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THE INFLUENCE OF PH ON THE ADSORPTION AND INTERACTION OF CHITOSAN WITH CELLULOSE

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The pH dependent adsorption behavior of chitosan onto a cellulose model surface was studied by quartz crystal microbalance with dissipation (QCM-D). The molecular level interactions between adsorbed chitosan layers were studied by atom force microscopy (AFM) colloidal probe force measurements in the liquid phase. Adsorption of chitosan increased with pH below the solubility limit of the polymer. The adsorption behavior could not be accounted for solely on the basis of electrostatic interactions; thus a specific interaction between the polymers existed. Swelling and viscoelastic properties of the adsorbed chitosan layer were strongly influenced by pH. At high pH, the layer deswelled and became more elastic due to insolubility of the chitosan. The colloidal probe force measurements showed a rise of electrosteric repulsion after adsorption of chitosan at pH 5. Above the solubility limit of the chitosan, at pH 7, the pull-off force and its range clearly increased compared to lower pH values, indicating that the wet adhesion between chitosan-coated cellulose surfaces increased. The presented results are discussed in relation to the ability of chitosan to improve the initial wet strength of paper.

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INTRODUCTION

Chitosan is a natural linear aminopolysaccharide (poly-β-(1-4) D-glucosamine) derived from chitin by deacetylation. Chitin (poly-β-(1-4) N-acetyl D-glucosamine) is the next most abundant biopolymer after cellulose, hemicellulose, and lignin, existing as a structural polymer in shells of crustaceans (and fungi), and thus providing an ample renewable source of chitosan. Generally, chitosan itself is not a well defined polymer but rather a class of polymers, chitin derivatives, with a degree of deacetylation over 70% and wide range of molecular weights (Rinaudo 2006; Rosca et al. 2005), therefore exhibiting also variation in material properties, such as solubility. Being renewable, biodegradable, biocompatible, and biofunctional as well as having bacterio- and fungistatic properties, chitosan has been widely studied and commercialized in the food and medical industries (Dutta et al. 2009; Gomez d'Ayala et al. 2008; No et al. 2007; Sashiwa and Aiba 2004) and has shown promises in regenerative medicine and gene delivery (Muzzarelli 2009).

Versatility of chitosan has been demonstrated in the textile (Hudson 1998; Strnad et al. 2007) and paper industries. In papermaking, chitosan has been found to be effective as a dry and wet strength agent (Allan et al. 1978; Laleg and Pikulik 1991;

Lertsutthiwong et al. 2002) as well as in coating (Kjellgren et al. 2006; Kuusipalo et al. 2005), sizing (Ashori et al. 2007), and retention (Li et al. 2004). The structural similarity of chitosan to cellulose (poly-β-(1-4) D-glucose) along with electrostatic attraction induces strong interaction between the polymers. These interactions and the possibility of chemical reactions between reactive groups have been suggested as explanation for the peculiar behavior of chitosan as an additive in papermaking (Li et al. 2004; Laleg and Pikulik 1992).

Cellulosic fibers are naturally anionic in charge, and cationic polymers are readily adsorbed onto fibers by electrostatic attraction. However, several neutral or even anionic polysaccharides, including xyloglucan and carboxymethyl cellulose (CMC), are irreversibly adsorbed onto cellulosic fibers as well. This has been attributed to specific structural interaction of the polymers with cellulose (Mishima et al. 1998). Because cellulosic fibers are chemically and physically heterogeneous, model surfaces of cellulose are excellent for studying adsorption phenomena and molecular interactions between materials (Ahola et al. 2008; Kontturi et al. 2006).

In this work the pH-dependent adsorption and adhesion behavior of chitosan on a cellulose model surface is studied by QCM-D and AFM, respectively. The objective is to clarify the specific interaction between the polymers and to reveal the function of chitosan from a papermaking point of view. A particular goal is to shed light on why chitosan has shown clear pH dependent behavior when applied as a paper strength additive (Allan et al. 1978; Laleg and Pikulik 1991; Myllytie et al. 2009). In addition, we perceive this type of approach as being useful for biomedical and materials sciences, in view of recent very sophisticated applications of chitosan and cellulose (Klemm et al. 2001; Muzzarelli 2009).

EXPERIMENTAL

Materials
Cellulose model surfaces

The cellulose model surfaces were obtained by depositing trimethylsilyl cellulose (TMSC) onto polystyrene-coated gold crystals by using the horizontal Langmuir–Schaefer (LS) dipping technique as described by Tammelin et al. (2006). The cellulose-coated crystals were allowed to swell in the appropriate electrolyte solution over night before the QCM-D experiments.

Water soluble polymers

Medium molecular weight chitosan (relative molecular mass of 400,000, Prod. no. 22742) was acquired from Fluka BioChemika (Buchs, Switzerland). The degree of deacetylation of the chitosan was approximately 85%. The polymer was purified by recrystallization as follows: Chitosan was dissolved in 1% acetic acid solution at a concentration of 10 g/L. The pH of the solution was adjusted to 10 using 1 M NaOH to precipitate the polymer. The solution was mixed at pH 10 for 4 hours. Then the precipitated polymer was centrifuged and washed with deionized water repeatedly until the conductivity of the excess solution was low enough for dialysis. The polymer was

transferred into a Spectra/Por (Spectrum Laboratories Inc., USA) dialysis tube (#1, MWCO of 6-8kDa) and was dialyzed against deionized water for 48 hours. After dialysis the polymer was filtrated, freeze-dried, and stored in a desiccator.

Polymer and buffer solutions

A stock solution of 0.1% glacial acetic acid in 0.5mM $NaHCO_3$ was prepared for the experiments. The purified chitosan was dissolved in the stock solution at a concentration of 100 ppm. The chitosan solutions were slowly mixed overnight to ensure full dissolution. Prior to the adsorption experiments the pH of the chitosan solutions was adjusted to a desired level with NaOH or HCl. The buffer solutions of different pH were prepared from the same stock solution by adjusting the pH to a desired level with NaOH or HCl.

Methods

Quartz crystal microbalance with dissipation (QCM-D)

Adsorption of chitosan on LS-cellulose model surfaces was studied with a QCM-D E4 instrument from Q-Sense AB (Sweden). The QCM-D technique enables simultaneous measurement of the adsorbed amount of polymer on a sensor surface and the viscoelastic properties of the adsorbed polymer layer. The sensor is a quartz crystal, in this case coated with a thin cellulose layer, which oscillates at a certain resonant frequency (f_o). The frequency decreases on adsorption as the coupled mass on the surface increases. Provided that the adsorbed layer is uniform and rigid, the change in frequency (Δf) is proportional to the adsorbed mass, according to the Sauerbrey equation (Höök et al. 1998; Sauerbrey 1959):

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

where *n* is a number of the overtone of the sensed frequency and C is a sensitivity constant for the device. The dissipation of energy during one cycle of oscillation provides information on the viscoelastic properties of the adsorbed layer. If the adsorbed layer is ideally elastic, no energy dissipation occurs by viscous losses and the dissipation is not affected. However, in most cases the adsorbed layer is not rigid but viscous, and energy dissipation is observed. The dissipation factor (*D*) is compared to the dissipation of the sensor surface in solution prior to adsorption (D_o). For a rigid adsorbed layer the change in dissipation (ΔD) is negligible, but for loose and viscous adsorbed layers ΔD increases with adsorbed amount. The interpretation of the QCM-D-data is described in detail elsewhere (Höök et al. 1998; Rodahl et al. 1995; Sauerbrey 1959).

Atom force microscopy (AFM) imaging

Structure and morphology of the LS-cellulose model surfaces (after the QCM-D adsorption experiments) were imaged using an atomic force microscope, AFM (Nanoscope IIIa multimode scanning probe microscope, Digital Instruments Inc., Santa Barbara, USA). The AFM images were scanned in tapping mode in air using silicon cantilevers (NSC15/AlBS) delivered by MicroMasch, Estonia. The drive frequency of the

cantilever was 310-350 kHz. The sizes of the images were 1 μm^2 or 25 μm^2, and the images were recorded on at least three different areas of the samples. No image processing except flattening was made. The imaging was performed at 30 to 40% relative humidity at 25°C.

AFM colloidal probe force measurements

The AFM colloidal probe technique (Butt 1991; Ducker et al. 1991) was used to study the surface forces between a cellulose sphere and the LS-cellulose model surface in the absence and presence of adsorbed chitosan at different pH. Adhesive properties of the system were assessed from the pull-off force on the separation of the surfaces.

The colloidal probes used were cellulose spheres (Kanebo Co., Japan) fabricated via the viscose process. The cellulose spheres carried a slight negative charge, and the crystallinity (cellulose II polymorph) of the spheres was 5-35% (Carambassis and Rutland 1999). The radius of the spheres was 15-30 μm, determined in situ in solution using an optical microscope and a digital camera.

A cellulose sphere was glued to the tipless end of an AFM cantilever with reported spring constants of 0.06 and 0.12 N/m (Veeco Instruments, USA). The spring constants of the cantilevers were determined by the thermal noise method, and the result was controlled by the reference spring method (Hutter and Bechhöfer 1993; Torii et al. 1996; Tortonese and Kirk 1997). Prior to the measurements, the surfaces were allowed to equilibrate in the respective electrolyte solution for several hours. For the sake of clarity, only one representative curve per system is presented. For the analysis of the pull-off force, at least 60 force curves were recorded to gain reliable statistics.

The raw data (cantilever deflection vs. piezo movement) were converted into force curves (force vs. separation) using a Scanning Probe Image Processor (SPIP) software (Image Metrology A/S, Denmark) and were further processed in Origin (OriginLab Co., USA) (Salmi 2009). A clear constant compliance region could not be reached for the all systems due to compressibility of the layers. This may lead to erroneous results if it is not taken into account (Rutland et al. 2004). In these cases, raw data (cantilever deflection vs. piezo movement) was transferred to force curves by using the sensitivity value obtained for cellulose-cellulose contact. The compressibility (load/indentation) of such surfaces was analyzed from the force curves. To facilitate a comparison to other studies, the forces in this study were normalized to the radius of the cellulose sphere used as the upper surface (Derjaguin 1934). The approach velocity of the surfaces was kept fairly low to minimize the hydrodynamic effect on the surface forces.

RESULTS AND DISCUSSION

### Adsorption of Chitosan onto Cellulose Studied by QCM-D

The adsorption of chitosan on the LS-cellulose model surfaces at different pH was studied using QCM-D. The measurements were done in the immersed state after swelling the surfaces in a starting buffer over night. Figure 1 shows QCM-D frequency and dissipation curves for adsorption of chitosan at pH 5 and subsequent steps of pH increments by different buffer solutions. In detail, first the chitosan (100 ppm) was

adsorbed at pH 5 on the model surface (0-30 min), then the unadsorbed polymer was rinsed off by a buffer of the same pH (10 min rinsing). Thereafter, buffer solutions of increasing pH were applied to the surface (>40 min). Changes in frequency (Δf) and dissipation (ΔD) were followed throughout the measurement. Figure 2 presents the QCM-D frequency and dissipation curves for chitosan adsorption at pH 6.5. Chitosan solution (100 ppm), adjusted to pH 6.5, was injected after 60 min measuring time (60-90 min). Then unadsorbed polymer was rinsed off with a buffer of pH 6.5 (10 min rinsing) followed by sequential pH increments (see Fig. 2). As a comparison, Fig. 3 shows changes in frequency and dissipation for plain a LS-cellulose model surface with increasing pH (same sequence of buffer solutions).
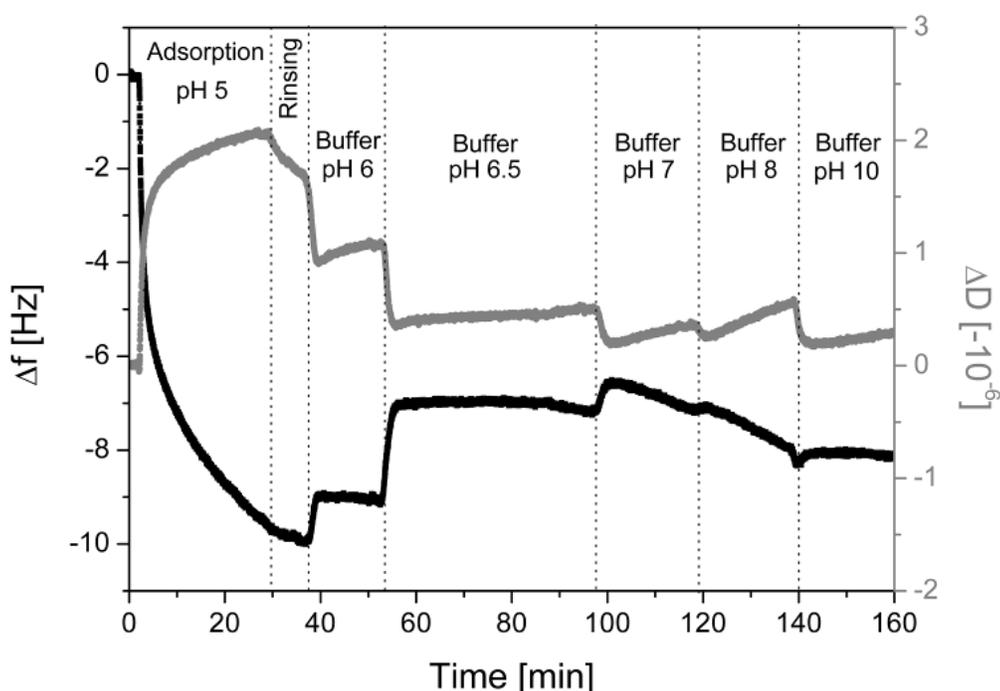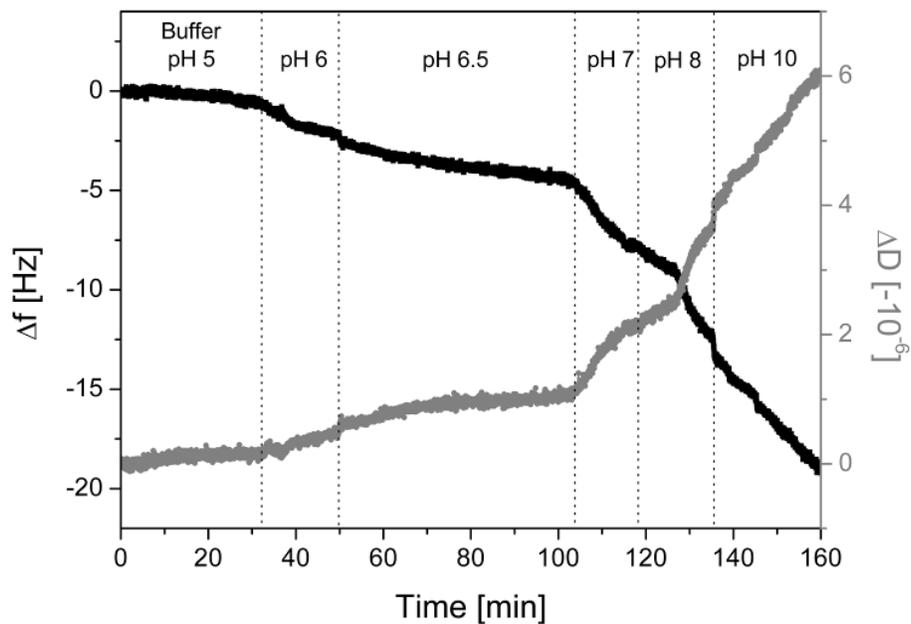

Fig. 1. QCM-D frequency and dissipation curves for chitosan adsorbed at pH 5 and the influence of gradual increase of pH on the adsorbed layer

As seen in Fig. 1, adsorption of chitosan at pH 5 induced a clear decrease in the frequency and increase in the dissipation. Rinsing the adsorbed chitosan layer by a buffer solution at pH 5 did not affect the frequency but it decreased the dissipation. This indicated that chitosan was irreversibly adsorbed on the surface (at pH 5) and that the rinsing compacted the adsorbed layer structure somewhat. The adsorption of chitosan did not reach equilibrium during the 30 min adsorption time, as seen from the shape of frequency curve (Fig. 1). However, the adsorption was considered to be sufficient for the evaluation of the effects of subsequent changes in pH by different buffer solutions.
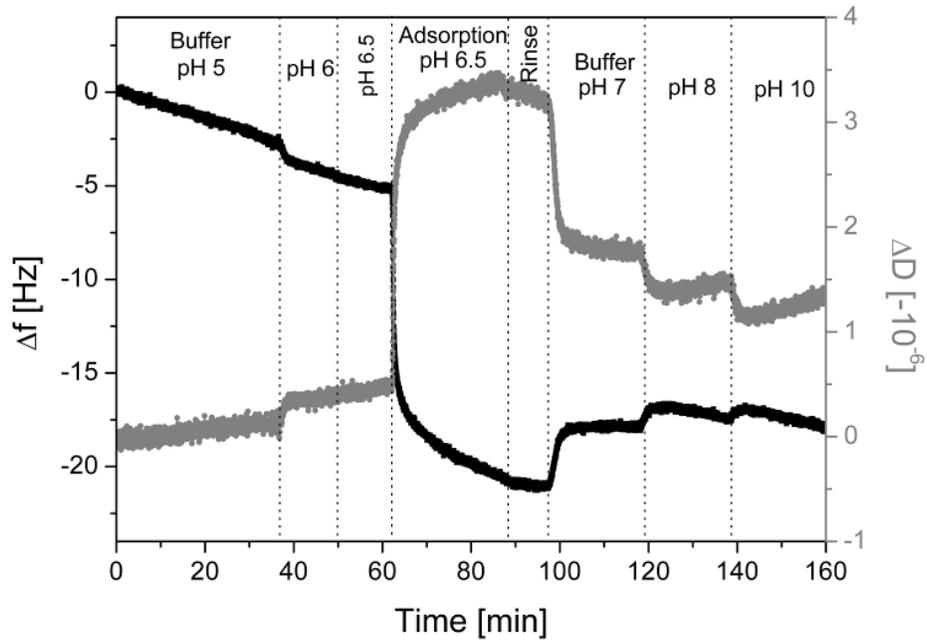
Fig. 2. QCM-D frequency and dissipation curves for chitosan adsorbed at pH 6.5 and the influence of gradual increase of pH on the adsorbed layer

Fig. 3. QCM-D frequency and dissipation curves for plain LS-cellulose model surface with gradual increase of pH

Since chitosan carries primary amine functional groups and therefore its charge and solubility are pH-dependent, changes in pH should have a clear influence on the properties of the adsorbed chitosan layer. Indeed, this was evidenced by the QCM-D experiments. When increasing the pH by changing the buffer from pH 5 to pH 6 (Fig. 1, time ~40 min), a sharp increase in frequency and a decrease in dissipation were observed. The same occurred when the buffer was changed from pH 6 to pH 6.5 (Fig. 1, time ~55 min). The observed behavior reflected the changes in the conformation and in the amount of associated water of the adsorbed chitosan layer. Although the observed changes could have been interpreted as desorption of the polymer, this was not the case, because the changes with pH were found to be reversible to a large extent (QCM-D data not presented). However, the possibility of exiguous desorption of chitosan from the surface by the pH changes could not be completely excluded. It seemed that the gradual increase of pH from pH 5 to pH 6.5 removed mainly water from the polymer layer (increase in frequency) and made the layer more rigid (reduced dissipation). Most likely, the chitosan was adsorbed in an extended conformation due to constrained linear molecular structure and higher charge at pH 5. The QCM-D results are in accordance with observed chain extension of chitosan at low pH and collapsed conformation at higher pH (Nordgren et al. 2009).

The solubility limit of the chitosan used was around pH 6.8, and above that the polymer precipitated from solution. At pH above the solubility limit (buffers from pH 7 to pH 10), the dissipation was quite small, but the frequency change (Δf) was still appreciable, about 6 Hz (Fig. 1, time >100 min). By comparing Figs. 1 and 3 it was evident that the adsorbed chitosan layer kept the cellulose model surface from excessive swelling by increasing pH, which was observed for the plain LS-cellulose model surface (Fig. 3). This could be due to the fact that at above pH 7, where the strong swelling of LS-cellulose surface began (Fig. 3), the adsorbed chitosan layer was already in an insoluble state, forming a kind of cover layer that protected/restrained the cellulose from swelling.

As expected, the adsorption behavior of chitosan at pH 6.5 (Fig. 2) was very similar to the adsorption at pH 5 (Fig. 1). More chitosan was adsorbed onto the surface because the negative charge of the cellulose was increased, and the positive charge of the chitosan was decreased at higher pH. The adsorbed amounts of chitosan at pH 5 and pH 6.5 after rinsing, calculated from Eq. 1, were 0.6 mg/m^2 and 1.0 mg/m^2, respectively. Because QCM-D senses the total increase of mass, the calculated values included the water associated with the chitosan molecules. Thus, the dry adsorbed amount of chitosan was not determined. However, at the pH where chitosan became insoluble, the decrease in the adsorbed amount can be mostly associated with dehydration of the polymer layer. The adsorbed amounts for chitosan originally deposited at pH 5 and pH 6.5, estimated at the pH where chitosan became insoluble (pH 8), were approximately 0.4 mg/m^2 and 0.7 mg/m^2, respectively. The difference in the calculated adsorbed amounts between soluble and insoluble state of chitosan mainly reflects the exclusion of water during the phase change, because desorption was not expected to occur (to a large extent).

The decrease in dissipation at above pH 6.5 suggested a clear transition in the viscoelastic properties of the adsorbed chitosan layer (Figs. 1 and 2). This should also have an influence on the interaction forces between an adsorbed chitosan layer and

cellulose. Also, the function of chitosan as wet web strength additive is achieved only when the polymer is adsorbed at high pH (Laleg and Pikulik 1991). In this condition, where the polymer is in an insoluble state, we have considered that the adsorption of chitosan is more like a precipitation of colloidal chitosan on fiber surfaces than adsorption in a strict sense, and that the viscoelastic properties of the fiber surfaces influence the attained wet web strength improvement (Myllytie et al. 2009). The recent observation on the origin of wet web strength (van de Ven 2008) combined with AFM colloidal probe techniques on model systems (Nordgren et al. 2009; Notley et al. 2009) can provide more insight to the mechanisms explaining how frictional and adhesive factors can affect the wet web strength of paper. On that account, the AFM colloidal probe technique was applied in order to complement the QCM-D experiments in this study.

It has been suggested that chitosan adsorption involves an interaction of non-electrostatic nature (Nordgren et al. 2009). The specific, non-electrostatic interaction between cellulose and chitosan was evidenced by a QCM-D experiment. QCM-D frequency and dissipation curves for chitosan adsorption at pH 2 are shown in Fig. 4.
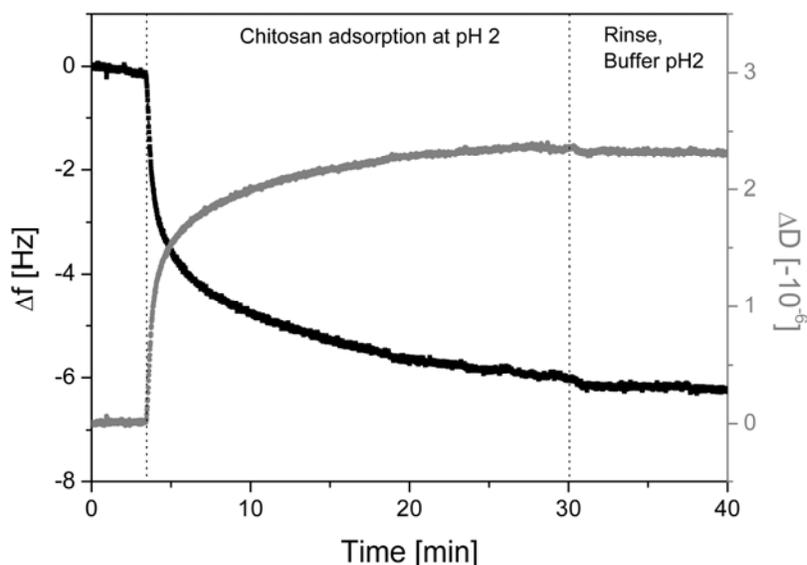
Fig. 4. QCM-D frequency and dissipation curves for chitosan adsorbed at pH 2 onto LS-cellulose model surface

At pH 2 where LS-cellulose surface was virtually uncharged and chitosan was fully protonated; i.e. in the absence of electrostatic attractive interaction, the polymer still adsorbed onto the cellulose surface (Fig. 4). Hence, our results also verified the presence of a specific non-electrostatic interaction between chitosan and cellulose. If only electrostatic interaction had been present, a cationic polymer would not have been adsorbed onto cellulose surface under conditions where the surface was uncharged. The adsorption mechanisms of chitosan, along with other linear 1-4-β-glucans, have been related to the structural similarity of the molecules (Mishima et al. 1998). In the case of

xyloglucan, a neutral polysaccharide that has a polymer backbone similar to cellulose, the adsorption mechanism onto cellulose has been related to hydrogen bonding between the xyloglucan and cellulose (Mishima et al. 1998; Zhou et al. 2007). Plausibly, similar mechanisms could influence the adsorption of chitosan on cellulose in the absence of electrostatic attraction. In addition, chemical reaction between chitosan and cellulose has been proposed to occur (Hosokawa et al. 1991; Laleg and Pikulik 1992), which may partly influence the adsorption.

AFM Colloidal Probe Force Measurements

To study in more detail the interfacial behavior of the adsorbed chitosan layer on cellulose surfaces, AFM colloidal probe experiments were done under similar conditions as the QCM-D measurements. The surface forces between a cellulose sphere and the LS-cellulose model surface on approach were measured at different pH using AFM, as presented in Fig. 5.

The surface force between cellulose surfaces was repulsive, and short-range prior to addition of chitosan (reference in Fig. 5). When chitosan was added (100ppm solution, pH 5), it adsorbed on the cellulose, resulting in a substantial increase in the magnitude and range of repulsion (Fig. 5, filled squares). On approach of the surfaces, the chitosan layers overlap and increased repulsion was observed due to the electrostatic and steric effects. When the pH was increased from pH 5 to pH 6.5, the range of repulsion between chitosan coated cellulose surfaces decreased clearly (Fig. 5, filled circles). This indicated a collapse of the chitosan layer, supporting the observation from the QCM-D experiments that the chitosan layer excluded water as the solubility of the chitosan decreased with pH.
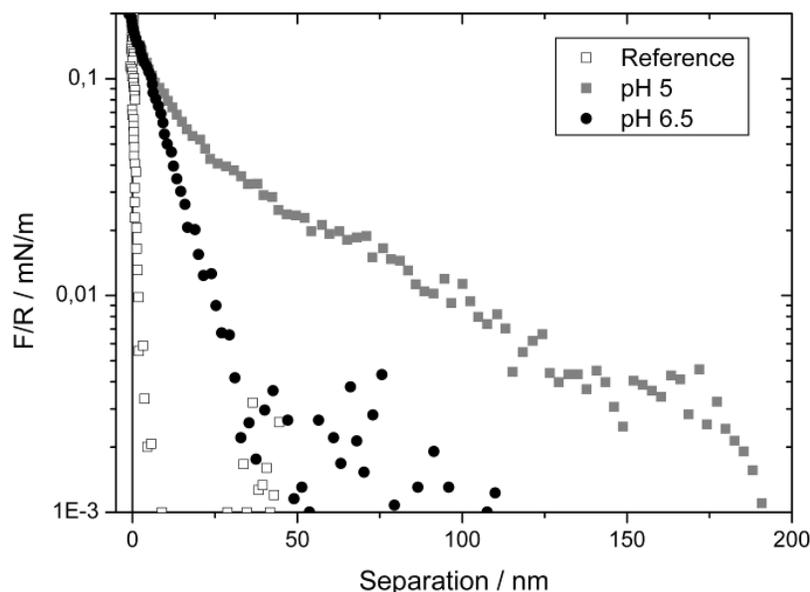
Fig. 5. Surface forces between approaching cellulose surfaces at different pH. Reference curve (open squares) is the surface force between cellulose surfaces (at pH 5) prior to chitosan addition. Filled symbols are for surface forces after chitosan adsorption.

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When the pH was increased further, the compressibility of the surface decreased (pH 7, pH 8, and pH 10) in such a way as to mask the effect of the chitosan-induced forces (Rutland et al. 2004; Salmi et al. 2007). The separation between the surfaces became indeterminate, and hence these forces are not shown in Fig. 5. Decrease in the compressibility indicates softening of the interface as pH increases. The effect of the surface starts to dominate over the effect of chitosan. Similar observations on the effect of pH on the swelling of a cellulose surface have been made by Ahola et al. (2008).

The adhesive properties of the interface were assessed from the pull-off force, i.e. from the force recorded upon retraction of the colloidal probe from the surface. The obtained values and ranges for the pull-off forces at different pH and applied loads are collected into Table 1.

Table 1. Maximum Magnitude and Range of the Pull-off Force between Chitosan Coated Cellulose Surfaces as a Function of pH and Load

Sample	Load [nN]	Pull-off force [mN/m]	Relative std. dev. [%]	Range [nm]
Reference*	6.2	13	136	25-40
pH 5	10.4	24	54	100-400
pH 6.5	11.3	25	87	50-400
pH 7	10.6	61	61	200-850
pH 8	10.4	46	28	200-850
pH 8	13.5	73	33	200-850
pH 8	17.9	93	13	**
pH 10	9.0	20	52	150-450

* reference is the pull-off force between pure cellulose surfaces prior to chitosan adsorption
** the shape of the pull-off force curve changed

The pull-off force between plain cellulose surfaces was low and short-range. The pull-off force as well as the range of the force increased slightly in the presence of adsorbed chitosan at pH 5 and pH 6.5, where chitosan was still water-soluble. However, when the pH was increased to pH 7 and pH 8, the pull-off force increased significantly (see Table 1). In addition, the range of the pull-off force was very long at these pH values. Doubtless, the change in the solubility of chitosan from soluble (at pH 6.5) into insoluble (at pH 7) affected the pull-off adhesion. At pH above the solubility limit of the polymer the chitosan layers favor the situation where water is excluded from between the layers, keeping the surfaces together and preventing the intrusion of water to contact with chitosan. On separation of the surfaces the chitosan molecules gradually detached from the other surface, which caused the saw-tooth pattern observed in the pull-off force curve (exemplified in Fig. 6). However, at pH 10, the observed pull-off force decreased to the same level as in pH 5 and 6.5. Probably, this was caused by gradual swelling of cellulose at the high pH. Furthermore, the effect of applied load on the pull-off force was evident; the pull-off force increased with load (Table 1, pH 8) as a result from more intimate contact between the surfaces. In addition, it was noticed that the shape of the force curves became more rounded as the applied load was doubled, indicating that the separation occurred rather by an elastic deformation of the interface than by gradual detachment of the molecules.
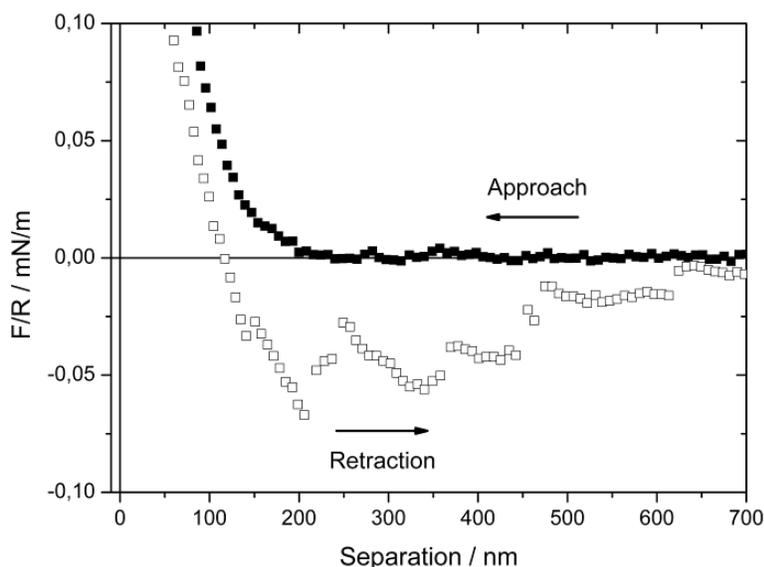
Fig. 6. Pull-off force (open symbols) between chitosan coated cellulose surfaces at pH 7. Filled symbols are for approaching data.

AFM Imaging

The morphology of the LS-cellulose model surfaces after adsorption experiments at QCM-D was studied by AFM. The surfaces were rinsed with deionized water before removal from measurement cells and drying. Figure 7a-c shows AFM images of reference LS-cellulose surface (a), and LS-cellulose surfaces after chitosan adsorption at pH 5 (b) and pH 6.5 (c).
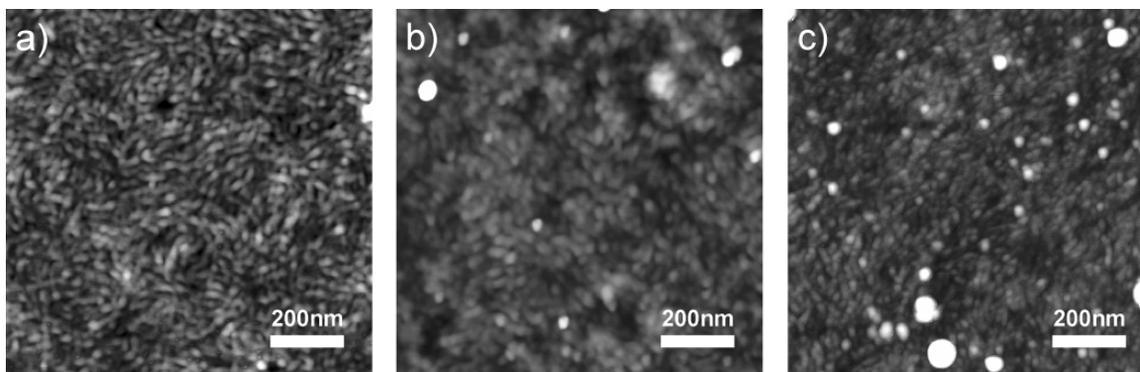
Fig. 7. AFM images of LS-cellulose surfaces after OCM-D adsorption experiments: a) reference, b) chitosan adsorption at pH 5, and c) chitosan adsorption at pH 6.5

The LS cellulose model surfaces seemed rather similar without chitosan (Fig. 7a) and after chitosan adsorption (Figs. 7b, c). The white round spots were present in all samples, and there was no marked difference in the overall occurrence of the features between the samples. Note that prior to removal from QCM-D cells the surfaces were kept in a buffer of pH 10, where the adsorbed chitosan was in an insoluble state, and

subsequent rinsing with deionized water, presumably, did not affect the state of adsorbed chitosan layer.

The indication from the QCM-D experiments that adsorbed chitosan layer protected the LS-cellulose model surface from excessive swelling, especially at pH above 7, may have several explanations. Charge neutralization of the carboxyl groups on cellulose by cationic chitosan could reduce the swelling power in the cellulose film with increasing pH. Indeed, the adsorption of cationic polyelectrolytes and the resultant charge neutralization of cellulose has been found to reduce the swelling of cellulose thin films (Enarsson and Wågberg 2009; Notley 2008). However, at high pH, where chitosan was deprotonized and virtually uncharged, the swelling of cellulose was still rather insignificant (Figs. 1-3). It is conceivable that a thin layer of adsorbed chitosan molecules have been formed over the cellulose film, which, in an insoluble state, could act as protective or constraining layer towards swelling. In addition, the specific non-electrostatic interaction between chitosan and cellulose, evidenced at pH 2, may partly influence the swelling behavior regardless of pH.

The observed swelling behavior may be related to the action of chitosan as a wet strength agent for paper (Allan et al. 1978), since decreased swelling of fibers has been proposed as a mechanism of permanent wet strength for polyamines, including poly(ethylene imine) and polyvinylamine (Linhart 2006). However, in this study the emphasis was on the pH-dependent adsorption behavior of chitosan, which have been related to wet web strength (and dry strength) of paper (Laleg and Pikulik 1991; Lertsutthiwong et al. 2002; Myllytie et al. 2009). The observed increase of wet adhesion between chitosan coated cellulose surfaces (by AFM colloidal probe technique) at pH above the solubility limit of chitosan can be related to the ability of chitosan to improve wet web strength of paper. Also, the finding that at pH 5 the adsorbed chitosan layer showed electrostatic and steric effects, i.e. behaved similarly as a common polyelectrolyte, combined with the fact that only dry strength of paper is affected at pH 5, gives support to this interpretation. The phase transition near the solubility limit of the polymer is crucial for the action of chitosan as strength additive. However, the experiments did not clarify whether the molecular level mechanism was chemical reactions and crosslinking (Hosokawa et al. 1991; Laleg and Pikulik 1992) or some other, such as increased tackiness of colloidal polymer particles near the solubility limit (Hubbe et al. 2006).

CONCLUSIONS

1. The adsorption of chitosan was influenced by electrostatic interaction, and the adsorbed amount was increased with pH below the solubility limit of the chitosan. However, also a specific, non-electrostatic, interaction was evidenced as chitosan was found to adsorb at low pH in the absence of electrostatic interactions.
2. Swelling and viscoelasticity of the adsorbed chitosan layer were affected by pH; at high pH the layer deswelled and became more elastic due to insolubility of the chitosan. In addition, the adsorbed chitosan layer protected the cellulose model film from pH induced swelling to some extent.

3. The AFM colloidal probe force measurements evidenced an electrosteric repulsive force on approach after adsorption of chitosan. Furthermore, the wet adhesion between chitosan coated cellulose surfaces clearly increased when the polymer changed from a soluble to an insoluble state. The ability of chitosan to improve initial wet strength of paper was partly accounted for the observed increase in wet adhesion.

ACKNOWLEDGMENTS

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