Arrangements of cationic starch of varying hydrophobicity on hydrophilic and hydrophobic surfaces

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ABSTRACT

Arrangements of cationic starches hydrophobized by acetylation (CS-acet) deposited from aqueous electrolyte solutions onto hydrophilized and hydrophobized silica surfaces were investigated by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and contact angle measurements. The influence of electrolyte composition, acetylation degree of cationic starch (DS_{ACET}), and deposition method was examined. On a hydrophobic substrate, CS-acet formed an open film with structure strongly dependent on DS_{ACET} and electrolyte composition of the solution. On a hydrophilic substrate, acetylation increased the hydrophobicity of the film when the starch was deposited by adsorbing. When deposition was made by spin coating, i.e., the CS-acet was forced onto the substrate, the hydrophobic tuning by acetylation was lost. The films deposited by spin coating were thicker and considerably rougher than those deposited by adsorbing.

1. Introduction

Biopolymer films of various thicknesses and morphologies have recently gained considerable attention. For instance, films of chitosan [1–3], cellulose [4–6], cellulose derivatives [7–10], and starch [11–13] for diverse purposes have been widely studied. Chemical modification of the biopolymer has a direct effect for film formation, both in case of thick films [14] as well as in the ultrathin regime [8,15]. Film formation depends strongly also on the deposition method. For example, in case of cellulose, films deposited by coagulation/regeneration [16] are very different from those prepared by spin coating [17] or Langmuir–Blodgett technique [18] and subsequent regeneration. In this fundamental study, the effect of chemical modification and deposition method on thin film formation of cationic starch has been investigated.

Starch is a natural and sustainable precursor for surface modifying polymers because of its availability, low price, biodegradability, non-toxicity, and chemical modifiability [19–21]. It is widely used e.g., in food, medical, textile, and paper industries [19]. Understanding the fundamental interactions taking place in starch film formation is essential for developing further applications for more complex systems. For instance, ultrathin layers of modified starch have a potential to substitute conventional surface sizing in papermaking [22].

To study the effect of chemical modification on ultrathin film formation, we have applied three cationic starch derivatives with varying degrees of hydrophobicity as coating materials. Arrangements of these starches were studied on hydrophilic and hydrophobic silica surfaces, which are well-defined substrates in surface science. Two distinct deposition methods, free adsorbing and forced spin coating, are likely to induce different molecular arrangements of the polymer on the substrate. Here, correlations between the molecular arrangements and film formation as well as the properties of film were evaluated. Also the influence of added electrolyte in starch solution on film formation was studied.

2. Materials and methods

2.1. Materials

2.1.1. Cationic starches

Three cationic potato starch derivatives with constant degree of cationization (0.15) and varying degrees of acetylation were used. Potato starch is a $(1 \rightarrow 4)$ linked poly-α-D-glucan and is a native blend of linear amylose ($\sim$25%) and the $(1 \rightarrow 6)$ branched amylopectin ($\sim$75%). Due to the high M_w of amylopectin, M_w of starch may reach tens of millions. Modification, such as cationization or acetylation, generally decreases the M_w of starch to some extent. The choice of samples in this study is summarized in Table 1. Cationic unacetylated potato starch (CS-acet0) was supplied by Ciba Specialty Chemicals (Raisio, Finland). A batch of cationic

Table 1
Properties of the starches studied.

	CS-acet0	CS-acet1	CS-acet2
Degree of cationization (DS_{CAT})	0.15	0.15	0.15
Degree of acetylation (DS_{ACET})	0	0.9	2.4
Reduced viscosity of 2 wt% solution (dl/g)[a]	5.04	2.02	1.74

[a] Measured in 0.1 mM NaCl; varying the electrolyte or its concentration did not have a marked effect on the values (results not shown).

starch (CS-acet1) was acetylated to a moderate degree, 0.9, and another batch (CS-acet2) to a high degree, 2.4. Chemical structures of the cationized and acetylated starch monomers are shown in Fig. 1.

The acetylation of cationic starch was performed according the method described in Ref. [23]. The degree of acetylation (DS_{ACET}) was determined by a titration method and confirmed by ^{1}H NMR spectroscopy as reported in Ref. [24]. The determination method involves the complete basic hydrolysis of the ester linkages and titration of the excess alkali. The degree of cationization (DS_{CAT}) for all starches was determined from the nitrogen content (N%) by the Kjeldahl method to verify that the cationic group still remains after the acetylation process (results shown in Ref. [22]).

Starch solutions: The starch was dissolved in aqueous electrolyte solution by heating and stirring the mixture in ∼90 °C for 30 min. Three different electrolyte solutions were used for each type of starch: 0.1 mM NaCl, 3 mM NaCl, and 1 mM NaHCO$_3$. All solutions were prepared at least 24 h before use. The concentration of the starch solutions used in model surface studies was 2 wt%. Independent of the electrolyte, the pH of CS-acet0 solutions was 7.9 and the pH of CS-acet1 and CS-acet2 solutions was 4.7. In addition, reduced viscosity values of the solutions are presented in Table 1.

2.1.2. Other chemicals

Distilled water was used in all experiments. NaCl, NH$_4$OH, HCl, and xylene were supplied by Merck (Darmstadt, Germany), H$_2$O$_2$ by J.T. Baker Chemicals (Deventer, The Netherlands), NaHCO$_3$, ethylene glycol, diiodomethane, and dimethyldichlorosilane by Fluka, and formamide by Sigma–Aldrich. All these chemicals were of analytical grade and were used without further purification.

2.1.3. Substrates

The SiO$_2$ surfaces used as base substrates were oxidized silicon wafers (Si 100 with a native oxide layer on top) supplied by Okmetic (Espoo, Finland).

Hydrophilic silica: The silicon wafers were cut into slides and then hydrophilized by cleaning (i) for 15 min in a boiling mixture of NH$_4$OH and H$_2$O$_2$ and (ii) for 15 min in a boiling mixture of HCl and H$_2$O$_2$. Slides were rinsed with water before and after the step (ii) and dried with nitrogen gas in the end. The treatment induces the formation of hydroxyl groups on the silica surface [25].

Hydrophobic silica: The hydrophobic silica slides were prepared by treating hydrophilized silica with solution of 20.5 µl dimethyldichlorosilane in 50 ml xylene overnight. After the treatment, the slides were rinsed with xylol and dried with pressurized air.
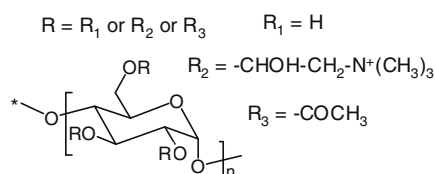
R = R$_1$ or R$_2$ or R$_3$ R$_1$ = H

OR   R$_2$ = -CHOH-CH$_2$-N$^+$(CH$_3$)$_3$

R$_3$ = -COCH$_3$

Fig. 1. Chemical structure of a modified starch monomer. All starches are cationically modified, which means a substitution by R$_2$ group to DS_{CAT} 0.15. Degree of acetylation (DS_{ACET}), i.e., substitution by R$_3$ group, is different for each starch: 0 for CS-acet0, 0.9 for CS-acet1, and 2.4 for CS-acet2.

The treatment induces the replacement of hydroxyl groups with dimethylsilyl groups on the silica surface [26].

2.2. Methods

2.2.1. Viscosity measurements

Viscosities of the 2 wt% starch solutions were determined with a computer-controlled Ubbelohde capillary viscometer system (Schott-Geräte, AVS 350). The correction factors of Hagenbach were used to calculate the real efflux times. The viscometer was cleaned using aqua regia, ion-exchanged water and distilled water. The viscometer was immersed in a bath thermostatted to 298.15 ± 0.01 K. The samples were allowed to equilibrate for 10 min in the thermostatic bath before measurements.

Several measurements were performed on each sample. The results of the viscosity measurements are presented as reduced viscosity values calculated from:

$$\eta_{red} = \frac{(t - t_0)/t_0}{c}, \tag{1}$$

where t is the measured efflux time, t_0 is the efflux time of the pure solvent, and c is the weight concentration of the polymer.

2.2.2. Deposition of polymers on substrates

Adsorbing: The substrate was immersed for 15 min in 2 wt% starch solution. The sample was then rinsed extensively with water and dried at room temperature by allowing the solvent to freely evaporate.

Spin coating: The 2 wt% starch solution was deposited on a static substrate and spin coated with a spinning speed of 2800 rpm and acceleration of ∼2000 rpm/s.

2.2.3. X-ray photoelectron spectroscopy (XPS)

A Kratos Analytical AXIS 165 electron spectrometer with a monochromatic A1 Kα X-ray source was used to analyze the elemental and chemical compositions of the sample surfaces. All spectra were collected at an electron take-off angle of 90° from sample areas less than 1 mm in diameter and using 100 W irradiation [27]. The spectra were recorded at three different spots on each sample and the analysis vacuum was monitored during the experiments with an in-situ reference sample. No X-ray induced degradation was detected during the experiments.

In this XPS study, three markers for the acetylated CSs were used (see Ref. [28]): the surface content of nitrogen (measured from low resolution spectra) and the relative abundances of C—O bonds (carbon with one bond to oxygen) and O—C=O bonds (carbon with three bonds to oxygen; acetyl group), both recorded from high resolution spectra on C 1s region and incorporated into the elemental surface concentrations.

The degree of cationization in the sample surface was determined from the ratio between detected amounts of N and C—O, by using a graph that represents the theoretical DS_{CAT} as a function of the value of the ratio N/C—O. After that, the degree of acetylation in the surface was calculated from the ratio between detected amounts of O—C=O and C—O, respectively, by using a graph that represents the theoretical DS_{ACET} as a function of the value of the ratio O—C=O/C—O.

The degrees of cationization and acetylation were determined from the XPS data only in the case of continuous films with full coverage over the substrate. In the case of films, which did not possess full coverage, the detected relative amount of silicon was used as an indication of the uncoverage of CS.

2.2.4. Atomic force microscopy (AFM)

A Nanoscope IIIa Multimode scanning probe microscope (Digital Instruments Inc., Santa Barbara, CA, USA) was used to