



# Multilayers of cellulose derivatives and chitosan on nanofibrillated cellulose



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## ABSTRACT

The aim of this work was to study the effect of solution conditions and polysaccharide structure on their Layer-by-Layer (LbL) deposition on nanofibrillated cellulose (NFC). Multilayer build-up of cellulose derivatives and chitosan on NFC model surfaces was studied using Quartz Crystal Microbalance with Dissipation (QCM-D) and Colloidal Probe Microscopy (CPM). The type of cationic polysaccharide was found to significantly affect the multilayer build-up and surface interactions. Cationic cellulose derivative quaternized hydroxyethyl cellulose ethoxylate (HECE) formed highly water-swollen layers with carboxymethyl cellulose (CMC), and the build-up was markedly influenced by both the ionic strength and pH. The ionic strength did not significantly influence the multilayer build-up of chitosan–CMC system, and adsorbed chitosan layers decreased the viscoelasticity of the system. Based on the results, it was also confirmed that electrostatic interaction is not the only driving force in case of the build-up of polysaccharide multilayers on nanofibrillated cellulose.

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## 1. Introduction

Nanostructured polyelectrolyte multilayers (PEMs), formed by “Layer-by-Layer” (LbL) deposition, have been of scientific interest since the discovery by Decher (Decher, Hong, & Schmitt, 1992) in the early 1990s. Due to the possibility to give materials desired properties by LbL adsorption of oppositely charged polyelectrolytes the interest in LbL materials virtually exploded in the 1990s and early 2000s. It has been shown that the potential of multilayers range from biosensors and small electronic devices to membranes and microcontainers for molecular encapsulation (Haberska & Ruzgas, 2009; Ho et al., 2000; Nolte & Fery, 2006; Zhao, Xu, & Chen, 2006). The possibility to modify also cellulosic surfaces using the LbL technique has been investigated from the fundamental level (Ahola, Myllytie, Österberg, Teerinen, & Laine, 2008; Aulin, Johansson, Wågberg, & Lindström, 2010; Eronen, Laine, Ruokolainen, & Österberg, 2012; Olszewska, Kontturi, Laine, & Österberg, 2013; Salmi, Nypelö, Österberg, &

Laine, 2009; Wågberg et al., 2008) to applied paper strength studies (Eriksson, Torgnysdotter, & Wågberg, 2006; Wågberg, Forsberg, Johansson, & Juntti, 2002). A general conclusion is that polyelectrolyte multilayers can enhance the fiber–fiber bond strength and are able to increase the tensile strength of paper. Therefore, continued studies considering multilayers on nanofibrillated cellulose (NFC) are highly motivated. Quartz Crystal Microbalance with Dissipation (QCM-D) and Colloidal Probe Microscopy (CPM) have been extensively used in studying the LbL build-up of different kinds of polyelectrolyte systems (Aulin, Varga, Claesson, Wågberg, & Lindström, 2008; Salmi et al., 2009). Traditionally, the cationic polyelectrolyte components in LbL deposition have been petroleum-based polyelectrolytes, i.e. polyacrylamide and polyethyleneimine (Eriksson et al., 2006; Salmi et al., 2009; Wågberg et al., 2008). However, there is a potential in using totally bio-based systems in LbL surface modification of cellulosic materials. Recently, interesting properties for layered structures involving polysaccharides, e.g. nanocellulose and xyloglucan, on cellulose have been reported (Jean, Heux, Dubreuil, Chambat, & Cousin, 2009; Olszewska et al., 2013). In addition, Haberska and Ruzgas (2009) studied the LbL deposition of chitosan and carboxymethyl cellulose (CMC) on a gold surface, and also the layer-by-layer assemblies of chitosan and other non-cellulosic polysaccharides has been studied (Crouzier, Boudou, & Picart, 2010; Kamburova, Milkova, Petkanchin, & Radeva, 2008; Lundin, Blomberg, & Tilton, 2010). However, the knowledge of polysaccharide-based polyelectrolyte

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multilayers on cellulose surfaces and especially nanofibrillated cellulose is very penurious.

The use of bio-based polysaccharides in cellulose surface modification has the advantage of irreversible adsorption to cellulosic surfaces due to the structural similarities (Eronen, Junka, Laine, & Österberg, 2011). This could be an advantage in, e.g. papermaking, where the solution conditions often are difficult to control. CMC, which is an anionic cellulose derivative used in industry for decades, is an interesting polyelectrolyte to use in multilayers, since it improves significantly paper strength properties (Blomstedt & Vuorinen, 2007; Laine, Lindström, Glad-Nordmark, & Risinger, 2002). Quaternized hydroxyethylcellulose ethoxylate (HECE) and chitosan were chosen and compared as the cationic polysaccharides for these experiments. HECE is a cationic cellulose derivative, chemically prepared and thus semi-green. Chitosan is a natural polysaccharide prepared from chitin by deacetylation, consisting of a glucosamine backbone, and is cationic at low pH. The interaction between chitosan and cellulosic materials has been studied to some extent (Holmberg et al., 1997; Liu & Berglund, 2012; Nordgren, Eronen, Österberg, Laine, & Rutland, 2009). An interesting property is that chitosan is known to increase wet-web strength of paper (Laleg & Pikulik, 1991). Since the adsorption of polysaccharides is not only electrostatically driven here is definitely a need to clarify the effect of polysaccharide structure vs. solution conditions on the layer properties. Herein, all the LbL polysaccharide deposition was investigated with CMC as the anionic polyelectrolyte, but the degree of substitution and molecular weight were varied. All in all, five bio based polyelectrolyte samples were therefore used in the experiments. A systematic comparison of different cellulose- or bio-based polysaccharide systems at different ionic strength and pH conditions was carried out in this work.

## 2. Materials and methods

### 2.1. Preparation of nanofibrillated cellulose and cellulosic model surfaces

The nanofibrillated cellulose (NFC) used for the cellulosic model surfaces was prepared by The Finnish Centre for Nanocellulosic Technologies, Espoo. The never-dried bleached kraft birch pulp originating from a Finnish pulp mill was washed into sodium form according to Swerin, Ödberg, and Lindström (1990) prior to disintegration of the fiber structure in a high pressure fluidizer (Microfluidics, M-Y). The disintegration was performed by 20 passes through the fluidizer. The final consistency of the NFC gel was ~2%. The cellulose model surfaces were prepared by spin coating a dilute nanofibrillar cellulose suspension on SiO<sub>2</sub>-crystals (QX303, Q-Sense AB, Västra Frölunda, Sweden) according to a method first suggested by Ahola, Salmi, Johansson, Laine, and Österberg (2008) and later modified by Eronen et al. (2011). Prior to cellulose deposition the SiO<sub>2</sub>-crystals were cleaned with 10% NaOH, ultrapure water and UV/ozonator (Bioforce Nanosciences, Ames, IA, USA), and an anchoring layer of polyethyleneimine (PEI, Polysciences Inc.) was adsorbed on the surface. A suspension of diluted, ultrasonicated and ultracentrifuged (10,400 rpm, 45 min) nanofibrillated cellulose dispersion was spin coated (3000 rpm, 1 min) on the crystal, carefully dried with nitrogen gas and finally heat-treated in an oven at 80 °C for 10 min. Spin coated model surfaces were conditioned overnight to exclude the effects of swelling during the measurements.

### 2.2. Chemicals and solutions

All chemicals used in the experiments were of analytical grade. Hydroxyethylcellulose ethoxylate, quaternized (Sigma–Aldrich),

**Table 1**

Properties of three different carboxymethyl cellulose grades according to the manufacturer (Sigma–Aldrich).

Sample name	Average $M_w$ (g mol <sup>-1</sup> )	DS
CMC1	90,000	0.7
CMC2	250,000	0.7
CMC3	250,000	1.2

chitosan (low molecular weight (230,000 g mol<sup>-1</sup>), Sigma–Aldrich) and three different carboxymethyl cellulose grades (Sigma–Aldrich) were all used as received. Ultrapure MilliQ-water (Millipore Synergy UV unit; Millipore S.A.S. Molsheim, France) was used for dilutions. The polymer solutions were prepared with a constant concentration of 0.1 g dm<sup>-3</sup>. Buffer solutions at pH 4.5, 7 and 8.5 were prepared from known amounts of salts. Acetic acid was used for dissolving chitosan. Fig. 1 presents the molecular structures of the polysaccharides.

### 2.3. Properties of the polysaccharides and nanofibrillated cellulose surfaces

Carboxymethyl cellulose with two different average molecular weights ( $M_w$ ) and two different degrees of substitution (DS) were used in the experiments. Some properties of the CMC samples are presented in Table 1.

The degree of deacetylation of chitosan was over 75% and charge density of HECE was 1.2 meq g<sup>-1</sup>. AFM height images of the dry NFC surfaces are shown in Fig. 2.

The properties of NFC model films are described in detail elsewhere (Ahola, Salmi, et al., 2008). Most importantly, the structure of cellulose is prevailed during the mechanical disintegration process of NFC manufacturing (Aulin et al., 2009). Hence the film consists of cellulose I and amorphous regions, and has a 63 µeq g<sup>-1</sup> charge density (Eronen et al., 2011).

### 2.4. Quartz Crystal Microbalance with Dissipation (QCM-D)

The QCM-D measurements were performed using an E-4 instrument (Q-Sense AB, Västra Frölunda, Sweden) with controlled flow. The flow rate used in these experiments was 0.1 ml min<sup>-1</sup>. The adsorption of one layer was continued until the adsorption rate leveled off and a plateau value was reached, which took approximately 30 min for the cationic polysaccharides and 40 min for CMC. Between each layer, the system was rinsed with buffer for 15 min. The QCM-D measures change in frequency and dissipation simultaneously at the fundamental resonance frequency, 5 MHz, and its overtones 15, 25, 35, 45, 55, and 75 MHz. The principle of the QCM-D is to utilize the piezoelectric properties of quartz. A quartz crystal is placed between a pair of electrodes. If an alternating voltage is applied, the crystal starts to oscillate and the resonance frequency ( $f$ ) of the oscillating crystal depends on the total oscillating mass, including water and other adsorbed molecules. When the dissipation values are low, the frequency decreases linearly with the mass according to the Sauerbrey Eq. (1) (Sauerbrey, 1959):

$$\Delta m = -\frac{C \cdot \Delta f}{n} \quad (1)$$

where  $\Delta m$  represents the change in mass (mg m<sup>-2</sup>),  $C$  is the mass sensitivity (0.177 mg Hz<sup>-1</sup> m<sup>-2</sup> for a 5 MHz quartz crystal),  $n$  is the overtone number and  $\Delta f$  is the change in frequency (Hz). In the case of polyelectrolyte adsorption on cellulosic materials, the adsorbed film is far from rigid and the Sauerbrey relation is no longer strictly valid. The swelling of viscoelastic cellulose surfaces, and soft polymers, will not fully couple to the oscillation of the crystal, and in these systems the Sauerbrey relation underestimates the mass

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