

Preparation of Langmuir/Blodgett-cellulose surfaces by using horizontal dipping procedure. Application for polyelectrolyte adsorption studies performed with QCM-D

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Abstract

A method of preparing model cellulose surfaces by the Langmuir–Blodgett (LB) technique with horizontal dipping procedure has been developed. The primary aim for the use of these surfaces was adsorption studies performed with the quartz crystal microbalance with dissipation (QCM-D) instrument. Hydrophobised cellulose (trimethylsilyl cellulose, TMSC) was deposited on the hydrophobic, polystyrene-coated QCM-D crystal. After 15 dipping cycles, the TMSC film fully covers the crystal surface. TMSC can easily be hydrolysed back to cellulose with acid hydrolysis. With this method a smooth, rigid, thin and reproducible cellulose film was obtained. Its morphology, coverage, chemical composition and wetting was further characterised using atomic force microscopy (AFM), X-Ray photoelectron spectroscopy (XPS), and contact angle measurements. The swelling behaviour and the stability of the cellulose film in aqueous solutions at different ionic strengths were studied using the QCM-D instrument. The swelling/deswelling properties of the cellulose film were those expected of polyelectrolytes with low charge density; some swelling occurred in pure water and the swelling decreased when the ionic strength was increased. No significant layer softening was detected during the swelling. The effect of electrolyte concentration and polymer charge density on the adsorption of cationic polyelectrolytes on the cellulose surface was also investigated. At low electrolyte concentration less of the highly charged PDADMAC was adsorbed as compared to low charged C-PAM. The adsorbed amount of PDADMAC increased with increasing ionic strength and a more compact layer was formed while the effect of electrolyte concentration on the adsorption of C-PAM was not as pronounced.

Introduction

Cellulose model films have been investigated by researchers for several years and the demand for such films is increasing due to the growing interest in the cellulose interactions in the field of paper-making chemistry. New, more accurate surface

analysis techniques such as QCM-D and AFM enable more specific research applications to obtain better understanding when dealing with e.g. cellulose–cellulose and cellulose–polyelectrolyte interactions.

Model cellulose surfaces have previously been produced by spin-coating (Neuman et al. 1993;

Geffroy et al. 2000; Gunnars et al. 2002; Kontturi et al. 2003; Fält et al. 2004) or Langmuir–Blodgett (LB) deposition (Schaub et al. 1993; Buchholz et al. 1996; Holmberg et al. 1997). All the above-mentioned techniques produce cellulose II films. In a recent study, an oriented cellulose I films was prepared using spin-coating and shearing (Edgar and Gray 2003). Swelling and water uptake capability of the model cellulose films were earlier studied by Fält et al. (2003) and by Rehfeldt and Tanaka (2003). The former group have studied the swelling of the spin-coated cellulose surfaces by using QCM-D and the latter group have compared the hydration forces of the spin-coated and LB-deposited cellulose films by using ellipsometry.

Spin-coating is a rapid and simple method for producing model cellulose surfaces. However, one disadvantage is that it is difficult to control the deposition and thickness of the layer during the spin-coating. The advantage of the LB-technique is that thin and smooth films can be deposited in a very controllable way (Roberts 1990; Petty 1996) since the transferring of the film onto the substrate surface can be followed *in situ* during the deposition.

This paper introduces a method to produce a smooth cellulose model film on a QCM-D crystal using LB-technique. Our intention is to model the main components present in wood fibre (cellulose, lignin and extractives) separately in order to better understand polymer–fibre component interactions. Preparation of lignin and extractive model surfaces is presented in Tammelin et al. (2005).

Quartz crystal microbalance with dissipation, QCM-D technique, is a relatively recently developed method for *in-situ* adsorption studies at the solid/liquid interface. It has been successfully used to study adsorption behaviour on mineral surfaces like gold and silica (Rodahl and Kasemo 1996; Rodahl et al. 1997; Merta et al. 2004; Tammelin et al. 2004). The monitoring of energy dissipation enables further interpretation of the viscoelasticity of the adsorbed layer (Voinova et al. 1999). Due to the sensitivity of the method, the model adsorbent surfaces must be thin, rigidly attached, fully covering the substrate and as inert and stable as possible.

The structure of the QCM-D crystal brings a few drawbacks which must be considered when depositing cellulose on the sensor surface. The different hydrophobicities of the different sides of the crystal and the risk of contamination of the

electrodes exclude the traditional vertical LB-dipping procedure used by Holmberg et al. (1997). In this study the horizontal dipping procedure is used to deposit trimethylsilyl cellulose (TMSC) onto the sensor surface. As shown by Lee et al. (1992), this procedure can be used to deposit multilayers.

In this paper the surface chemistry and coverage of the LB-cellulose film prepared by a horizontal dipping procedure was characterised using XPS and the smoothness of the film was characterised using AFM. In contrast to mineral surfaces, all model cellulose surfaces swell in water solutions. This is an important parameter that has to be taken into account in adsorption experiments. Thus, the swelling of the model film in different aqueous electrolyte solutions as well as the reproducibility of adsorption experiments are described. Two polyelectrolytes of low and high charge density were adsorbed at different ionic strengths on cellulose surface. The adsorbed amount, the layer formation and the conformation of the polyelectrolytes on the cellulose were studied using QCM-D.

Experimental

Materials

Cellulose

Trimethylsilyl cellulose (TMSC, Figure 1) was prepared by silylation of microcrystalline cellulose powder from spruce (Fluka) with hexamethyl disilazane in the following way, as first suggested by Greber and Paschinger (1981) and Cooper et al. (1981). One gram of cellulose was added to 50 ml of water and the suspension was left in refrigerator over night. Eight gram of dry lithium chloride (LiCl) was dissolved in 100 g of dimethyl acetamide (DMA) at 100 °C. The cellulose was filtrated and washed with first 3 × 20 ml methanol and then 2 × 20 ml DMA before dissolution in cold DMA/LiCl-solution. Nitrogen (g) was bubbled into the solution for 1 h whereupon the cellulose solution was heated to 80 °C and 10 ml of hexamethyl dizilasane was added slowly while stirring. When the mixture had cooled down the product was filtered and rinsed with methanol. The TMSC was further purified by re-crystallization. The TMSC was dissolved in a small amount of chloroform and precipitated in methanol while

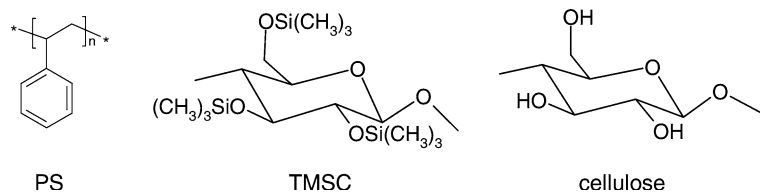


Figure 1. Molecular structure of polystyrene, TMSC and cellulose.

stirring. The product was filtrated and rinsed with methanol and dried in vacuum. The purity of the product was established using FTIR.

In Figure 2 the FTIR spectra of pure cellulose and TMSC are shown. There is still a weak O–H stretching band at 3500 cm^{-1} , indicating that there are some unsubstituted OH-groups left in the cellulose backbone of TMSC. This is as expected, since the OH-groups were never fully substituted. The degree of substitution as determined by XPS varied between 2.1 and 2.3 in different synthesis batches. The peaks at $2900\text{--}2960\text{ cm}^{-1}$ are due to CH_3 , CH_2 and CH stretching. The sharp peaks at 1253, 879, 849 and 756 are due to Si-CH_3 stretching and deformation and Si-O-C vibration. These peaks are not at all present in pure cellulose.

TMSC deposited on the polystyrene QCM-D crystal was converted to cellulose by desilylation. The QCM-D crystal was kept for at least 1 min in the atmosphere above a 10% aqueous HCl solution according to Schaub et al. (1993). The completeness of the desilylation reaction was verified using XPS and contact angle measurements.

Polyelectrolytes

Two cationic polyelectrolytes, cationic polyacrylamide (C-PAM), kindly donated by Kemira Oyj,

Finland and PDADMAC (Allied Colloids Ltd., Yorkshire, England) were used in the adsorption studies on the cellulose surface. C-PAM was fractionated by filtration in a tangential flow ultrafiltration system (Filtron Technology Corp., Northboro, MA; Minisette), using a membrane with a cutoff between 100,000 and 500,000. PDADMAC was ultrafractionated with in an Amicon ultrafiltration unit prior to the analysis using a cutoff $> 300,000$ (Laine et al. 1996). The molecular weight of C-PAM, as determined from the intrinsic viscosity, was 220,000 and the charge density was 0.91 meq g^{-1} . The charge density of PDADMAC was 6.13 meq g^{-1} corresponding to one charge per monomer unit.

All other chemicals were of p.a. grade if not otherwise specified.

QCM-D crystals

The sensor crystals used were AT-cut quartz crystals supplied by Q-sense AB, Gothenburg, Sweden. They are thin (0.3 mm) with $f_o \approx 5\text{ MHz}$ and $C \approx 0.177\text{ mg m}^{-2}\text{ Hz}^{-1}$. The crystals were spin-coated with polystyrene (Figure 1) by the supplier. The polystyrene surface was hydrophobic, the contact angle values of pure water on the crystal surface were $95^\circ \pm 2^\circ$.

Methods

FTIR

A Bio-Rad FTS 6000 research grade FTIR spectrometer equipped with a photoacoustic cell (MTEC300) was used to determine the completion of the silylation reaction and the purity of the TMSC.

Preparation of cellulose film

Silylated cellulose was deposited on a hydrophobic QCM-D crystal using LB-technique. A KSV Mini

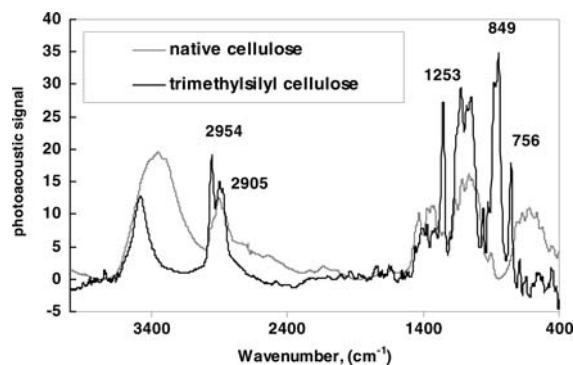


Figure 2. FTIR-PAS spectrum of TMSC (black line). For comparison the spectrum of cellulose (grey line) before synthesis is also shown.

trough system developed by KSV Instruments LTD, Helsinki, Finland was used to record the Langmuir isotherms and carry out the depositions. A special horizontal dipping procedure (Figure 3) was used to deposit TMSC on the polystyrene coated QCM-D crystal (Lee et al. 1992).

For the LB-deposition, 4 mg TMSC was dissolved in 10 ml chloroform. Sufficient amount of solution was spread on the water subphase in an LB-trough to reach a TMSC monolayer. The chloroform was allowed to evaporate for 15 min and afterwards the water surface contains only TMSC molecules. TMSC molecules were compressed with the barriers (shown in Figure 3) so that they form a continuous film and the surface pressure and the surface area per monomer unit were monitored simultaneously in the LB-trough.

The surface pressure versus area (π - A) isotherm shown in Figure 4a was recorded using a compression rate of 5 mm min^{-1} . The surface pressure was measured using the Wilhelmy plate-method (Roberts 1990). The surface pressure increases strongly when the surface area per monomer is less than 90 \AA^2 . The monolayer can be compressed to a surface pressure of about 23 mN m^{-1} . Above this pressure the slope of the isotherm changes indicating disruption of the film. Depositions were made at a constant surface pressure of 15 mN m^{-1} , see Figure 4b.

Figure 3 schematically describes the horizontal dipping procedure and the deposition of the TMSC layer on the hydrophobic polystyrene QCM-D crystal. The QCM-D crystal was mounted on the dipper with a suction pad. The crystal was horizontally pressed onto the TMSC film with a speed of 3 mm min^{-1} and immersed approximately 0.2 mm into the subphase (Figure 3b). The crystal was kept in contact with the TMSC monolayer for 30 s and was then lifted at a velocity of 3 mm min^{-1} , see Figure 3c. After that the crystal was allowed to dry for 15 min and then again lowered into contact. The barriers were keeping the surface pressure in the LB-trough at a constant value of 15 mN m^{-1} throughout the deposition cycle. Theoretically, during one dipping cycle a bilayer of TMSC is attached on the polystyrene surface as shown in Figures 3d and 3e. TMSC molecules are stiff and hence they are not as well orientated on the water surface as e.g. surfactant molecules are. Because of this stiffer structure one dipping cycle do not lead to a fully covering bilayer film, but a network of TMSC molecules is attached on the surface. This network also contains holes which are covered when the amount of dipping cycles is increased. The sufficient amount of dipping cycles needed for achieving a fully covering TMSC film was 15.

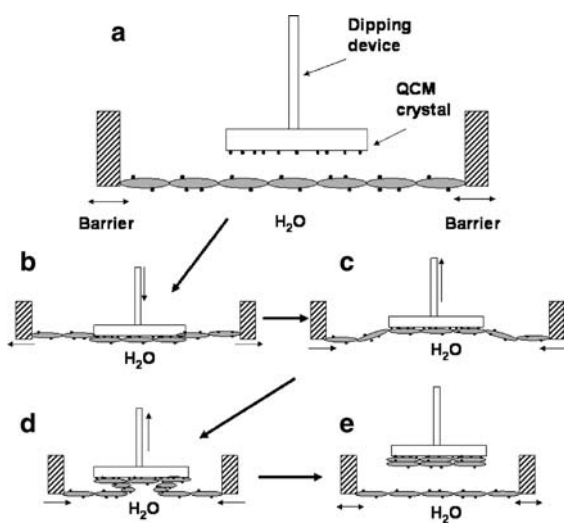


Figure 3. A schematic drawing of the horizontal dipping procedure for LB-deposition. The horizontal arrows represent the barrier movements and the vertical arrows represent the movements of the dipping device during one dipping cycle. The ovals illustrate the TMSC molecules and black spots illustrate the hydrophobic parts of TMSC and polystyrene.

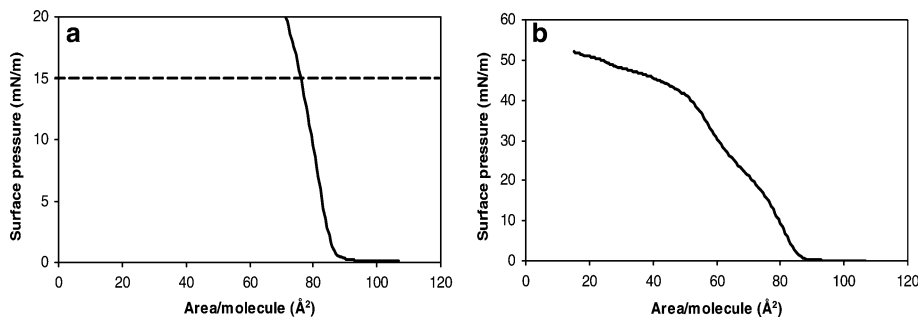


Figure 4. (a) Langmuir isotherm of TMSC on water. The dashed line indicates the surface pressure at which the TMSC is deposited. (b) Behavior of the cellulose film at higher surface pressures.

AFM

Atomic force microscopy was used to verify the cellulose deposition and the coverage of the crystal surface. AFM measurements were made with a Nanoscope IIIa Multimode scanning probe microscope from Digital Instruments Inc., Santa Barbara, CA, USA. The images were scanned in tapping mode in air using silicon cantilevers (Pointprobes, type=NCH) delivered by Nanosensors, Neuchald, Switzerland. No image processing except flattening was made. At least 10 areas on each sample were measured.

XPS

X-ray photoelectron spectroscopy was used to measure the chemical composition of the polystyrene, TMSC and cellulose (after desilylation) surfaces. The XPS measurements were performed with a Kratos Analytical AXIS 165 electron spectrometer at the Center for Chemical Analysis, Helsinki University of Technology, using a monochromated Al K α X-ray source. The experiments were carried out on dried QCM-D crystal samples, according to the standardised procedure developed for cellulosic materials (Johansson et al. 1999; Johansson 2002; Koljonen et al. 2003). In order to improve the statistic and also to average out the heterogeneities of the samples, both survey scans and the regional spectra were recorded on at least three different spots on each sample. All spectra were collected at an electron take-off angle of 90° from sample areas less than 1 mm in diameter and using only 100 W irradiation. The total exposure times were kept below 20 min per spot since long exposures to X-rays are known to easily degrade organic specimen (Johansson et al. 2004). No sample degradation was detected.

Contact angle

The sessile drop method was used for contact angle measurements employing a CAM 200 (KSV Instruments LTD, Finland) video camera based on fully computer controlled contact angle meter. Determination of contact angles is based on analysis of drop shape using the full Young–Laplace equation. The measurements were performed at room temperature using pure water. The drop volume was about 5 μ l. The contact angle on at least three different spots was measured on each sample.

QCM-D

The swelling of the cellulose layer and the adsorption of polyelectrolyte were studied using a quartz crystal microbalance with dissipation, the QCM-D instrument, from Q-Sense, Gothenburg, Sweden (Rodahl et al. 1995). With QCM-D, the changes in frequency and dissipation can be followed simultaneously at the fundamental resonance frequency (5 MHz) and its three overtones (15, 25 and 35 MHz). The interpretation of QCM-D data is described in detailed elsewhere (Rodahl et al. 1995).

If the adsorbed mass is evenly distributed, rigidly attached and small compared to the mass of the crystal, the shift in the resonant frequency is related to the adsorbed mass by the Sauerbrey equation (Höök et al. 1998).

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

where Δm is the adsorbed mass per unit surface, $\Delta f = f - f_o$ is the frequency shift, n is the overtone number (in the present case $n = 1, 3$ or 5) and C is a

constant that describes the sensitivity of the device to changes in mass.

Results

Preparation of the LB-cellulose film

In the LB-technique, when using a vertical dipping procedure, a monolayer is formed every time the substrate passes through the air/water interface. When using a horizontal dipping procedure, the substrate is pressed in contact with the liquid interface. A bilayer of the film is formed when the substrate is withdrawn and the liquid and substrate are separated. This is the case when using fatty acids and other surface active agents with flexible structures (Lee et al. 1992; Petty 1996). However, the 4-*O*-glycosidic bonded cellulose backbone of TMSC is stiffer and thus it does not form as dense monolayer on the water surface. As a consequence, more dipping cycles are needed to form a cellulose film that fully covers the substrate surface.

The horizontal dipping procedure shown in Figure 3 was used to avoid contamination of the electrode side of the QCM-D sensor crystal. However, it was also found that the difference in hydrophobicity between the electrode side and the sensor side of the crystal interferes with the TMSC deposition. Thus, the traditional vertical dipping procedure could not be used.

The deposition of the film on a solid substrate is measured by a transfer ratio. This is defined as the ratio between the decrease in the area of the film in the LB-trough during the deposition and the area of the substrate. In this case, the transfer ratio describes the ratio between the decrease in surface area of the TMSC film and the surface area of the polystyrene coating on the QCM-D crystal. Figure 5 shows the transfer ratio versus layer number. In the ideal situation the transfer ratio when the solid substrate is brought into contact with the liquid interface should be zero and upon withdrawing of the substrate it should be two, i.e. during the dipping cycle a uniform bilayer is formed. In the present case, when TMSC attaches on the hydrophobic crystal surface, the ratio upon withdrawing is between 2 and 4. During the deposition the film probably also transfers to the edges of the crystal which are not covered with

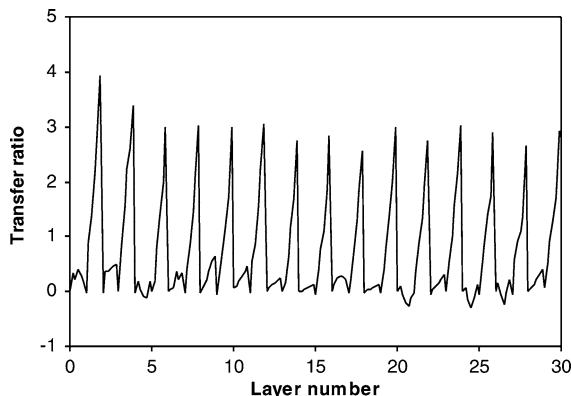


Figure 5. Transfer ratio of the TMSC versus layer number.

polystyrene (the edges are not taken into account in the transfer ratio calculations). One deposition cycle do not lead to a uniform TMSC film structure as discussed later when the film morphology and chemistry is further characterised, although the transfer ratio values are optimal. Transfer ratio values below zero would mean that the TMSC film is detaching from the crystal surface. As Figure 5 shows, more or less constant amount of TMSC film transferred onto the substrate surface after every dipping cycle and no detachment of the film was observed.

Characterization of the LB-cellulose film

Morphology

Figure 6 shows the AFM topography images of polystyrene, TMSC and cellulose surface after 3 and 15 dipping cycles. Sometimes, but not always, a few holes in the polystyrene layer were found as seen in Figure 6a. If the crystal was not sufficiently covered with polystyrene the deposition of TMSC did not succeed. After deposition of TMSC the structure of the surface clearly changes as can be seen from Figure 6 b. The rms roughness of the $1 \mu\text{m} \times 1 \mu\text{m}$ topography image was 0.8 nm. After three deposition cycles the crystal surface was not fully covered by cellulose as seen in Figure 6c and it contains holes. After 15 deposition cycles only the cellulose structure was seen. A smooth and thin cellulose surface was achieved with rms roughness of approximately 0.4 nm determined from a $1 \mu\text{m} \times 1 \mu\text{m}$ topography image. The TMSC film is rougher than the cellulose because

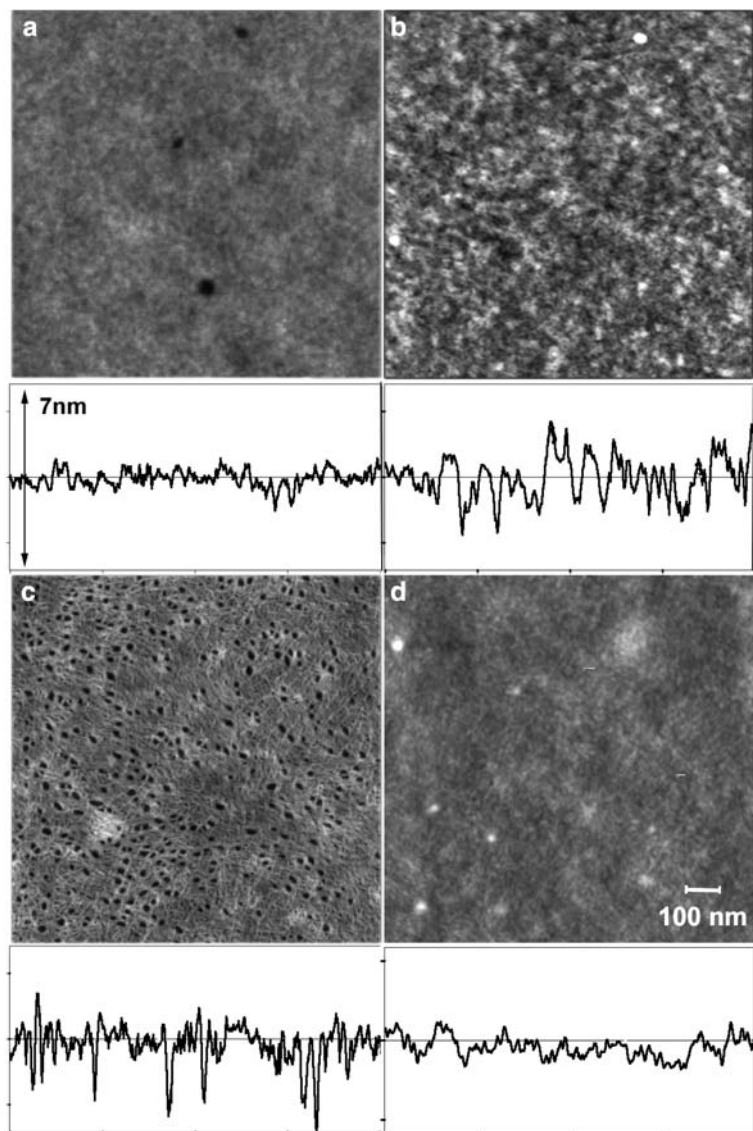


Figure 6. AFM topography images of (a) polystyrene, (b) TMSC and cellulose after (c) 3 and (d) 15 dipping cycles. Height profiles of the surfaces are also shown. The image size is $1 \times 1 \mu\text{m}$.

the three methyl silyl groups are much larger than one hydroxyl group. The transformation from a rough TMSC film to a cellulose film containing holes to finally a smooth and homogeneous cellulose film is clearly visible when comparing the line profiles of the images in Figures 6b–d.

Chemical composition of the surface

The elementary compositions of polystyrene, TMSC and cellulose surfaces were determined using XPS. The atomic ratios between oxygen and

carbon and between silicon and carbon as well as the relative amounts of different carbons are shown in Table 1 and the curve-resolved XPS spectra of the C1s peak for polystyrene, TMSC and cellulose are shown in Figure 7. The atomic ratio of silicon to carbon and the relative abundance of carbon–silicon bonds in the TMSC sample indicate the degree of silylation (DS). The silicon–carbon ratio of 0.14 (DS 2.1) indicates that 70% of all possible carbon–hydrogen bonds were changed to silicon groups. After desilylation of the

Table 1. O/C atomic ratio, Si/C atomic ratio and relative amounts of different carbons for PS, TMSC and cellulose.

Material	O/C	Si/C	C-CH C1	C-O C2	C=O C3	O-C=O C4	C-Si
Polystyrene	0.006	0.001	100	–	–	–	–
TMSC (this study)	0.36	0.14	7	39	9	0.9	4
TMSC (theoretical, DS = 3.0)	0.33	0.20	–	33	7	–	60
TMSC (theoretical, DS = 2.1)	0.41	0.14	–	41	8	–	51
TMSC (Holmberg et al. 1997)	0.42	0.14	4	38	9	0.5	48
Cellulose 6 layers (this study)	0.12	0.002	84	13	3	0.4	–
Cellulose 30 layers (this study)	0.66	–	19	65	15	1	–
Cellulose (theoretical)	0.83	–	–	83	17	–	–
Bleached kraftwood (Laine et al. 1994)	0.80	–	6	75	18	1	–
Cellulose (Holmberg et al. 1997)	0.80	0.0025	7	75	18	1	–

cellulose, the carbon–silicon bonds have disappeared indicating that the desilylation process has succeeded and all silicon groups were replaced by hydrogen.

Polystyrene consists completely of C–C type carbons, i.e. carbons without oxygen neighbours (C1). Hence, the C–C concentration was 100 ± 0 (Figure 8). In the polystyrene spectrum (Figure 7),

the shake-up satellite band is due to the transitions in π -electrons of aromatic rings. The amount of carbon–carbon component in the crystal after 3 dipping cycles of cellulose is still very high (84%), see Figure 8 and Table 1. Pure cellulose has no C–C component of the C1s signal, and consequently we believe that these bonds origin from the underlying polystyrene and, as the AFM images

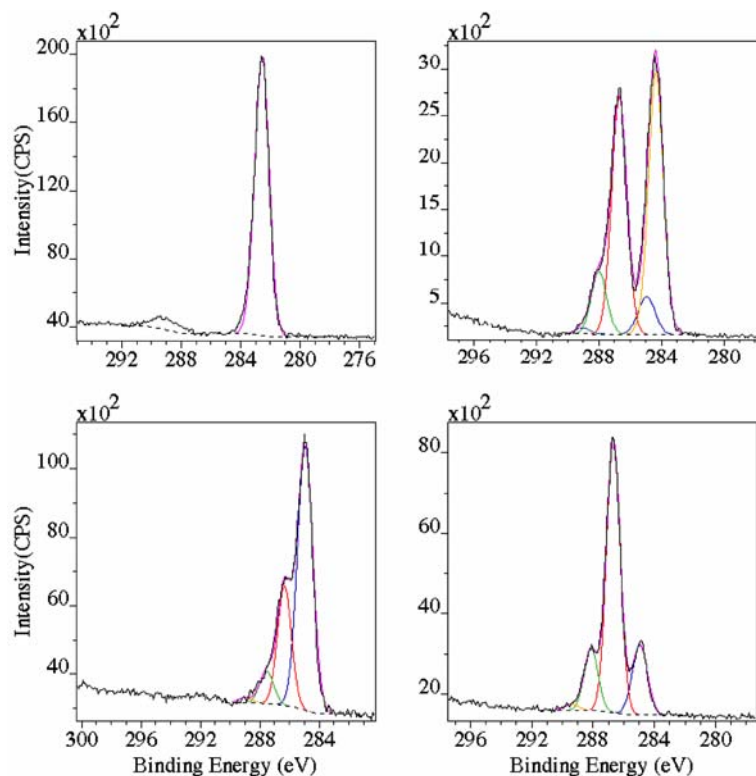


Figure 7. Curve-resolved XPS spectra of the C1s peak for polystyrene, TMSC film and cellulose films (3 and 15 dipping cycles).

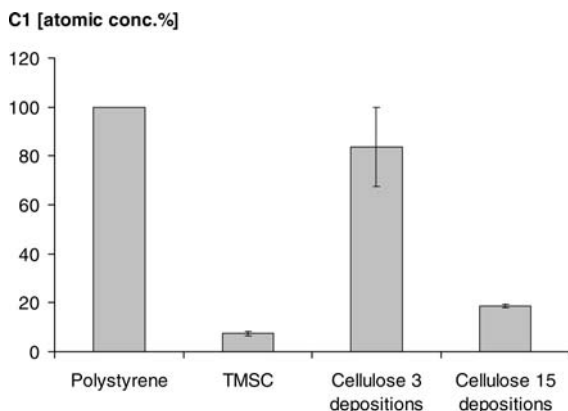


Figure 8. Relative amount of carbon bonded to only hydrogen or other carbon atoms for polystyrene, TMSC and cellulose of after 3 and 15 dipping cycles.

taken after 3 dipping cycles showed, the cellulose molecules do not fully cover the polystyrene surface. The standard deviation of the C–C carbon for the cellulose film after three dipping cycles is also very high, showing that the film is heterogeneous (Figure 8).

The relative abundance of C–C type carbons decreased notably when more cellulose was deposited onto the crystal. Correspondingly, the oxygen–carbon ratio increased. The standard deviation of the relative abundance of C–C carbon is much lower after 15 deposition cycles as compared to only 3 deposition cycles. The relative abundance of C–C type carbons and the oxygen–carbon atomic ratio of the crystal after 15 dipping cycles of cellulose still deviated from the theoretical values and the results obtained by Holmberg et al. (1997) for similar LB-cellulose films. About 1–2% of the C–C component is almost always detected, even for pure cellulose samples, due to adsorption of airborne contaminants (Johansson et al. 2004). However, this cannot be the only contribution to the C–C peak in this case. The analysing depth in XPS measurements is 5–10 nm. Probably the whole cellulose film of 15 depositions was so thin that XPS still detected the underlying polystyrene layer (high amount of C1 carbon), although the cellulose film fully covers the surface as was seen by AFM. Holmberg deposited 86 cellulose layers on hydrophobised mica in which case the oxygen–carbon ratio was near the theoretical value. The results from the AFM images together with the fact that the standard deviation of the C–C carbon of the cellulose film after 15

depositions is low, confirms that the surface is homogeneous and fully covered with cellulose.

Wetting

The measurements of static contact angles for polystyrene, TMSC and cellulose surfaces gave the following values: $95^\circ \pm 2^\circ$ for polystyrene, $78^\circ \pm 1^\circ$ for TMSC and $31^\circ \pm 3^\circ$ for cellulose. The values are rather well in accordance with literature; Schaub et al. (1993) reported contact angles of 25° for LB cellulose and Carlsson and Ström (1995) reported contact angles of 30° for unextracted bleached kraft pulp. The standard deviations for all surfaces, polystyrene, TMSC and cellulose, are almost at the same level (± 1 – 3°). This indicates that the deviations do not derive from the preparation or e.g. from the poor desilylation of the cellulose surface but probably from air-borne contamination of the surface and from the normal instrumental error.

Stability of the LB-cellulose coated quartz crystals

Swelling of the LB-cellulose film

In dilute aqueous solutions polyelectrolyte molecules swell due to the osmotic pressure created by the counter-ions. According to the theory of swelling behaviour of polyelectrolytes, the swelling ability of a polymer increases with increasing charge density of the polymer and decreases with increasing ionic strength of solution (Flory 1953).

Figure 9 shows the behaviour of pure polystyrene coated crystal and crystal with LB-cellulose deposited on polystyrene at sequentially increased ionic strength. In studies of the stability, water penetration and possible swelling behaviour with the QCM-D, a decrease in frequency is thought to indicate water penetration into the layer structure. Changes in dissipation describe changes in structural properties such as layer softening and thickening during these processes. A higher dissipation response corresponds to softer layers. As Figure 9 shows the swelling effects were more pronounced with the slightly negatively charged cellulose film¹ but also the uncharged polystyrene layer showed changes in the layer structure when it was kept in contact with water and electrolyte

¹Osterberg (2000) determined an area per charge of 460 nm^2 for the similar kind of LB-cellulose surface.

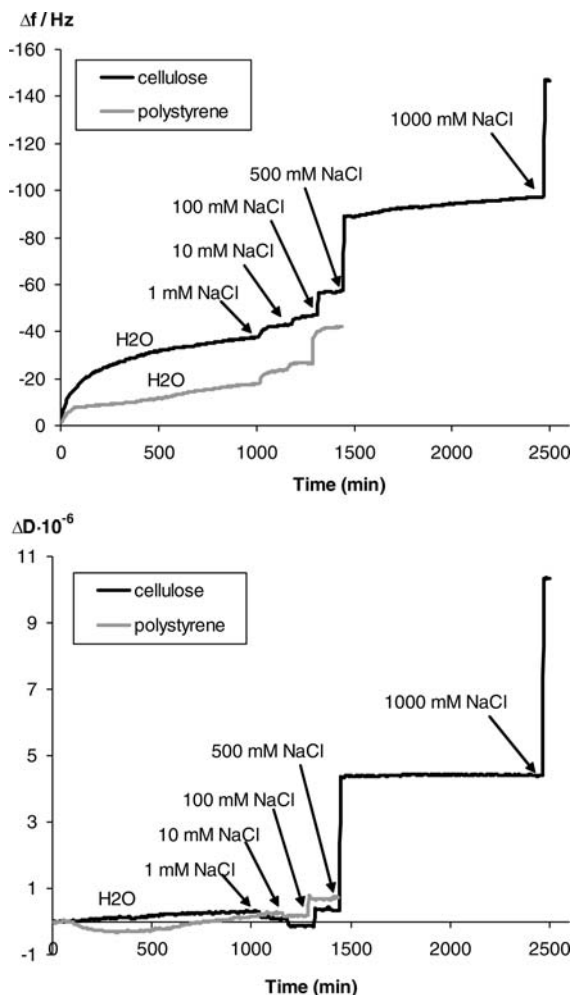


Figure 9. Change in frequency and dissipation as a function of time during the swelling of polystyrene and cellulose films in water/aqueous electrolyte solutions with increasing ionic strength at pH 7. Electrolyte concentration increases sequentially. $f_o = 5$ MHz, $n = 3$.

solutions. After 900 min more water had penetrated into the cellulose structure, as seen by the larger frequency change. In both cases the low increase in dissipation ($\Delta D < 0.5 \cdot 10^{-6}$) indicates that a slight swelling of the film but no considerable layer softening occurred. When the electrolyte concentration was slightly increased (1 and 10 mM NaCl) the change in dissipation of the cellulose film decreases and there seems to be some decrease in swelling. Such deswelling was not seen with polystyrene due to the negligible charge of the film. After electrolyte addition the dissipation change remained more or less constant for polystyrene.

At higher electrolyte concentrations (100, 500 and 1000 mM NaCl) changes in the bulk properties of the solution screen the effects of water penetration and swelling/deswelling of the film. The frequency and dissipation response also depends on the density and viscosity of the bulk liquid. The very sharp changes in frequency and dissipation observed immediately after electrolyte additions were so rapid and large that it seems very unlikely that they could be due to water penetration and swelling/deswelling of the film. This so called bulk effect is a commonly known effect when using QCM-D. The following values for the frequency and dissipation changes are measured for the quartz crystal when pure water is replaced by 100 mM NaCl: $\Delta f_{15 \text{ MHz}} = \sim -8$ Hz and $\Delta D_{15 \text{ MHz}} = 1.2 \times 10^{-6}$. The almost constant values of Δf and ΔD after the sharp peak originating from the bulk effect (Figure 9), imply that the physical properties of the films did not depend on time. The low changes detected were smaller than the maximum drift of the instrument which is 2 Hz/h and $0.2 \cdot 10^{-6} \text{ h}^{-1}$ at 15 MHz (Q-Sense 2000).

Figure 10 shows the behaviour of the cellulose film when the electrolyte concentration was initially adjusted to the desired level (1, 10 and 100 mM NaCl). In all three cases the amount of water that penetrates into the cellulose film is almost the same (the final change in frequency is equal) and the structure of the film stays rigid ($\Delta D < 0.5 \cdot 10^{-6}$) regardless of the ionic strength of the system. This result shows that the LB-cellulose film was stable and rigidly attached on the polystyrene crystal and that the increase in ionic strength did not significantly change the layer properties. Both the effects, swelling and water penetration, were seen concomitantly. Thus, these effects cannot be separated by this experiment. The cellulose surface can be regarded as fully swelled and stabilized when frequency and dissipation responses attain the drifting response of the instrument. The cellulose film was fully stabilized after 6.5 h.

Adsorption of cationic polyelectrolytes on LB-cellulose

The repeatability of the QCM-D measurements

Figure 11 shows the change in frequency and the change in dissipation for three parallel adsorption

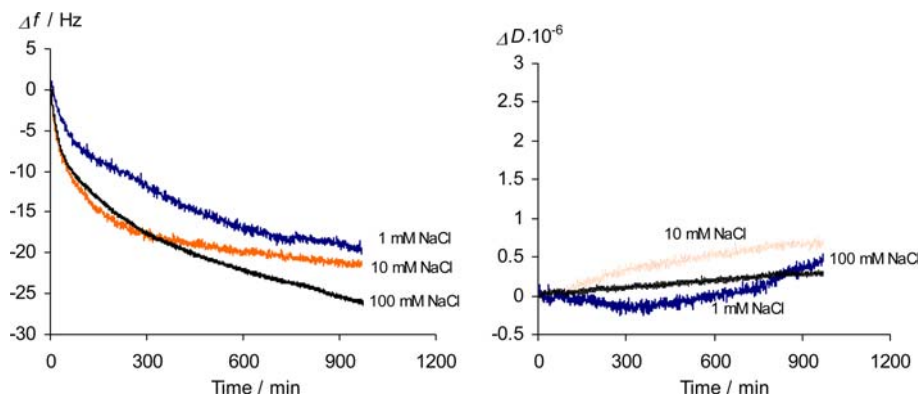


Figure 10. Change in frequency and dissipation as a function of time during the swelling of cellulose films in aqueous solutions of different electrolyte concentrations at pH 7. The desired electrolyte concentration was initially adjusted. $f_o = 5$ MHz, $n = 3$.

experiments of low charge C-PAM ($M_w = 220,000$ and charge density 0.91 meq g^{-1}) on LB-cellulose coated crystals at pH 8. The final change in frequency after 30 min of adsorption was -38.7 ± 1.2 Hz, whereas the final change in dissipation was $(2.4 \pm 0.01) \cdot 10^{-6}$.

Effect of charge density of polymer and solution electrolyte concentration

In Figure 12 the change in frequency and the change in dissipation after 60 mins of adsorption of low and high charged polyelectrolytes on cellulose as a function of ionic strength are shown. Three separate adsorption experiments were done with fresh polyelectrolyte solutions for each point. These two polyelectrolytes adsorb differently onto cellulose. For the high charged PDADMAC, the adsorbed amount (seen as higher change in frequency) and the dissipation increase clearly, upon

increasing the electrolyte concentration in solution. This is as expected when considering the conformation of the polyelectrolytes in solution (Fleer et al. (1993)). A highly charged polyelectrolyte will have an extended conformation in solution due to inter- and intra-molecular repulsion between charged segments. It will consequently also adsorb onto the cellulose surface in a rather flat conformation at low ionic strength. Thus, only a small amount of polymer is enough to fully cover the surface as is seen as the low Δf value. The rather flat conformation is evident from the quite low ΔD value.

When the ionic strength is increased (10 and 100 mM NaCl) PDADMAC in solution adopts a more coiled conformation due to the reduced repulsion between the charged segments. The persistence length of the polymer coil decreases and hence more polymer molecules can fit to adsorb

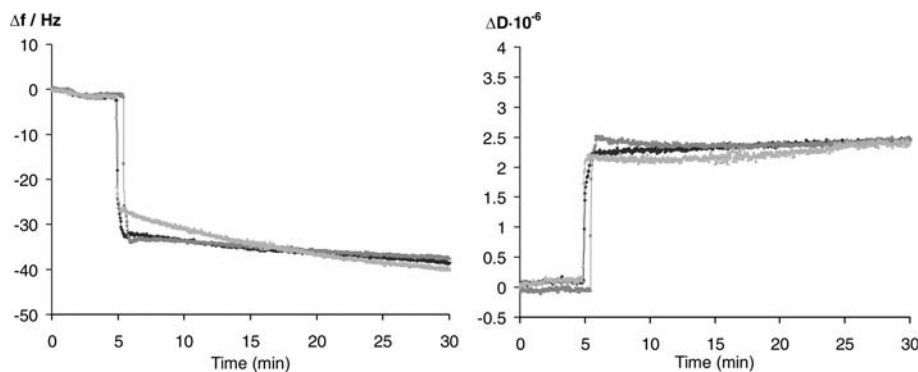


Figure 11. Change in frequency (left) and dissipation (right) as a function of time for three parallel adsorptions of low charge C-PAM (charge density 0.91 meq g^{-1} , $M_w = 220,000$) at pH 8 on LB-coated cellulose surface. $f_o = 5$ MHz, $n = 3$.

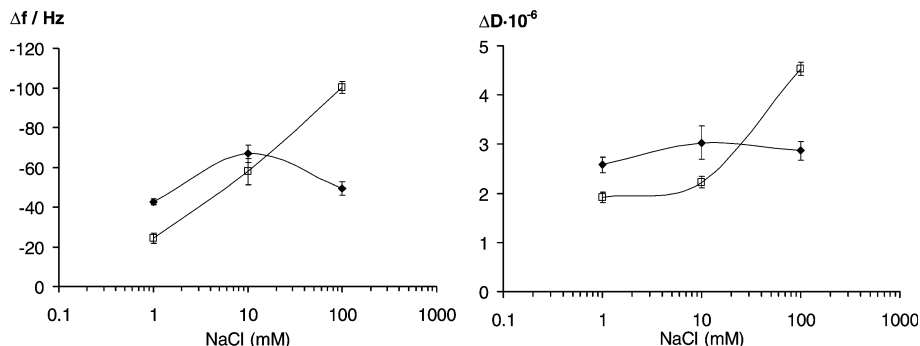


Figure 12. Change in frequency (left) and change in dissipation (right) as a function of ionic strength for adsorption of 0.5 g l^{-1} cationic polyelectrolytes at pH 8 on LB-cellulose surface. \blacklozenge low charge C-PAM, 0.91 meq g^{-1} , $M_w = 220,000$ and \square high charge PDADMAC, 6.13 meq g^{-1} , $M_w > 300,000$. $f_o = 5 \text{ MHz}$, $n = 3$, $t = 60 \text{ min}$.

onto the cellulose surface seen as higher adsorbed amount, see Figure 12.

The change in conformation upon increasing the electrolyte concentration is not as pronounced with the low charged C-PAM. C-PAM molecule has a moderately coiled conformation already at low ionic strength and consequently the polymer chains are more extended out to the solution phase. Both frequency and dissipation changes for C-PAM shown in Figure 12 are larger than those for PDADMAC indicating more mass attached on the cellulose surface. Slight increase in ionic strength (10 mM NaCl) reduces the persistence length of the C-PAM coil and again more polymer can adsorb onto the cellulose surface (higher change in frequency). When the ionic strength further increases the adsorbed amount and

dissipation decreases. This effect might have two explanations. Either the polymer adopts an even more compact conformation, the polymer layer further contracts and water expels from the layer structure or the attractive electrostatic effects between the cellulose surface and C-PAM are screened and the adsorption decreases.

To further investigate the effect of polyelectrolyte charge density on the conformation of the formed layer, the QCM-D data is presented as change in dissipation vs. change in frequency. Figure 13 compares the Δf and ΔD responses for low and high charge density polyelectrolytes adsorbed on cellulose surface from two different electrolyte concentrations. The slopes of the curves are calculated to clarify the changes in viscoelastic properties during the adsorption process. The

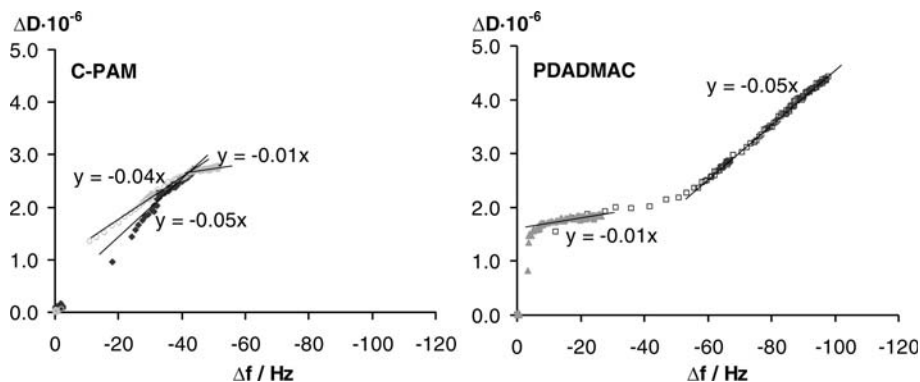


Figure 13. Change in dissipation factor as a function of the change in frequency for adsorption of 0.5 g l^{-1} low charge C-PAM (left) and high charge PDADMAC (right) at pH 8 in 1 mM and 100 mM NaCl on LB-cellulose surface. Low charge C-PAM, 0.91 meq g^{-1} , $M_w = 220,000$ and high charge PDADMAC, 6.13 meq g^{-1} , $M_w > 300,000$. $f_o = 5 \text{ MHz}$, $n = 3$. \blacklozenge C-PAM in 1 mM NaCl, \circ C-PAM in 100 mM NaCl, \blacktriangle PDADMAC in 1 mM NaCl, \square PDADMAC in 100 mM NaCl.

steepness of the slope and the changes in the slope during the adsorption describe the softening or packing of the layer structure. The steeper the $\Delta D/\Delta f$ curve is the more dissipative the layer is i.e. more energy is bounded per the frequency change unit. If two slopes can be distinguished as the adsorption proceeds the layer properties are altering. If the curve becomes steeper the layer is becoming softer and more mobile, whereas packing of the layer is observed as a decrease in the slope steepness. By comparing the slopes calculated during the different stages of the adsorption process, the content of entrapped water together with the conformation of the polyelectrolyte can be estimated.

The few points in the beginning of the curves in Figure 13 correspond to the initial contact between polymer and surface and they are neglected from the layer structure analysis. When considering the slow viscoelastic changes it is more interesting to investigate the $\Delta D/\Delta f$ changes after the fast initial adsorption stage.

Regardless of the ionic strength of the system, the curves are rather similar for the low charged C-PAM indicating a fairly similar structure of the adsorbed layer, see Figure 13. This is as expected since this polymer is substantially coiled already at low electrolyte concentrations. An increase in ionic strength generates a slightly more compact structure. However, the conformation of this polyelectrolyte is moderately extended in to the solution phase regardless of the ionic strength. In the case of C-PAM at high ionic strength two slopes can be distinguished from the adsorption data. At the end of the adsorption the slopes turns to be more gentle indicating better packing of the C-PAM molecules. As time proceeds the extended loops and tails become more coiled, and part of the bounded water is released from the layer and the layer conformation becomes denser.

The slope of the $\Delta D/\Delta f$ curve for the highly charged PDADMAC in 1 mM NaCl shown in Figure 13 is almost zero indicating an increase in mass while the layer rigidity stays relatively constant. The conformation of the layer does not change during the adsorption but the layer becomes denser as more polymer fills the surface. The change in dissipation is higher than intuitively would be expected for the highly charged PDADMAC. The reason for the moderately dissipative PDADMAC layer is the low amount of

anionic sites on the cellulose surface for the polymer to attach to. As a consequence, PDADMAC forms a water containing layer with trains and tails. Increase in ionic strength leads to more coiled conformation and a more packed structure. The adsorbed amount considerably increases and the perfectly linear $\Delta D/\Delta f$ relationship indicates a dense and compact PDADMAC layer.

Discussion

Our results show that using the LB-technique with horizontal dipping procedure, a smooth and reproducible cellulose film can be deposited on polystyrene-coated quartz crystals. The LB-technique is slow and needs a special computerised trough system. However, the film deposition is better controlled when compared to the quick and simple spin-coating technique. We found that 15 dipping cycles produced a thin, evenly distributed and fully covering cellulose layer. The film is rigidly attached film and stable also at high ionic strengths and, hence, is well suitable as a substrate for adsorption studies with the QCM-D.

When using cellulose model surfaces, pure cellulose interactions can be investigated. With this approach, in contrast to using wood fibres, no interfering traces from hemicelluloses, extractives or lignin are present. Although a real pulp fibre consists of the materials mentioned above, our intention is to study the affinities of each of these components separately in order to increase our understanding of the important interactions between cellulose and the other components present in wood fibres. The methods to prepare the model surfaces for lignin and extractives are described elsewhere (Tammelin et al. 2005). The cellulose surface developed in this investigation is a good model for studying interactions in systems consisting of mainly pure cellulose having a very low charge. Native cellulose has almost no charge and, for instance, the negative charge of fully bleached kraft pulp is relatively low.

We found that the TMSC slowly degraded during storage, especially if it was exposed to sunlight or humidity. When the degree of silylation had decreased below a certain level, good transfer ratios were no longer obtained. In these cases the transfer ratio was sometimes negative when

bringing the crystal into contact with the water surface indicating that the film detached from the crystal. Thus, the transfer ratio is a good measure of the success of deposition. By following the transfer ratio during LB-deposition it was possible to ensure that the quality of the film to be used in QCM-D measurements was always adequate. This opportunity to check the film quality already during preparation is a clear advantage of the LB technique compared to spin-coating and casting methods.

Holmberg et al. (1997) found that the thickness of ten LB deposited cellulose layers in air was about (4 ± 0.5) nm when measured with the surface force apparatus and (5 ± 1.2) nm when measured by ellipsometry. After swelling of the film in aqueous solution the thickness was increased by about 40%. In the present study the thickness of the cellulose film was not determined, but rough values could be estimated from AFM images. After 3 dipping cycles the surface was not fully covered by cellulose and the depth at maximum determined from AFM image, using the Nano-scope image processing depth profiling tool was about 2.3 nm (Figure 6). Accordingly, after 15 deposition cycles of cellulose the film should have a thickness of about 11.5 nm. From the thickness values reported earlier (Holmberg et al. 1997) a corresponding thickness of 12–15 nm could be calculated, depending on the analysing technique used. Thus, the estimated thickness values obtained in this investigation are well in accordance with earlier results.

Assuming that the mass change detected after water addition onto the crystal originates from the film's capability to uptake water, the water content of the fully swollen films can be calculated. Assuming that the film is rigid, the total mass of swollen film can be calculated from the Sauerbrey equation (Equation 1). At the stage where the film is regarded as fully swollen (Figure 9), the amount of water inside the film is about 2.2 mg m^{-2} .

The approximations underlying the Sauerbrey equation are valid since the dissipation change is low ($\Delta D < 1 \cdot 10^{-6}$) and the frequency changes follow the order of the overtone (–12 Hz at 5 MHz, –38 Hz at 15 MHz, –63 Hz at 25 MHz and –94 Hz at 35 MHz). This result indicates a rigid layer where the water has penetrated into the small cavities in the cellulose network and it is

oscillating with the cellulose, without significantly changing the layer's viscoelastic properties.

If the thickness had increased by 40%, as found by Holmberg et al. (1997), the film thickness would have increased from 11.5 to 16.4 nm and the maximum amount of water inside the film would have been 4.9 mg m^{-2} , corresponding to a frequency change (according to Equation 1) of –83 Hz at 15 MHz.² As Figure 10 shows, the final change in frequency was only –38 Hz at 15 MHz. The mass increase on the crystal is mainly due to water penetration but also slight swelling/deswelling behaviour is detected since dissipation decreases at higher ionic strengths (1 and 10 mM NaCl). However, in the frequency range of 5–35 MHz, the cellulose film behaves as a fully elastic film also at higher ionic strengths, which shows that the film is stable and rigid.

The reason for the differences in the amounts of water imbibed after swelling analysed by SFA (Holmberg et al. 1997), ellipsometry (Holmberg et al. 1997) and QCM-D is still unclear, but it is well known that different techniques may give very different values for the thickness of polymer films (Fleer et al. 1993, p. 43). SFA and ellipsometry are static measuring methods while during QCM-D measurement the crystal oscillates at a high frequency. Moreover, ellipsometry and QCM-D do not give absolute thickness or mass values, they are only estimated or calculated from models using other quantities such as refractive index or frequency change. It is noteworthy that, although the thickness values obtained by different techniques vary, the observed trends in the swelling behaviour are the same. The low swelling observed is in agreement with the results obtained by Fält et al. (2003) for a spin-coated low charge cellulose film and also with observations for wood fibres with low charge (Laine 1994).

According to the theory (Fleer 1993) the maximum adsorbed amount of polyelectrolyte on an oppositely charged surface should be lower, the higher its charge density is because less polymer is required for charge neutralisation and the adsorbed layer is flatter. Addition of electrolyte weakens the electrostatic interactions of the system which has two consequences. On the one hand, the

²These values were obtained by calculating the mass of a cylinder of water with height of 4.9 nm and area of $7.85 \times 10^{-5} \text{ m}^2$ (the area of the quartz crystal)

attraction between the polyelectrolyte and the oppositely charged surface is screened, and on the other hand the osmotic pressure, which makes the polyelectrolyte molecule swell, decreases causing an decrease in the radius of the molecule (repulsion between the charged segments decreases). As shown in Figure 12 both polyelectrolytes behave exactly this way. At low ionic strength more C-PAM is adsorbed when compared to PDADMAC. Increase in ionic strength (10 mM NaCl) reduces the persistence length of the polymer and more polymer fit on the surface. At high ionic strength (100 mM NaCl) the adsorption of PDADMAC still increases but the adsorbed amount of C-PAM is lowered.

According to our knowledge the polyelectrolyte adsorption on cellulose has not been studied using QCM-D. However, the results are well in accordance with earlier studies of the effect of electrolyte on polyelectrolyte adsorption on kraft fibres (Lindström and Wågberg 1983; Wågberg 2000). They also found that an increase in ionic strength screens electrostatic forces, the polymer becomes coiled and low charged polymer adsorbs less due to the disappeared attraction towards the surface. Highly charged PDADMAC still adsorbs since these interactions are not totally screened in 100 mM NaCl. Horvath (2003) showed that the adsorbed amount of PDADMAC on bleached softwood kraft pulp do not decrease until the NaCl concentration exceeds 1 M.

When comparing the $\Delta D/\Delta f$ curves for C-PAM in Figure 13 at different ionic strengths it is not evident that the formed layer is less strongly bound on the cellulose surface at high ionic strength due to the fact that the dissipation factor is more or less the same as it is at low ionic strength. The other equally important factor, which has an effect on the mass change detected, is the amount of water coupled to the polymer film. When the polyelectrolyte molecule contracts, the water expels from the layer, and the mass on the crystal surface decreases. A slight decrease in dissipation might be due to the more compact and densely packed polymer conformation. We can only speculate about the strength of the bonding between polymer and the cellulose surface on the basis of these results. A more detailed analysis of the viscosity and elasticity of the formed layers and an analysis of hydrodynamic thickness would further clarify the layer

properties. We intend to do this analysis in a forthcoming publication.

We believe that this LB-cellulose model surface enables a safe interpretation of experimental results due to its uniformity in morphology and structure and its stability and rigidity under various conditions in the liquid phase. Variations originating from the cellulose surface itself are minimised, which is very important when dealing with such sensitive analysis methods as QCM-D. Previous interaction studies between xylan and cellulose have also showed the feasibility of this particular model surface (Paananen et al. 2003, p. 269).

Conclusions

The LB-technique is a suitable method to produce thin and smooth cellulose films on hydrophobic polystyrene coated QCM-D crystals. By using a horizontal dipping procedure and a sufficient number of dipping cycles a uniformly distributed cellulose film is obtained. This cellulose model surface was primarily developed to fulfil the demands of adsorption studies performed with the QCM-D instrument, but it is also useful in other analysis techniques where a smooth surface is needed, e.g. in surface force measurements performed with AFM. The proper use of the LB-cellulose surface requires accounting for the slow stabilising and swelling of the cellulose film and the effects of different conditions such as ionic strength and pH affect the behaviour of the cellulose film. The adsorption experiments conducted on LB-cellulose showed the feasibility of the model surface. The adsorbed amount of cationic polymer and the physical properties of the adsorbed layers were repeatable. The dependence of the adsorption and layer properties on charge density of the polyelectrolyte and ionic strength were well in accordance with results obtained for polymer adsorption on pulp fibres. With the QCM-D instrument it was possible to obtain new, interesting information about the layer properties of the adsorbed polyelectrolyte.

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References

- Buchholz V., Wegner G., Stemme S. and Ödberg L. 1996. Regeneration, derivatization and utilization of cellulose in ultrathin films. *Adv. Mater.* 8: 399–402.
- Carlsson G., Ström G. and Annergren G. 1995. Water sorption and surface composition of untreated or oxygen plasma-treated chemical pulps. *Nord. Pulp Pap. Res. J.* 10: 17–23.
- Cooper G.K., Sandberg K.R. and Hinck J.F. 1981. Trimethylsilyl cellulose as precursor to regenerated cellulose fiber. *J. Appl. Polym. Sci.* 26: 3827–3836.
- Edgar C.D. and Gray D.G. 2003. Smooth model cellulose I surfaces from nanocrystal suspensions. *Cellulose* 10: 299–306.
- Fleer G.J., Cohen Stuart M.A., Scheutjens J.M.H.M., Cosgrove T. and Vincent B. 1993. *Polymers at Interfaces*. Cambridge, Chapman & Hall, University Press.
- Flory P.J. 1953. *Principles of Polymer Chemistry*. Ithaca Cornell University Press, New York.
- Fält S., Wågberg L. and Vesterlind E-V. 2003. Swelling of model films of cellulose having different charge densities and comparison to the swelling behavior of corresponding fibers. *Langmuir* 19: 7895–7903.
- Fält S., Wågberg L., Vesterlind E-V. and Larsson P.T. 2004. Model films of cellulose II – improved preparation method and characterization of the cellulose film. *Cellulose* 11: 151–162.
- Geffroy C., Labeau M.P., Wong K., Cabane B. and Cohen Stuart M.A. 2000. Kinetics of adsorption of polyvinylamine onto cellulose. *Colloids Surf. A* 172: 47–56.
- Greber G. and Paschinger O. 1981. Silyl-derivate der cellulose. *Das Papier* 35: 547–554.
- Gunnars S., Wågberg L. and Cohen Stuart M.A. 2002. Model films of cellulose: I Method development and initial results. *Cellulose* 9: 239–249.
- Holmberg M., Berg J., Stemme S., Ödberg L., Rasmusson J. and Claesson P. 1997. Surface force studies of Langmuir–Blodgett cellulose films. *J. Colloid Interface Sci.* 186: 369–381.
- Horvath A.E. 2003. *Appropriate Conditions for Polyelectrolyte Titration to Determine the Charge of Cellulosic Fibers*. Licentiate Thesis, Royal Institute of technology, Stockholm, Sweden.
- Höök F., Rodahl M., Brzezinski P. and Kasemo B. 1998. Energy dissipation kinetics for protein and antibody–antigen adsorption under shear oscillation on a quartz crystal microbalance. *Langmuir* 14: 729–734.
- Johansson L.-S. 2002. Monitoring fibre surfaces with XPS in papermaking processes. *Microchim. Acta* 138: 217–223.
- Johansson L.-S., Campbell J., Koljonen K., Kleen M. and Buchert J. 2004. On surface distributions in natural cellulosic fibres. *Surf. Interface Anal.* 36: 706–710.
- Johansson L.-S., Campbell J.M., Koljonen K. and Stenius P. 1999. Evaluation of surface lignin on cellulose fibers with XPS. *Appl. Surf. Sci.* 144–145: 92–95.
- Koljonen K., Österberg M., Johansson L.-S. and Stenius P. 2003. Surface chemistry and morphology of different mechanical pulps determined by XPS and AFM. *Colloids Surf. A* 228: 143–158.
- Kontturi E., Thüne P.C. and Niemantsverdriet J.W.H. 2003. Cellulose model surfaces – simplified preparation by spin coating and characterization by X-ray photoelectron spectroscopy, infrared spectroscopy, and atomic force microscopy. *Langmuir* 19: 5735–5741.
- Laine J., Buchert J., Viikari L. and Stenius P. 1996. Characterization of unbleached kraft pulps by enzymatic treatment, potentiometric titration and polyelectrolyte adsorption. *Holzforschung* 50: 208–214.
- Laine J., Stenius P., Carlsson G. and Ström G. 1994. Surface characterization of unbleached kraft pulps by means of XPS. *Cellulose* 1: 145–160.
- Lee S., Virtanen J.A., Virtanen S.A. and Penner R.M. 1992. Assembly of fatty acid bilayers on hydrophobic substrates using a horizontal deposition procedure. *Langmuir* 8: 1243–1246.
- Lindström T. and Wågberg L. 1983. Effects of pH and electrolyte concentration on the adsorption of cationic polyacrylamides on cellulose. *Tappi J.* 66: 83–85.
- Merta J., Tammelin T. and Stenius P. 2004. Adsorption of complexes formed by cationic starch and anionic surfactants on quartz studied by QCM-D. *Colloids Surf. A* 250: 103–114.
- Neuman R.D., Berg J.M. and Claesson P.M. 1993. Direct measurement of surface forces in papermaking and paper coating systems. *Nord. Pulp Pap. Res. J.* 8: 96–104.
- Österberg M. 2000. The effect of a cationic polyelectrolyte on the forces between two cellulose surfaces and between one cellulose and one mineral surface. *J. Colloid Interface Sci.* 229: 1–8.
- Paananen A., Österberg M., Rutland M., Tammelin T., Saari-nen T., Tappura K. and Stenius P. 2003. Interaction between cellulose and xylan – An AFM and QCM study. In: Gaten-holm P. and Tenkanen M. (eds.), *864Hemicelluloses: Science and Technology*, American Chemical Society. ACS Symp. Ser., Washington, DC, pp. 269–290.
- Petty M.C. 1996. *Langmuir–Blodgett Films. An Introduction*. Cambridge University Press, Cambridge.
- Q-Sense D300 User Manual, Q-Sense AB 2000.
- Rehfeldt F. and Tanaka M. 2003. Hydration forces in ultrathin films of cellulose. *Langmuir* 19: 1467–1473.
- Roberts G. 1990. *Langmuir–Blodgett Films*. Plenum Press, New York.
- Rodahl M., Höök F., Fredriksson C., Keller C.A., Krozer A., Brzezinski P., Voinova M. and Kasemo B. 1997. Simultaneous frequency and dissipation factor QCM measurements of biomolecular adsorption and cell adhesion. *Faraday Discuss* 107: 229–246.
- Rodahl K., Höök F., Krozer A., Brzezinski P. and Kasemo B. 1995. Quartz crystal microbalance setup for frequency and Q-factor measurements in gaseous and liquid environments. *Rev. Sci. Instrum.* 66: 3924–3930.
- Rodahl M. and Kasemo B. 1996. On the measurement of thin liquid overlayers with the quartz-crystal microbalance. *Sensors Actuators A* 54: 448–456.

- Schaub M., Wenz G., Wegner G., Stein A. and Klemm D. 1993. Ultrathin films of cellulose on silicon wafers. *Adv. Mater.* 5: 919–922.
- Tammelin T., Merta J., Johansson L-S. and Stenius P. 2004. Viscoelastic properties of cationic starch adsorbed on quartz studied by QCM-D. *Langmuir* 20: 10900–10909.
- Tammelin T., Österberg M., Saarinen T., Johansson L-S. and Laine J. 2005. Development of model surfaces for different pulp fibre components. The 13th ISWFPC Conference Proceedings, vol. 2, 16–19 May 2005, Auckland, New Zealand, pp. 59–66.
- Voinova M., Rodahl M., Jonson M. and Kasemo B. 1999. Viscoelastic acoustic response of layered polymer films at fluid-solid interfaces: continuum mechanics approach. *Phys. Scr.* 59: 391–396.
- Wågberg L. 2000. Polyelectrolyte adsorption onto cellulose fibres – A review. *Nord. Pulp Pap. Res. J.* 15: 586–597.