The Effects of Cellulosic Fiber Charges on Polyelectrolyte Adsorption and Fiber-Fiber Interactions

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The Effects of Cellulosic Fiber Charges on Polyelectrolyte Adsorption and Fiber-Fiber Interactions

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Abstract

The surface charges of cellulosic fibers contribute to several papermaking operations that influence the manufacture and final properties of paper. This thesis investigates the effect of the surface charges on wet-end chemistry, e.g. through the interaction of cationic polyelectrolytes with the fiber surface charges, and on the network strength of pulp suspensions. The polyelectrolyte titration method was used to investigate the interaction of the fiber charges with cationic polyelectrolytes. Techniques were developed to fluorescent label the adsorbing cationic polyelectrolyte in order to visualize the adsorption behavior. Fluorescent confocal laser scanning microscopy (CLSM) was used to determine the extent to which the cationic polyelectrolyte adsorbs into the porous fiber wall. It was shown that the polyelectrolyte charge density limits the adsorption to the surface under electrolyte-free conditions. Adsorption into the fiber wall only occurs for two conditions: 1) if the molecular mass is sufficiently low or 2) the electrolyte concentration is high enough to screen the charges along the polyelectrolyte backbone but not the interactions between the polyelectrolyte and the fiber charges.

Aside from the polyelectrolyte properties, the fiber charge density contributes to the adsorption behavior of cationic polyelectrolytes. The fiber charge profile was altered by bulk and surface carboxymethylation. The electrolyte concentration at which a deviation from 1:1 stoichiometry occurs was shown to be dependent on the amount of surface charges, such that the deviation in stoichiometry occurs at a higher electrolyte concentration for pulps having a higher surface charge. A hypothesis was developed to test the conditions at which the deviation in adsorption stoichiometry occurs, which was defined as the critical electrolyte concentration (CEC). It was found that the CEC corresponded to the electrolyte concentration at which the distance between the fiber charges was on the order of the Debye length. Electron spectroscopy for chemical analysis (ESCA) was used as an independent calibration procedure to validate for which a 1:1 stoichiometry occurs. The analysis with ESCA agreed well with the polyelectrolyte titration method for measurement of fiber surface charges. When measured under appropriate conditions, i.e. electrolyte concentration and molecular properties, the fiber surface charge can accurately be measured by the polyelectrolyte titration method.
The charge profiles of various pulp types and treatments were also examined. Having been established as a valid technique, the polyelectrolyte titration method was again used to measure the surface charge while conductometric titration was used to measure the total charge content. The amount of bulk and surface charges vary depending on the pulping method and type of wood, although the ratio between the bulk and surface charge (i.e. the charge ratio) is similar for chemical pulps. The mechanical pulp has a higher charge ratio because it contains more fines material than chemical pulp. Bleaching of the chemical pulp decreases the amount of bulk and surface charges, although the charge ratio remains essentially constant. However, methods such as beating or carboxymethyl cellulose (CMC) grafting are available to increase the charge ratio.

The effect of the charge profile on fiber-fiber interactions was studied on both a microscopic and macroscopic level. Colloidal probe microscopy (CPM) was used to investigate the microscopic interactions between two cellulose surfaces. Cellulose surfaces, prepared by spin-coating a dissolving pulp onto silica, were used to model the fiber surface, which is too rough for surface force measurements. The charge density of the model surface was increased by CMC grafting. Results showed that increasing the surface charge density created large electrosteric repulsions, due to CMC the chains protruding out from the surface. These interactions on the microscopic scale affect the fiber network strength, which was measured with a parallel plate rheometer. When the repulsion is increased between the fibers, caused by the increase in the surface charge, fiber flocs break apart more easily due to a reduced friction between the fiber surfaces.

The forces acting on the fiber network can also be mechanical in origin. The fiber length and flexibility were altered in order to study the influence of mechanical surface linking and elastic fiber bending on the fiber network strength. Using the storage modulus ($G'_0$) as a measure of fiber network strength, longer fibers were found to create a stronger network due to an increased amount of fiber contacts. Flexible fibers have a lower network strength than stiff fibers because the fibers come to rest in a less strained position such that the the influence of elastic fiber bending on the fiber network strength is predominant.

**KEYWORDS:** Adsorption, electrolyte, polyelectrolyte, polyelectrolyte titration, stoichiometry, fluorescence, CLSM, carboxymethylation, ESCA, charge ratio, colloidal interactions, mechanical forces, network strength, floc, CPM, rheometer
Preface

It is well established that the charge content of cellulosic fibers is important for various unit operations in the papermaking process, such as wet-end chemistry, de-watering, sizing and flocculation, as well as the final paper properties.

It is important to distinguish charges in the fiber bulk (total charge = bulk charge) from charges on the fiber surface, which affect fiber-fiber bonding and interactions with high molecular mass additives (e.g. retention aids) and additives that are particulate in nature, such as latex and sizing dispersions. The total charge is most conveniently measured using conductometric titration. Surface charge is measured using the polyelectrolyte titration method by titrating with a high molecular mass cationic polyelectrolyte. The polyelectrolyte titration method and its theoretical basis is one important issue in this thesis.

The amount of surface charges are also important for reducing fiber flocculation, which results in a better formation. It is important for the papermaker to understand the nature of fiber flocculation and the forces acting between the fiber surfaces. Therefore, this thesis has also focused on how surface charges affect flocculation.

Polyelectrolyte adsorption is a fairly well known method for determining the surface charge of fibers. There are, however, various factors that affect the adsorption behavior, namely the polyelectrolyte charge density and molecular mass, the fiber charge profile and ionic strength. The relationship between the polyelectrolyte properties and the adsorption to cellulosic fibers is presented in Paper I. Poly(AM-co-DADMAC) was synthesized to have varying molecular mass and charge density in order to serve as a model high charge density polyelectrolyte. The poly(AM-co-DADMAC) was then fluorescent labeled such that the extent to which adsorption occurs in the fiber wall could be visualized by confocal laser scanning microscopy (CLSM). This technique was combined with polyelectrolyte titration to elucidate the effect
of molecular mass, polyelectrolyte charge density and the ionic strength on the adsorption behavior. **Paper II** presents the influence of the fiber properties on polyelectrolyte adsorption. For this purpose, high charge density poly-diallyldimethylammonium chloride (poly-DADMAC) was adsorbed in various electrolyte concentrations onto fibers having different charge profiles, which were achieved by bulk and surface carboxymethylation. A requirement for accurate determination of the surface charge is a 1:1 stoichiometry between the adsorbed polyelectrolyte charges and the fiber surface charges. This work validated the hypothesis that the distance between the fiber charges must be smaller than the thickness of the electrostatic double layer, \( \kappa^{-1} \), in order for a 1:1 stoichiometry to prevail. This is in agreement with self-consistent mean-field theories. Furthermore, **Paper II** also employed the surface sensitive ESCA technique as an independent calibration procedure for the polyelectrolyte titration method.

Several publications have shown that a vast amount of different conditions have been employed to measure the surface charge using the polyelectrolyte titration method. Since the charge distribution influences various unit operations in the papermaking process, the amount of charges on the fiber surface is of importance. **Paper III** compares the charge profile for several types of pulps and treatments.

Surface charges are assumed to affect the local interactions responsible for the fiber network strength. Flocs, which are created in a flowing suspension due to colloidal and mechanical interactions, are undesirable due to their negative effect on sheet formation. **Paper IV and V** present the influence of colloidal and mechanical forces on the fiber network strength and the factors that govern these interactions.
List of Publications

This thesis is based on the following papers:

I. *Polyelectrolyte Adsorption on Cellulosic Fibers: I. High Charge Density Polyelectrolytes.*

II. *On the Indirect Polyelectrolyte Titration of Cellulosic Fibers. Conditions for Charge Stoichiometry and Comparison with ESCA.*

III. *Indirect Polyelectrolyte Titration of Cellulosic Fibers. Surface and Bulk Charges of Cellulosic Fibers.*

IV. *Influence of Colloidal Interactions on Fiber Network Strength.*
    Horvath, A. E. and Lindström, T. (2006), Accepted for publication in Journal of Colloid and Interface Science

V. *The Influence of Mechanical Surface Linking and Elastic Fiber Bending on Fiber Network Strength.*
Other relevant disseminations not included in the thesis:

1. **Effects of cellulose surface modification surface friction as probed by colloidal probe microscopy (CPM)**

2. **Surface- and Bulk Charge Determination of Cellulosic Fibers - Traps and Possibilities.**

3. **Polyelectrolyte Charge Titration of Cellulosic Fibres.**

4. **Appropriate Conditions for Polyelectrolyte Titration to Determine the Charge of Cellulosic Fibers**

5. **Fiber Network Strength**

6. **The Influence of Charges on Fiber Network Strength.**

7. **Polyelectrolyte Adsorption on Cellulosic Fibers: II. Low Charge Density Polyelectrolytes**
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1 Introduction

In order to understand fiber-fiber interactions as well as the interactions between fibers and cationic polyelectrolytes, it is important to distinguish the charges on the fiber surface (surface charges) from charges in the fiber cell wall (bulk charges). The charges on cellulosic fibers mainly originate from dissociation of ionic groups, where carboxyl acid groups are the major contributor to the fiber charge during normal papermaking conditions (Sjöström, 1989). Different components in wood carry carboxyl groups and these groups can also be created during pulping and bleaching operations. The surface charge on fibers and fines are important because the number of charges determines the interaction with cationic additives. The bulk charges are important for fiber swelling as well as the interaction between fibers during pressing/consolidation in the drying section of the paper machine (Lindström, 1992). Bulk charges and surface charges may also define many chemical aspects of bonding between fibers. A large number of bulk charges contribute to the swelling and flexibilization of fibers, thus increasing the relative bonded area. Therefore, paper strength properties are often closely related to the swelling properties of the pulp. Ionized acidic groups on the fiber surface also provide the fibers with an increased bond strength per unit area (Laine et al., 2003b).

The adsorption mechanism for polyelectrolyte adsorption to cellulosic fibers is a fundamentally important process. Polyelectrolytes having a large range in molecular mass and charge density are used throughout paper production for various wet-end applications (Lindström, 1989). Even though the adsorption behavior of cationic polyelectrolytes has been studied for many years, it has yet to be resolved to what extent polyelectrolytes adsorb into the fiber wall. Moreover, it is unclear whether changes in the adsorption behavior are a consequence of a deviation from stoichiometry on the fiber surface or the polyelectrolyte penetrating into the fiber cell wall. Polyelectrolyte properties, such as charge density and molecular mass, the fiber charge profile and ionic strength are factors affecting the adsorption
behavior. Due to the importance of the charge profile, it is of great interest to be able to measure the surface charges. One method for determining the surface charge is the indirect polyelectrolyte titration technique (Horn, 1978). Direct polyelectrolyte titration was pioneered by Terayama (1952), who determined the concentration of a cationic polyelectrolyte solution by titration with an anionic polyelectrolyte in the presence of a cationic indicator. Direct polyelectrolyte titration was later applied to cellulosic fibers (indirect titration) by Winter et al. (1986). The method was regarded as an ion-exchange process such that a 1:1 charge stoichiometry takes place, i.e. one polyelectrolyte charge adsorbs for every available fiber charge. At least three criteria must be met for a 1:1 stoichiometry to prevail when measuring the surface charge content: (1) a high charge density of the cationic polyelectrolyte, (2) a sufficiently high molecular mass of the cationic polyelectrolyte and (3) a sufficiently low electrolyte concentration. Furthermore, there must be an absence of non-electrostatic interactions between the polyelectrolyte and the fiber. There are, however, numerous examples throughout the open literature that used various conditions, specifically regarding molecular mass and ionic strength, for determining the surface charge (Ampulski, 1985; Wågberg et al., 1988; Zhang et al., 1994; Höök, 1995; Laine and Stenius, 1997). This prompted the further investigation of the appropriate conditions for surface charge determination.

Because the charge content of fibers strongly affects the adsorption of polyelectrolytes as well as fiber swelling and strength properties (Lindström, 1992), it is of interest to compare the charge content of different types of pulp fibers. Various types of wood, pulping procedures and bleaching sequences that alter the charge profile are used throughout the papermaking industry. There are also methods available to change the relationship between bulk and surface charges, denoted in this thesis as the charge ratio. As the charge ratio changes, unit operations such as dewatering, consolidation and fiber flocculation will be affected. The relationship between the bulk and surface charge content is therefore of interest. Fiber flocs are especially undesirable as they have a negative impact on formation, strength and opacity (Kerekes et al., 1985). These properties could be improved if the strength of these flocs, i.e. the network strength, can be reduced. It is also of interest to study which forces govern the fiber-fiber interactions and how they affect the fiber network strength.

The aim of this thesis is threefold. The first aspect is to investigate the adsorption behavior of cationic polyelectrolytes in regards to the fiber charge density, polyelectrolyte properties and ionic strength. The second aspect focus on the measurement of surface charge density by determining the appropriate conditions for polyelectrolyte titration. The final aspect is to elucidate the effect surface charges have on the fiber network strength.
2 Background

2.1 The origin of charge

Wood mainly consists of three substances that are either physically or chemically attached to each other: cellulose, hemicellulose and lignin. Cellulose and hemicellulose are polysaccharides that are built from different carbohydrates. Lignin consists of phenylpropanoic units bonded together in a three dimensional network structure. Apart from these three substances, wood also contains extractives and other materials in smaller amounts. The relative composition of wood also depends on the tree species.

Various fiber properties, such as fiber structure and chemical composition, are used to produce paper with different properties. Generally, long fibers improve paper strength properties if the sheet can be formed without large variations in grammage, i.e. fiber flocs. Fiber dimensions depend on the pulping method used to separate the fibers. For example, fibers from wooden materials swell when components are removed by conventional pulping chemicals. Fibers also swell when they are subjected to mechanical treatments, such as beating and refining (Kerr and Goring, 1975).

Ionizable functional groups are an important factor in various unit operations and influence the final paper properties (Scallan, 1983; Lindström, 1989, 1992; Eklund and Lindström, 1991). Carboxylic acid groups are the primary functional groups ionized during normal papermaking conditions (neutral and weakly acidic). A rather high pH is required to ionize phenolic hydroxyl groups and strong alkali is needed to ionize such weak acids as alcoholic hydroxyl groups (Sjöström, 1989). The carboxyl groups give pulp fibers an anionic charge. The majority of these carboxyl groups are uronic acid type and are mainly attached to xylan. Native wood carries only a few charges because the carboxyl groups are esterified to various degrees depending on the wood species. The esters are then hydrolyzed during bleaching of mechanical pulps, giving rise to an increased amount of carboxyl groups.
Wood chips of chemi-mechanical (CTMP) and chemi-sulfite pulps are treated with sulfite to introduce sulfonic acid groups. The extent of sulfonation, which depends on the pulping and impregnation conditions, is higher for softwood pulps than for hardwood pulps. The ion-exchange capacity decreases during delignification of the sulfite pulp as the contents of both the residual lignin, where the sulfonic acid groups are introduced, and the hemicellulose decrease (Lindström, 1992), see Figure 1(a).

During kraft pulping (Figure 1(b)), the carboxyl group content decreases because of the dissolution of acidic polysaccharides, particularly xylan (Sjöström, 1989). The major part of the carboxylic groups present in xylan originates from hexenuronic acids (Buchert et al., 1995). Hardwood has a higher charge content than softwood due to a higher xylan and uronic acid content (Laine et al., 1996). Laine et al. (1996) found that two types of acidic groups are present in unbleached kraft pulp. The lower $pK_\alpha$-value corresponds to uronic acid, while the higher $pK_\alpha$-value corresponds to carboxylic acid groups bound to the lignin residues.

Carboxylic acid groups are created during the bleaching of chemical pulp, but the amount of acidic groups decreases due to the dissolution of lignin and hemicellulose (Gellerstedt and Lindfors, 1987; Sjöström, 1993).
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It has been shown by Buchert et al. (1995) that ozone and chlorine dioxide almost completely destroy the hexenuronic acids, whereas peroxide and oxygen have no effect. Only a small amount of carboxylic acid groups are introduced during bleaching as aldehydic groups are created when bleaching agents oxidize the polysaccharide chain. Depending on the prevailing bleaching conditions, the aldehydic groups are either oxidized to carboxylic acid groups or initiate a peeling reaction of the polysaccharide chain (Sjöström, 1993).

2.2 The importance of fiber charges on papermaking

Cellulosic fibers produced in the papermaking process behave as polyelectrolytic gels due to their anionic charge (Lindström and Carlsson, 1978; Scallan and Grignon, 1979). The charges within the gel cause electrostatic repulsions that result in swelling of the fiber. Therefore, the degree of fiber swelling is dependent on the amount of charges, ionic strength and the type of counter-ion (Lindström, 1992).

It was recognized early on that the amount of charges within the fiber cell wall, i.e. bulk charges, give rise to swelling, which affects the rate of beating and paper strength. Walecka (1957) utilized a method where hydroxyl groups are substituted with carboxyl groups (carboxymethylation) in order to increase the bulk charge content. However, even though the swelling gives an increased bonded area that increases the paper strength, it has a negative effect on the water removal during wet pressing.

Whereas bulk charges contribute to swelling and create an increased bonded area, the charges at the fiber surface provide the fibers with an increased bond strength per unit area (Barzyk et al., 1997a,b; Laine et al., 2003b). The surface charges are also important for the interaction between fibers and cationic chemical additives (Lindström, 1989). The importance of surface and bulk charges on paper machine operations and final paper properties are summarized in Table 1. The surface charges are also important for fiber-fiber interactions, which generate the fiber network strength (Kerekes et al., 1985).
Table 1: Effects of charges on paper machine operations and paper properties.

<table>
<thead>
<tr>
<th>Surface charges</th>
<th>Bulk charges</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strength properties</td>
<td>+ +</td>
<td>Laine et al. (2003b)/ Lindström (1986)</td>
</tr>
<tr>
<td>Pressability</td>
<td>0 - -</td>
<td>Carlsson et al. (1977)</td>
</tr>
<tr>
<td>Retention</td>
<td>+ 0</td>
<td>Eklund and Lindström (1991)</td>
</tr>
<tr>
<td>Sizing</td>
<td>+ + 0</td>
<td>Lindström and Glad-Nordmark (2006)</td>
</tr>
<tr>
<td>Wet-strength</td>
<td>+ + 0</td>
<td>Laine et al. (2002)</td>
</tr>
<tr>
<td>(PAMAM-EPI)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial wet-strength</td>
<td>+ 0</td>
<td>Mešić (2002)</td>
</tr>
</tbody>
</table>

2.3 Polyelectrolyte adsorption theory

Electrostatic interactions are important for the adsorption of polyelectrolytes onto an oppositely charged surface (Hesselink, 1977; Cohen Stuart et al., 1991). The charge density of both the polyelectrolyte and the surface affects the adsorption. The electrolyte concentration, valency of the ions and pH are important factors as well. In the presence of a monovalent electrolyte, polyelectrolyte adsorption onto an oppositely charged surface can either increase or decrease with increasing electrolyte concentration. If the interactions are purely electrostatic, self-consistent lattice theories (Fleer et al., 1993) predict that the adsorption decreases due to the electrolyte screening both the segment-segment repulsion and the segment-surface attraction. In cases where non-electrostatic interactions are present, the repulsion between segments dominates the adsorption such that the screening of the repulsions at high electrolyte concentration causes the polyelectrolyte to behave as an uncharged polymer in solution. At higher electrolyte concentrations, the polyelectrolyte will adopt a conformation on the surface having loops and tails, which increases the amount adsorbed. These cases are illustrated in Figure 2, where the adsorbed amount is plotted as a function of electrolyte concentration for various values of the adsorption energy parameter, $\chi_s$, which expresses the non-electrostatic affinity for the surface.

For pure electrosorption ($\chi_s=0$), adsorption monotonically decreases with increasing electrolyte concentration due to screening of the attraction between the polyelectrolyte and the surface charges. However, the screening effect is almost negated when a non-electrostatic interaction ($\chi_s>0$) is present. The adsorption exhibits an increase before decreasing slightly
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Figure 2: Adsorbed amount as a function of electrolyte concentration for different values of $\chi_s$, the non-electrostatic interaction with the surface (van de Steeg et al., 1992).

when the electrolyte concentration is increased. Higher $\chi_s$ values clearly enhance adsorption at high electrolyte concentrations, as repulsion between the polyelectrolyte charges are screened such that the polyelectrolytes adsorb to the surface in loops and tails, which act to increase the adsorbed amount. According to scaling theory (Dobrynin et al., 2001), adsorption will first increase at low ionic strength before decreasing at high ionic strength. Experiments have also shown that this is the case for various polyelectrolytes onto silica (Cohen Stuart et al., 1991; Shubin, 1997), latex (Shubin et al., 1997) and cellulose (Tanaka et al., 1979; Lindström and Wågberg, 1983; van de Steeg et al., 1993).

The adsorption of polyelectrolytes onto a flat substrate has also been discussed by Netz and Joanny (1999) and Netz and Andelman (2003). These authors went beyond self-consistent mean-field theories and considered lateral correlation effects. An adsorption phase diagram was presented for strongly charged polyelectrolytes as a function of the substrate charge density and the inverse screening length. At constant substrate charge density, charge compensation occurs at low electrolyte concentrations. Increasing the electrolyte concentration causes overcharging of the substrate, followed by desorption of the polyelectrolyte. This also affects the formation of, for instance, polyelectrolyte multilayers (Decher, 1997; Netz and Joanny, 1999).
2.4 Polyelectrolyte adsorption to cellulosic fibers

Polyelectrolyte adsorption to cellulosic fibers is complicated by the porous nature of the fiber. It was shown by Alince and van de Ven (1997) that fibers contain macro pores ∼75 nm in diameter and micro pores having a diameter of about 4 nm. Others have shown that the average pore size is in the order of 30-40 nm (Duchesne and Daniel, 1999; Andreasson et al., 2003). However, the pore size depends on the type of fiber and measurement technique (Maloney et al., 1997). Taking into account that fibers contain charged groups on the surface and in the cell wall, it is understandable that polyelectrolyte adsorption is governed by electrostatic interactions. It has been shown that the adsorption of highly charged cationic polyelectrolytes in electrolyte-free conditions occurs at a 1:1 charge stoichiometry (Winter et al., 1986). Due to the the porous nature of the fiber, the extent the polyelectrolyte adsorbs into the fiber cell wall will be dependent on the molecular conformation of the polyelectrolyte in solution. Wågberg and co-workers (Wågberg and Ödberg, 1989; Wågberg and Hägglund, 2001) reasoned that adsorbed amount of poly-DADMAC increases as the molecular mass decreases due to penetration into the fiber wall. Similar results were reported by Tanaka et al. (1990) for low charge density polyelectrolytes. To compensate for the fiber charges, a high charge density polyelectrolyte will adsorb to a lower amount than a low charge density polyelectrolyte having similar molecular mass.

The adsorption behavior changes in the presence of an electrolyte. At moderate electrolyte concentrations, the adsorption increases due to a deviation from a 1:1 stoichiometry. This deviation can be attributed to the partial screening of the charges within and between polyelectrolyte chains, causing the polyelectrolyte to adsorb in a more coiled conformation. An additional increase in the electrolyte concentration decreases adsorption as the screening allows the polyelectrolyte to behave as an uncharged polymer in solution. Finally, the adsorption ceases when the charges between the fiber and polyelectrolyte are completely screened (Tanaka et al., 1979; Lindström and Wågberg, 1983; van de Steeg et al., 1993).

2.5 Polyelectrolyte titration (PET)

The indirect polyelectrolyte titration method is commonly employed to determine the adsorbed amount of polyelectrolyte (Horn, 1978). The direct polyelectrolyte titration technique was pioneered by Terayama (1952). The
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technique is based on complexing a cationic polyelectrolyte by titration with an anionic polyelectrolyte in the presence of a cationic indicator, typically orthotoluidine blue (OTB). The color of the uncomplexed OTB indicator is blue, and the color changes to pink when it complexes with the excess anionic polyelectrolyte. This wavelength displacement is called metachromasy, and is the basis for the polyelectrolyte titration method. The complex formation can be written as:

\[ A + C \xrightarrow{K_1} AC \]  

\[ A + I \xrightarrow{K_2} AI \]  

where A is an anionic polyelectrolyte, C is a cationic polyelectrolyte and I is the indicator.

In order for this method to work, the complex formation with the cationic polyelectrolyte must occur faster than the complex formation with the indicator i.e. \( K_1 \gg K_2 \). The polyelectrolyte titration procedure is basically independent of molecular mass (Horn, 1978) and the polyelectrolyte complex is stoichiometric with respect to charge if the charge density of the polyelectrolytes is sufficiently high (Horn, 1979) or the ionic strength is sufficiently low (Tanaka, 1983a,b; Sjödin and Ödberg, 1996; Kam and Gregory, 1999). Winter et al. (1986) developed the method to be used for charge determination of cellulosic fibers (indirect titration). This method is based on a 1:1 stoichiometric relationship between the adsorbed polyelectrolyte charges and the charges on the fiber. Several publications from the STFI-group (Wågberg et al., 1985, 1987, 1988, 1989; Wågberg and Ödberg, 1989; Winter et al., 1986) have shown that this condition is valid if the electrolyte concentration is sufficiently low. Kokufuta and Takahashi (1986) found that stoichiometry prevails between poly-DADMAC and silica in deionized water, but deviates in ionic solutions.

2.6 Forces acting on a fiber network

Surface charges are important as they affect the interactions between fibers and chemical additives, such as cationic polyelectrolytes, as well as fiber-fiber interactions. The fiber-fiber interactions are important for the formation of the paper web. It is desirable to form a web as uniform as possible. However, different chemical and mechanical forces create local fiber concentrations higher than the average, i.e. fiber flocs are formed. Flocs are
undesirable due to their negative impact on various paper properties, such as formation, strength (Hallgren and Lindström, 1988), opacity (Jordan, 1985; Wahren, 1987) and printability (Huang and LePoutre, 1994). The mechanisms responsible for fiber flocculation, illustrated in Figure 3, can be divided into colloidal interactions, mechanical surface linking and elastic fiber bending (Kerekes et al., 1985).

\[ \kappa^{-1} = \sqrt{\frac{\varepsilon_w \varepsilon_0 k_B T}{2e^2 \sum n_{\infty,i} z_i^2}} \]  

where \( \varepsilon_w \) is the dielectric constant of water, \( \varepsilon_0 \) is the permittivity in vacuum, \( k_B \) is Boltzmann’s constant, \( T \) is the absolute temperature, \( z \) is the valency of a \( z:z \) electrolyte, \( e \) is the elementary charge and \( n_{\infty,i} \) is the number concentration of counter-ions in the bulk solution.

The thickness of the double layer decreases with increasing ionic strength, affecting the interactions between two approaching surfaces (Israelachvili, 1992). A commonly known theory for illustrating the interactions between two particles in aqueous solution is the DLVO-theory (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948). The DLVO-theory describes the interplay between the van der Waals force and the electrostatic double layer force. However, other forces, such as hydration and steric forces, become
important at very small separations. In the case where a polymer is adsorbed to the surfaces, the surfaces will experience a steric force when the adsorbed chains start to overlap. The polymer will adopt a denser conformation, resulting in an entropy loss, and a steric repulsion occurs (Napper, 1983). In the case of adsorbed polyelectrolytes, the repulsive force is a combination of the electrostatic and steric interaction and the force is termed electrosteric.

It was once believed that colloidal interactions were responsible for floculation. Moreover, Mason (1954) reasoned that mechanical surface linking was the major contributor for floc formation. Mechanical surface linking, Figure 3(b), is caused by the kinks and curl of the fibers and the fibrillated fiber surfaces, which act to entangle each other. Hence, mechanical surface linking inherently depends on surface fibrillation, fiber stiffness and the degree that the fibers are bent. Elastic fiber bending, depicted in Figure 3(c), was introduced by Meyer and Wahren (1964). They hypothesized that fibers coming to rest in a strained position produce normal forces between the fibers that are built into the network, causing frictional forces that inhibit the fibers from sliding. Therefore, elastic fiber bending is strongly dependent on the number of contacts per fiber, fiber stiffness and the coefficient of friction between the fibers.

The relative importance of the different forces is dependent on the pulp consistency. Elastic fiber bending is more important at higher consistencies and the significance of colloidal interactions is more pronounced at lower consistencies (Kerekes et al., 1985). Mechanical surface linking may be more important for fibers that are very curled.
3 Measurement techniques

3.1 Adsorption isotherms

Polyelectrolyte adsorption onto cellulosic fibers is commonly measured using the polyelectrolyte titration method, which served as the basis for Papers I-III. The adsorbed amount of polyelectrolyte and the equilibrium concentration in solution can be calculated from the inflection point in the (direct) polyelectrolyte titration curve. The adsorbed amount of polyelectrolyte as a function of the equilibrium concentration is then compiled in an adsorption isotherm, see Figure 4.

A theoretical adsorption isotherm for the adsorption of a cationic polyelectrolyte would have two distinct features. Firstly, a vertical line would exist on the ordinate as the polyelectrolyte is completely adsorbed at low addition levels. Therefore, no remaining polyelectrolyte would be left in the solution, resulting in an equilibrium concentration of zero. Secondly, a plateau region in the adsorbed amount would exist at higher equilibrium concentrations, represented by the dashed line in Figure 4, because the additional polyelectrolyte remains in solution once the available surface charges are saturated (Lindström, 1989). In practice, adsorption isotherms deviate from this prediction, which can be attributed to three main effects:

1. The polydispersity of the adsorbing polyelectrolyte causes curved isotherms because the higher molecular mass material is preferentially adsorbed at the accessible fiber surfaces, displacing the lower molecular mass material (Cohen Stuart et al., 1980).

2. A low molecular mass polyelectrolyte has higher accessibility to charges in the fiber cell wall than a high molecular mass polyelectrolyte (Wägberg et al., 1987).
Figure 4: An adsorption isotherm and the principle of extrapolating back to zero equilibrium polyelectrolyte concentration in order to determine the adsorbed amount of polyelectrolyte charges. IEC = Ion Exchange Capacity. (Lindström, 1989)

3. A decrease in the stoichiometry for the adsorbed polyelectrolyte chains, which is most probably due to an increased interaction between the polyelectrolyte chains on the fiber surface. This factor is expressed as an expansion of the adsorbed polyelectrolyte layer out from the surface (Wågberg and Ödberg, 1989), resulting in a deviation of the charge stoichiometry such that more adsorption can occur.

In order to compensate for the polyelectrolyte expansion mechanism (3), the number of adsorbed charges can be evaluated from the adsorption isotherm by an extrapolation of the linear region to zero polyelectrolyte concentration, as seen in Figure 4. The charge ratio can be calculated if the total charge is determined, preferably by conductometric titration (Katz et al., 1984). The charge ratio (Wågberg and Ödberg, 1989) can then be calculated according to Equation 4:

$$\text{Charge ratio} = \frac{\text{number of adsorbed polyelectrolyte charges}}{\text{total number of fiber charges}}$$

(4)

A charge ratio of unity means that all fiber charges can be reached by the adsorbing polyelectrolyte. The charge ratio drops drastically, i.e.
the adsorption decreases, above a critical molecular mass because larger molecular mass polyelectrolytes have less accessibility to the charges in the fiber pores and will almost only be adsorbed on the fiber surface.

3.2 Confocal Laser Scanning Microscopy (CLSM)

Confocal laser scanning microscopy (CLSM) (employed in Paper I) is used to obtain high resolution images and three-dimensional reconstructions. The basic concept of CLSM was originally developed by Minsky in the 50's, but it wasn't until the 1980's (Minsky, 1988) that advances in computer and laser technology led to a growing interest in confocal microscopy. CLSM is unique in the fact that it can take optical cross-sections from within semitransparent and biological samples. Compared to conventional widefield optical microscopy, CLSM has the ability to control the depth of field, to reduce the background information away from the focal plane and can produce blur-free images of thick specimens at various depths.

The principle behind CLSM is that a laser is focused by an objective lens into a small focal volume within a fluorescent specimen. The laser causes the specimen to fluoresce. The laser scans over the plane of interest and an image is obtained pixel by pixel and line by line. The brightness of a resulting pixel correspond to the relative intensity of the detected fluorescent light. Information can be collected from different focal planes and a three-dimensional picture of a specimen can be created by assembling a stack of two-dimensional images from successive focal planes.

Non-fluorescing samples must be treated with fluorescent dyes to become visible by CLSM. This approach has been used for various applications within industrial research (Schrof et al., 1998), including research on dye diffusion into nylon fibers (Song et al., 2000) and polyelectrolyte adsorption (Regismond et al., 1999) using fluorescent labeled polymers.

3.3 Electron Spectroscopy for Chemical Analysis (ESCA)

Paper II utilized electron spectroscopy for chemical analysis (ESCA) for obtaining chemical information about the surface of solid materials. ESCA, also known as x-ray photoelectron spectroscopy (XPS), was developed by Siegbahn and co-workers in the mid-50’s. Later improvements in computer technology and x-ray optics allowed ESCA to be further developed for the chemical characterization of surfaces.
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ESCA uses an x-ray beam to excite the surface of a solid sample, resulting in the emission of photoelectrons. The photoelectrons interact with the atoms of the material, such that the intensity of the escaping electrons decreases exponentially as the analysis depth increases. The analysis depth has been reported to be between 6 and 12 nm for polymeric materials (Ashley and Williams, 1980). An energy analysis of the photoelectrons provides both elemental and chemical bonding information about the surface.

3.4 Colloidal Probe Microscopy (CPM)

Atomic force microscopy (AFM), first developed by Binnig et al. (1986) for the imaging of surfaces, has become a very powerful instrument for studying forces on the molecular level. For normal force measurements, a cantilever tip approaches a surface and the deflection of the tip is used to measure the forces between the tip and the surface. However, it can be difficult to interpret the force data as the radius of curvature of the tip, i.e. the contact area, may be too small for accurate calculations. Ducker et al. (1991, 1992) further developed the AFM by attaching a colloidal probe to give the tip of the cantilever a well-defined geometry. This technique is generally termed colloidal probe microscopy (CPM). CPM was primarily used in Paper IV.

![Figure 5: Schematic of the setup of a colloidal probe microscope.](setup.pdf)

For CPM, schematically shown in Figure 5, a colloidal sphere is attached to a cantilever and the sample is placed on a piezo-electric scanner, which can translate in the x, y and z directions. A laser beam reflects off
the cantilever and into a photo diode, registering the deflection of the cantilever tip as a voltage. A typical normal force interaction in pure water between a glass surface and a glass colloidal probe (Zauscher, 2000) is shown in Figure 6. Several characteristics can be noted:

1. At large separations the surfaces barely interact and there is little deflection of the cantilever.

2. As the separation is reduced, the cantilever begins to deflect away from the approaching surface, indicating an electrostatic repulsive force.

3. When the surface force exceeds the cantilever stiffness, the probe will jump into contact with the surface due to attractive van der Waals forces.

4. After contacting the surface, the cantilever deflects in a region of constant compliance as the surface continues to move toward the cantilever. The onset of this constant compliance region defines the apparent zero separation. Once the zero separation distance is determined, the actual separation can be calculated by adding the cantilever deflection to the piezo displacement.

5. Upon retraction, an adhesive force may arise (seen as negative PSD voltage) until the cantilever finally detaches from the surface.

Figure 6: Data illustrating a normal force measurement for the approach and retraction of two surfaces. (Zauscher, 2000)
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3.5 Rheological measurements

The network strength of a pulp suspension can be measured through oscillatory rheological measurements. Two techniques are typically employed to measure the network strength: a Couette-type rheometer (Mason, 1954; Thalén and Wahren, 1964b,c,a; Bennington et al., 1990; Swerin, 1995; Wikström and Rasmuson, 1998; Dalpke and Kerekes, 2005) and a parallel plate rheometer (Swerin, 1995; Zauscher, 2000; Youn and Lee, 2002). A parallel plate rheometer applying small amplitude oscillations under controlled strain was employed in Papers IV and V.

For parallel plate measurements, one of the plates is oscillated at a preset amplitude (controlled strain). The force transferred through the suspension is used to the opposite plate to measure the shear modulus, $G^*$. $G^*$ can be divided into its real and imaginary parts, $G^* = G' + iG''$. $G'$, commonly referred to as the storage modulus, gives information about the elastic character of the pulp suspension. $G''$ is termed the loss modulus and describes the viscous character of the pulp suspension. For a perfectly elastic solid, $G'$ is equal to the shear modulus, $G^*$, and $G''$ is zero (Bird et al., 1987). For pulp suspensions, $G'$ is a measure of the elastic force acting on the fiber suspension. A typical measurement of the storage modulus of a pulp suspension is presented in Figure 7.

![Figure 7: Determination of the storage modulus at the plateau, $G'_0$, critical strain, $\gamma_c$, and yield stress, $\tau = G'_0 \cdot \gamma_c$, from a typical rheological measurement.](t.pdf)
The storage modulus is independent of the applied strain at low strains, such that \( G'_0 \) can be defined as the plateau value of the storage modulus. Above a critical strain, \( \gamma_c \), the storage modulus decreases with applied strain. The critical strain marks the onset for the breakage of the network structure in the fiber suspension (Swerin and Ödberg, 1992) and can be determined from the intersection of the tangent lines from the two distinct regions, as shown in Figure 7. The yield stress (\( \tau \)), calculated as \( \tau = G'_0 \cdot \gamma_c \), is also a measure of the network strength. For pulp suspensions, \( \tau \) can be viewed as the stress needed to deform the fiber network.
4 Results and Discussion

The adsorption of polyelectrolytes is highly relevant for the papermaking process. Polyelectrolyte adsorption is strongly influenced by the polyelectrolyte properties, fiber properties and adsorption conditions. Paper I examines the effect that the polyelectrolyte charge density and molecular mass have on the adsorption in various electrolyte concentrations. Paper II then continues with the influence that the fiber charge profile has on polyelectrolyte adsorption in different electrolyte concentrations. Furthermore, a hypothesis regarding the conditions where a 1:1 stoichiometry prevails was validated, as this is important for accurately measuring the surface charge using the polyelectrolyte titration method. This method is used in Paper III to investigate the relationship between surface and bulk charges of various pulps and their treatments. A surface selective method to increase the surface charge content was utilized to investigate the effect of surface charges on the fiber network strength in Paper IV. Colloidal forces do not solely govern the fiber network strength, and in Paper V the influence of mechanical forces is also reported.

4.1 Effect of polyelectrolyte properties on polyelectrolyte adsorption

Despite the fact that polyelectrolyte adsorption onto cellulosic fibers has been extensively studied, there are still aspects of polyelectrolyte adsorption to be clarified. Due to the porous and fibrillar nature of the fiber surface, it is difficult to resolve whether changes in adsorption behavior are due to changes in the conformation of the adsorbed polyelectrolyte on the fiber surface or to penetration of the adsorbed chain into the fiber cell wall. High charge density copolymers of acrylamide (AM) and diallyldimethylammonium chloride DADMAC, i.e. poly(AM-co-DADMAC), have been
synthesized in order to study the effect of the polyelectrolyte properties on the adsorption behavior.

Fluorescent labeling technique have been developed to compliment polyelectrolyte titrations. Confocal laser scanning microscopy (CLSM) has been used to visualize the location that the fluorescent copolymers adsorbed into the fibers. Adsorption and diffusion can be studied qualitatively from fluorescent intensity profiles obtained from optical cross-sections of the fiber.

4.1.1 Adsorption of high charge density polyelectrolytes

Poly-DADMAC is a widely used polyelectrolyte that to has a high charge density, specifically having a theoretical charge density of 6.19 meq/g. However, poly-DADMAC is limited in its ability to form covalent bonds with fluorescent labels. In order to be fluorescent labeled, AM can be copolymerized with DADMAC, as AM readily forms covalent bonds with most fluorescent labels. The charge density of the copolymer, $\varepsilon$, can also be controlled by the AM concentration, as AM is non-ionic. Moreover, the molecular mass $M_w$ can be controlled by the extent of copolymerization reaction. This approach was used in Paper I to synthesize copolymers with varying charge density and molecular mass that can be fluorescent labeled. The degree of fluorescent labeling is slightly greater for copolymers having a lower charge density, as the amount of AM is higher in these copolymers. However, the effect of the fluorescent groups on the polyelectrolyte charge density were shown to be minimal, suggesting that the degree of substitution is low enough to ensure that the molecular properties of the original copolymer were retained.

Adsorption isotherms depicting the adsorption of copolymers with varying charge density onto a never-dried, oxygen bleached kraft pulp under electrolyte-free conditions are presented in Figure 8. The adsorbed mass depends on the charge density, such that a lower charge density results in a higher adsorbed mass. However, it is unclear whether the increase in the adsorbed mass is a result of the copolymer penetrating into the fiber cell wall or the copolymer adsorbing in a more coiled conformation on the fiber surface that allows for additional adsorption. The adsorption of the fluorescent labeled copolymers gives information regarding the extent to which the copolymers adsorb into the fiber cell wall.

Fluorescent CLSM images and the corresponding intensity profiles in the fiber radial direction are presented in Figure 9. The difference in the fluorescent intensity at the fiber surface is the result of two factors. First, the adsorbed mass is different for each copolymer. Second, the degree of
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Figure 8: Isotherms for poly(AM-co-DADMAC) having variations in the charge density but a similar molecular mass ($M_w \sim 4 \cdot 10^5$ Da) adsorbed onto a never-dried, oxygen bleached softwood kraft pulp. (Paper I)

Figure 9: Fluorescent CLSM images of adsorbed poly(AM-co-DADMAC) having variations in the charge density ($\varepsilon$) but a similar molecular mass, $M_w \sim 4 \cdot 10^5$ Da. A never-dried, oxygen bleached softwood kraft pulp was used. Image (a) Copolymer A having $\varepsilon = 1.95$ meq/g, (b) Copolymer B having $\varepsilon = 3.40$ meq/g, (c) Copolymer C having $\varepsilon = 5.04$ meq/g and (d) untreated reference fiber. (Paper I).
substitution of the fluorescent label for each copolymer is slightly different, such that the degree of substitution is higher for lower charged copolymers. Although it is difficult to resolve from Figure 9 if the thickness of the adsorbed layer extends from the fiber surface or resides partly within the fiber wall, the layer thickness is essentially the same for all copolymers. This would indicate that the changes in the adsorbed mass do not occur from the copolymers penetrating into the fiber cell wall.

Polyelectrolyte adsorption has also been shown to be affected by molecular mass, such that decreasing the molecular mass increases the adsorbed mass (Wågberg and Öberg, 1989; Swerin and Wågberg, 1994). The explanation for the increase is that the low molecular mass polyelectrolyte is able to penetrate into the fiber cell wall. The effect of molecular mass was also investigated with the copolymers. The number of adsorbed charges as a function of equilibrium concentration are presented in Figure 10 for copolymers having varying molecular mass but a similar charge density ($\varepsilon \sim 3$ meq/g). Two copolymers having a higher charge density ($\varepsilon \sim 5$ meq/g) have also been included in order to clarify the effect of molecular mass at another charge density.

**Figure 10:** Adsorption isotherms for poly(AM-co-DADMAC) with varying molecular mass but similar charge density onto a never-dried, oxygen bleached softwood kraft pulp. (Paper I)
An effect of the molecular mass can be seen for copolymers having \( \varepsilon \sim 3.4 \text{ meq/g} \). Although almost all of the isotherms collapse onto the same curve, regardless of charge density and molecular mass, the isotherm of Copolymer F indicates a much larger adsorption. A reasonable explanation is that Copolymer F is able to penetrate into the fiber cell wall. This effect is only noted at sufficiently low molecular mass. However, the same trend does not occur for low molecular mass copolymers having a higher charge density. The highly charged copolymers (\( \varepsilon \sim 5 \text{ meq/g} \)) are most likely limited in the extent they can penetrate into the fiber wall by their extended conformation. It can be seen in Figure 10 that Copolymer D, despite a low molecular mass, does not adsorb to a greater amount, indicating it is most likely restricted to the fiber surface. Therefore, it appears that adsorption can only increase below a critical molecular mass and charge density. The extent the copolymer adsorb into the fiber cell wall was confirmed by the fluorescent CLSM images found in Figure 11.

**Figure 11:** Fluorescent CLSM images for the adsorption of poly(AM-co-DADMAC) having different molecular mass but a charge density of \( \sim 3.4 \text{ meq/g} \): (a) high molecular mass (\( M_w = 4.0 \times 10^5 \text{Da} \)), (b) moderate molecular mass (\( M_w = 1.1 \times 10^5 \text{Da} \)) and (c) low molecular mass (\( M_w = 8.0 \times 10^3 \text{Da} \)) onto a never-dried, oxygen bleached softwood kraft pulp. (Paper I).
The difference in the fluorescent intensity at the fiber surface is only due to an increase in the adsorbed mass, as the degree of substitution of the fluorescent label is essentially the same for the three copolymers due to their similar charge density. For copolymers having $\varepsilon \sim 3$ meq/g, only the lowest molecular mass copolymer, Copolymer F, is able to penetrate into the fiber cell wall. This is indicated by the thickness of the fluorescent intensity peak at the fiber surface, seen in Figure 11c. It can also be seen that Copolymer F has adsorbed into the fiber lumen, as Figure 11c exhibits a small fluorescent peak on the inside of the fiber walls. It is possible that the low molecular mass copolymer can adsorb through macropores or breakages in the fiber cell wall. This phenomenon may be kinetic in nature, such that higher molecular mass may also adsorb into the lumen, only at a slower rate.

The adsorption behavior of cationic polyelectrolytes onto cellulosic fibers has been shown to change drastically in the presence of electrolyte (Tanaka et al., 1979; Lindström and Wågberg, 1983; van de Steeg et al., 1993). The effect of the electrolyte concentration on the adsorbed mass is presented in Figure 12 for copolymers that vary in charge density. The adsorbed mass is fairly constant at low electrolyte concentrations. The slight difference in adsorbed mass is attributed to the variation in charge density. The electrolyte is not sufficient to screen the charges and the copolymer chains adsorb in an extended conformation due to electrostatic repulsion between the charges along the backbone. It is therefore expected that a 1:1 stoichiometry prevails under these conditions. This will be further investigated in Chapter 4.2 (Paper II).

![Graphs](a) Adsorbed mass (b) Adsorbed charges

**Figure 12:** Adsorption of poly(AM-co-DADMAC) as a function of electrolyte concentration for copolymers having a varying charge density onto a never-dried, oxygen bleached softwood kraft pulp. Copolymer A having $\varepsilon = 1.95$ meq/g, Copolymer E having $\varepsilon = 3.37$ meq/g and Copolymer C having $\varepsilon = 5.04$ meq/g. (Paper I)
The adsorbed mass begins to increase for all three copolymers at moderate electrolyte concentrations ($\sim 10^{-3} \text{M } \text{NaHCO}_3$). The effect of the electrolyte concentration on the adsorption is greatest for the copolymers having a lower charge density. Further increasing the electrolyte concentration starts to effectively screen the charges, causing the repulsion between the copolymer charges to decrease and the copolymer to adopt a more coiled conformation. A maximum in the adsorbed amount is achieved near $10^{-1} \text{M } \text{NaHCO}_3$ for all three copolymers. At electrolyte concentrations above $10^{-1} \text{M } \text{NaHCO}_3$, the copolymer interactions with the fiber charges are completely screened and the adsorbed mass sharply decreases towards zero. As both DADMAC and AM monomers have been shown to exhibit only electrostatic interactions with cellulose (Ishimaru and Lindström, 1984; Wågberg, 2000), it can be expected that further increases in the electrolyte concentration will cease adsorption entirely.

![Fluorescent CLSM images for the adsorption in $10^{-1} \text{M } \text{NaHCO}_3$ of poly(AM-co-DADMAC) having varying charge density onto a never-dried, oxygen bleached softwood kraft pulp. Image (a) Copolymer A having $\varepsilon =$1.95 meq/g, (b) Copolymer E having $\varepsilon =$3.37 meq/g and (c) Copolymer C having $\varepsilon =$5.04 meq/g. (Paper I).](image)

**Figure 13:** Fluorescent CLSM images for the adsorption in $10^{-1} \text{M } \text{NaHCO}_3$ of poly(AM-co-DADMAC) having varying charge density onto a never-dried, oxygen bleached softwood kraft pulp. Image (a) Copolymer A having $\varepsilon =$1.95 meq/g, (b) Copolymer E having $\varepsilon =$3.37 meq/g and (c) Copolymer C having $\varepsilon =$5.04 meq/g. (Paper I).

Fluorescent CLSM images and the corresponding intensity profiles are presented in **Figure 13** for the adsorption in $10^{-1} \text{M } \text{NaHCO}_3$ for the copolymers presented in **Figure 12**. The difference in adsorbed mass can
be explained by the penetration depth, i.e. the thickness of the fluorescent intensity peak at the fiber surface. It is apparent that the penetration depth decreases with increasing copolymer charge density. It can also be seen from light scattering experiments (see Paper I) that the copolymers behave as uncharged polymers in solution at this electrolyte concentration. Although the charge density does not alter the molecular conformation at $10^{-1} \text{M} \ NaHCO_3$, the charge density still causes interactions with the fiber charges. There is a considerable adsorption at $10^{-1} \text{M} \ NaHCO_3$ because the fiber-copolymer interactions are not fully screened. Otherwise, adsorption would not occur. Because the interactions with the fiber charges are governed by the copolymer charge density, it can be inferred that localized interactions with the fiber wall occur as the copolymer attempts to penetrate into the fiber pores. This could lead to a kinetic process that is essentially dependent on the charge density. A possible explanation for this is that the copolymers with a higher charge density ($\varepsilon = 5.04 \text{ meq/g}$) adsorb to a lesser extent into the fiber wall because they diffuse at a slower rate. It may be said that the charge density create localized interactions that retard the copolymer from penetrating the cell wall and also increase the activation energy to jump through the cationic field, i.e. the adsorbed polyelectrolyte layer, at the fiber surface.
4.2 Effect of fiber properties on polyelectrolyte adsorption

The fiber charge density is an equally important factor as the polyelectrolyte charge density for polyelectrolyte adsorption onto cellulosic fibers. In order to change the charge density in a controlled manner, an untreated pulp was bulk (Walecka, 1957) and surface (Laine et al., 2000) carboxymethylated (Paper II). Bulk carboxymethylation is based on substituting hydroxyl groups for carboxylic acid groups by treating the fibers with monochloroacetic acid in isopropanol. The degree of substitution (DS) is controlled by the amount of monochloroacetic acid added to the fibers. For surface carboxymethylation, high molecular mass carboxymethyl cellulose (CMC) was grafted onto the fiber surface under specific conditions, making it possible to increase the surface charge content with the amount of CMC grafted. Table 2 shows the total charge density, as determined by conductometric titration (Katz et al., 1984), and the surface charge, as determined by polyelectrolyte titration using high molecular mass poly-DAMAC (Mw = 9.2 · 10^5 Da), for the carboxymethylated pulps.

Table 2: Total charge density and surface charge density for bulk carboxymethylated (DS = 0-0.076) and CMC surface grafted fibers (0-14 mg/g grafted CMC). All the pulps were never dried during preparation. (Paper II and IV)

<table>
<thead>
<tr>
<th>Pulp treatment</th>
<th>Total charge (µeq/g)</th>
<th>Surface charge (µeq/g)</th>
<th>Charge ratio</th>
<th>Surface selectivity†</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS 0.000</td>
<td>37</td>
<td>1.7</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>DS 0.009</td>
<td>89</td>
<td>4.1</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>DS 0.045</td>
<td>314</td>
<td>16</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>DS 0.076</td>
<td>506</td>
<td>34</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>0 mg/g CMC</td>
<td>34</td>
<td>1.6</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>4 mg/g CMC</td>
<td>45</td>
<td>10</td>
<td>0.22</td>
<td>0.75</td>
</tr>
<tr>
<td>14 mg/g CMC</td>
<td>74</td>
<td>21</td>
<td>0.29</td>
<td>0.49</td>
</tr>
</tbody>
</table>

†) ∆ surface charge / ∆ total charge

Each method increases both the surface charge and the total charge of the fiber. However, bulk carboxymethylation introduces charges uni-
formly throughout the the fiber cell wall, whereas surface carboxymethylation mainly introduces charges on the surface, shown as an increase in the charge ratio. The CMC molecule has a molecular mass of $\sim 10^6$ Da, such that it will be grafted mainly onto the fiber surface. The decrease in surface selectivity at high grafting levels is due to surface swelling (Laine et al., 2003a). When the amount of grafted CMC increases, the fiber surface swells because of electrostatic repulsions between CMC chains. This results in some of the pores and cavities opening up, allowing more CMC chains to be grafted below the surface of the fiber.

4.2.1 Effect of electrolyte concentration on polyelectrolyte adsorption onto fibers with different charge profiles

The bulk and surface carboxymethylated pulps were used to investigate the effects of electrolyte concentration on polyelectrolyte adsorption onto fibers with different charge profiles. The adsorption of high molecular mass poly-DADMAC (Mw = $9.2 \cdot 10^5$ Da) onto fibers that were bulk carboxymethylated to different degrees is shown in Figure 14 at various electrolyte concentrations. At $10^{-5}$M NaHCO$_3$ the charge ratio is 0.05 for all pulps except for the pulp carboxymethylated to a DS of 0.076. This suggests that the added charges are distributed evenly throughout the fiber and the treatment is not surface selective. The higher surface charge ratio exhibited by the highest DS (0.076) is probably due to extensive swelling of the fiber, resulting in an increased surface area and accessibility to more of the fiber charges for the adsorbing poly-DADMAC. Another significant observation is that the onset for the increase in the adsorption is shifted towards higher electrolyte concentrations for pulps having a higher surface charge.

The data in Table 2 indicates that it is possible to increase the charge ratio from 5% to 30% by grafting CMC to the fiber surface. Figure 15 presents the results for the adsorption of poly-DADMAC to fibers having different surface charges in various electrolyte concentrations. The adsorption of poly-DADMAC is less sensitive to changes in the electrolyte concentration for pulps having a higher surface charge.
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Figure 14: The charge ratio of bulk carboxymethylated pulps as a function of the NaHCO$_3$ concentration. The adsorbing polyelectrolyte was poly-DADMAC having a molecular mass of 9.2·10$^5$ Da. (Paper II)

Figure 15: The charge ratio of CMC grafted pulps at different NaHCO$_3$ concentrations. The adsorbing polyelectrolyte was poly-DADMAC having a molecular mass of 9.2·10$^5$ Da. (Paper II)
4.2.2 Investigation of the deviation from a 1:1 stoichiometry

Adsorption at a 1:1 stoichiometry is important for measuring the surface charge, as the amount of surface charges is determined from the amount of polyelectrolyte charges adsorbed. A prerequisite for a 1:1 adsorption stoichiometry is the absence of non-electrostatic interactions. At a low electrolyte concentrations (e.g. $<10^{-4}$M $\text{NaHCO}_3$ in Figure 14 and Figure 15) the distance between the charges ($d$) will be smaller than the thickness of the diffuse electric double layer, $\kappa^{-1}$ (Netz and Andelman, 2003). The interaction between the fiber surface and the polyelectrolyte, illustrated in Figure 16(a), can be considered as the interaction of two mean-fields rather than point-charges (Netz and Andelman, 2003).

![Figure 16: Schematic of polyelectrolyte adsorption at (a) low and (b) high electrolyte concentration. $\kappa^{-1}$ is calculated according to Equation 3. (Paper II)](image)

Adsorption increases when the electrolyte concentration is sufficient to screen the polyelectrolyte charges. This is attributed to the thickness of the double layer becoming smaller than the distance between the charges as the electrolyte concentration increases ($d > \kappa^{-1}$, see Figure 16(b)). At higher electrolyte concentrations the polyelectrolyte and fiber charges begin to behave as discrete charges instead of as a mean-field. Also, the conformation of the polyelectrolyte in solution will change with the electrolyte concentration. When the electrolyte concentration is further increased, the polyelectrolyte charges will be further screened from each other and the repulsion will decrease. The polyelectrolyte can adsorb in loops and tails instead of a flat conformation, which occurs at low electrolyte concentrations. The deviation from a 1:1 stoichiometry will be more profound at...
higher electrolyte concentrations, resulting in an increase in the adsorption. At very high electrolyte concentrations, the adsorption eventually ceases because the electrolyte completely screens the polyelectrolyte charges from interacting with the fiber charges.

It was of interest to determine the electrolyte concentration at which the stoichiometry starts to deviate from 1:1, i.e. the electrolyte concentration that fulfills the limiting condition of $d > \kappa^{-1}$. Fibers having different charge profiles were used to test this hypothesis (see Table 2). A critical electrolyte concentration (CEC) was introduced to define the electrolyte concentration where the apparent surface charge had increased by 20% (see Figure 17). $\kappa^{-1}$ was then calculated of each CEC and plotted against the geometric distance between the charges on the surface, which was calculated according to Equation 5:

$$
d = \sqrt[3]{\frac{V_S}{\sigma_S \cdot N_A}} = \sqrt[3]{\frac{W R V_{Na} \times 5\%}{\sigma_S \cdot N_A}}$$

where $V_S$ is the "surface volume", $\sigma_S$ is the surface charge density, $N_A$ is Avogadro’s number and $W R V_{Na}$ is the water retention value for the untreated pulp in its sodium form.

Because the surface of a wet fiber is ill-defined, a "surface volume" was introduced as a more straightforward way to define and calculate the dis-
distance between fiber charges. It can be seen in Table 2 that approximately 5% of the total charges are located in this ”surface volume” for bulk carboxymethylated pulps. If the location of the charges and the swelling are uniform throughout the fiber wall, the surface volume can be calculated as 5%×WRV$_{Na}$, using the WRV as a measure of the fiber swelling (Scallan and Carles, 1972). The results of this approach are shown in Figure 18. It can be seen that $d \approx \kappa^{-1}$ (the dashed line represents where $d = \kappa^{-1}$) for all the different pulp treatments. The hypothesis that $d \ll \kappa^{-1}$ must be satisfied in order for a 1:1 stoichiometry to prevail was therefore validated to be a useful and simple assumption.

It should be noted that this concept is similar to predictions based on lateral correlation effects in polyelectrolyte adsorption theory (Netz and Joanny, 1999; Netz and Andelman, 2003), for which the concept of a mesh size for the adsorbed polyelectrolytes was introduced. Polyelectrolyte adsorption theory assumes that the adsorbed polyelectrolyte forms a disordered surface pattern with chains crossing each other. The average distance between the crossings is characterized by a certain mesh size, $\xi_s$. Charge overcompensation is predicted when $\xi_s$ becomes on the order of $\kappa^{-1}$. If the mesh size is associated with the charge distance, the present model is identical to the model of Netz and coworkers.
4.3 Verification of the polyelectrolyte titration method by ESCA

The polyelectrolyte titration method was verified with ESCA (Electron Spectroscopy for Chemical Analysis) in Paper II. ESCA has been shown to detect the amount of nitrogen on a surface at a reported analysis depth of 6-12 nm for polymeric materials (Ashley and Williams, 1980). High molecular mass \(9.2 \times 10^5\) Da and low molecular mass \(7.0 \times 10^3\) Da poly-DADMAC were adsorbed onto highly charged (bulk carboxymethylated) fibers having a total charge density of 506 \(\mu\)eq/g in \(10^{-5}\)M \(NaHCO_3\). The adsorbed mass was determined by polyelectrolyte titration. Handsheets were made from the fibers and the amount of nitrogen was analyzed using ESCA. The results are displayed in Figure 19.

As can be seen in Figure 19(a), the adsorbed amount of the lower molecular mass poly-DADMAC is about ten times higher when determined by polyelectrolyte titration. This is expected as the lower molecular mass poly-DADMAC accesses the charges in the fiber pores, whereas the high molecular mass poly-DADMAC can only reach the charges on the fiber surface. The surface nitrogen content determined by ESCA (Figure 19(b)) shows a similar adsorbed amount regardless of the molecular mass. It is expected in the case of a 1:1 stoichiometry that the surface nitrogen content would be the same for a given fiber surface. Even though it may appear that the fibers treated with the high molecular mass poly-DADMAC have a
somewhat higher nitrogen content, it was concluded that a reasonable agree-
ment is obtained in the ESCA analysis between the two polyelectrolytes as
the thickness of the adsorbed layer is about the same for each molecular
mass. These results give further credence to the hypothesis that the surface
charge of cellulose can be determined by polyelectrolyte titration using high
molecular mass poly-DADMAC.
4.4 Surface and bulk charges of cellulosic fibers

Paper II also determined that the fiber surface charge can be measured with polyelectrolyte titration using a high molecular mass polyelectrolyte (poly-DADMAC Mw ~10^6 Da) at low ionic strength (10^{-5}M NaHCO_3). In 10^{-5}M NaHCO_3, the thickness of the electrostatic double layer is 1000 Å for a monovalent electrolyte, which is also the interaction distance for the polyelectrolyte at the interface. If the thickness of the fiber cell wall is sufficiently small, this distance cannot be ignored and the charge ratio could be affected. However, if fibrils protrude out from the fiber surface, the polyelectrolyte titration procedure will measure the total charge rather than the fibril surface charge, as the thickness of the fibrils is of the same order as the double layer thickness.

In Paper III, the relationship between the total charge (as determined by conductometric titration (Katz et al., 1984)) and the surface charge (measured by polyelectrolyte titration) was presented for various pulps. Pulps from different mills in Sweden were studied, as they had been subjected to different bleaching sequences and treatments. Fibers from several types of pulping processes, noted in Table 3, were also used. Although the total and surface charge vary to a large extent between the different types of pulping, the charge ratio does not change significantly for chemical (kraft) and semi-chemical (NSSC) pulping. However, the (thermo)mechanical pulping (TMP) process gives a much higher charge ratio due to the large amount of fines material released during pulping. Fines material has a higher specific surface area, resulting in an increased charge ratio.

Table 3: Charge profiles for different types of unbleached pulp from various mills in Sweden. (Paper III)

<table>
<thead>
<tr>
<th>Company/Mill</th>
<th>Treatment type</th>
<th>Total charge (µeq/g)</th>
<th>Surface charge (µeq/g)</th>
<th>Charge ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stora Enso/Skoghall</td>
<td>Kraft/SW</td>
<td>107</td>
<td>3.4</td>
<td>0.032</td>
</tr>
<tr>
<td>M-real/Husum</td>
<td>Kraft/HW</td>
<td>137</td>
<td>6.3</td>
<td>0.049</td>
</tr>
<tr>
<td>Billerud/Skärblacka</td>
<td>NSSC/HW</td>
<td>156</td>
<td>6.0</td>
<td>0.038</td>
</tr>
<tr>
<td>Holmen/Hallsta</td>
<td>TMP/SW</td>
<td>83</td>
<td>11</td>
<td>0.133</td>
</tr>
</tbody>
</table>

A bleaching sequence was examined by collecting pulp after each bleaching stage and measuring the charge content, see Table 4. The number of charges decreases as the κ number (lignin removal) decreases. The charge
density increases after the first bleaching stage due to oxidation of end groups and cleavage of polysaccharide chains, forming aldehydic end groups that can be oxidized to carboxylic acid groups (Sjöström, 1993). Although the total and surface charge change through the bleaching sequence, the charge ratio remains fairly constant (the deviation from the charge ratio 0.05 in Table 4 is however significant).

Table 4: Bleaching sequence for softwood (60:40 spruce:pine) kraft pulp from Stora Enso, Skoghall. (Paper III)

<table>
<thead>
<tr>
<th>Bleaching sequence</th>
<th>Kappa number</th>
<th>Total charge (µeq/g)</th>
<th>Surface charge (µeq/g)</th>
<th>Charge ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unbleached</td>
<td>34.8</td>
<td>107</td>
<td>3.4</td>
<td>0.032</td>
</tr>
<tr>
<td>O</td>
<td>18.8</td>
<td>115</td>
<td>5.9</td>
<td>0.051</td>
</tr>
<tr>
<td>O OP</td>
<td>10.7</td>
<td>98</td>
<td>4.8</td>
<td>0.049</td>
</tr>
<tr>
<td>O OP D</td>
<td>4.0</td>
<td>59</td>
<td>3.1</td>
<td>0.053</td>
</tr>
<tr>
<td>O OP D Q</td>
<td>3.6</td>
<td>62</td>
<td>2.8</td>
<td>0.045</td>
</tr>
<tr>
<td>O OP D Q PO</td>
<td>1.9</td>
<td>58</td>
<td>2.6</td>
<td>0.045</td>
</tr>
</tbody>
</table>

The effect of mechanical treatment can be seen in Table 5, where a fully bleached softwood kraft pulp was investigated with the fines material being removed before beating. The total charge is constant as charges are not created during the mechanical treatment. On the other hand, the surface charge increased because more surface is exposed as fines material are released during beating. It is also possible to increase the charge ratio with this treatment, which could therefore be used as a measure for the extent of beating.

Table 5: Effect of beating on the charge ratio of a never-dried, ECF-bleached (ODQPDP) softwood kraft pulp from M-real, Husum. The fines material was removed using a screen with 100 µm slots prior to beating. (Paper III)

<table>
<thead>
<tr>
<th>PFI revolutions</th>
<th>Total charge (µeq/g)</th>
<th>Surface charge (µeq/g)</th>
<th>Charge ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>37</td>
<td>1.7</td>
<td>0.046</td>
</tr>
<tr>
<td>1000</td>
<td>37</td>
<td>2.6</td>
<td>0.070</td>
</tr>
<tr>
<td>5000</td>
<td>38</td>
<td>4.9</td>
<td>0.129</td>
</tr>
<tr>
<td>10000</td>
<td>40</td>
<td>6.0</td>
<td>0.150</td>
</tr>
</tbody>
</table>
The Effects of Cellulosic Fiber Charges on Polyelectrolyte Adsorption and Fiber-Fiber Interactions

4.5 Fiber Network Strength

4.5.1 Colloidal forces

It is well-known that the fiber charge content is an important factor for the final paper properties. CMC-grafting can be utilized to increase the surface charge (Papers II and III), and this method was used to study the influence of colloidal interactions on the fiber network strength (Paper IV). However, cellulosic fibers are not suitable to use for micro-scale measurements due to their rough and fibrillated surface. Instead, model cellulosic surfaces are required for techniques such as colloidal probe microscopy (CPM). Gunnars et al. (2002) developed methods for preparing cellulose films by spincoating a dissolving pulp onto a silica surface. Normal force measurements can therefore be made by mounting a cellulose bead to a cantilever tip and bringing the model cellulose surfaces into contact. The surface charge density was increased by grafting high molecular mass CMC ($M_w \sim 10^6$ Da) onto the cellulosic surfaces using the heating stage of the CPM.

![Figure 20: Force as a function of separation between two approaching cellulosic surfaces with attached CMC (CMC) and without (Ref). The expected surface charge densities are ▲ 2.90 \, \mu\text{eq/g} and ◦ 24.9 \, \mu\text{eq/g. The experiments were carried out in } 10^{-5}\text{M NaCl with the surfaces in their sodium form. (Paper IV)}](image)

For untreated surfaces (surface charge density of 2.9 \, \mu\text{eq/g}), the forces are purely repulsive on approach and no attractive van der Waals forces, as
can be seen in Figure 20. The repulsive forces at large surface separations are electrostatic in nature, but as the surfaces approaches each other (around 10 nm) a steep increase in the repulsion occurs. This repulsion can be ascribed as being electrosteric, a combination of electrostatic and steric repulsions. The electrosteric repulsion dramatically increased when the the surface charge density increased from 2.9 µeq/g to an expected 25 µeq/g, due to CMC chains extending from the surface.

Upon retraction, the force-separation curve does not follow the curve displayed upon approach. The large hysteresis occurring for the CMC-treated surfaces is probably due to the CMC chains extending from the surface. Lowack and Helm (1998) found that the hysteresis was dependent on the distance that the surfaces are compressed, such that the force-separation curves were irreversible if the surfaces were separated by a distance smaller than the distance that the polyelectrolyte chains extended out in solution. Hence, a rather large hysteresis would be expected as the CMC is a rather long chain extending out from the surface.

To investigate the influence of the surface charge density on the fiber network strength, the reference fibers (surface charge density 1.6 µeq/g) were grafted with various amounts of carboxymethyl cellulose (CMC) such that the surface charge density was increased to 10, 17 and 21 µeq/g respectively. The apparent yield stress of these fiber networks is presented as a function of fiber consistency in Figure 21.

![Figure 21](image.png)

**Figure 21:** The dependence of the apparent yield stress on the consistency for a bleached kraft pulp having different surface charge densities. The power law dependence is given after each charge density. All pulps are in their sodium form and the measurements were performed in deionized water. (Paper IV)
The effect of fiber consistency on the apparent yield stress follows a power law dependence, $\tau = aC^b_w$, as has been previously reported (Swerin and Ödberg, 1992; Wikström and Rasmuson, 1998; Dalpke and Kerekes, 2005). The values of $a$ and $b$ vary between different laboratories and between measurement methods. The yield stress should therefore be interpreted as an apparent yield stress. Moreover, the power law exponent increases with increasing surface charge density. This conforms with the view that colloidal interactions affect the rheological behavior more at low pulp consistencies, whereas mechanical interlocking dominates the interactions at higher consistencies (Kerekes et al., 1985). The decrease in the apparent yield stress with increasing surface charge density is linked to an increased repulsion, resulting in a lower friction between fibers.

The conformation of the CMC grafted to the fiber surface will strongly depend on the pH and electrolyte concentration. The conformation of the CMC at the surface is referred to as the surface swelling of the cellulose and can be quantified. A good measure for total fiber swelling is the water retention value (WRV) (Scallan, 1983). Paper IV contains measurements of the fiber network strength in different electrolyte concentrations and for different counter-ions. The WRV was measured for all samples, and the apparent yield stress is presented as a function of the WRV in Figure 22.

![Figure 22](all.pdf)

**Figure 22:** The dependence of the apparent yield stress on swelling (WRV) for all bleached kraft pulps having varying charge densities. The WRV was determined from the pulps in Paper IV.

The apparent yield stress decreases for all consistencies as the swelling increased. The apparent yield stress also has a negative power law dependence on the WRV ($\tau = a \cdot WRV^{-b}$). The slope is approximately the same
at a consistency of 2 w-% and 4 w-%, whereas the slope is greater for a consistency of 1 w-%. This implies that lower fiber consistencies are influenced more by electrosteric interactions, while mechanical forces are more important at higher consistencies.

4.5.2 Mechanical forces

**Paper V** presents the dependence of the network strength on mechanical forces by altering the number of contact points and fiber stiffness. Two pulps having distinct properties were used. A bleached commercial pulp that was beaten 4000 revolutions in a PFI mill served as the more flexible pulp. The pulp was fractionated into different fiber lengths in a Bauer-McNett fractionator. A stiffer pulp was prepared by laboratory cooking and bleaching chips sawn to different thicknesses. The fiber network strength was measured from the different fractions, and the storage modulus at small amplitude oscillation, $G'_0$, as a function of the fiber length can be seen in **Figure 23**.

![Figure 23: Dependence of the fiber length on the storage modulus for unbeaten fibers and fibers beaten 4000 revolutions in a PI-mill. (Paper V)](image)

Longer fibers have a larger number of fiber-fiber contacts, which results in stronger networks. This is in agreement with Dalpke and Kerekes (2005), who found a clear influence of the fiber length on the apparent yield stress. The beaten pulp had a lower $G'_0$, which is a consequence of the fiber flexibility. Beating the pulp decreases the fiber wall stiffness and creates a more
flexible fiber. As the flexibility increases, less tension can build up in the network because the fibers comes to rest in a less strained position, resulting in a decreased network strength.

The critical strain is presented in Figure 24 as a function of fiber length. The small decrease in $\gamma_c$ with increasing fiber length is somewhat surprising, as it would be expected that a lower strain would be applied before a network having fewer contact points starts to break apart. However, this resembles a rubbery network, where the strain to failure decreases with an increased number of contact points per molecule. Simulations have shown that a lower strain is required to break flocs created from a more flexible fiber (Switzer and Klingenberg, 2003). The unbeaten fibers would therefore be expected to exhibit a higher critical strain. Although this is not the case, it can be explained by the fact that the beaten fibers have a more fibrillated and rough surface, increasing the influence of mechanical surface linking.

Figure 24: Critical strain as a function of the fiber length for unbeaten fibers and fibers beaten 4000 revolutions in a PFI-mill. (Paper V)
5 Conclusions

This thesis investigated the effects of cellulosic fiber charges on polyelectrolyte adsorption and fiber-fiber interactions. It has been shown that the charge density of the adsorbing polyelectrolyte essentially governs the adsorption to cellulosic fibers. Under electrolyte-free conditions, cationic polyelectrolytes typically adsorb to the fiber surface. The adsorbing polyelectrolyte will only penetrate into the fiber cell wall if the molecular mass is sufficiently low and the charge density is not too high. In the presence of electrolyte, a 1:1 adsorption stoichiometry will only prevail at low electrolyte concentrations, whereas adsorption increases with increasing electrolyte concentration until the electrostatic interactions become completely screened. The adsorbing polyelectrolyte may penetrate into the fiber wall, although it at high electrolyte concentrations was inferred that this process is kinetic in nature. Adsorption into the fiber cell wall is governed by the charge density, such that localized interactions with the fiber wall occur as the polyelectrolyte attempts to penetrate into the fiber pores. This process is thought to depend on the charge density of the polyelectrolyte, which interacts with the fiber pores and slows the diffusion process.

The adsorption of polyelectrolytes onto cellulosic fibers is also affected by the surface charge density of the fiber. Bulk and surface carboxymethylation can be used to introduce charges in the fiber cell wall and on the fiber surface, resulting in a selective modification of the charge profile. In the presence of electrolyte, a deviation from a 1:1 stoichiometry occurs at a higher electrolyte concentration for fibers having a higher surface charge density. This effect was attributed to the fact that the distance between the fiber charges decreases as the charge density increases. A higher electrolyte concentration is then required before the distance between the fiber charges exceeds the thickness of the double layer, which causes a deviation from a 1:1 stoichiometry. The onset of the deviation from a 1:1 stoichiometry was defined by a critical electrolyte concentration (CEC). A good agreement was found between the thickness of the electric double layer at the
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CEC and the distance between the fiber charges. It was concluded that the distance between the fiber charges must be smaller than the diffuse electric double layer in order for a 1:1 stoichiometry to prevail. ESCA was used as an independent method to confirm the results from polyelectrolyte titration. The results from ESCA agreed well with the results from polyelectrolyte titration and it was concluded that polyelectrolyte titration is a viable method for measuring the fiber surface charge when performed under the appropriate conditions.

The amount of bulk and surface charges for various types of pulp and treatments were examined using the polyelectrolyte titration method. It was found that even though the amount of surface charges changes, the ratio between the surface and bulk charges remains fairly constant for chemical pulps. The (surface) charge can be increased through beating or CMC-grafting. The charge ratio (surface charges divided by the bulk charges) can also be used as a measurement of the rate of beating.

The investigation of the influence of charges on fiber network strength revealed that grafting CMC onto the fiber surface results in a large electrosteric repulsion. This repulsion is caused by the CMC chains protruding from the surface into solution. The increased repulsive force is expected to decrease the friction between the fibers. Results showed the the increase in surface charge decreased the fiber network strength. It can be concluded that the relative influence of colloidal forces are large compared to mechanical forces at low fiber concentration (\(\sim 1\text{ w-\%})\). The mechanical forces responsible for the fiber network strength indicated that longer fibers increase the network strength, as they contain a larger amount of fiber contacts. However, by the fiber flexibility also contributes to the network strength. Stiffer fibers create a stronger fiber network because the fibers come to rest in a more strained position. Therefore, the influence of elastic fiber bending is the predominant mechanism at higher consistencies.
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Stockholm, September 28th, 2006

Elisabet Horvath
The Effects of Cellulosic Fiber Charges on Polyelectrolyte Adsorption and Fiber-Fiber Interactions

Literature


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