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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.

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_2-crystals (QSX303, 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_2-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, ultrasonificated 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), chitosan (low molecular weight (230,000 g mol^{-1}), 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^{-3}. 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.

Table 1
Properties of three different carboxymethyl cellulose grades according to the manufacturer (Sigma–Aldrich).

Sample name	Average M_w (g mol^{-1})	DS
CMC1	90,000	0.7
CMC2	250,000	0.7
CMC3	250,000	1.2

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^{-1}. 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^{-1} 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^{-1}. 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 Δm represents the change in mass (mg m^{-2}), C is the mass sensitivity (0.177 mg Hz^{-1} m^{-2} for a 5 MHz quartz crystal), n is the overtone number and Δf 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

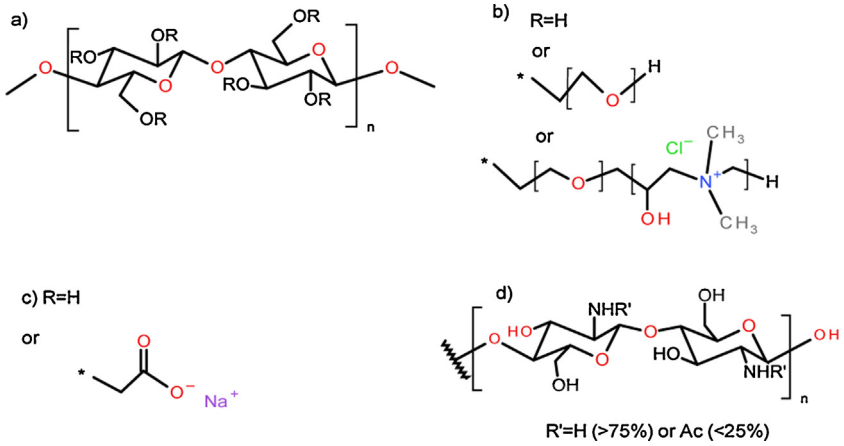

Fig. 1. Molecular structures of (a) cellulose backbone, (b and c) substituents in HECE and CMC, respectively, and (d) structure of chitosan.

adsorbed at the surface. In other words, the soft films dampen the oscillations of the crystal, seen as dissipation of energy. The definition of D in Eq. (2) is dependent on the dissipated (lost) energy per oscillation cycle, E_{lost} (J) and E_{stored} (J) is the energy stored in the oscillator.

$$D = \frac{E_{lost}}{2\pi E_{stored}} \quad (2)$$

Another model that takes into account the viscoelasticity is Johannsmann' model for viscoelastic thin films (Johannsmann, Mathauer, Wegner, & Knoll, 1992):

$$\hat{m}^* \approx m_0 \left(1 + \hat{J}(f)\frac{f^2 \rho d^2}{3}\right) \quad (3)$$

where $\hat{J}(f)$ is the shear compliance, f is the resonance frequency in liquid, d is the thickness of the film and ρ is the density of the fluid. The true sensed mass (m_0) can be obtained from the intercept of the equivalent mass (m^*) and the square of the resonance frequency in liquid. Both the cellulose films used as well as adsorbing polysaccharides bind water and hence the changes in Δf and ΔD are due to both bound water and adsorbed polysaccharide. Actually up to 90% of the observed mass for polysaccharide adsorption on cellulosic surfaces is due to coupled water (Eronen et al., 2011).

2.5. Colloidal Probe Microscopy (CPM)

The surface forces were studied with the colloidal probe technique (Ducker, Senden, & Pashley, 1991) and an atomic force microscope (NanoScope IIIa multimode, Digital Instruments Inc., Santa Barbara, USA). Precipitated spheres of cellulose II, regenerated via the viscose process (Kanebo Co., Japan), were used as colloidal probes. These spheres where 5–35% crystalline and slightly negatively charged (Carambassis & Rutland, 1999). The radius of the attached spheres was 18–30 μm, as determined in situ in electrolyte solution by using optical imaging. The lower surface was a spin-coated NFC film on a silica wafer. The spring constant of the cantilever was determined by the thermal noise method (Hutter & Bechhloefer, 1993) prior to gluing the cellulose sphere on the tip. The surface force, which is determined from the deflection of the cantilever, was calculated using Hooke's law and normalized using the radius of the cellulose sphere.

3. Results and discussion

3.1. Effect of pH and electrolyte concentration on the multilayer build-up of polysaccharides on NFC

The multilayer build-up of six different systems in controlled solution conditions was monitored by QCM-D. Three different pHs (4.5, 7 and 8.5) and three ionic strengths (0.00056 mol L^{-1}, 0.01 mol L^{-1} and 0.02 mol L^{-1} [Na^+]) were used. Prior to polysaccharide addition, the pre-swollen NFC films were rinsed with buffer solution in order to get a horizontal baseline. The multilayer build-up was initiated by adsorbing a cationic polysaccharide on the slightly anionic NFC surface. The system was rinsed with buffer after the adsorption had leveled off to remove any unattached

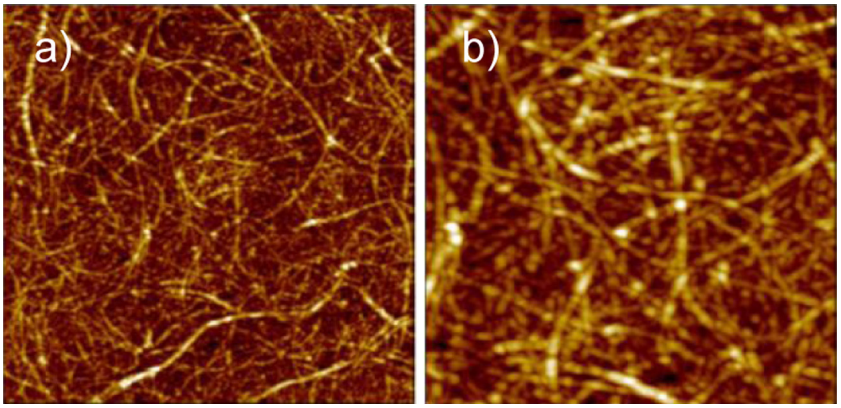

Fig. 2. An AFM height image of the NFC model surface. The image size is (a) 25 μm^2 and (b) 4 μm^2. The root mean square roughness (RMS) values were 3.9 nm and 3.6 nm for (a) and (b), respectively. The z-scales were 33 nm for (a) and 28 nm for (b).

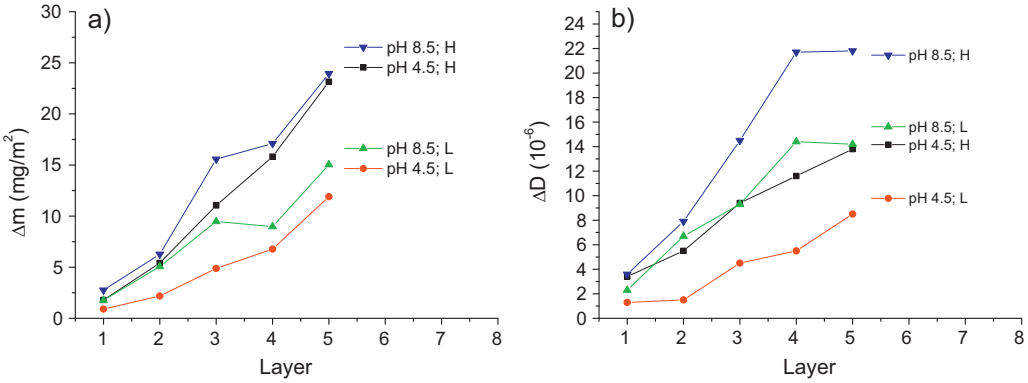

Fig. 3. (a) The adsorbed mass calculated using the Johannsmann equation (Johannsmann et al., 1992) and (b) the change in dissipation for multilayer build-up of HECE and CMC2 on cellulose in two different pHs (■ and ● at pH 4.5 and ▲ and ▼ at pH 8.5) and ionic strengths (● and ▲ at 0.00056 mol L^{-1} (L) and ■ and ▼ at 0.02 mol L^{-1} (H)). The system was rinsed with buffer between each layer. The solid lines are only guide for the eye.

material, and an anionic polysaccharide was added. By repeating this procedure several times, the LbL formation could be studied for each system. All experiments were at least duplicated in order to ensure reproducible results. The pH, ionic strength and the properties of the polyelectrolytes were all varied systematically to analyze their effect on layer properties and interactions between components. The major technique used to study this was QCM-D, and the results from these measurements are presented in Figs. 3–5 and show all the trends seen in this study. Fig. 3 presents the calculated (Eq. (3)) adsorbed amount (a) and change in dissipation (b) for five polyelectrolyte layers on a NFC surface.

Both the adsorbed mass per unit surface area and dissipation clearly increased during the multilayer build-up in case of the HECE–CMC system (Fig. 3). At higher ionic strength (H) the adsorbed amount is higher at both pHs which can be seen from Fig. 3a. This is common in case of polyelectrolyte multilayers and the reason is the coiled conformation of the polyelectrolytes in solution at higher electrolyte concentration resulting in more loops and tails when the polyelectrolyte is adsorbed on a surface (Antipov, Sukhorukov, & Mahwald, 2003; Dubas & Schlenoff, 1999). Also from the dissipation measurements, cf. Fig. 3b, changes with more layers are obvious. i.e. the system is clearly more dissipative at higher ionic strength and at higher pH, which indicates more swollen layers.

The carboxyl groups in both CMC and NFC are fully dissociated at pH 8.5 in solution (Hoogendam et al., 1998), which results in more swelling compared to pH 4.5 conditions due to the Donnan effect (Donnan, 1924) seen as higher energy dissipation of the system (Fig. 3). In addition, at higher pH the amount of adsorbed HECE slightly increases, because of the more significant electrostatic interaction between cationic HECE and the anionic NFC surface. All in all, pH had a marked effect on the layer build-up. An increase in adsorbed mass is detected when the fifth layer (HECE) is adsorbed but the dissipation energy is not changed. In addition, the fourth layer (CMC) does not increase the adsorbed mass but increases the dissipation energy. The reason for this is that CMC, having a higher charge at pH 8.5, and thus ionic complexation occurs between CMC and the underlying HECE, releasing counterions and thus removing bound water observed as a decrease in layer viscosity, as has been observed previously for adsorption of cationic polymers on cellulose (Ahola, Salmi, et al., 2008; Wang et al., 2011). At lower pH, where the carboxyl groups of CMC are less dissociated, non-ionic interactions dominate the layer build-up. As a consequence densification of the layer is not observed. In order to investigate how the type of cationic polysaccharide affects the layer build-up, the experiments were also conducted with chitosan as the cationic polyelectrolyte. CMC2 was adsorbed LbL with both chitosan and HECE at both 0.02 mol L^{-1} and 0.00056 mol L^{-1} electrolyte concentration. Fig. 4 shows the adsorbed mass and dissipation response for the CMC2–chitosan and CMC2–HECE system. This comparison between chitosan and HECE were performed at pH 4.5 because chitosan is only soluble and cationic at acidic conditions.

From a comparison of the systems in Fig. 4, it is clear that the chitosan–CMC system behaves differently from the HECE–CMC system. Chitosan is suggested to be fully charged at pH 4.5 (Claesson & Ninham, 1992), whereas the carboxyl groups in CMC and the cellulosic surface are not fully charged at these conditions. Based on the

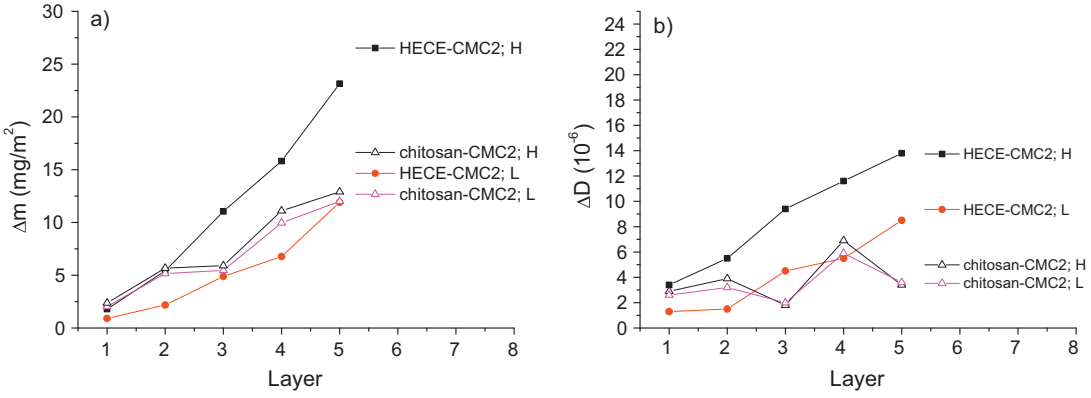

Fig. 4. (a) The adsorbed mass calculated using the Johannsmann equation (Johannsmann et al., 1992) and (b) the change in dissipation for multilayer build-up of chitosan–CMC2 and HECE–CMC2 in 0.02 mol L^{-1} (Δ for chitosan and ■ for HECE) and 0.00056 mol L^{-1} (Δ for chitosan and ● for HECE) ionic strength and pH 4.5 (NaAc/HAC-buffer) on a NFC model surface. The system was rinsed with buffer between each layer. The solid lines are only guide for the eye.

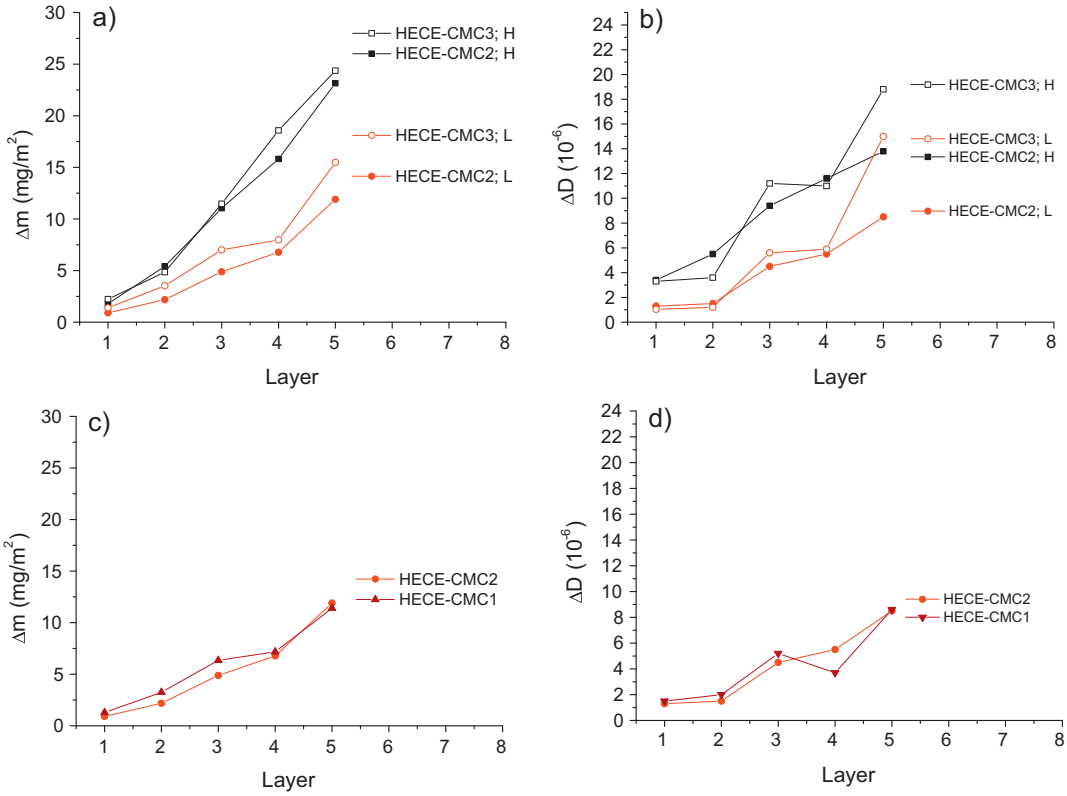

Fig. 5. (a) The effect of CMC DS on the multilayer build-up with HECE at pH 4.5, and at higher (H) and lower (L) ionic strength, (b) the effect of the CMC DS on the dissipation energy at pH 4.5, and at higher (H) and lower (L) ionic strength, (c) the effect of the M_w of CMC on the multilayer build-up at pH 4.5 at $I = 0.00056$ mol L^{-1} and (d) the effect of the M_w of CMC on the dissipation energy at pH 4.5 at $I = 0.00056$ mol L^{-1}. The solid lines are only guide for the eye.

QCM-D results it seems that chitosan is able to densify the system and release some bound water seen as decreased dissipation energy (Fig. 4). This kind of densification behavior has also been seen for some other cationic polyelectrolytes such as polydiallyldimethylammonium chloride (Enarsson & Wågberg, 2009) on cellulose, and it has been proven by parallel surface plasmon resonance (SPR) and QCM-D measurements that the adsorbed mass is increasing when polydiallyldimethylammonium chloride is added (Ahola, Myllytie, et al., 2008; Ahola, Salmi, et al., 2008) although this cannot be seen in the QCM-D data. However, the most pronounced difference between the HECE–CMC system and the chitosan–CMC system is that the ionic strength did not affect the amount of adsorption in the chitosan–CMC2 system, while the opposite was true for the HECE–CMC2 system. This could be explained by the rigid structure of chitosan (Rinaudo, 2006).

Finally, the effect of the *DS* and M_w of CMC on the multilayer build-up of polysaccharides on cellulosic surfaces was studied with HECE as the cationic polysaccharide (Fig. 5).

Neither the charge density nor the molecular weight of CMC has any substantial effect on the multilayer build-up for the studied cellulose derivative systems. The most influential parameters are pH and ionic strength. Nevertheless, the dissipation energy (viscoelasticity of the film) is affected by both molecular weight, cf. the fourth layer in Fig. 5d, and charge density, cf. Fig. 5b of the CMC.

The degree of dissociation (α) for the CMC samples at this pH is 0.7 for CMC2 (DS 0.7) and 0.6 for CMC3 (DS 1.2) (Hoogendam et al., 1998). These degree of dissociation values correspond to a charge density of 2.6 mmol g^{-1} and 3.5 mmol g^{-1}, respectively. The only major difference seen using the QCM-D was the viscoelastic behavior of the system, cf. Fig. 5b. Suggesting that non-electrostatic interactions due to similar backbone structure play a role in the layer build-up but effective charge of the polymers affects the amount of bound water. Higher charge leads to ionic complexation and removal of water. All in all, it is evident that the effect of pH and ionic strength is more pronounced than the effect of CMC charge density on the layer build-up with HECE on the NFC model surfaces. The molecular weight of CMC, which was varied from 90,000 to 250,000 g mol^{-1}, did not cause major difference in the build-up of multilayers (Fig. 5). This has been previously noticed for synthetic polyelectrolytes on cellulose (Saarinen, Österberg, & Laine, 2009). In order to make statistical analysis of the data and to evaluate the optimal conditions for the layer build-up of CMC–HECE on cellulose, the experiments were also conducted at pH 7 and intermediate ionic strength (0.01 mol L^{-1} [Na+]) (supporting information). Based on the statistical analysis, the layer build-up of the cellulose derivative system on NFC surface reaches maximum at pH 7 and at high (0.02 mol L^{-1}) ionic strength.

3.2. Forces between multilayer-coated cellulosic surfaces

The selection of systems for Colloidal Probe Microscopy (CPM) measurements was based on the QCM-D results. Since the two cationic polysaccharides had an opposite effect on the viscoelastic properties of the NFC film it was decided to study the influence of these multilayer systems on the surface interaction between cellulosic surfaces. The measurements were done at pH 4.5 and $I = 0.02$ mol L^{-1}. All in all, four polyelectrolyte layers were formed. For reference the forces between the bare cellulosic surfaces, the NFC film and cellulose sphere, were measured. Then a 0.1 g L^{-1} solution of cationic polyelectrolyte was added, the system was let to stabilize, the excess polyelectrolyte was rinsed off with buffer and the forces between the surfaces were measured. After this the anionic polyelectrolyte was added, the excess removed, and so on. The results from these CPM measurements are presented in Fig. 6. Fig. 6a shows the HECE–CMC2 system and Fig. 6b shows the chitosan–CMC2 system at pH 4.5 and 0.02 mol L^{-1} ionic strength.

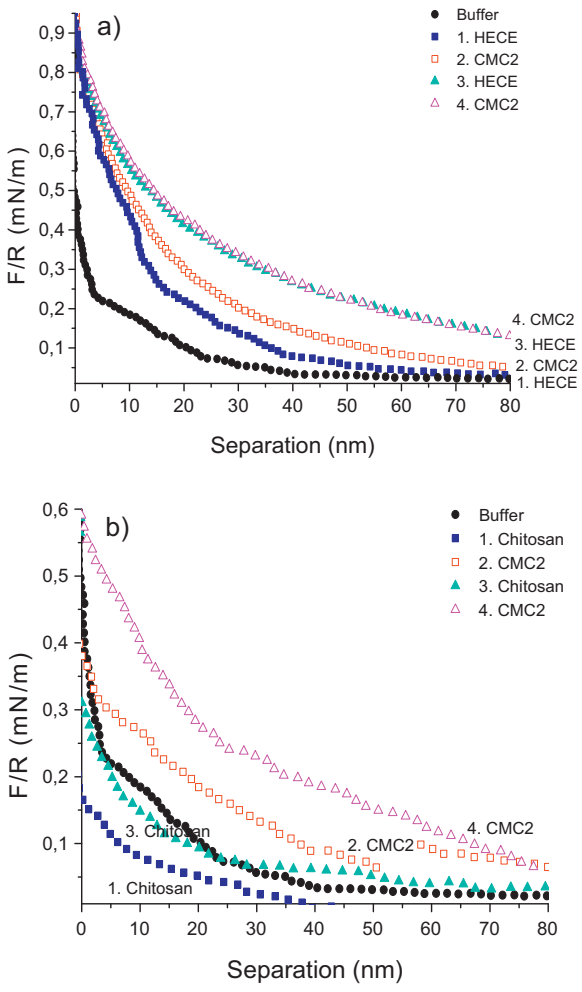

Fig. 6. CPM results showing the interaction forces of cellulose, HECE or chitosan coated and CMC2 (*DS* 0.7; M_w = 250,000 g mol^{-1}) coated surfaces at pH 4.5 (NaAc/HAC-buffer) and I = 0.02 mol L^{-1}. The forces between two cellulosic surfaces are marked with black spheres (●). The system was rinsed with buffer solution after each layer and the forces were measured after the rinsing (1. ■, 2. □, 3. ▲ and 4. △).

The forces between two cellulose surfaces in the buffer solution are monotonically repulsive (Fig. 6). The observed force between the reference cellulosic surfaces was repulsive due to the electrostatic repulsion between slightly negatively charged cellulosic surfaces, and due to steric effect between surfaces (Holmberg et al., 1997). The following HECE and CMC layers were able to substantially increase the range of repulsion between the surfaces. Steric repulsion is most probably the reason for this increase, as it cannot be explained by electrostatic repulsion alone. All in all, the HECE–CMC2 system was able to increase the range of repulsion between cellulosic surfaces at least in the case of three polysaccharide layers. This means that polysaccharide multilayers were formed on NFC using this system as could also be noticed from the QCM-D results in Fig. 4. Comparing the chitosan–CMC2 with this system, the major difference is that the range of repulsion clearly decreased as a result of the adsorbed chitosan layer. This could indicate that chitosan adsorbs flat on the both surfaces and is able to densify the underlying layers decreasing the steric repulsion between the surfaces. Based on the QCM-D data, the dissipation energy (related to the viscoelasticity) of the chitosan–CMC2 system was decreased as a result of adsorbed layers of chitosan which also supports that chitosan adsorbs flat (resulting in less steric repulsion) on the underlying layer and possibly even removes bound water from the system. However, the CMC layers adsorbing on top

Table 2
The pull-off forces of different layers for the chitosan–CMC2 system and HECE–CMC2 system. The force measurements were conducted at pH 4.5 (NaAc/HAC-buffer) and I = 0.02 mol L^{-1}. The reference pull-off force (REF) is the pull-off force between the cellulose sphere and the NFC surface.

Chitosan–CMC system	Pull-off force (mN/m)	HECE–CMC system	Pull-off force (mN/m)
Cellulose–NFC	−0.08 ± 0.02	Cellulose–NFC	−0.10 ± 0.05
1st chitosan layer	−0.32 ± 0.11	1st HECE layer	−0.06 ± 0.03
2nd CMC layer	−0.08 ± 0.01	2nd CMC layer	−0.04 ± 0.03
3rd chitosan layer	−0.11 ± 0.04	3rd HECE layer	−0.03 ± 0.01
4th CMC layer	−0.07 ± 0.01	4th CMC layer	−0.07 ± 0.02

of chitosan markedly increased the range of repulsion even to the same level as in the case of the cellulose derivative system. This implies that the interaction forces between the multilayer-coated cellulosic surfaces are dominated by the outermost polysaccharide layer which has also been noticed in case of polyelectrolyte multilayer systems on cellulose (Cranston, Gray, & Rutland, 2010; Wågberg et al., 2002). All in all, the effect of thin, molecular layers of these polysaccharides has a marked effect on the surface interaction and viscoelasticity of the NFC film.

3.3. Pull-off forces of multilayer-coated cellulosic surfaces

For further comparison of the two systems, the maximum pull-off forces of the CPM measurements were compared. The pull-off forces are presented in Table 2.

The pull-off forces, shown in Table 2, between two cellulosic surfaces are as previously observed very low (Ahola, Salmi, et al., 2008). Neither of the two cellulose derivatives could increase the adhesion between the surfaces. However, the adsorption of a chitosan layer clearly increased the pull-off force between the cellulosic surfaces. The increase in pull-off force for the chitosan-coated cellulosic surfaces is most probably due to the ability of chitosan to adsorb on a cellulosic substrate and decrease steric repulsion between the surfaces. This enables the surfaces to come close enough to let the attractive van der Waals forces dominate. However, the second chitosan layer has almost the same pull-off force as the CMC layer, which could mean that the second chitosan layer and the CMC layer are already partly overlapping.

4. Conclusions

The effect of solution conditions on the multilayer build-up of two different cationic polysaccharides and CMC on nanofibrillated cellulose was investigated. The cationic cellulose derivative HECE formed a highly water-swollen multilayer structure with CMC and the layer build-up could be altered by changing the pH and ionic strength. An increase in ionic strength resulted in a higher amount of adsorption because of changes in HECE and CMC conformation resulting in more loops and tails. It was noticed that CMC was able to neutralize the charge of the HECE layer only at alkaline conditions because of the higher degree of dissociation of the carboxylic acid groups of CMC. The chitosan–CMC system in contrast was much more rigid to changes in ionic strength. In fact, the ionic strength did not markedly affect the layer build-up, and based on the QCM-D results chitosan was able to remove bound water from the system while adsorbing.

Steric repulsion dominated the interactions between the cellulosic surfaces. However, the range of repulsion could be decreased by multilayers of chitosan and CMC. In addition, chitosan also increased the adhesion between the cellulosic surfaces in aqueous media. It is clear from the data that the layer build-up and interaction of these polysaccharide systems on nanofibrillated cellulose is not only electrostatically driven. This understanding of the effect

solution conditions as well as build-up of polysaccharide layers on NFC is highly valuable in terms of surface modification of NFC with bio-based polysaccharide systems in aqueous media.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.02.061.

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