysis," *Macromol. Biosci.* 8(12), 1108-1115.
- Picout, D. R., Ross-Murphy, S. B., Jumel, K., and Harding, S. E. (2002). "Pressure cell assisted solution characterization of polysaccharides. 2. Locust bean gum and tara gum," *Biomacromol.* 3(4), 761-767.
- Picout, D. R., Ross-Murphy, S. B., Errington, N., and Harding, S. E. (2003). "Pressure cell assisted solubilization of xyloglucans: Tamarind seed polysaccharide and detarium gum," *Biomacromol.* 4(3), 799-807.
- Picout, D. R., and Ross-Murphy, S. B. (2007). "On the Mark-Houwink parameters for galactomannans," *Carbohydr. Polym.* 70(2), 145-148.
- Pitkänen, L., Virkki, L., Tenkanen, M., and Tuomainen, P. (2009). "Comprehensive multidetector HPSEC study on solution properties of cereal arabinoxylans in aqueous and DMSO solutions," *Biomacromol.* 10(7), 1962-1969.
- Pääkkö, M., Ankerfors, M., Kosonen, H., Nykänen, A., Ahola, S., Österberg, M., Ruokolainen, J., Laine, J., Larsson, P. T., Ikkala, O., and Lindström, T. (2007). "Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels," *Biomacromol.* 8(6), 1934-1941.
- Ren, J.-L., Peng, F., Sun, R.-C., and Kennedy, J. F. (2009). "Influence of hemicellulosic derivatives on the sulfate kraft pulp strength," *Carbohydr. Polym.* 75(2), 338-342.
- Robinson, G., Ross-Murphy, S. B., and Morris, E. B. (1982). "Viscosity-molecular weight relationship, intrinsic chain flexibility and dynamic solution properties of guar galactomannan," *Carbohydrate Res.* 107(1), 17-32.
- Rodahl, M., Höök, F., Krozer, A., Brzezinski, P., and Kasemo, B. (1995). "Quartz crystal microbalance setup for frequency and Q-factor measurements in gaseous and liquid environments," *Rev. Sci. Instrum.* 66(7), 3924-3930.
- Rojas, O. J., and Neuman, R. D. (1999). "Adsorption of polysaccharide wet-end additives in papermaking systems," *Colloids Surf. A* 155(2-3), 419-432.
- Saito, T., Nishiyama, Y., Putaux, J.-L., Vignon, M., and Isogai, A. (2006). "Homogeneous suspensions of individualized microfibrils from TEMPO-catalyzed oxidation of native cellulose," *Biomacromol.* 7(6), 1687-1691.
- Sauerbrey, G. (1959). "The use of quartz oscillators for weighing thin layers and for microweighing," *Zeitschrift für Physik* 155, 206-222.

- Schmidt, U., Hild, S., Ibach, W., and Hollricher, O. (2005). "Characterization of thin polymer films on the nanometer scale with confocal Raman AFM," *Macromol. Symp.* 230(1), 133-143.
- Siró, I., and Plackett, D. (2010). "Microfibrillated cellulose and new nanocomposite materials: A review," *Cellulose* 17(3), 459-494.
- Sjöström, E. (1993). "Wood polysaccharides," In *Wood Chemistry: Fundamentals and applications*. Academic Press, San Diego (CA), 49-67.
- Stelzer, G. I., and Klug, E. D. (1980). "Carboxymethylcellulose," In *Handbook of Water-soluble Gums and Resins*, R. L. Davidson, (ed.) McGraw-Hill, New York, 4.1-4.28.
- Syverud, K., and Stenius, P. (2009). "Strength and barrier properties of MFC films," *Cellulose* 16(1), 75-85.
- Swanson, J. W. (1950). "The effects of natural beater additives on papermaking fibers," *Tappi* 33(9), 451-462.
- Swerin, A., Ödberg, L., and Lindström, T. (1990). "Deswelling of hardwood kraft pulp fibers by cationic polymers: The effect on wet pressing and sheet properties," *Nordic Pulp Pap. Res. J.* 5(4), 188-196.
- Taipale, T., Österberg, M., Nykänen, A., Ruokolainen, J., and Laine, J. (2010). "Effect of microfibrillated cellulose and fines on the drainage of kraft pulp suspension and paper strength," *Cellulose* 17(5), 1005-1020.
- Tammelin, T., Paananen, A., and Österberg, M. (2009). "Hemicelluloses at interfaces: Some aspects of the interactions," In *The Nanoscience and Technology of Renewable Materials*, L. A. Lucia and O. J. Rojas (eds.), Wiley-Blackwell Publishing Ltd, Chichester, 149-172.
- Teeri, T. T., Brumer III, H., Daniel, G., and Gatenholm, P. (2007). "Biomimetic engineering of cellulose-based materials," *Trends Biotechnol.* 25(7), 299-306.
- Turbak, A. F., Snyder, F. W., and Sandberg, K. R. (1983). "Microfibrillated cellulose, a new cellulose product: Properties, uses, and commercial potential," *J. Appl. Polym. Sci., Appl. Polym. Symp.* 37, 815-827.
- Westbye, P., Svanberg, C., and Gatenholm, P. (2006). "The effect of molecular composition of xylan extracted from birch on its assembly onto bleached softwood kraft pulp," *Holzforschung* 60(2), 143-148.
- Whitney, S. E. C., Brigham, J. E., Darke, A. H., Grant Reid, J. S., and Gidley, M. J. (1998). "Structural aspects of the interaction of mannan-based polysaccharides with bacterial cellulose," *Carbohydr. Res.* 307(3-4), 299-309.
- Voinova, M. V., Rodahl, M., Jonson, M., and Kasemo, B. (1999). "Viscoelastic acoustic response of layered polymer films at fluid-solid interfaces: Continuum mechanics approach," *Phys. Scr.* 59(5), 391-396.
- Zheng, G., Cui, X., and Yang, C. (2010). "Surface-wave-enabled darkfield aperture for background suppression during weak signal detection," *Proc. Natl. Acad. Sci. U.S.A.* 107(20), 9043-9048.
- Zhou, Q., Rutland, M. W., Teeri, T. T., and Brumer, H. (2007). "Xyloglucan in cellulose modification," *Cellulose* 14(6), 625-641.

Article submitted: May 12, 2011; Peer review completed: July 17, 2011; Revised version received and accepted: Sept. 2, 2011; Published: Sept. 5, 2011.