Interactions of a cationic cellulose derivative with an ultrathin cellulose support

Tamilselvan Mohan [a], Cíntia Salomão Pinto Zarth [b], Aleš Doliška [a], Rupert Kargl [c], Thomas Grießer [d], Stefan Spirk [a,*], Thomas Heinze [b,1], Karin Stana-Kleinschek [a,1]

[a] Laboratory for Characterization and Processing of Polymers, Faculty of Mechanical Engineering, University of Maribor, Smetanova 17, SI-2000 Maribor, Slovenia
[b] Institute for Organic Chemistry and Macromolecular Chemistry, Centre of Excellence for Polysaccharide Research, Friedrich Schiller University of Jena, Humboldtstraße 10, D-07743 Jena, Germany
[c] Institute of Chemistry, Karl-Franzens-University Graz, Heinrichstraße 28/III, A-8010 Graz, Austria
[d] Chair of Chemistry of Polymeric Materials, University of Leoben, Otto-Glöckel-Straße 2, A-8700 Leoben, Austria

ARTICLE INFO

ABSTRACT

The adsorption behavior of cellulose-4-[*N*-methylammonium]butyrate chloride (CMABC) on two hydrophilic substrates is studied, namely nanometric cellulose model thin films and silicon dioxide substrates. The adsorption is quantified in dependence of electrolyte concentration and pH value using a quartz crystal microbalance with dissipation (QCM-D). In case of CMABC, at high ionic strengths (25–100 mM NaCl) high adsorption is observed at pH 7 (Δf_3: -15 to -17 Hz) while at lower ionic strengths (1–10 mM) less CMABC (Δf_3: -2 to -12 Hz) is deposited on the cellulose surfaces as indicated by the frequency changes using QCM-D. A change in pH value from 7 to 8 reveals an increase in adsorption. Atomic force microscopy shows that the coating of cellulose thin films with CMABC changes the morphology from a fibrillar to a particle like structure on the surface. The surface wettability with water increases with an increasing amount of CMABC on the surface compared to neat cellulose model films. At lower pH values (3 and 5), CMABC does not adsorb onto the cellulose model thin films. XPS is used to validate the results and to determine the nitrogen content of the surfaces. In addition, adsorption of CMABC onto another hydrophilic and negatively charged substrate, silicon dioxide coated quartz crystals, cannot be detected at different pH values and electrolyte concentrations as proven by QCM-D.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

In the past years, there has been growing interest in the development of biomimetic materials based on polysaccharides (Ishimaru & Lindström, 1984; Teeri, Brumer, Daniel, & Gatenholm, 2007; Zhou, Rutland, Teeri, & Brumer, 2007). In particular, cellulosic materials offer several promising perspectives for the design and preparation of such materials due to their intrinsic properties. It is known that the properties of cellulosic fibers such as mechanical strength or biocompatibility can be altered during chemical modifications. One methodology to overcome a disadvantageous harsh chemical treatment is to perform a compatibilization, which is usually done by coating cellulose fibers with structurally similar but water soluble derivatives (Christiernin et al., 2003; Eronen, Junka, Österberg, & Laine, 2011; Fras Zemljic, Stenius, Laine, & Stana-Kleinschek, 2011; Kondo, Koschella, Heublein, Klemm, & Heinze, 2008). In this context, the most commonly used material is carboxymethyl cellulose (CMC), which can be immobilized on different kinds of cellulose based supports (Liu, Choi, Gatenholm, & Esker, 2011). In many cases, the approach toward the attachment of CMC has been very pragmatic, for instance by using click chemistry or enzymes (Brumer, Zhou, Baumann, Carlsson, & Teeri, 2004; Filpponen et al., 2012). Moreover, a huge amount of technical studies does exist which use CMC or xyloglucans for the improvement of the properties of papers and fibers (Ahrenstedt, Oksanen, Salminen, & Brumer, 2008; Blomstedt, Kontturi, & Vuorinen, 2007; Fras Zemljic, Stenius, Laine, & Stana-Kleinschek, 2008; Laine et al., 2000; Laine, Lindström, Nordmark, & Risinger, 2000, 2002; Rakkolainen et al., 2009). In almost all of these studies, the adsorption can be controlled by variation of electrolyte concentration and pH value. However, the monitoring of adsorption on real samples such as fibers is sometimes tricky, laborious and requires a combination of analytical techniques. A more elegant way to investigate the adsorption behavior of water soluble cellulose derivatives onto a solid cellulose substrate is the use of cellulose model thin films in combination with a highly surface sensitive technique such as a quartz crystal microbalance with dissipation (QCM-D). The QCM-D method allows a monitoring of the adsorption process in real time and in situ, which reduces experimental errors in the course of the analysis, while providing high sensitivity (resolution: ∼0.1 Hz; ca. 2 ng cm^{-2}).

Amorphous cellulose model films can be prepared by exposing spin coated trimethysilyl cellulose (TMSC) to vapors of hydrochloric acid (Kontturi, Thüne, & Niemantsverdriet, 2003; Mohan et al., 2011; Schaub, Wenz, Wegner, Stein, & Klemm, 1993). Recently, the kinetics of this conversion was investigated by means of X-ray reflectivity (Kontturi & Lankinen, 2010), Raman spectroscopy (Woods, Petkov, & Bain, 2011), and QCM-D (Mohan, Spirk, Kargl, Doliška, Ehmann, et al., 2012) and it was shown that the amorphous nature of these films is also retained upon heating (Mohan, Spirk, Kargl, Doliska, Vesel, et al., 2012). Potential applications of cellulose model films include polyelectrolyte adsorption (Liu et al., 2011), enzymatic digestion (Cheng et al., 2011; Suchy et al., 2011; Mohan, Kargl, Doliška, et al., 2012) and biomolecule immobilization (Kargl, Mohan, Köstler, et al., 2012; Löscher, Ruckstuhl, Jaworek, Wegner, & Seeger, 1998; Mohan, Kargl, Köstler, et al., 2012; Orelma, Filpponen, Johansson, Laine, & Rojas, 2011; Orelma, Teerinen, Johansson, Holappa, & Laine, 2012), to mention just a few. While anionic (at pH 7) CMC has been used to immobilize biomolecules on such films (Mohan, Kargl, Köstler, et al., 2012), the use of cationic cellulosic polymers has not been demonstrated so far for this purpose. However, positively charged surfaces possess an enormous potential regarding the immobilization of biomolecules such as DNA and proteins (Orelma et al., 2011). Therefore, we became interested whether we can control the adsorption behavior of a water soluble cationic cellulose derivative onto thin solid cellulose supports. In this paper, the adsorption behavior of cellulose-4-[N-methylammonium]butyrate chloride (in the following referred to as cationic cellulose or CMABC) on cellulose substrates is investigated as a function of electrolyte concentration and pH value of the polymer solution. The results are set into contrast with the adsorption of CMABC on silicon dioxide substrates. For this purpose, a quartz crystal microbalance with dissipation (QCM-D) is employed to quantify the amount of deposited cationic cellulose.

2. Experimental

2.1. Materials and methods

Trimethylsilyl cellulose (TMSC), with a degree of substitution (DS) of 2.55 with $M_w = 175.000$ g mol^{-1}, and $M_n = 36.000$ g mol^{-1} was used as starting material for the cellulose model film preparation (Köhler, Liebert, & Heinze, 2008). Cellulose-4-[N-methylamino]butyrate hydrochloride with degree of substitution (DS) of 0.86 and degree of polymerization (DP) of 415 (DP$_n$) and 1188 (DP$_w$), denoted in this work as cationic cellulose (CMABC), was synthesized from cotton linters (Fluka) via the ring-opening reaction of N-methyl-2-pyrrolidone (NMP, Acros) with p-toluenesulfonyl chloride (TosCl, Fluka) as previously reported (Zarth, Koschella, Pfeifer, Dorn, & Heinze, 2011). QCM-D gold (QSX-301) and SiO$_2$ coated crystals (QSX-303) were purchased from LOT-Oriel (Germany). Sodium chloride (NaCl, $\geq$99.0%) was obtained from Sigma–Aldrich. A MilliQ water system was the source of pure water (resistivity = 18.2 MΩ cm at 25 °C) used for sample preparation and for measurements. For the QCM-D measurements, cellulose-4-[N-methylamino]butyrate hydrochloride ($c = 1$ mg ml^{-1}, native pH: 4) is dissolved in NaCl electrolyte solution (1, 10, 25, 50, 100 mM) and adjusted to different pH values (3, 5, 7, 8) using 0.1 M HCl and 0.1 M NaOH, respectively.

2.2. Substrate cleaning and film preparation

In the course of the cleaning procedure, the Au coated QCM sensors were soaked in a mixture of H$_2$O/H$_2$O$_2$ (30 wt.%)/NH$_4$OH (5:1:1, v/v/v) for 10 min at 70 °C, then immersed in a "piranha" solution containing H$_2$O$_2$ (30 wt.%)/H$_2$SO$_4$ (1:3, v/v) for 60 s, followed by rinsing with water and finally dried in a stream of nitrogen. For cellulose film preparation, TMSC (10 g l^{-1}) was dissolved in toluene and 50 μl of the solution were deposited on the static Au-crystal and subjected to spin coating ($v = 4000$ rpm, $a = 2500$ rpm s^{-1}, $t = 60$ s). The regeneration of the spin coated TMSC to cellulose was performed by vapor phase hydrolysis according to a modified literature procedure (Kontturi et al., 2003). A detailed description of the spin coating and regeneration procedure can be found elsewhere (Mohan et al., 2011; Mohan, Spirk, Kargl, Doliska, Vesel, et al., 2012). Resulting cellulose film thickness is 25 ± 1 nm.

The SiO$_2$ coated QCM sensors were cleaned by treatment with a "piranha" solution for 60 s, rinsing with water and drying in a stream of nitrogen.

2.3. Quartz crystal microbalance with dissipation (QCM-D)

A QCM-D instrument (model E4) from Q-Sense, Gothenburg, Sweden was used. The instrument simultaneously measures changes in the resonance frequency (Δf) and energy dissipation (ΔD) when the mass of an oscillating piezoelectric crystal changes upon adsorption on the crystal surface (Marx, 2003; Rodahl et al., 1997). Dissipation refers to the frictional losses that lead to damping of the oscillation depending on the viscoelastic properties of the material. Thus, by measuring the frequency and dissipation it is possible to analyze the state of molecular layers bound to the sensor surface during the adsorption and/or desorption process. For a rigid adsorbed layer that is fully coupled to the oscillation of the crystal, Δf_n is given by the Sauerbrey equation

$$\Delta m = -\frac{C \Delta f_n}{n} \tag{1}$$

where Δf_n is the observed frequency shift, C is the Sauerbrey constant (17.7 ng Hz^{-1} cm^{-2} for a 5 MHz crystal), n is the overtone number ($n = 1, 3, 5, \ldots$), and Δm is the change in mass of the crystal due to the adsorbed layer. The mass of a soft film is not fully coupled to the oscillation and the Sauerbrey relation is not valid since energy is dissipated in the film during the oscillation. The damping (or dissipation) (D) is defined as

$$D = \frac{E_{\text{diss}}}{2\pi E_{\text{stor}}} \tag{2}$$

where E_{diss} is the energy dissipated, and E_{stor} is the total energy stored in the oscillator during one oscillation cycle. The QCM-D records the change in D (ΔD) as a function of adsorption time. For the data analysis in this study, the changes in the third overtone's frequency and dissipation (Δf_3, ΔD_3) were determined.

The regenerated cellulose film attached to Au-crystals was mounted in the QCM-D chamber. Before the adsorption measurements, in each run pure MilliQ water was pumped into the chamber for 15 min to ensure the stability of the baseline frequency. In a subsequent step, MilliQ water was replaced by electrolyte solutions and equilibrated until the frequency remained at a stable level. Afterwards, the frequency was reset to zero and CMABC ($c = 1$ mg ml^{-1}, dissolved in MilliQ water with electrolyte at adjusted pH) was allowed to adsorb onto the cellulose surfaces for 90 min. In the end, the surfaces were rinsed with electrolyte solutions (30 min) and MilliQ water (30 min) to remove loosely attached material and the changes in frequency and dissipation were calculated. All experiments were conducted in continuous flow mode at a flow rate of 0.1 ml min^{-1}. The temperature was kept at 21.0 ± 0.1° C for the duration of the measurement. All measurements were repeated three times in order to ensure the reproducibility of the results. Experiments have been performed at pH values of 3, 5, 7 and 8, respectively, for all substrates.