Multilayers of Low Charge Density Polyelectrolytes on Thin Films of Carboxymethylated and Cationic Cellulose

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Abstract

Multilayers with low charge density polyelectrolytes assembled on thin films of cellulose were studied by piezoelectric microgravimetry. The substrates were produced from colloidal suspensions of cotton fibers before and after modification with cationic and anionic groups via epoxy intermediates of quaternary ammonium and carboxymethylation, respectively. Two different levels of ionicity were used for each cellulosic substrate in order to investigate the role of the supporting surface in the buildup of the multilayer. It was found that while electrostatic interactions were leading factors in the assembly of high molecular weight, low charge density polyelectrolytes, other effects such as van der Waals and secondary cooperative forces played important roles. The charge properties of the substrate and the adsorbing polymer were relevant to the behavior of the self-assembled multilayers. Sequential additions of weak polyelectrolytes formed viscoelastic layers on all cellulose substrates. Adsorption of the first layer depended heavily on the charge characteristics of the substrate while the buildup of subsequent layers was mainly affected by the outermost adsorbed polymer. The polyelectrolyte multilayer formation with highest total adsorbed mass occurred on unmodified cellulose surfaces; therefore, in the case of the low charge density polyelectrolytes studied, substrate ionicity and functionalization may not be a requirement. Finally, the effect of anionic weak polyelectrolytes added after the first adsorbed polymer pair is highlighted in the context of reported observations for polyelectrolytes of high charge density.

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Keywords
Polyelectrolyte multilayer, adsorption, cationic cellulose, anionic cellulose, cotton, adhesion, QCM

1. Introduction

Electrostatic polymer layer-by-layer assembly through non-covalent interactions was introduced in the nineties [1–5] and since then it has been applied in a number
of materials with tailored structures. Highly charged polyelectrolytes can produce charge reversal upon adsorption on oppositely charged surfaces. On the other hand, similarly charged molecules can repel each other allowing for self-regulation of adsorption and formation of a single layer. Oppositely charged molecules that are added to the system can then be adsorbed on the first layer, thereby forming a second layer. These steps can be repeated cyclically to form multilayer structures on a given substrate [1].

While good adhesion of a layer to the base substrate depends on electrostatic interactions and ionic bonds, the buildup of successive layers is mainly affected by the properties of the outer adsorbed polymer layer. In fact, the influence of the substrate is typically lost after a few layer-by-layer deposition cycles. Therefore, the conformation of a given polymer in a multilayer is controlled by the intrinsic nature of the polyelectrolyte and the conditions used during adsorption more than by the properties of the substrate [1, 6–10]. For the first five deposition steps, the amount of adsorbed polymer normally increases before leveling off [1, 11]. The surface charge of the substrate determines how long it takes to reach such condition. However, as long as the polyelectrolytes create an electrostatic equilibrium, constant growth is eventually observed [1, 7–10, 12]. In these latter cases experimental evidence of a linear increase of film thickness with the number of deposited layers, independent of the nature of the initial substrate, has been reported [11, 13–16].

A large number of polyelectrolytes have been used to create a variety of nanosstructured coatings on solid substrates [12, 17–19]. One of the most studied system is the pair poly(allylamine hydrochloride) (PAH) and poly(styrene sulfonate) (PSS) [20–24]. A number of other more complex, functionalized polyelectrolytes have also been investigated, especially to take advantage of secondary chemical interactions. Above all, one of the features of the layer-by-layer or multilayer deposition technique is that as long as the appropriate oppositely charged pair is chosen almost any charged macromolecule can be used [25].

Although electrostatic self-assembly has been widely investigated, certain details of the process are still not clearly understood. The behavior of highly charged, strong polyelectrolyte chains has attracted most of the interest in layer-by-layer adsorption, [26]. On the other hand, for weak polyelectrolytes such as polyacids or polybases, variations in pH can affect the balance of charges and, therefore, the thickness and stability of the adsorbed layers. As a consequence, most of the work with weak polyelectrolytes has centered on the effect of solution pH [6, 26, 27].

It is apparent that weak polyelectrolytes allow for a precise control over the physical characteristics of the multilayers. For example, in contrast to the case of strong polyelectrolytes which often adsorb as molecularly thin layers, weak polyelectrolytes can be deposited with a high percentage of their chains as protruding loops and tails under salt or pH conditions that minimize their charge. Therefore, much thicker polymer multilayers can be assembled, depending on the polymer concentration, pH, ionic strength, etc. [28].
Applications of polyelectrolyte multilayers in cellulosic systems have exploded in recent years [29]. However, as is the case for mineral surfaces, most of the polymer pairs investigated have consisted of strong polyelectrolytes or low molecular mass, weak polyelectrolytes. While the main findings in such endeavors have helped tremendously to understand fundamental issues in multilayer deposition, some factors still deserve attention. Therefore, the buildup of polyelectrolyte multilayer on cellulose was investigated after selecting a polymer pair that was considered relevant to papermaking and textiles. Such systems, for example, involving high molecular mass, low charge density polyacrylamides are expected to offer some interesting possibilities in the development of strong inter-fiber adhesion and bonding [30, 31]. The main objectives of this work included the elucidation of the effect of the electrostatic charge of the substrate and the first adsorbed, precursor polymer on the structure of the multilayer formed. The conditions used were such that charge reversal was unlikely to occur and therefore non-electrostatic effects were expected to be dominant.

2. Experimental

2.1. Materials and Methods

Standardized TIC-400 woven cotton fabrics (Textile Innovators, Inc., Windsor, NC) were used as a source of cellulose in all experiments. The precursor for cationization of cotton was 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHTAC) which was available as a 69% aqueous solution under the name of CR-2000 (Dow Chemical) and was used as received. Carboxymethylation of cotton was carried out with mono-chloroacetic acid, 99% (Acros Organics). The polyelectrolytes used to assemble polymer multilayers on cellulose (modified or unmodified) were random copolymers based on acrylamide and were provided as a gift by Harima Chemicals, Inc. (Japan). The weak cationic and anionic groups in the acrylamide copolymer consisted of N,N-dimethyl aminopropyl acrylamide (DMAPAA) and itaconic acid (IA), respectively.

The cationic polyelectrolyte carried 5 mol% of DMAPAA units and had a molecular mass of \(2.98 \times 10^6\) Da while the anionic polyelectrolyte carried 4 mol% of IA units and had a molecular mass of \(3.23 \times 10^6\) Da. Therefore, the macromolecules used in this study can be classified as weak polyelectrolytes of low charge density and high molecular mass. For simplicity, these polybase and polyacid will be referred to by the abbreviations of the active (charged) component, i.e., DMAPAA and IA, respectively. Aqueous stock solutions of 0.2 g/l polymer concentration were prepared using 0.1 mM sodium chloride as background electrolyte. Before use the pH of the DMAPAA and IA solutions was adjusted to 7 by addition of HCl or NaOH, as needed. At this pH the streaming potential in aqueous solution was measured to be +3 and \(-17\) mV for the cationic and anionic polyelectrolytes, respectively.
Other chemicals used included dimethyl sulfoxide, DMSO (Fisher Scientific, Pittsburgh, PA); N-methylmorpholine-N-oxide, NMMO (50 wt% concentration, Sigma-Aldrich, St. Louis, MO); polyethyleneimine, PEI (BASF, Charlotte, NC); sodium hydroxide (50 wt% aqueous solution, Fisher Scientific, Pittsburgh, PA). Polyelectrolyte solutions for charge titration consisted of aqueous solutions (0.003 and 0.0025 N) of the potassium salt of poly(vinylsulfonic acid) (PVSK, 170 kDa) and 0.002 N aqueous solution of poly(diallyldimethyl ammonium chloride) (poly-DADMAC, 400–500 kDa), both of which were supplied by Sigma-Aldrich (St. Louis, MO). All experiments were performed with deionized water from an ion-exchange system (Pureflow, Inc., Graham, NC) which was further processed in a Milli-Q® Gradient unit (Millipore) to ensure ultrapure water (resistivity greater than 18 M\(\Omega\)).

2.1.1. Cationic Cotton

Cotton fabrics (cut to squares of 30.5 cm) were made cationic by reaction with 2,3-epoxypropyl trimethyl ammonium chloride (EPTMAC) following the procedure reported elsewhere \[32, 33\]. The efficiency of cationization was found to depend on time, temperature and pH and therefore these conditions were carefully controlled. Briefly, EPTMAC was produced by mixing aqueous solutions of 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHTAC, 69%) and sodium hydroxide (50 wt%). The sodium hydroxide acted as a base catalyst for CHTAC to form EPTMAC, which is an epoxy intermediate that is reactive with cellulose. Two different CHTAC concentrations, 188 and 376 g/l, were used while keeping the same molar ratio of CHTAC to sodium hydroxide, 1:1.8 \[32\]. The reactive EPTMAC solution was pad-applied immediately on the cotton specimens at 100% wet pickup to minimize hydrolysis reactions that would otherwise reduce the effectiveness of the treatment \[34\]. The samples were then dried at 45°C and cured at 115°C for 10 min in a forced air oven. The cured fabrics were washed with cold water; neutralized with dilute acetic acid (2 g/l); washed again with cold water and centrifuged and air-dried. Finally, the specimens obtained were cut into 2.54-cm squares. Randomized samples were then cut from the cationic cotton into very small sizes and mixed for later use in polyelectrolyte titration by the streaming current and the streaming potential methods. They were also used in nitrogen elemental analysis and to manufacture thin films of cationic cellulose (see later sections).

2.1.2. Anionic (Carboxymethylated) Cotton

Cotton fabrics (cut to squares of 30.5 cm) were made anionic by carboxymethylation using a simple, two-step procedure reported elsewhere \[35, 36\]. First, the fabric samples were soaked for 10 min in 20% sodium hydroxide aqueous solution, padded to 100% wet pickup and dried at 45°C for 12 min. Separately, a solution of mono-chloroacetic acid was neutralized by a weak base, sodium carbonate, to form a sodium chloroacetate solution. Two different chloroacetate solution concentrations were prepared, 95 and 195 g/l, in order to produce two different levels of anionicity in cellulose. This was done by soaking for 5 min the pre-treated fabrics
in the respective aqueous solutions of chloroacetate, padding to 100% wet pickup, curing for 30 min at 85°C and washing with water. Acidification with 2 g/l acetic acid and washing again with water was finally performed before air-drying for storage until use. Randomized samples were cut from the carboxymethylated cotton specimens, as explained in the case of cationic cellulose.

2.1.3. Nitrogen Analysis
The nitrogen content in the fabric samples was determined using an Elemental Analyzer (Perkin-Elmer PE 2400 CHN, Norwalk, CT, USA). Soybean leaves were used to calibrate the instrument. Internal standards NBS 1572-citrus leaves and NBS 1564-wheat flour were used to confirm the calibration. The elemental analysis was based on the classical method of Pregal and Damas [37] which included the combustion of the samples in a pure oxygen environment. The products of combustion were passed through a separation zone and a thermal conductivity detector column was used to separate the gas mixture and to measure the nitrogen content. The total cationic charges were obtained by considering the difference in the percentages of nitrogen in functionalized and untreated cotton fabrics. The molar % of N per unit mass of fabric was expressed in µeq/g units.

2.1.4. Acid–Base Titration
A procedure different than the elemental analysis used for cationic cotton was employed to quantify the total negative charges of carboxymethylated (anionic) cotton fibers. The anionic content of the samples was quantitatively determined by acid–base titration adopted from previous work [38] and reported as µeq/g fabric. Briefly, small pieces (less than 3 mm × 3 mm) were cut from different parts of the treated sample and soaked overnight in 0.5% aqueous hydrochloric acid solution. Multiple filtration and washing cycles with water (until the filtrate was chloride ions free, as determined by the silver nitrate drop test) were performed and the sample obtained was dried at 105°C for 3 h. The sample was then weighed accurately to 0.25 g and soaked overnight at room temperature in 25 ml of 0.05 N NaOH aqueous solution. A blank run was also carried out (with no fabric sample). Then, both the soaked and blank samples were titrated with 0.05 N aqueous HCl solution using phenolphthalein indicator to determine the volume consumed until the end points. The difference of the volumes consumed was then used to determine the amount of negative groups in the anionic cotton.

2.1.5. Preparation of Cellulose Thin Films
Thin films of unmodified, anionic and cationic cellulose from cotton fibers were used as substrates for polyelectrolyte multilayers. Sensors used in quartz crystal microgravimetry (see later sections) consisted of gold-coated AT-cut quartz crystals (Q-Sense Inc., Sweden) that were spin-coated with cellulose solutions [39–41]. The bare gold sensors were first cleaned using a mixture of ammonium hydroxide and hydrogen peroxide and UV-ozone treatments. In the UV-ozone treatment, the incident UV light oxidized any spuriously adsorbed organic matter that might have remained on the surface of the sensor. Clean gold sensors were then immersed in
a diluted polyethyleneimine (PEI) solution before spin-coating the respective cellulose solutions. PEI was thus adsorbed from the solution onto the sensor and was used as an anchoring layer between the sensor surface and the cellulose thin film.

Spin coating the sensor with solutions of unmodified, anionic or cationic cellulose was performed to create uniform thin films. The dissolution of the samples of cotton fibers was accomplished with N-methylmorpholine-N-oxide (NMMO) solvent, which resulted in colloidal suspensions of the respective cellulose for spin-coating [39, 40]. For the purpose of facilitating dissolution in NMMO, the respective cotton fibers were cut into very small pieces, and then 0.025 g of each fiber sample was immersed in 2.5 ml water/NMMO (50% w/w) solution and heated at 115°C. When the cotton fibers were almost dissolved 7.5 ml dimethyl sulfoxide (DMSO) was added to adjust the concentration and viscosity of the mixture and to facilitate spin coating.

The cellulose solutions were spin-coated on the sensors at 5000 rpm for 40 s ( Laurell Technologies, model WS-400A-6NPP, North Wales, PA). The cellulose-coated sensors were then removed from the spin-coater and dried in an oven at 80°C for 2 h and then soaked in water for at least 4 h. Afterwards, they were washed thoroughly with water, dried with a gentle nitrogen gas jet and stored at room temperature in a clean container until use. Typical ellipsometric thicknesses and AFM RMS roughness of the obtained cellulose films were in the range of 15–30 nm and 2.5–3 nm (for 2 µm × 2 µm scan size), respectively. Before any polymer multilayer assembly, the respective cellulose-coated sensor was allowed to fully swell by immersion in water overnight.

2.1.6. Quartz Crystal Microgravimetry and Polyelectrolyte Multilayers
Adsorption of anionic and cationic polyelectrolytes to build up macromolecular multilayers onto the cellulose films was investigated by a Quartz Crystal Microbalance with Dissipation monitoring (QCM), model QCM-D300 (Q-Sense, Gothenburg, Sweden). The temperature during the experiments was controlled within 0.02°C and maintained at 25°C with a built-in Peltier element. Quartz crystal microgravimetry involved piezoelectric resonators that underwent electric polarization due to applied mechanical stresses (piezoelectricity). During the measurement, the cellulose-coated crystal was mounted in a thermostatic liquid chamber, which was designed to provide a rapid, non-perturbing exchange of the liquid in contact with one side of the sensor. This system allowed for the measurement of up to 4 harmonics. In this study, the frequency shift and the change in energy dissipation were recorded at ca. 15, 25 and 35 MHz, corresponding to the third, fifth and seventh overtones \((n = 3, 5 \text{ and } 7, \text{ respectively})\). Only the normalized frequency shifts for the third overtone \((\Delta f_3/3)\) and the change in dissipation \(\Delta D\) were used to illustrate the adsorption profiles but also higher harmonics were factored in the calculation of adsorbed mass.

In order to study the amount of polyelectrolyte that was adsorbed on the cellulose films, fresh polymer solutions (0.2 g/l) were prepared with background ionic strength of 0.1 mM NaCl. Before running the polyelectrolyte solutions, frequency
and dissipation baselines were obtained by running polyelectrolyte-free salt solution; this typically required ca. 4 h to allow the cellulose film to stabilize and produce constant $f$ and $D$ signals, which were set to zero (baseline). Frequency and dissipation were then registered for 10 min and then $f$ and $D$ were monitored continuously after injection of ca. 1 ml of the respective polyelectrolyte solution using a low flow rate (0.12 ml/min). Time was allowed to elapse until constant $f$ and $D$ values were obtained and then 3 ml of the electrolyte, polymer-free solution was used to rinse out any excess or unbound polymer, using the same injection rate of 0.12 ml/min. The adsorbed amount or areal mass is usually calculated from simple, linear relations involving the frequency shift. For simplicity and to avoid the use of correlations or models that require a number of assumptions, the measured frequency shifts are presented in this study. In some few cases the adsorbed mass was calculated by using various QCM overtones and by employing the Voigt model in the QCM software (QTools, Q-Sense). Nevertheless, it should be kept in mind that the (negative) changes of frequency associated with the injection of polymer solutions can be taken as indicative of trends in the adsorbed mass.

Multiple, successive injections of cationic DMAPAA and anionic IA polyelectrolyte solutions (0.2 g/l concentration in 0.1 mM NaCl background solution, pH 6.9) were conducted in order to produce self-assembled multilayers on the unmodified, cationic or anionic cellulose substrates. Trends in the adsorbed mass were followed as a function of time or as a function of the injection step in the form of QCM frequency plots, as explained above. In the discussion that follows two cases were considered relative to the precursor or first adsorbed polymer layer, regardless of the type of cellulose thin film used: (1) cationic DMAPAA polyelectrolyte added first and (2) anionic IA polyelectrolyte added first.

3. Results and Discussion

3.1. Cationic Charges of CHTAC-Treated Cotton Fibers

The percent of nitrogen present as quaternary ammonium in the cationic fabric samples was determined by elemental analysis. Similar procedure was applied to unmodified fibers which resulted in a nitrogen content of about 0.02%. This small amount of nitrogen was related to the presence of naturally-occurring impurities in cotton including proteins, pectins and waxes. It is worth noting that the treatment of cotton with CHTAC produced a distinctive change in the measured nitrogen content from which the total charges in cationic cotton, reported in units of µeq/g of cellulose, was calculated. These total charges amounted to $591 \pm 20$ and $791 \pm 20$ µeq/g in the case of cotton that was treated with 188 and 376 g/l CHTAC solution concentrations, respectively. Finally, nitrogen content for the anionic fabrics (from carboxymethylation treatment) was determined to be the same as that of unmodified cotton.

For the cationic fabrics more detailed evaluation of the charge density of the samples was performed by polyelectrolyte titrations with PVSK and poly-DADMAC
aqueous solutions using complementary streaming current (SC) and streaming potential (SP) techniques. Results from these measurements were taken as indicative of the surface charge, as opposed to that determined by bulk elemental N analysis, which was indicative of the total charge. While details of SC and SP procedures are given elsewhere [42, 43] for brevity only the final results are reported here as follows: For the lower cationic treatment level the surface charge of the cationic cotton measured by SC and SP titrations were calculated to be $98 \pm 4$ and $114 \pm 12$ µeq/g, respectively. Here the standard deviations were obtained from five different tests performed on the different samples. Within the experimental error good agreement between these values was noted. In the case of the higher cationic treatment level, the surface charge of the cationic cotton was determined to be $157 \pm 5$ and $166 \pm 9$ µeq/g, according to the SC and SP titration techniques, respectively. Therefore, the contribution of the surface charges to the total measured charge was ca. 18 to 20%, for both the low and high level of cationization.

3.2. Anionic Charges of Carboxymethylated Cotton Fibers

The total charges determined by acid–base titration amounted to $822 \pm 33$ and $1028 \pm 32$ µeq/g in the case of cotton that was treated with 95 and 190 g/l chloroacetate solution concentrations, respectively. As in the case of cationic cotton, SC and SP polyelectrolyte titrations were performed. For the lower carboxymethylation treatment level the surface charges of the anionic cotton measured by SC and SP titrations were calculated to be $151 \pm 15$ and $151 \pm 10$ µeq/g, respectively. The standard deviations were obtained from five different tests performed on different samples. In the case of the higher anionic treatment level the surface charge of the cationic cotton was determined to be $229 \pm 15$ and $201 \pm 6$ µeq/g, according to the SC and SP titration techniques, respectively. Therefore, the contribution of the surface charge to the total measured charge was ca. 18 to 21%, for both the low and high level of anionic treatment.

3.3. Polyelectrolyte Multilayers on Thin Film of Cellulose from Unmodified Cotton

Injection of solutions of cationic DMAPAA in fully swollen and pre-equilibrated thin films of unmodified cellulose produced an immediate drop in frequency accompanied by a rise in energy dissipation (see later discussion). These shifts indicated that DMAPAA adsorbed rapidly on the cellulosic substrate, most likely driven by electrostatic interactions. After rinsing with the background electrolyte solution, anionic IA polyelectrolyte solution was injected leading to a further frequency drop. Then, background electrolyte was injected to rinse out excess IA polymer. This procedure produced the first polyelectrolyte layer pair and the process was repeated sequentially three more times. Afterwards, a cap, final layer consisting of cationic polyelectrolyte was adsorbed.

In each injection step it was noted that polyelectrolyte adsorption occurred very fast, as judged by a sharp reduction in frequency that occurred within seconds (see Fig. 3 for similar behaviors in the case of other systems) but the slower dynamics
that followed required about 5–10 min for the $f$ signal to reach a constant value. Upon rinsing with background electrolyte, regardless of the type of polymer added before the rinsing step, only a marginal change in frequency (increased $f$) was noted. This was taken as indication that there was a minimum or negligible amount of loosely bound polymer molecules at the surface.

The evolution of frequency with time is not covered in the remainder of this discussion but instead attention will be placed on the shifts in effective, after rinsing, frequency that followed each polyelectrolyte injection. For unmodified cellulose the main observation was that upon injection of the third and fifth polymer solutions, i.e., injection of An$_2$ and An$_3$ after formation of the respective cationic polyelectrolyte layers Cat$_2$ and Cat$_3$, the frequency shift was positive (dip in the $-\Delta f$ plot shown in Fig. 1). This can be explained by two possible phenomena that could have occurred at the surface of the outer layer: (a) molecules from the cationic layer (Cat$_2$ and Cat$_3$) were partially removed after injection of the anionic polyelectrolyte solution, thereby reducing the effective mass and (b) water was expelled upon addition of the anionic polymer, producing a more collapsed layer with less coupled water (which increases the vibration frequency). The most likely possibility, from the large change in frequency, is that the second and third cationic layers (Cat$_2$ and Cat$_3$) had larger affinity with the flowing IA anionic polyelectrolyte, compared to the polymer layers already assembled on the surface. Therefore, polyelectrolyte complexes were formed and rinsed out. If this hypothesis is correct it would high-

![Figure 1](image-url)  
**Figure 1.** Normalized frequency shift after successive additions of polyelectrolyte solution (each followed by rinsing with water) to thin films of cellulose deposited on QCM sensors from unmodified and cationic cotton fibers (treated at two different levels, low and high cationic charge). A precursor layer consisting of (cationic, Cat) DMAPAA, which was injected first, was followed by rinsing with water and injection of (anionic, An) IA, for a total of seven polymer additions (as indicated by the respective subscripts tagged to the Cat and An steps). The temperature and pH during the experiments were maintained at 25°C and pH 7, respectively. Lines are added as a guide to the eyes.
light the fact that the net binding of the adsorbed polymer depends on the balance of interactions between the ‘immobilized’ polymer located underneath, as well as the assembled structure on the surface and the incoming polymer present in solution. Interestingly, this behavior was only observed for the second and third cationic layers. Similar behaviors, as will be presented in later sections, were observed in the case of carboxymethylated and cationic cellulose.

In the following discussion, experiments with two different addition protocols are presented, as a function of the precursor layer formed by the first polyelectrolyte added, namely, (a) buildup of polyelectrolyte multilayer with first polyelectrolyte addition consisting of cationic DMAPAA and (b) buildup of a polyelectrolyte multilayer with first polyelectrolyte addition consisting of cationic IA. Thin films of cellulose from cationic and anionic cotton, functionalized at two different levels, will also be considered.

3.4. Polyelectrolyte Multilayer on Thin Films of Cationic Cellulose with (Cationic) DMAPAA as Precursor Layer (Cat1)

Similar general observations regarding the dynamics of the process described for polymer adsorption on unmodified cellulose substrates apply in the case of films of cationic cellulose. Despite the existence of positive charges on the film of cationic cellulose, the first injection of cationic (DMAPAA) polyelectrolyte produced a reduction in frequency consistent with the occurrence of adsorption (see Fig. 1, Cat1 frequency change). Since DMAPAA had a low charge density and low streaming potential, it is likely that non-electrostatic interactions were accountable for the small adsorption observed. Such interactions could include van der Waals forces and secondary cooperative interactions such as H bonding, ionic and hydrophobic–hydrophobic forces. However, as also expected from contributions of electrostatic repulsion, adsorption was the smallest for the highly cationic cellulose while intermediate and maximum adsorption was observed for the lower cationic and unmodified cellulose, respectively.

After rinsing Cat 1 with polymer-free solution, the anionic polymer (An1) was injected and extensive adsorption was noticed, as can be concluded from the large frequency shift shown in Fig. 1, for all cellulose surfaces. As was the case for unmodified cellulose films, the next cationic layer also added mass to the assembled structure but after rinsing with electrolyte solution (that produced only small changes in frequency) and after injection of the next anionic polymer solution (An2), an increase in frequency was observed (see the dip in the plot shown in Fig. 1). Again, it is hypothesized that macromolecules from the outer cationic layer were removed from the surface, forming complexes with the anionic polyelectrolyte added. Similar features were observed in the next pair of polyelectrolyte injections.

It is interesting to note that the charge density at pH 7 for the anionic polyelectrolyte was several times larger than that for the cationic one (see the Materials Section). Therefore, a weak binding of the lower charge density cationic polymer to the underneath multilayer structure is expected, which facilitated partial removal
upon injection of the anionic polymer. Finally, it was observed that the growth of the polymer multilayer was somewhat linear for the first three polymer layers; but a less pronounced change in mass growth was apparent during later deposition stages. A multilayer system with 3.5 layer pairs was easily built on cellulose, as shown in Fig. 1; however, the robustness of the assembly diminished if further layer addition was attempted.

3.5. Polyelectrolyte Multilayer on Thin Films of Carboxymethylated (Anionic) Cellulose with (Cationic) DMAPAA as Precursor Layer (Cat₁)

Compared to the cases previously discussed, the use of carboxymethylated cellulose implied a large extent of adsorption upon injection of the first cationic polyelectrolyte, Cat₁. Moreover, the extent of adsorption, taken as the negative of the frequency shift, was largest for the cellulose film with the highest charge density, followed by the lower and unmodified cellulose substrates (see Fig. 2). The trends in QCM frequency observed after addition of subsequent polyelectrolytes are similar to those described before for cationic cellulose. However, contrary to the former case of cationic cellulose, a larger mass of polymer layers was built on the anionic cellulose, with the cellulose with highest anionicity displaying the largest total mass of adsorbed layers. It is worth noting that in the case of cationic cellulose, the largest multilayer mass occurred on the unmodified or lower charged density cellulose substrates (see Fig. 1). These observations highlight the importance of the electrostatic

![Figure 2](image_url)
Figure 3. Normalized frequency and dissipation shifts, $\Delta f_3/3$ (filled circles) and $\Delta D_3$ (open circles), after successive additions of polyelectrolyte solution (each followed by rinsing with water) to thin films of cellulose deposited on QCM sensors from carboxymethylated cotton fibers (low anionic charge). A precursor layer consisting of (cationic, Cat) DMAPAA, which was injected first, was followed by rinsing with water and injection of (anionic, An) IA, for a total of seven polymer additions (as indicated by the respective subscripts tagged to the Cat and An steps). The inset shows the time evolution of the same frequency and dissipation signals as a raw QCM plot and it is added to illustrate the dynamics of the process. The temperature and pH during the experiments were maintained at 25°C and pH 7, respectively. Lines are added as a guide to the eyes.

interactions in the buildup of multilayer structures and also the effect of the first, precursor layer adsorbed.

Figure 3 shows the dissipation profile for one of the systems and it is used to illustrate the trends in the energy dissipation, which are related to the softness and degree of hydration of the adsorbed layer. A large shift in dissipation occurred after each polymer addition. However, what is remarkable here is that while the second and third injection of the anionic polyelectrolyte produced an increase in frequency (see the dip in the frequency profile), the dissipation kept growing. This may indicate that upon contact with arriving ionic polyelectrolyte if it is assumed that partial removal of the pre-adsorbed cationic polyelectrolyte occurred, such change was not
### Table 1.
Comparison of the areal mass of first (precursor) adsorbed layer (DMAPAA) and second anionic polyelectrolyte IA layer on the different substrates tested

<table>
<thead>
<tr>
<th>Thin film of cellulose (substrate)</th>
<th>Adsorbed areal mass of precursor layer of DMAPAA polymer after rinsing (ng/cm²)</th>
<th>Cumulative adsorbed areal mass of second layer of IA polymer after rinsing (ng/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High degree of cotton carboxymethylation (highly anionic cellulose)</td>
<td>463</td>
<td>555</td>
</tr>
<tr>
<td>Low degree of cotton carboxymethylation (low anionic cellulose)</td>
<td>352</td>
<td>425</td>
</tr>
<tr>
<td>Unmodified cellulose from cotton</td>
<td>238</td>
<td>393</td>
</tr>
<tr>
<td>Low cationicity cellulose from cotton</td>
<td>130</td>
<td>480</td>
</tr>
<tr>
<td>High cationicity cellulose from cotton</td>
<td>52</td>
<td>375</td>
</tr>
</tbody>
</table>

accompanied by a reduction in the coupled water that otherwise would have led to a more collapsed or denser layer. Instead, the adsorbed layer became more expanded or dissipative, as was confirmed by the calculated thickness of the multilayer (see below).

To close, and with the aim to elucidate the effect of the substrate in the multilayer assembly, a summary of the calculated areal mass and thickness of the precursor cationic and secondary, anionic polymer layers adsorbed on the different cellulose substrates is presented in Table 1. These results are based on the model of Voinova et al. [44] to quantify the adsorbed mass and thickness, which uses frequency and dissipation data for the different overtones registered during the QCM experiments. Caution should be exercised in the interpretation of these data since QCM mass is very sensitive to water coupled to the adsorbed layer at the surface; in other words, the figures should be taken only as relative values. After examination of Table 1, it can be noted, as expected, that the maximum adsorbed mass for the precursor layer was present on highly carboxymethylated, or highly anionic, cellulose. On the other hand, the minimum adsorption occurred on the cellulose film with the highest level of cationicity. More interesting though is the fact that the adsorbed cationic layer equalized the differences between the different substrates and therefore, as a result, the accumulated mass (after adsorption of the second anionic polymer layer) tended to be somewhat similar for the different cases studied.

#### 3.6. Polyelectrolyte Multilayer on Thin Films of Cellulose with (Anionic) IA as Precursor Layer (An₁)

In this section only the thin films produced from both high charge density cationic and anionic cellulose as well as those from unmodified cellulose will be discussed. Figure 4 shows the shift in QCM frequency after addition of polyelectrolytes, using the same protocols as those explained before in connection with Figs 1 and 2. Here, however, the precursor or first polyelectrolyte layer was the anionic polyelectrolyte,
Figure 4. Normalized frequency shift after successive additions of polyelectrolyte solution (each followed by rinsing with water) to thin films of cellulose deposited on QCM sensors from unmodified, cationic and anionic cotton fibers (the last two cases corresponding to the highest level of treatment). A precursor layer consisting of (anionic, An) IA, which was injected first, was followed by rinsing with water and injection of (cationic, Cat) DMAPAA, for a total of seven polymer additions (as indicated by the respective subscripts tagged to the An and Cat steps). The temperature and pH during the experiments were maintained at 25°C and pH 7, respectively. Lines are added as a guide to the eyes.

IA. It can be observed that this first added polymer only adsorbed on the cationic cellulose substrate, i.e., negligible shifts in frequency were observed for the anionic and unmodified cellulose thin films. However, the most distinctive feature was the observation that upon addition of the second cationic polyelectrolyte the extent of adsorption was clearly higher in the cases of unmodified and carboxymethylated cellulose. Furthermore, the polyelectrolyte assembly grew to a larger degree in the case of these two substrates, compared to cationic thin films of cellulose.

In all cases (Figs 1–4) partial removal of the second and third added DMA-PAA cationic polyelectrolyte layers occurred upon addition of the following anionic IA polymer. Among all experimental conditions, the substrate that produced the largest adsorbed net mass of multilayered polyelectrolytes was unmodified cellulose with precursor anionic polyelectrolyte. Paradoxically, this condition led to an initial minimum adsorption but provided after addition of the cationic polyelectrolyte the largest amount of available cationic charges (upon adsorption of the first cationic polymer layer) for the next, anionic layer to build upon. This observation is especially relevant to the polymers used here, which were low charge density, high molecular mass.

3.7. Effects of Precursor Layers and Substrate Type

When the first polyelectrolyte injected was anionic, the adsorbed mass of the second, cationic polymer added depended heavily on a balance of charges between the substrate and the first layer. On the anionic cellulose film, the areal mass of
cationic polymer (2nd injection) was almost 475 ng/cm², which was similar to the areal mass calculated when cationic polymer was added first to the same substrate (see Table 1). The same observation holds in the case of unmodified cellulose substrates. This is reasonable because the anionic polymers adsorbed very little (or did not adsorb) when added first to the anionic and unmodified cellulose. However, the areal mass of the cationic polymer on the cationic film of cellulose was lower than 100 ng/cm² (see Table 1) while it reached ca. 300 ng/cm² when it was added (on the same substrate) after an anionic, first polymer layer.

These observations, once again, highlight the importance of the protocols used when low charge density polymers are used in the fabrication of polyelectrolyte multilayers. Comparing the cumulative frequency shifts, which are related to the adsorbed mass, for different injecting sequences of polyelectrolyte solutions, it is paradoxical to observe that the larger accumulation of polymer occurred in the case of cellulose films from unmodified cotton.

Our observations agree with those made in [45] in that the formation of polyelectrolyte multilayers depends both on the nature of the substrate prior to treatment and on the balance of charges of added polyelectrolytes. However, it has been proposed that the first polyelectrolyte layer needs to adsorb strongly on the substrate and charge reversal is required as the basis for formation of polyelectrolyte multilayers on mineral surfaces [46] as well as on cellulose [45, 47]. For high molecular weight, low charge density polymers, where adsorption also is driven by non-electrostatic interactions (van der Waals forces, H bonding, ionic and hydrophobic interactions) this requirement may be relaxed.

An interesting feature in work published on weak polyelectrolyte (based on poly(acrylic acid) or anionic polyacrylamides, among others) multilayers on cellulose is the fact that upon addition of the anionic polymer in the respective step, a small increase in the QCM frequency, accompanied by a reduction in dissipation, has been observed after it passed through a maximum for each cationic layer [29, 45, 48]. Such effect has been proposed to be due to polyanions replacing the water in the polycation layer, leading to a more rigid and compact layer [45, 49]. Alternatively, it has also been explained by desorption of polyelectrolyte molecules [48, 50] or a restructuring of the polyelectrolytes in the adsorbed layers [29, 50].

It may be a coincidence that all reports indicate this phenomenon as only happening when the anionic polymer is introduced. Our experimental results also point to similar features, but they are made more evident since low charge density, high molecular mass polyelectrolytes were used in the present investigation. Our results indicate clearly that some of the cationic polymer was removed from the outer layer. For the reasons explained above, if the cationic polymer is the outermost layer, the multilayer will show a lower viscosity and shear modulus [48]. The nature of the outer layer, in fact, will affect greatly the properties of the system, for example, the hydration, surface energy, contact angle, etc. A large influence on adhesion and joint strength for polymer multilayer-coated fibers is expected since the strength depends heavily on the nature of the last layer. Overall, and as noted by other au-
thors, polyelectrolyte multilayer treatment of cellulosic materials can significantly affect adhesion between fibers and, therefore, paper strength [45, 48, 51–54]. A very relevant system such as that of low molecular mass, low charge density polyelectrolytes was explored here. In such cases, polyelectrolyte multilayers can enhance inter-fiber adhesion due to polymer–polymer interpenetration and by increased viscoelastic losses that occur during the rupture of a paper sheet under strain. Even though no attempt was made to apply the discussed polymers to actual papermaking fibers, the main conclusions reported here can be useful in directing formulations for such systems.

4. Conclusions

Adsorption onto films of cellulose obtained from unmodified and functionalized (anionic and cationic) cotton fibers was studied with weak anionic and cationic polyelectrolytes using the QCM-D technique. The following conclusions can be made:

(1) The charge properties of the substrates and the polymers were relevant to the outcome of polyelectrolyte multilayers obtained by self-assembly.

(2) Sequential additions of weak polyelectrolytes formed multiple, viscoelastic layers on all cellulose substrates.

(3) Adsorption of the first layer depended heavily on the charge characteristics of the substrate while adsorption of further layers depended on the overall balance of interactions.

(4) Adsorption occurred as a result of a combination of electrostatic as well as non-electrostatic interactions.

(5) For the cationic polyelectrolyte the adsorbed mass of the first layer, on the different cellulose films, increased with the anionicity of the surface.

(6) Adsorption of negatively charged polymer occurred only on the cationic cellulose film. However, while the first layer deposition depended on the charge density of the cellulose film, the second layer adsorption, comprised of anionic polyelectrolyte, depended both on the substrate and the first, precursor adsorbed layer.

(7) In all cases the second and successive adsorbed cationic layers were partially removed when anionic polyelectrolyte was added. This effect was explained by the fact that the charge density of the cationic polymer was much lower than that of the anionic counterpart.

(8) The polyelectrolyte multilayer with highest mass was produced on the unmodified cellulose surface. Therefore, when adsorbing multilayers of weak polyelectrolytes substrate functionalization, either to make it cationic or an-
ionic, may not be a requisite. Overall, the results presented allow for a better understanding of polyelectrolyte adsorption and reveal that the extent of adsorption and conformation of the adsorbed species is a result of the balance of the charge properties.

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References