

EFFECT OF POLYMER ADSORPTION ON CELLULOSE NANOFIBRIL WATER BINDING CAPACITY AND AGGREGATION

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Polymer adsorption on cellulose nanofibrils and the effect on nanofibril water binding capacity were studied using cellulose nanofibril films together with quartz crystal microbalance with dissipation (QCM-D) and surface plasmon resonance (SPR). The experiments were performed in the immersed state, and special attention was paid to the effect of polymer properties on the water content and viscoelastic properties of the polymer/fibril layer. The dry mass of the adsorbed polymers was determined using SPR. The type of the adsorbed polymer strongly affected the water content and viscoelastic properties of the nanofibril film. The adsorption of a highly charged flocculating polymer, PDADMAC, caused dehydration of the film, which was also detected as nanofibril film stiffening. The adsorption of xyloglucan introduced a dispersing effect to the nanofibril film, which was detected as a loosening and softening of the nanofibril/polymer layer. A dispersing effect was also achieved with carboxymethyl cellulose (CMC), but CMC did not adsorb irreversibly on the nanofibril surfaces. In addition to the nanofibril film studies, the effect of polymer adsorption on cellulose nanofibril suspension aggregation was demonstrated using confocal laser scanning microscopy (CLSM). Xyloglucan was shown to open the nanofibril aggregate structures and act as a dispersing agent, whereas the other polymers studied did not have as significant an effect on aggregation.

Keywords: Adsorption; Polymer; Cellulose nanofibril; MFC; QCM-D; SPR; CLSM

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INTRODUCTION

Recent developments in cellulosic fibre disintegration have made it possible to produce nanofibrillar cellulose with nanometer scale width and high aspect ratio with reasonably low energy consumption (Pääkkö et al. 2007; Wågberg et al. 2008; Saito et al. 2007). These cellulose nanofibril materials differ greatly from cellulosic fibres. High aspect ratio and specific surface area combined with high strength and flexibility are characteristic for cellulose nanofibrils (Pääkkö et al. 2007). Functional hydroxyl groups in cellulose enable chemical modifications for further applications (Andresen and Stenius 2007; Andresen et al. 2007). In addition, biocompatibility, non-toxicity, and biodegradability of cellulose nanomaterials are important properties that can be utilized in biochemical and biomedical applications (Klemm et al. 2006). All of these features and the wide abundance of cellulose make cellulose nanofibrils a very promising material for nanotechnology (Berglund 2005; Klemm et al. 2006; Hubbe et al. 2008).

Probably the most characteristic feature of cellulose fibrils in aqueous suspensions is the formation of a highly water-containing entangled network, which behaves as a pseudoplastic gel (Herrick et al. 1983; Pääkkö et al. 2007). This is due to the large specific surface area and high aspect ratio of the nanofibrils and leads to extremely good strength properties of the network (Berglund 2005). The entangled, gel-like structure has been shown to affect many interfacial phenomena of nanofibrils in aqueous conditions such as swelling and surface interactions (Ahola et al. 2008a). The water retention capacity of nanofibrils is mainly an undesirable phenomenon, because it affects many potential applications, for example, the water removal efficiency in papermaking.

Utilization of cellulose nanofibrils in e.g. nanocomposites (Berglund 2005; Hubbe et al. 2008) or paper manufacture (Ahola et al. 2008b) often includes mixing nanofibrils with other materials, especially polymers. Strategies to mix nanofibrils and polymers in aqueous media include layer-by-layer deposition (Wågberg et al. 2008; Aulin et al. 2008; Ahola et al. 2008b) or complex formation (Ahola et al. 2008b). Although the interactions between polymers and cellulose have been widely studied and are well understood, these studies mainly concentrate on cellulosic fibres (Wågberg 2000) or regenerated cellulose model surfaces (Kontturi et al. 2006). The nature of the interaction between cellulose and polymers is strongly affected by the polymer properties, i.e. functional groups, charge properties, molecular weight, structure, etc. (Wågberg 2000). Furthermore, the type of interaction affects the properties of the nanofibril/polymer layer or complex. Due to the gel-like structure of nanofibril suspensions, the adsorption of polymers is expected to strongly affect the water content of the nanofibrils.

Cellulosic fibres are challenging subjects of study due to their small size, roughness, porosity, and heterogeneity. Therefore, to fundamentally study the interactions of cellulose with other matters, model systems are employed (Kontturi et al. 2006). In our recent paper we introduced a method to prepare cellulose I model films by spin-coating aqueous nanofibril suspensions onto silica substrates (Ahola et al. 2008a). The model films can be used for fundamental studies of e.g. swelling, surface forces, enzymatic hydrolysis, and adsorption, using sophisticated surface chemical methods. Although hydration of polyelectrolyte multilayers has been widely studied (Schönhoff et al. 2007), the hydration of cellulose nanofibril films upon polymer adsorption has not been previously studied, to the knowledge of authors. In this work, cellulose nanofibril model films were utilized to study polymer adsorption and hydration of the films using quartz crystal microbalance with dissipation (QCM-D) and surface plasmon resonance (SPR).

Three different types of polymers were used in this paper. The polymers were chosen because it was known from previous studies that they interact with cellulose by different mechanisms. A cationic polyelectrolyte, poly(diallyldimethylammonium chloride), PDADMAC, is a synthetic flocculating polyelectrolyte that adsorbs electrostatically on cellulose by forming dense layers (van de Ven 2000). Xyloglucan is a neutral polysaccharide that has been shown to have a dispersing effect on cellulose (Zhou et al. 2007). It has been assumed to interact with cellulose through hydrogen bonding (glucose-glucose attraction). Carboxymethyl cellulose (CMC) is an anionic cellulose derivative that also has a dispersing effect on cellulose (Beghello 1998; Yan et al. 2006); but irreversible adsorption (co-crystallization) of CMC on cellulose requires higher temperature and high electrolyte concentration (Laine et al. 2000). However, it has been shown

that even if the CMC adsorption is reversible, the dispersing effect still exists (Beghella 1998; Jokinen et al. 2006).

In this study the effect of adsorbed polymer and type of the polymer/nanofibril interaction on water content and viscoelastic properties of cellulose nanofibril model films were investigated using QCM-D. SPR measurements were performed to determine the dry adsorbed mass of the polymers to distinguish between the adsorption of polymer and binding of water. In addition, the effect of polymer adsorption on aggregation of cellulose nanofibril suspensions was demonstrated using confocal microscopy.

EXPERIMENTAL

Materials

Cellulose nanofibrils

Cellulose nanofibrils were disintegrated from delignified sulphite pulp at STFI-Packforsk, Stockholm, Sweden using a high-pressure fluidizer (Microfluidizer M-110EH, Microfluidics Corp., Newton, U.S.) according to the procedure described by Pääkkö et al. (2007). The procedure combines an enzymatic pre-treatment of delignified pulp fibres with mechanical shearing before the final disintegration of the fibres in the fluidizer.

Polymers

Polymers used were commercial samples of PDADMAC, xyloglucan, and CMC. PDADMAC (Salcare SC 30, Ciba Specialty Chemicals Ltd) was ultrafractionated with an Amicon ultrafiltration unit using a cutoff $M_w > 300\,000$ and the retained portion of the polymer was used. The charge density of PDADMAC was 6.13 meq/g. Tamarind xyloglucan (Megazyme, Ireland) and CMC (Finnfix WRM, CP Kelco, Finland) were used as delivered.

Model films

In order to prepare transparent, stable dispersions from the 2% nanofibril gels for model surface preparation, the gel was diluted with Milli-Q water to 1.67 g/L, stirred with an ultrasonic microtip for 10 min at 25% amplitude setting, and centrifuged at 10400 rpm (10000 G) to remove remaining fibril aggregates using an Optima L-90K ultracentrifuge from Beckman Coulter, USA. The clear supernatant was used for spin-coating. Substrates used for film preparation were either silica QCM-D crystals (Q-Sense AB, Västra Frölunda, Sweden) or gold SPR chip substrates (Biacore, GE Healthcare, Sweden). 3-aminopropyltrimethoxysilane (APTS) was used as an anchoring substance to improve the coverage of the fibrils on silica. Washed silica substrates were immersed into 1% v/v APTS/toluene solution for 40 min, rinsed with toluene, and dried in an oven at 60 °C for 30 min. In the case of the gold SPR surfaces, poly(vinylamine) (PVAm) (Lupamin 9095, BASF) was used as an anchoring substance. The substrates were immersed in 1 g/L aqueous PVAm solution for 10 min followed by rinsing with Milli-Q water and drying with nitrogen gas. The model films were prepared by spin-coating the fibril dispersion onto the substrates at 3000 rpm for 45 s. The spin-coated surfaces were rinsed with water, dried gently with nitrogen gas, and heat-treated in an oven at 80 °C for 10 min. The

differences between the substrates and anchoring substances, when comparing the QCM and the SPR surfaces, do not significantly change the nanofibril film properties and the surfaces are hence considered comparable. The preparation of the nanofibril films is presented in more detail by Ahola et al. (2008a).

Methods

Quartz Crystal Microbalance with Dissipation (QCM-D)

Polyelectrolyte adsorption on cellulose nanofibril model films was studied using the quartz crystal microbalance with dissipation (QCM-D) device from Q-sense, Västra Frölunda, Sweden. The experiments were performed using the Q-Sense E4-instrument, which is designed for controlled flow measurements. The QCM-D device measures simultaneous changes in frequency and dissipation (frictional losses due to viscoelastic properties of the adsorbed layer) at the fundamental resonance frequency, 5 MHz, and its overtones 15, 25, 35, 45, 55, and 75 MHz. Without adsorbate the crystal oscillates at a resonant frequency f_0 , and upon adsorption the resonance frequency decreases to f . For uniform, rigidly adsorbed films the change in frequency, Δf , is proportional to the adsorbed mass per unit surface, Δm , according to the Sauerbrey equation (Sauerbrey 1959; Höök et al. 1998):

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

where n is the overtone number and C is a device sensitivity constant. The relation is valid when the adsorbed mass is small compared to the mass of the crystal. The dissipation measurements in QCM-D give information about the visco-elastic properties of the adsorbed layer. When the voltage applied to the QCM-D is cut off, the amplitude decays due to frictional losses in the system. The decay rate depends on the visco-elastic properties of the adsorbed layer, the surrounding solution, and the crystal itself. A rigid adsorbed layer gives no change in the dissipation energy, but for loose, visco-elastic adsorbing layers there is an increase in dissipated energy as a function of adsorption. The interpretation of the QCM-D-data is described in more detail elsewhere (Rodahl et al. 1995; Sauerbrey 1959; Höök et al. 1998). Prior to measurements, the cellulose nanofibril films were allowed to swell in a 1 mM NaHCO₃/1 mM NaCl solution overnight.

Surface Plasmon Resonance (SPR)

SPR was used to study the adsorption of polymers on cellulose nanofibril model films. The adsorption of polymers was measured using a Biacore 1000 instrument with a continuous flow system (GE Healthcare, Sweden). The SPR technique is based on the phenomenon of total internal reflection of light (Schasfoort and Tudos 2008). Light travels through a glass plate that is coated with a noble metal. At the glass/metal interface some of the light is reflected and some of the light is “lost” into the metal layer. At a certain critical angle of the travelling light this loss is at its greatest, and the angle is called the surface plasmon resonance angle. This phenomenon is a consequence of the oscillation of mobile electrons (surface plasmons) at the surface of the metal layer.

Coupling of incident light to the surface plasmon wave results in loss of energy and a reduction in the intensity of the reflected light. The resonant frequency of the surface plasma wave depends on the refractive index of the medium on the other side of the metal layer. Molecules adsorbing on the surface change the solute and solvent concentration profiles and thus the refractive index within the evanescent wave range. The surface plasmon resonance angle is therefore altered to find a minimum in the reflected light intensity. The difference in the angle and the corresponding difference in the refractive index are represented as a change in resonance unit, ΔRU .

Dry mass of adsorbed polymers was calculated based on the SPR results and compared to QCM-D results, which give the combined amount of the adsorbed polymer and water that binds on the surface. The adsorbed mass is proportional to ΔRU according to

$$\Delta m_{SPR} = C_{SPR} \Delta RU, \quad (2)$$

where C_{SPR} is a proportionality constant, which is different for different adsorbed species. Since the SPR method is mostly used in protein research, the C_{SPR} constants are only given for proteins by the instrument suppliers. Hedin et al. (2007) have determined the constant for a cellulose derivative, ethyl(hydroxyethyl) cellulose using refractometer. This constant (0.080 ng/cm^2) was used in the present work to calculate the adsorbed mass of PDADMAC and xyloglucan. The constant may introduce a small error to the calculated adsorbed mass values because it has been determined for a different polymer. All SPR experiments were carried out at 25°C with a flow rate of $5 \mu\text{L/min}$. The running buffer was $1 \text{ mM NaHCO}_3/1 \text{ mM NaCl}$ containing 0.005% surfactant P20.

Confocal Laser Scanning Microscopy (CLSM)

The effect of polymers on the aggregation of nanofibril suspensions was studied by confocal microscopy. Confocal images were recorded with a Zeiss LSM 5 Duo laser-scanning confocal microscope (Carl Zeiss, Germany). An argon laser (488 nm) was selected as a light source, and the objective used was $10\times$ Plan-Apochromat (air immersion) objective. Polymer solutions ($0.25 \text{ m}\%$) of CMC, PDADMAC, and xyloglucan were prepared in Milli-Q water. 1 mL of cellulose nanofibril suspension (5 g/L), 0.3 mL of polymer solution, and 3.2 mL of Milli-Q water were mixed in a test tube. The suspensions were mixed by turning the test tubes periodically. Sampling for the microscopy was done after 45 min adsorption time. Prior to sampling, the suspensions were mixed to keep the volume fraction of particles in the samples constant. The cover slips were sealed to the microscope slides with nail polish in order to prevent detachment of the cover slip and drying of the samples during microscopy measurements. Average aggregate diameters were determined from the images as an average of 20 measurements, using image analysis.

RESULTS AND DISCUSSION

The adsorption of PDADMAC, xyloglucan, and CMC on cellulose nanofibril model surfaces was studied using QCM-D. The experiments were performed in the

immersed state, and the surfaces were stabilized in an electrolyte solution (1 mM NaCl in 1 mM NaHCO₃, pH 8) until a horizontal baseline was obtained. During this stabilization step the films swelled extensively, as has earlier been shown by Ahola et al. (2008a). The decrease in frequency upon swelling was about 80 Hz. Figure 1 shows QCM-D frequency curves for the situation in which the polymers were adsorbed on the water-swollen nanofibril model surfaces. At (t) = 10 min the polymer solution (0.1 g/L) was injected. The polymer injection caused different kinds of responses to the frequency profiles, depending on the polymer adsorbed. The adsorption of xyloglucan introduced a decrease in frequency, indicating that the polymer adsorbed onto the surface. The adsorption was rather slow, and it did not reach equilibrium within the time range studied (over 4 hours). Similar adsorption profiles for xyloglucan on regenerated cellulose surfaces have been obtained by Bodin et al. (2007). CMC addition caused a slow decrease in frequency, also indicating that the polymer slowly adsorbed on the surface. However, buffer rinsing of the surface after the polymer adsorption caused desorption of CMC, i.e. the frequency increased to the zero level, indicating that all the CMC desorbed from the surface. The injection of PDADMAC caused a sudden increase in frequency, indicating lightening of the surface. The adsorption was very fast, and it stabilized in a few minutes. Since it has been shown that PDADMAC has an electrostatic attraction to cellulose (e.g. Wågberg 2000), the mass decrease of the sensor surface was concluded to be due to removal of water from the swollen nanofibril film as PDADMAC adsorbed on the surface.

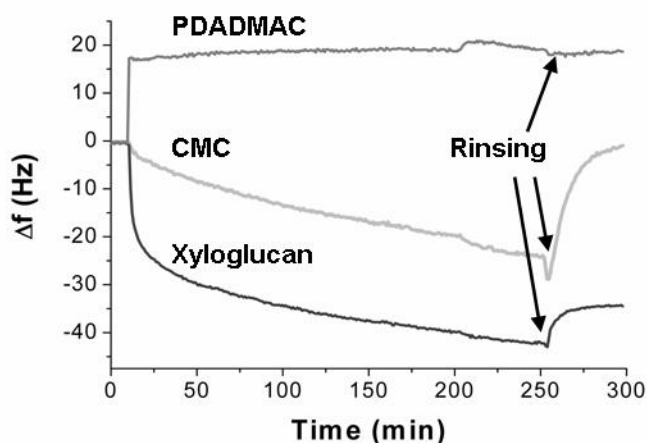


Fig. 1. QCM-D data (3rd overtone) showing change in resonant frequency as PDADMAC, CMC, and xyloglucan (0.1 g/L) adsorb on cellulose nanofibril film (1 mM NaCl in 1 mM NaHCO₃, pH 8). The starting level is a fully water-swollen film.

The corresponding QCM-D energy dissipation curves are presented in Fig. 2. Xyloglucan and CMC adsorption caused an increase in energy dissipation, indicating loosening of the nanofibril film upon adsorption. The increase was more pronounced for the CMC adsorption. However, after rinsing with buffer, CMC desorbed, causing a sudden decrease in the energy dissipation back to the zero level. QCM-D detects not only the dry mass of adsorbed polymer but also the mass of coupled water in the adsorbed layer. The loosening of the nanofibril film (increase in dissipation) upon xyloglucan and CMC adsorption indicates that more water binds to the surface. Xyloglucan and CMC

polymer chains adsorb on the cellulose surface with an extended conformation, which leads to high water content not only in the nanofibril film but also in the adsorbed polymer layer. Adsorption of PDADMAC caused an inverse response to the dissipation profile i.e. the energy dissipation decreased as PDADMAC adsorbed on the nanofibril film, indicating stiffening of the film. The conformation of adsorbed chains is rather flat (Saarinen et al. 2009), and hence, the adsorbed PDADMAC layer contains less water than the adsorbed xyloglucan and CMC layers. The stiffening can be partly due to water removal from the nanofibril film caused by charge neutralization on the fibril surface as highly cationic PDADMAC adsorbs on anionic cellulose nanofibrils. The charge neutralization leads to a reduction in the swelling forces and results in flattening of the entangled nanofibril network. On the other hand, in the swollen state the hydroxyl groups in cellulose nanofibrils bind water through hydrogen bonding. Xyloglucan and CMC adsorption did not decrease the amount of hydrogen bonds between the cellulose surface and water. However, PDADMAC does not bind water like xyloglucan and CMC. Upon PDADMAC adsorption the nanofibrils had fewer opportunities to form hydrogen bonds with water, and hence, deswelling occurred.

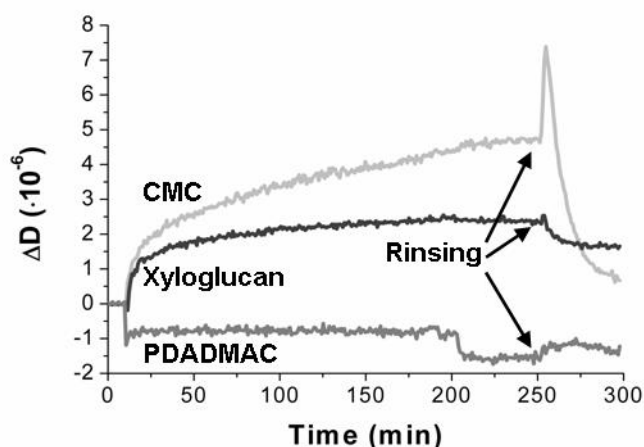


Fig. 2. QCM-D data (3rd overtone) showing change in energy dissipation as PDADMAC, CMC, and xyloglucan (0.1 g/L) adsorb on cellulose nanofibril film (1 mM NaCl in 1 mM NaHCO₃, pH 8).

The QCM-D results showed that the type of interaction between the substrate and the polymer strongly affected the nanofibril-polymer layer properties. Xyloglucan adsorbs onto the cellulose surface through glucose-glucose attraction, which occurs via hydrogen bonding (Zhou et al. 2007). Upon adsorption the energy dissipation increases, indicating loosening of the film as more water binds into the film. In other words, xyloglucan has a dispersing effect on cellulose nanofibrils. The interaction between CMC and nanofibrils is repulsive, because both CMC and cellulose nanofibrils are anionic, and thus, CMC is not irreversibly adsorbed onto cellulose nanofibrils at low electrolyte concentrations. CMC also has glucose-glucose attraction with cellulose, but at low electrolyte concentrations the electrostatic repulsion prohibits the adsorption through the interaction between the polysaccharide backbones. However, it was shown that as long as CMC was present on the surface, the energy dissipation was very high, indicating a very high water content of the layer. As already mentioned, CMC can be irreversibly attached on cellulose at higher electrolyte concentrations and at elevated temperatures. However,

the use of high electrolyte concentration causes a collapse in the swollen nanofibril structure due to reduction in the swelling forces and hence, the procedure was not applied here. These results correlate with earlier studies made for cellulosic fibres, in which xyloglucan and CMC were shown to have similar dispersing effects (Yan et al. 2006).

The adsorption of PDADMAC had an opposite effect on the highly swollen nanofibril film properties. The strong electrostatic interaction between PDADMAC and nanofibrils densified the film and resulted in water removal from the layer. Notley (2008) and Saarinen et al. (2009) did not observe the same effect for less-swollen low-charged regenerated cellulose films; the PDADMAC adsorption on low-charged cellulose caused a decrease in frequency and increase in dissipation upon adsorption. However, for highly anionic carboxymethylated regenerated cellulose films Notley (2008) also observed water removal upon PDADMAC adsorption. The cellulose nanofibrils used here were low-charged cellulose, in contrast to the highly charged cellulose that Notley used. However, the deswelling phenomenon observed here upon PDADMAC adsorption was similar to what Notley observed for highly anionic cellulose. These results indicate that the low charged cellulose nanofibrils act similarly to highly charged cellulose due to the entangled and highly swollen network structure of the fibrils.

Determination of the dry mass of the adsorbed polymer is not possible using QCM-D, which senses the combined amount of polymer adsorbed and water bound into the film. Especially the adsorbed amount of PDADMAC was impossible to determine based on the QCM-D results due to the water removal from the film upon adsorption. To verify the polymer adsorption on cellulose nanofibril model films, SPR was used to measure the dry adsorbed mass of PDADMAC and xyloglucan. Because of desorption of CMC in the QCM-D experiments it was not used in the SPR adsorption experiments. The same conditions as in the QCM-D measurements were used, i.e. 0.1 g/L polymer solution in 1 mM NaCl and 1mM NaHCO₃ at pH 8. The SPR measurements were also performed in the immersed state and the nanofibril surfaces were stabilized in the buffer solution before injecting the polymer solution. Swelling of the nanofibril film caused drifting effects of the baseline due to opening of the film structure upon swelling in the buffer solution. The drift can cause a small error to the measurements, but this drift did not significantly affect the interpretation of the adsorbed amounts of the polymers.

Injection of both xyloglucan and PDADMAC caused an adsorption of the polymers, as shown in Fig. 3. The shape of the adsorption profiles was similar to those observed in the QCM-D measurements i.e. the adsorption kinetics were slower for the xyloglucan adsorption compared to the PDADMAC adsorption. Surprisingly, buffer rinsing after PDADMAC adsorption caused a mass increase. This may be caused by conformational changes, i.e. opening of the surface structure upon rinsing. Such an effect was observed as a change in the refractive index, which is further proportional to the adsorbed mass. The dissipation curve in Fig. 2 also showed a slight increase upon buffer rinsing after PDADMAC adsorption, which again indicates opening of the surface structure. It is noteworthy that the adsorbed mass values obtained were not equilibrium values, because especially xyloglucan adsorption was very slow. However, the adsorbed amounts of xyloglucan and PDADMAC could be compared with each other. The total adsorbed mass of water and polymer from the QCM-D results was calculated by the Sauerbrey equation (1), and the changes in frequency (at t = 30 min) correspond to mass

changes of 2.5 mg/m^2 and -1.1 mg/m^2 for xyloglucan and PDADMAC, respectively. The respective dry adsorbed masses of xyloglucan and PDADMAC from the SPR measurements were about 0.4 mg/m^2 and 0.2 mg/m^2 ; i.e. the adsorbed mass was twofold higher for xyloglucan, indicating a larger adsorbed amount. The results indicate that the water content of the adsorbed xyloglucan layer was about 80%. The corresponding percentage could not be determined for the PDADMAC layer because of the negative total adsorbed amount in the QCM-D experiments. Because PDADMAC adsorbs with a flat conformation and the adsorbed layer is much denser than the xyloglucan layer, the PDADMAC layer is believed to have significantly lower water content. However, the adsorption of PDADMAC was evident. This strongly indicates that the observed increase in frequency in the QCM-D experiments was due to water removal from the nanofibril film as PDADMAC adsorbs on the surface. Thus, combined QCM-D and SPR results further highlight the effect of the polymer type on properties and water binding capacity of the nanofibril/polymer mixture.

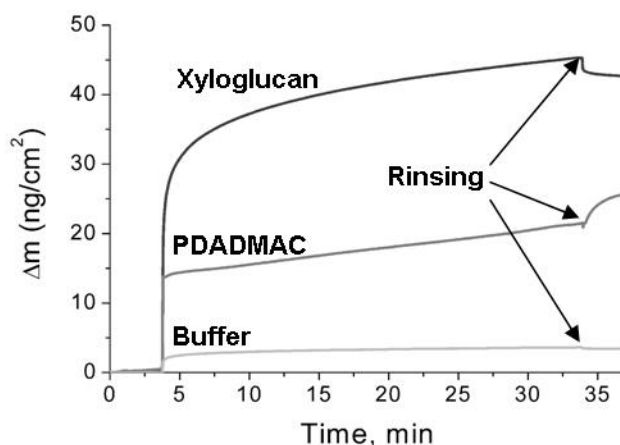


Fig. 3. Calculated Δm values from SPR experiments showing adsorbed amount of PDADMAC and xyloglucan (0.1 g/L) on cellulose nanofibril film (1 mM NaCl in 1 mM NaHCO₃, pH 8).

To further study the nanofibril/polymer interactions, aggregated nanofibril suspensions were mixed with xyloglucan, PDADMAC, and CMC, and the aggregate structure of these nanofibril/polymer mixtures was characterized using CLSM (see Fig. 4). The images revealed that the reference nanofibril suspension (Fig. 4a) was strongly aggregated, and no individual smaller aggregates or fibril bundles could be seen. The average aggregate diameter was determined to be about $180 \mu\text{m}$. Compared to the reference, the xyloglucan/nanofibril mixture (Fig. 4b) shows significantly smaller aggregate size (about $21 \mu\text{m}$). This further demonstrates the dispersing effect of xyloglucan on cellulose nanofibril suspensions, which was suggested based on the QCM-D results. The results also correlate with the studies made using cellulosic fibres, which showed a dispersing effect when xyloglucan was used (Yan et al. 2006). PDADMAC and CMC did not have such a strong effect on the nanofibril aggregation. Surprisingly, PDADMAC addition (Fig. 4c) did not cause further flocculation of the material. PDADMAC adsorption introduced a fraction of smaller aggregates and fibril bundles in

the suspension, but also larger dense fibril aggregates were present. The average diameters of the small and large aggregates were about 23 μm and 120 μm , respectively. This was unexpected, because PDADMAC is used as a fixative in the paper industry (McNeal et al. 2005), i.e. it agglomerates colloidal anionic substances in process waters and also surface fibrils on cellulosic fibres. The observed partial dispersing effect under the conditions used here can be due to electrostatic repulsion between the fibrils when PDADMAC adsorbs on the surfaces and renders the aggregates cationic. In addition, the PDADMAC polymer chains were linear, relatively short, and highly charged, and thus, under the conditions used here, the effect of PDADMAC was not strong enough to further flocculate the already aggregated nanofibril suspensions. CMC addition (Fig. 4d) introduced a very small dispersing effect but not as strong as what was observed with xyloglucan. This is due to the fact that CMC was not irreversibly adsorbed onto the nanofibrils. The average aggregate diameter was about 130 μm . However, irreversible adsorption of CMC has been shown to have a stronger dispersing effect on cellulosic fibres (Yan et al. 2006), and this effect would presumably apply also for the nanofibril suspensions if elevated temperatures and electrolyte concentrations were used.

It is noteworthy that in Figs. 4a-d oriented interference patterns of the laser light can be seen. The interference patterns are due to excess water between the microscope slide and the cover slip because pressing of the samples was avoided during sample preparation.

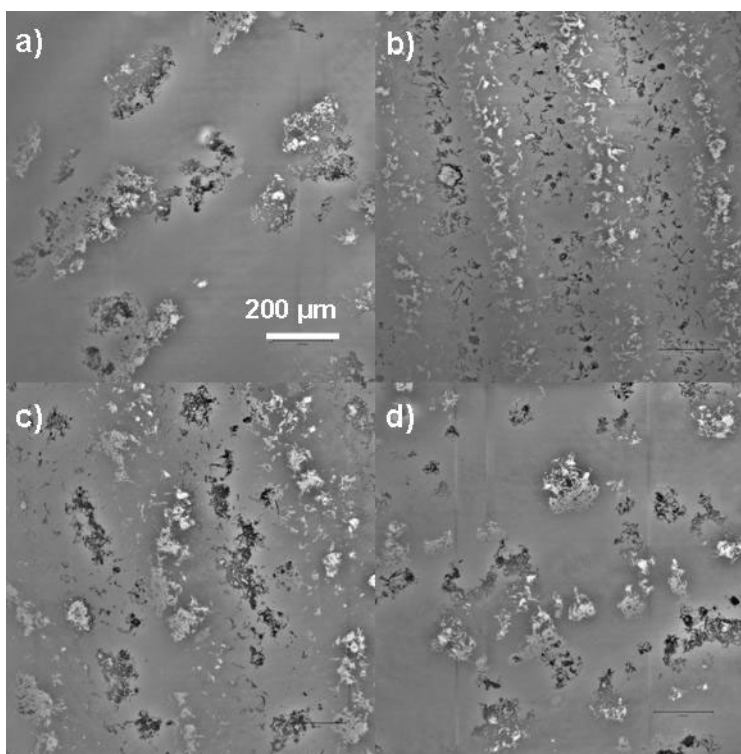


Fig. 4. Confocal microscopy images of a) aggregated cellulose nanofibrils, and fibrils mixed with b) xyloglucan, c) PDADMAC, and d) CMC.

The results obtained indicated that the type of the polymer adsorbed had a strong effect on nanofibril film layer properties and water content on the interfacial level, but it also affected the nanofibril suspension aggregation on a more macroscopic level. The dispersing effect of xyloglucan was evident from the QCM-D results, as well as from the nanofibril aggregate microscopy images. The strong water removal effect of PDADMAC in the QCM-D experiments did not fully correlate with the aggregation results, which showed, surprisingly, a slight dispersing effect for PDADMAC. These results are believed to be due to several simultaneous interfacial phenomena, i.e. water removal and densification of the aggregates upon adsorption of PDADMAC, and electrostatic stabilization of fibrils when they are covered with cationic PDADMAC under the conditions used. Thus, by optimizing the charge ratio of the nano-fibril/polymer mixture, one can also electrostatically stabilize nanofibril suspensions using cationic polymers. Based on the results obtained, it can be stated that if nanofibrils are mixed with polymers in novel applications in materials science, it is essential to optimize the water binding capacity of the mixture by choosing a suitable type of polymer/nanofibril interaction. It is noteworthy that the use of water-removing polymers may result in decreased mechanical strength properties due to decreased surface area of the fibrils caused by the fibril network collapse. Furthermore, it is important to have stable, well dispersed mixtures in order to stay at the nanoscale and avoid unwanted aggregation of the substances. This can be achieved by using dispersing polymers or by optimizing the nanofibril/polymer charge ratio in order to achieve electrostatic stabilization of the suspension.

CONCLUSIONS

1. The type of the polymer adsorbed has a strong effect on nanofibril film layer properties and water content on the interfacial level, but it also affects the nanofibril suspension aggregation on a more macroscopic level.
2. Adsorption of xyloglucan causes a dispersing effect of the nanofibrils and water uptake in the nanofibril/polymer layer, whereas adsorption of PDADMAC causes water removal and densification of the nanofibril/polymer layer. CMC adsorption causes a dispersing effect, but the adsorption is not irreversible under the conditions used.
3. Xyloglucan can break nanofibril aggregates and act as a dispersing agent in suspensions. If cationic polyelectrolytes are mixed with nanofibrils, further flocculation can be avoided and dispersing effects can be achieved mainly through electrostatic stabilization (charge reversal).

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