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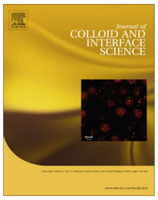

Charge regulation and energy dissipation while compressing and sliding a cross-linked chitosan hydrogel layer

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ABSTRACT

Interactions between a silica surface and a surface coated with a grafted cross-linked hydrogel made from chitosan/PAA multilayers are investigated, utilizing colloidal probe atomic force microscopy. Attractive double-layer forces are found to dominate the long-range interaction over a broad range of pH and ionic strength conditions. The deduced potential at the hydrogel/aqueous interface is found to be very low. This situation is maintained in the whole pH-range investigated, even though the degree of protonation of chitosan changes significantly. This demonstrates that pH-variations change the concentration of counterions within the hydrogel to keep the interior close to uncharged, which is similar to what has been observed for polyelectrolyte brushes. Changes in pH and ionic strength affect the adhesion force and the friction force between the silica surface and the hydrogel layer, but not the friction coefficient. This suggests that the main energy dissipation mechanism arises from processes occurring within the hydrogel layer, rather than at the silica/hydrogel interface, and we suggest that it is related to stretching of polymer chains between the cross-linking points. We also find that an increased cross-linking density, from 40% to 100%, in the hydrogel reduces the friction coefficient.

1. Introduction

Chitin is one of the most abundant polysaccharides in nature, being second only to cellulose in the amount produced annually by biosynthesis. Chitosan (CHI) is a linear β-(1,4)-linked polysaccharide that is obtained by deacetylation of chitin. One important structural feature of this polysaccharide is the presence of primary amines, providing responsive properties with respect to changes in pH and ionic strength. At low pH, the amines are protonated and chitosan is soluble in water. However, it becomes poorly soluble in water already at pH-values slightly above the pK_a. The pK_a of chitosan depends on the degree of acetylation, but is often reported to be in the order of 6.0–6.5 [1,2]. This is lower than the pK_a for the monomeric unit, glucosamine, which has a pK_a of 7.6 [3]. The pK_a value of chitosan may, however, vary when cross-linked or if it forms complexes with oppositely charged polyelectrolytes. For instance, the pK_a values of the primary amine groups of cross-linked chitosan hydrogels has been found to consist of two populations, with the major population having a significantly higher pK_a than glucosamine [4,5].

Interactions between adsorbed chitosan layers were first reported by Claesson and Ninham, who demonstrated how changes in solution pH affected interactions between preadsorbed layers on mica substrates [6]. Later, Kampf and Klein measured not only surface forces but also friction forces, and the effect of cross-linking using sodium hexametaphosphate (SHMP) [7]. In particular, they noted an increase in friction force due to cross-linking of a single adsorbed chitosan layer. In this study we explore interactions between a chitosan hydrogel and a silica colloidal probe, both under compression and shear. The preparation and characterization of our chitosan-based hydrogel layer is described in detail elsewhere [4,5]. In this paper we report how pH, ionic strength and cross-linking time affect surface forces and friction. Our study sheds light on how the nature of the layer affects long-range double-layer forces and how the surface charge density deduced from such measurements is affected by solution pH and ionic strength. The data suggests that most of the charge in the hydrogel is inter-

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nally compensated, rendering the effective surface charge density very low even when chitosan is highly charged. The friction forces observed are generally high, significantly higher than reported for a single layer of chitosan [7,8]. We discuss this finding in terms of intralayer dominated energy dissipation.

2. Experimental section

2.1. Materials

Chitosan (CHI) with a degree of deacetylation of 75–85% (M_w = 50,000–190,000 g/mol) and low molecular weight poly(acrylic acid) (PAA) (M_w = 1800 g/mol) were purchased from Sigma–Aldrich. 3-glycidoxypropyltrimethoxysilane (GPS) with 98% purity, 50 wt% glutaraldehyde aqueous solution (GA), glacial acetic acid (HAc) with 99.7% purity, acetone with 99.9% purity, sodium hydroxide (NaOH) pellets with 99.99% purity, hydrochloric acid (HCl, ACS reagent grade), sodium chloride with 99.5% purity, sodium carbonate with 99% purity and sodium bicarbonate with 99.5% purity were used as received from Sigma–Aldrich. The water was purified by employing a Milli-RO Plus unit connected to a Milli-Q Plus 185 system, and filtered through a 0.2 μm Millipak filter prior to use. The resistivity of the purified water was 18.2 MΩ cm, and its total organic carbon content did not exceed 2 ppb.

2.2. Chitosan hydrogel preparation

Thermally oxidized silicon wafers with a ≈100 nm thick silicon dioxide layer were obtained from Wafer Net, Germany. The wafers were cleaned with 2% Hellmanex (Hellma GmbH) solution for 30 min and then washed with copious amount of Milli-Q water. Clean substrates were immersed in 18% GPS/acetone solution for 22 h and then rinsed with acetone several times. The GPS coated surface was heated at 100 °C for 1 h prior to use. Chitosan (100 ppm) and PAA (200 ppm) solutions containing 30 mM NaCl were used for building polyelectrolyte multilayers by sequential adsorption. Glutaraldehyde solution (2.5 wt%) was used to cross-link chitosan in the multilayers, and 0.2 M carbonate buffer at pH 9 was employed to facilitate removal of some PAA from the cross-linked multilayers. The preparation and characterization of the chitosan hydrogel layers are described in our previous works [4,5].

2.3. Colloidal probe – atomic force microscope

Surface force and friction measurements were performed using an atomic force microscope, Nanoscope Multimode III Pico Force (Bruker). Rectangular tipless cantilevers (CSC12F, Mikromasch, Tallinn, Estonia) with approximate dimension of 250 μm in length and 35 μm in width were used. The normal and torsional cantilever spring constants were determined by thermal noise analysis as suggested by Sader et al. [9]. The lateral photodetector sensitivity, δ (V/rad), was calibrated using the method of tilting the AFM head as described by Pettersson et al. [10].

After calibration of the spring constants, the colloidal particle, a silica sphere of radius ≈10 μm, was attached to the cantilever by using an Eppendorf Micromanipulator 5171, a Nikon Optiphot 100S reflection microscope and high-temperature melting epoxy glue (Shell Epikote 1009). The particle size was measured using a Nikon Optiphot 100S reflection microscope, employing image analysis with National Instrument Vision Assistant 8.0. The cantilever carrying an attached colloidal particle was cleaned by UV irradiation for 15 min to remove any organic residue on the tip. The fused silica liquid cell was cleaned with 2% Hellmanex for 30 min followed by rinsing with water prior to use.

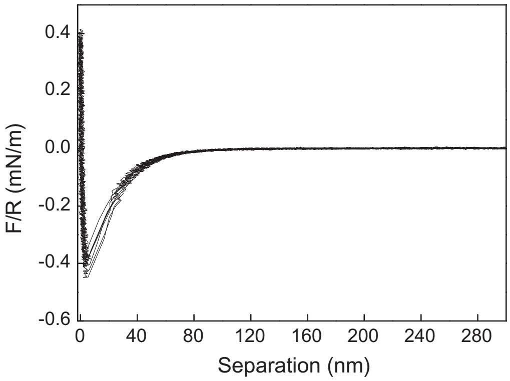

Fig. 1. Eight consecutive approach force curves between a spherical silica probe and a 20 min cross-linked chitosan hydrogel grafted to a silica wafer measured across 0.1 mM NaCl at pH 5.7. The force is normalized by the silica particle radius.

The surface forces were measured with a constant approach and retraction speed of 400 nm/s. Fig. 1 shows the typical reproducibility of the force measurements, and in the remaining figures we show one representative force curve for each condition explored. The force, F, normalized by the sphere radius, R, is equal to $2\pi G_f$, where G_f is the free energy of interaction per unit area between two flat surfaces according to the Derjaguin approximation [11]. After changes in pH or salt concentration the system was left to equilibrate for 30 min before new measurements were performed.

Friction force measurements were performed by sliding the surfaces backwards and forwards while registering the cantilever torsional angle [12,13]. The process was repeated ten times at each normal load using a sliding length of 10 μm in each direction and a scan rate of 1 Hz, giving a sliding speed of 20 μm/s.

2.4. Data analysis

The normal deflection sensitivity was determined from the measurement between two hard silica surfaces in 1 mM NaCl at pH 5.7, and the value determined for this system was used in the analysis of all force curves [14]. The long-range double-layer forces encountered in this study were analyzed in the non-linear Poisson–Boltzmann approximation, using either constant surface charge or constant surface potential boundary conditions [15,16] as outlined in a recent publication [17].

The calculations require input values for the electrostatic double-layer potential at the two surfaces and the Debye screening length. In all cases we used the Debye screening length corresponding to the known salt concentration of the solution, and the potential at the silica-solution interface was taken from values reported in the literature. This leaves the double-layer potential at the hydrogel-solution interface as the only free parameter, which can be determined by adjusting the calculated forces to the measured forces at large separations.

3. Results and discussion

We consider two types of hydrogels, both prepared by sequential adsorption of chitosan and PAA on a silica substrate. The multilayer consists of 11 layers of chitosan and 10 layers of PAA, and will be referred to as 11/10 CHI/PAA. These multilayers were subsequently cross-linked to produce two kinds of hydrogels with different cross-linking densities. The two types of hydrogels will be referred to as HC-hydrogels and LC-hydrogels, where HC and LC stand for high cross-linking (100% cross-linking density) and low cross-linking (40% cross-linking density), respectively. Some key properties of these hydrogel layers are summarized in Table 1