

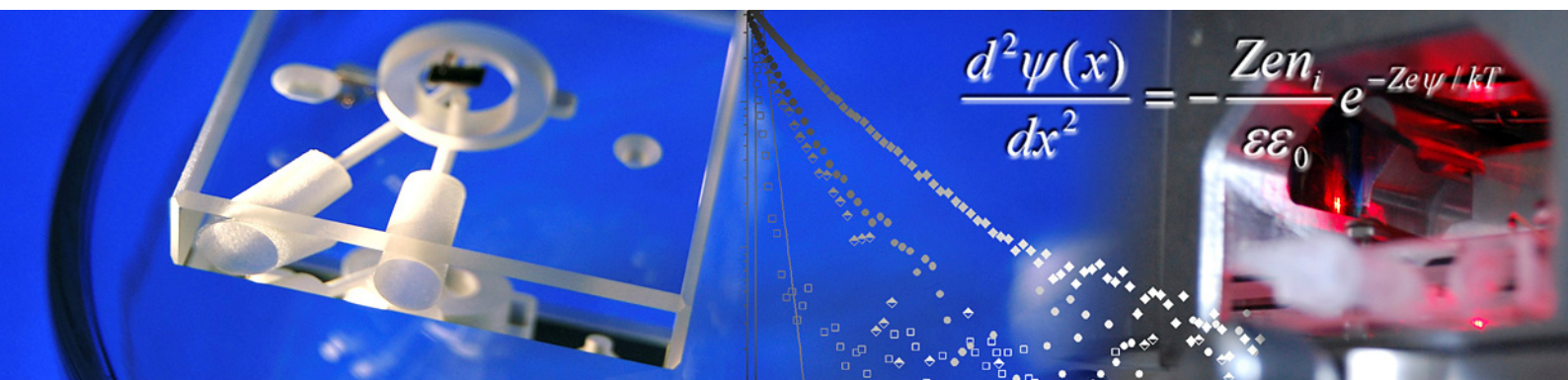
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SURFACE INTERACTIONS IN POLYELECTROLYTE-CELLULOSE SYSTEMS AND THEIR IMPLICATIONS FOR FLOCCULATION MECHANISMS

Doctoral thesis

Jani Salmi



TEKNILLINEN KORKEAKOULU
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HELSINKI UNIVERSITY OF TECHNOLOGY
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<p>Abstract</p> <p>The overall purpose of this work was to gain a better understanding on how the different polyelectrolyte systems affect on the interactions between cellulose surfaces, and thus how the different flocculation systems worked on a molecular level. The focus was on studying the effect of cationic polyelectrolytes, polyelectrolyte complexes and architectures formed by polyelectrolyte and nanoparticles on interactions. The main part of the results was obtained using atomic force microscope (AFM).</p> <p>The forces between cellulose surfaces in cationic polyelectrolyte solutions depended on the molecular weight and charge density of the polyelectrolyte. Repulsion at high polymer concentrations was mainly steric in the solution of high molecular weight, low charged polyelectrolyte, whereas repulsion was mainly electrostatic in the solution of the low molecular weight, high charged polyelectrolyte. Also forces on separation were different. While a sharp minimum was found in the presence of a polyelectrolyte with high charge density and low molecular weight close to charge neutralization point, the detachment was gradual and long ranged for a polyelectrolyte with low charge density and high molecular weight. The main mechanism for flocculation was bridging in both cases.</p> <p>The interactions between adsorbed polyelectrolyte complex layers were mainly steric and repulsion was long ranged, even at low polymer concentration. The largest complex, formed by high molecular weight, low charged polyelectrolytes, showed the longest ranged repulsion and the best dewatering behaviour. In contrast to single polymer systems, the pull-off force was long ranged even in high polymer concentrations. It was concluded that the flexible and large complex was beneficial for flocculation, when the anionic polyelectrolyte can act as a link between the complex layers.</p> <p>The stratifying of silica nanoparticles and cellulose nanofibrils (NFC) with polyelectrolyte were compared. The adsorption and repulsion increased during the layer formation in the silica nanoparticle systems, whereas the second addition of cationic polyelectrolyte decreased repulsion in the case of nanofibrillar cellulose multilayer formation due to the collapse of the topmost nanofibrils. A high repulsion between nanofibril covered surfaces indicated together with high dissipation changes that NFC formed loose and thick layer containing a large amount of water. Silica nanoparticles were concluded to be able to penetrate inside the loose polyelectrolyte structure due to their small size. On the other hand, NFC formed individual layers between the polyelectrolyte layers.</p>			
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Tiivistelmä <p>Tutkimuksen tarkoituksena oli selvittää, kuinka erilaiset polyelektrolyttisysteemit vaikuttavat voimiin selluloosapintojen välillä, ja siten ymmärtää, kuinka erilaiset flokkulaatiomekanismit toimivat molekyyalitasolla. Tutkimuksessa keskityttiin kationisten polyelektrolyyttien, polyelektrolyttikompleksien ja polyelektrolyytti-nanopartikkeli-kerrosten vaikutukseen pintavoimiin, joita tutkittiin atomivoimamikroskoopilla (AFM).</p> <p>Vuorovaikutukset selluloosapintojen välillä kationisessa polyelektrolyyttiliuoksessa riippuivat polyelektrolyytin molekyylipainosta ja varaustiheydestä. Korkeissa polyelektrolyyttipitoisuuksissa repulsio oli pääasiassa steeristä korkean molekyylipainon ja matalan varaustiheyden polyelektrolyytin ollessa kyseessä, kun taas repulsio oli pääasiassa sähköstaattista matalan molekyylipainon ja korkean varaustiheyden polyelektrolyytin tapauksessa. Myös irrottamisvoimat olivat erilaiset ko. tapauksissa. Terävä minimi havaittiin lähellä pintavarauksen neutraloitumispistettä matalan molekyylipainon ja korkean varaustiheyden polyelektrolyytillä, mutta irtoaminen oli vaihtelevaa ja kauaskantoista korkean molekyylipainon ja matalan varaustiheyden polyelektrolyytin tapauksessa. Flokkulaation päämekanismina todettiin olevan silloittuminen.</p> <p>Pintavoimat polyelektrolyttikompleksikerrosten välillä olivat pääasiassa steerisiä. Repulsio ulottui pitkälle jopa matalilla polymeeripitoisuuksilla. Kauskantoisin repulsio ja paras vedenpoistovaikutus havaittiin mitattaessa isointa kompleksia sisältävässä liuoksessa. Kompleksi oli muodostettu korkean molekyylipainon ja matalan varaustiheyden vastakkaismerkkisistä polyelektrolyyteistä. Havainnot irrottamisvoimissa olivat erilaiset verrattuna yksikomponenttisysteemiin. Irrottamisvoima oli pitkäkantoista jopa korkeissa polymeeripitoisuuksissa. Tästä pääteltiin, että joustava ja iso kompleksi oli edullinen flokkulaatiolle. Keskeisin mekanismi oli se, että anioninen polyelektrolyytti toimi sitovana linkkinä polyelektrolyttikompleksikerrosten välillä.</p> <p>Kokeissa monikerroksilla havaittiin, että adsorptio ja repulsio kasvoivat kerrostumisen aikana piidioksidinanopartikkeli-systeemeissä, kun taas selluloosanofibrillien muodostama kerros painui kasaan toisessa polyelektrolyytin lisäyksessä. Korkea repulsio nanofibrillikerrosten välillä yhdessä korkean dissipaation kanssa ilmaisivat, että nanofibrillit muodostivat löyhän ja paksun kerroksen, joka sisälsi paljon vettä. Piidioksidinanopartikkelit pystyivät tunkeutumaan polyelektrolyttikerroksen sisään pienestä koostaan johtuen toisin kuin nanofibrillit muodosti itsenäisiä kerroksia verkottumistaipumuksensa takia.</p>			
Asiasanat Pintavoima, AFM, flokkulaatio, selluloosa, polyelektrolyytti, polyelektrolyttikompleksi, polyelektrolyttimonikerros, nanopartikkeli			
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To Jaana with love

In memory of Jussi 1975-2004

PREFACE

This study was carried out in the Department of Forest Products Technology at Helsinki University of Technology during 2001-2009. It has been a long and rough journey for me. I have learned a lot of science but also of me and life. Many deserves a word of thank for supporting and helping me during this process.

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I am grateful to my supervisor Professor Janne Laine for trusting and believing in me through these years. We planned this thesis together right from the beginning and he guided me with his great knowledge in this field. I am indebted to my advisor Docent Monika Österberg for her time and patience. Her guidance in writing has been invaluable. She always found time to help me and to discuss with me. I thank Professor Emeritus Per Stenius. Per is perfect idol for any young scientist. His enthusiasm for science and his kindness are admirable. In addition, I have been privileged to work with young and talented scientists. I am grateful to all my co-authors Dr. Susanna Ahola, Dr. Juha Lindfors, Tiina Nypelö and Dr. Leena-Sisko Johansson. It was joy working with them.

Former Laboratory of Forest Products Chemistry at TKK is probably the one of the best working places. I thank all past and present colleagues for creating nice and supporting atmosphere. Especially I thank Ritva Kivelä, Marja Kärkkäinen and Anu Anttila for laboratory assistance and Delphine Miquel for helping me with NFC surfaces. Dr. Arja Paananen (VTT) is acknowledged for valuable discussion about AFM. Librarian Kati Mäenpää is thanked for her help in literature acquisitions and for nice conversations when we were in neighboring offices. I thank Esa Pirttinen for his friendship and interdisciplinary discussions during lunch breaks. In addition, Dr. Joseph Campbell is thanked for the linguistic revision of the manuscript.

I would not survive through this without my supporting and caring friends, Ari and Tuija. I am grateful to them for their friendship and for listening me whenever something was bothering me. In addition, I am indebted to Ari for his expertise with the cover image. I am grateful to my sister Eeva for her love and support and to my sister Leena's family for being my second home. I thank my parents, sisters, brothers and the rest of the family and friends just for being there for me always when needed.

I owe my deepest gratitude and love to Jaana for being the light and warmth of my life, for endlessly encouraging me, for believing me, for loving in me.

Espoo, April 27th, 2009

Jani Salmi

LIST OF PUBLICATIONS

This thesis is mainly based on the results presented in five publications which are referred as Roman numerals in the text. Some additional published and unpublished data is also related to the work.

- Paper I** Salmi, J., Österberg, M., Stenius, P. and Laine, J. (2007). Surface Forces between Cellulose Surfaces in Cationic Polyelectrolyte Solutions: The Effect of Polymer Molecular Weight and Charge Density. *Nordic Pulp and Paper Research Journal* 22(2), 249-257.
- Paper II** Salmi, J., Österberg, M. and Laine, J. (2007). The Effect of Cationic Polyelectrolyte Complexes on Interactions Between Cellulose Surfaces. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 297(1-3), 122-130.
- Paper III** Ahola, S., Salmi, J., Johansson, L.-S., Laine, J. and Österberg, M. (2008). Model Films from Native Cellulose Nanofibrils. Preparation, Swelling, and Surface Interactions. *Biomacromolecules* 9, 1273-1282.
- Paper IV** Salmi, J., Nypelö, T., Österberg, M. and Laine, J. (2009). Layer Structures Formed by Silica Nanoparticles and Cellulose Nanofibrils with Cationic Polyacrylamide (C-PAM) on Cellulose Surface and Their Influence on Interactions. *BioResources* 4(2), 602-625.
- Paper V** Xiao, L., Salmi, J., Laine, J. and Stenius, P. (2009). The Effects of Polyelectrolyte Complexes on Dewatering of Cellulose Suspension. *Nordic Pulp and Paper Research Journal*, accepted.

Author's contribution to the appended joint publications:

- I-II** Jani Salmi was responsible for the experimental design, performed the main part of the experimental work, analysed the corresponding results, and wrote the manuscript (responsible author).
- III-IV** Jani Salmi was responsible for the experimental design with co-authors, performed the AFM experiments, analysed the corresponding results, and wrote the corresponding part of the manuscript.
- V** Jani Salmi was responsible for the experimental design with co-authors, analysed the main part of results, and wrote the manuscript (responsible author).

LIST OF KEY ABBREVIATIONS

A-PAM	anionic polyacrylamide
AFM	atomic force microscope
C-PAM	cationic polyacrylamide
CD	charge density
cnp	charge neutralization point
DLVO	Derjaguin, Landau, Verwey and Overbeek
M_w	molecular weight
NFC	nanofibrillar cellulose
NP	nanoparticle
PDADMAC	poly(diallyldimethylammonium chloride)
PE	polyelectrolyte
PEC	polyelectrolyte complex
PEM	polyelectrolyte multilayer
QCM-D	Quartz crystal microbalance with dissipation monitoring
REF	reference (surface force between cellulose surfaces)
RMS	root mean square
SNP	silica nanoparticle

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1 INTRODUCTION AND THE OUTLINE OF THE STUDY

The properties of surfaces can be modified by adjusting solution properties or by adding polymers or nanoparticles, and thus affect interactions between surfaces. Polymers or nanoparticles can be added either sequentially forming layered structures or together as a complex. For versatile possibilities, they are used to control stability (or flocculation) in macroscopic systems – up to industrial scale. The understanding of the relationship between interactions and stability, and the effect of solution properties and additives are important to a variety of industries, also to the paper industry.

A widely studied and well-understood way to modify the interactions is to add a single polymer, but it is also a starting point to more complex systems. The effect of a single cationic polyelectrolyte on interactions in cellulosic systems has been extensively reviewed (Hartley 1999; Hodges 2002; Claesson et al. 2005). We try to elucidate this field further in **paper I**, where a comparison between different molecular weights and charge densities of a cationic polyelectrolyte was considered in order to clarify the effect of polyelectrolyte properties on the flocculation mechanism. In the macro scale, the adsorption of polyelectrolyte can cause charge neutralization or a bridging attraction favoring flocculation, or on the other hand, it can cause charge reversal or steric repulsion favoring stabilization. The mechanism depends upon the polyelectrolyte layer structure. One component systems are reported to be beneficial e.g. in papermaking, improving retention and shear stability (Lindström 1989; Dickinson and Eriksson 1991; Swerin et al. 1996; Solberg and Wågberg 2003).

Taking one step further, two polymers can be added to build up more sophisticated layer structures to affect the interactions. Surface forces between polyelectrolyte multilayers, PEMs, (sequential addition) and polyelectrolyte complexes, PECs, (premixed addition) have been studied to some extent (Lowack and Helm 1998; Blomberg et al. 2004; Kulcsar et al. 2004 and 2005; Gong et al. 2005; Notley et al. 2005). Surface forces between multilayer structures are mostly determined by the outer layer of the system, whereas the effect of PECs is depending on the properties of PEC. The effect of PECs was more closely studied in **paper II**.

The surface to be modified plays an important role when considering the system stability. In this thesis, three different cellulose surfaces were used: mostly amorphous cellulose sphere containing also cellulose II regions, low charged nanofibrillar cellulose I surface and high charged carboxymethylated nanofibrillar cellulose I surface. Nanofibrillar cellulose (NFC) surfaces were developed in **paper III**. The NFC surface consisting the areas of crystalline cellulose I and amorphous regions and having fibrillar structure serves as excellent models for the pulp fiber surface. In this context, the effect of salt and pH on surface forces between cellulose surfaces was studied. Adjusting the properties of solution is the simplest way to affect colloidal stability. In this way, electrostatic double layer forces and the behavior of system can be changed directly.

NFC surface was also used in **paper IV**, where nanoparticles were studied together with polyelectrolytes. Microparticles and nanoparticles have been noted to improve the papermaking process (Andersson and Lindgren 1996; Swerin and Ödberg 1996); however, interactions in nanoparticle-polyelectrolyte systems have been rarely studied (Sennerfors et al. 2000). To understand the structure of nanoparticle-polyelectrolyte assembly, the surface forces in these systems and the mechanism behind flocculation phenomena, we have studied the effect of silica nanoparticles and cellulose nanofibrils on adsorption on cellulose and on interactions between cellulose surfaces using two addition strategies in **paper IV**.

The final step at work was to deepen the understanding of the PEC system behavior learned from the surface force measurements. The solution properties of the PECs and the effect of PECs on dewatering were studied in **paper V**. Already a low amount of anionic component in the complex was found to show a large effect on surface forces and to be clearly beneficial for dewatering. All in all, a dual polymer system has shown superior properties compared to one component systems in papermaking (Petzold et al. 1998; Wågberg et al. 2002; Gärdlund et al. 2003; Nyström et al. 2003; Eriksson et al. 2005; Lingström 2006) and the mechanism behind this are further discussed in Chapter 4.3 and in **papers II and V**.

Some of these forces are well-known, as well as the effect of polymers in flocculation on a practical level have been well studied. However, the link between surface forces

and the flocculation mechanism has not been thoroughly studied. Most of the studies reported in literature have been made on mineral surfaces, despite the fact that the base surface may have an influence e.g. on multilayer structures in the few first layers and on the polymer introduced interactions (Wågberg et al. 2008). The need for the utilization of the cellulose surfaces was obvious. Indeed, in this thesis, we have studied the effect of polymeric surface modification on surface forces between cellulose surfaces using atomic force microscope. The aim of this work is to clarify the surface forces in flocculation and to deepen the understanding of the molecular level mechanisms of flocculation in papermaking. These results can be generalized and utilized in other industrial processes.

2 BACKGROUND

2.1 Surface forces

Interactions between surfaces, or colloidal particles, are often a combination of different types of forces (Israelachvili 1992). Generally, surface forces have been widely studied with direct force measurement methods (Hartley 1999; Hodges 2002; Butt et al. 2005; Claesson et al. 2005), and the connection between measured forces and the DLVO theory is well established. However, there are several other forces in technical processes than those described in DLVO theory. In this section, the main types of interactions relevant to cellulosic systems in aqueous environment are described briefly to give background information for the experiments.

2.1.1 DLVO forces

The DLVO theory describes the interactions between charged surfaces (Derjaguin and Landau 1941; Verwey and Overbeek 1948). The DLVO forces are the sum of the van der Waals forces and the electrostatic double-layer forces. The theory predicts that electrostatic double-layer forces dominate at large separations, when the ionic strength is low enough, while van der Waals forces become dominating at short separations.

The van der Waals forces consist of three different types of forces that originate from time-dependent dipoles in atoms or molecules. These are Keesom forces for permanent dipoles, Debye interactions for permanent dipole and induced dipole, and London dispersion interactions for two induced dipoles. To calculate the van der Waals forces between two macroscopic surfaces, the Hamaker-method assuming pairwise additivity can be used (Hamaker 1937). The different force contributions are integrated over all pairs of molecules. The interaction energy per unit area between two flat, parallel surfaces, $W_{fl/fl}$, at a separation X , is given in the following equation:

$$W_{vdW}(X)_{fl/fl} = -\frac{A_H}{12\pi X^2} \quad (2.1)$$

where A_H is the material dependent Hamaker constant. To avoid drawbacks of the assumptions in Hamaker approach, the Lifshitz theory can be used to calculate the Hamaker constant (Lifshitz 1956). In this approach, the effect of neighboring atoms and the influence of medium are taken into account. Furthermore, the Hamaker constant depends on separation decaying more rapidly at distances beyond about 5 nm due to retardation effects. The van der Waals interactions between identical bodies in a medium are always attractive, as it is case in the cellulose-cellulose system.

Electrostatic double-layer forces are present between charged surfaces in liquids containing electrolyte (Israelachvili 1992). The charging of the surface may be due to several different mechanisms including desorption of lattice ions, dissociation of surface groups or adsorption of charged species. A system strives for electroneutrality and hence, in the presence of electrolyte, surface charge is balanced by an oppositely charged region of counterions. Some of these are very strongly bound to the surface in the so-called Stern layer. Others form a diffuse layer around the surface containing more counterions than the bulk solution and containing also co-ions. The diffuse layer neutralizes the charge of the surface. The Poisson-Boltzmann equation (2.2) describes the distribution of ions in the diffuse double-layer as a function of the separation from surface, x , and it assumes ions as point charges and non-interacting. When the Poisson-Boltzmann distribution is integrated twice, it gives the surface potential ψ , the electric field and the counterion density at any point x .

$$\frac{d^2\psi(x)}{dx^2} = -\frac{Zen_i}{\epsilon\epsilon_0} e^{-Ze\psi/kT} \quad (2.2)$$

where Z is the valency of counterions, e the electron charge, n_i the ion concentration, ϵ the dielectric constant of water, ϵ_0 the permittivity of the vacuum, k the Boltzmann constant and T the temperature. However, the solution of the Poisson-Boltzmann equation can not be done exactly and analytically; either numerical solutions or analytical approximations are needed (Chan 1983). Only the analytical approximation can be mathematically fitted to experimental data. Overlap of similar electrical double-layers give rise to repulsive osmotic pressure originating from the entropy loss of the ions. The interaction energy between identical surfaces can be calculated from

the pressure caused by the overlapping double-layers by integrating from the separation X to infinity. Assumptions of boundary conditions are needed in the solution. The assumption of constant potential or of constant charge gives the lower and upper limits of the interactions energies, respectively. The linearized solution of Poisson-Boltzmann equation for constant charge (2.3) and constant potential (2.4) leads to the following equations:

$$W_{\sigma}(X)_{fl/fl} = 2Z^2 n_i kT \left(\frac{e\psi_s}{kT} \right)^2 \kappa^{-1} \left(\coth \frac{\kappa X}{2} - 1 \right) \quad (2.3)$$

$$W_{\psi}(X)_{fl/fl} = 2Z^2 n_i kT \left(\frac{e\psi_s}{kT} \right)^2 \kappa^{-1} \left(1 - \tanh \frac{\kappa X}{2} \right) \quad (2.4)$$

which are valid at distances larger than the Debye length and provided the surface potential is low (< 25 mV) (Derjaguin et al. 1987). Here, ψ_s is the surface potential and κ^{-1} is the Debye length, which is the inverse parameter of the Debye-Huckel parameter describing the decay length of the electrical double-layer. The Debye length (2.5) indicates the distance from the surface where the distribution of ions in the solution is affected by the presence of a charged surface. The Debye length decreases when the electrolyte concentration increases.

$$\kappa^{-1} = \sqrt{\frac{\epsilon \epsilon_0 kT}{\sum_i e^2 Z_i^2 n_i}} \quad (2.5)$$

In DLVO theory, it assumed that the van der Waals and electrostatic interactions are independently additive. To obtain the *DLVO interactions*, the equations (2.3) or (2.4) and (2.1) are summed. However, it is more realistic to assume that the real surface force is somewhere between the two boundary conditions (2.3 and 2.4). The charge regulation model is one proposed intermediate solution (Ninham and Parsegian 1971).

Further, the surface forces between two macroscopic surfaces are calculated using the Derjaguin approximation assuming that the radius of the sphere is much larger than the distance between surfaces. In the Derjaguin approximation, the force can be

obtained by integrating the forces acting on small circular regions from the surface and from the opposite surface. This leads to different equations for different arrangements of the bodies, where the interaction energy is multiplied by the radii (r_i) of the spheres (Derjaguin 1934). Equations for two spheres (2.6) and for a sphere and a plate (2.7) are presented in the following:

$$F_{DLVO}(X)_{sph/sph} = 2\pi \frac{r_1 r_2}{r_1 + r_2} W_{DLVO}(X)_{flt/flt} \quad (2.6)$$

$$F_{DLVO}(X)_{sph/flt} = 2\pi r_1 W_{DLVO}(X)_{flt/flt} \quad (2.7)$$

The numerical solutions of DLVO forces for two identical surfaces with surface potentials of 20 mV, assuming constant potential or constant charge are shown in Figure 1 along with the contribution of van der Waals forces. The comparison between numerical solutions (symbols) and the linearized Poisson-Boltzmann equations (lines) shows that the approximations deviate from numerical solutions only close to contact, below the separation of the Debye length, 9.6 nm, where the approximations are not valid anymore. The resultant surface potential, according to eq. (2.3) and (2.4), are 18.2 mV for the constant charge approximation and 19.7 mV for the constant potential approximation, giving less than 10% error compared to the numerical solutions. Besides, the DLVO theory often fails to describe the interactions at very short separations. This can be because the continuum theory breaks or there are other non-DLVO forces present (Israelachvili 1992).

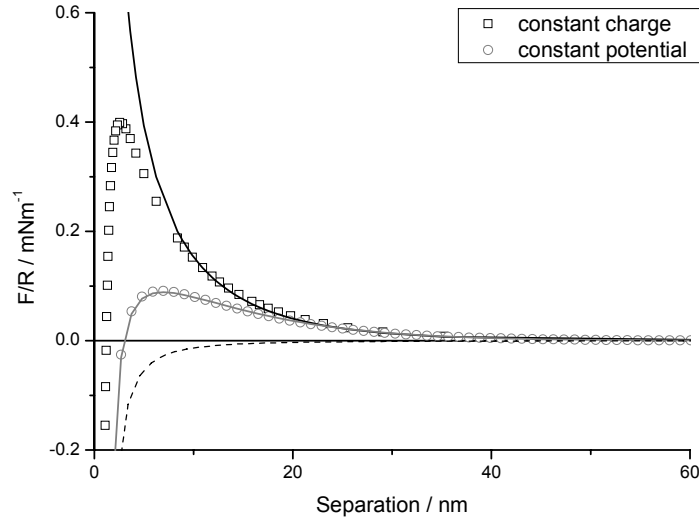


Figure 1. Example of calculated surface forces using DLVO theory between similarly charged surfaces. The symbols illustrate numerical solutions of the DLVO theory assuming constant charge (\square) and constant potential (\circ). $\psi_s = 20$ mV and $\kappa^{-1} = 9.6$ nm for 1:1 electrolyte. The solid lines represent the linearized solutions of Poisson-Boltzmann equation fitted to the numerical solution of the DLVO theory for constant charge (black) and constant potential (grey). The resultant surface potentials are 18.2 mV for constant charge and 19.7 mV for constant potential. A dashed line indicates the effect of van der Waals forces ($A_H = 0.8 \cdot 10^{-20}$ J).

2.1.2 Polymer induced forces

In many natural systems, it is not enough to assume contributions of only van der Waals forces and electrostatic double-layer forces. E.g. in the presence of the polymers, the DLVO theory is often not adequate to describe the interactions. The surface itself might be polymeric, or polymers may adsorb to the surface and thus influence the interactions. In addition, simply the presence of the polymers in solution may affect the forces (e.g. depletion force). A polymer adsorbed on the surface has tails and loops extending out into the solution. Depending on the solution properties, the surface forces may be either attractive or repulsive, when two polymer layers overlap. In a good solvent at high surface coverage, the surface force is repulsive (Figure 2A.), which is a common case in this study. The reason for osmotic repulsion is the loss of the entropy due to reconfiguration of polymer chains and the loss of

enthalpy due to reduced solvent-polymer contacts, when polymer layers are overlapping. This repulsion is called *steric repulsion*. On the other hand, the surface force is attractive in a poor solvent due to the enthalpy gain, when polymer-solvent contacts are replaced by polymer-polymer contacts (Figure 2A.). However, steric repulsion is also present at short separation.

The simplest cases of steric repulsion are rather well described. The steric force depends on adsorption or grafting density, surface affinity, polymer structure, the structure of the polymer layer and solvency condition. The steric force can be calculated based on lattice mean field theory or scaling theory (Dolan and Edwards 1974; de Gennes 1979, 1987 and 1982; Milner et al. 1988; Fleer et al. 1993). Scaling theory has been further developed involving charged end-grafted polymers by Pincus (1991). It was concluded that the polyelectrolyte layer diminishes the effect of Debye screening due to the polymer elasticity. The model of a three force regime was presented. Interactions are mostly electrostatic before the overlap of polymer layers. When the layers are overlapping, two effects contribute - the steric effect from the entropy loss of polymer and compressing of the polymer charges. Polymer brushes having a fixed and well-defined layer structure are ideal cases. In the case of an adsorbed polymer, when the structure is more random and the polymer is not anchored to the surface, two force regimes of steric repulsion can be observed (Sonntag et al. 1982). Weaker repulsion at larger separations is due to the overlap of the tails, and stronger repulsion at smaller separations when also the loops are overlapping. However, these cases are still rather limited regarding the systems in this thesis. Here, the polymers were charged, random co-polymers and freely adsorbing; also, the addition of a second component in the system complicated the situation further. In two component systems, the system is often kinetically trapped in the non-equilibrium state (Decher and Schlenoff 2003). Furthermore, adsorbed layers were not in thermodynamic equilibrium during the approach of surfaces, when polymer layers were overlapping because of the limited time.

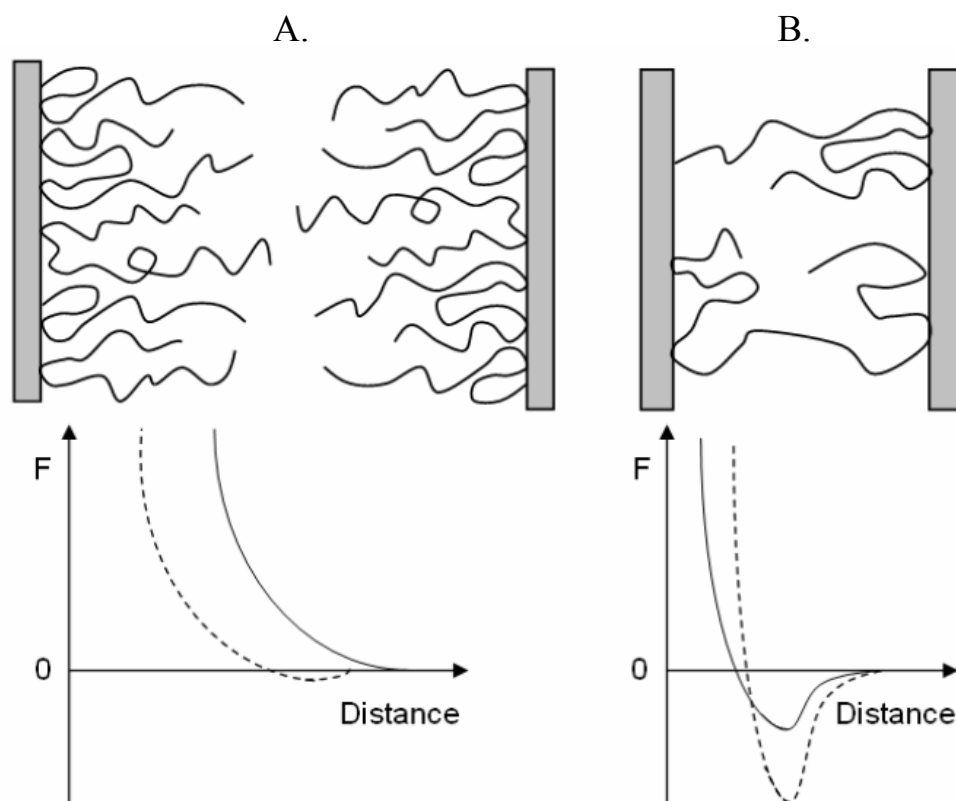


Figure 2. Interaction forces between polymer-coated surfaces. Graph A. shows the interaction between polymer-coated surfaces with high surface coverage in a good solvent (solid line) and in a poor solvent (dashed line). In graph B. the corresponding situation is shown for polymer-coated surfaces with low surface coverage. The scales are arbitrary. (According to Israelachvili, 1992; Hiemenz and Rajagopalan, 1997.) Image by courtesy of Arja Paananen (2007).

At low surface coverage of polymer, an attractive force called *bridging* is possible (Figure 2B.). In this case, the polymer can attach (adsorb) to both surfaces forming a bridge between them (La Mer and Healy 1963; Almog and Klein 1985; Ji et al. 1990). The mechanism behind the attraction is that the system gains enthalpy from the decrease of polymer-solution contact. After the bridge formation, the polymer experiences an entropy gain at first, when the surfaces come closer. If the polymer is oppositely charged compared to the surface, bridging can occur when part of polyelectrolyte crosses the electrostatic double-layer (Åkesson et al. 1989; Miklavic et al. 1990). When the surfaces are separating, bridging can keep surfaces together due to energetic binding. Bridging adhesion is relatively long ranged (Rand et al. 1979; Biggs 1995).

When the polymer is charged, double-layer forces can also affect the interactions. This type of force is often referred to as *electrosteric force*, which is a more specified description of steric force (Poptoshev and Claesson 2002). However, it is not always unambiguous to distinguish steric and electrosteric force, and thus in this thesis steric force is used to describe forces also in the case, when there might be an electrostatic contribution.

Another subtype of steric force is *hydration-steric force* (Israelachvili 1992; Rutland and Christenson 1990). This force includes the effect of bound water in polymer layer. Because some of the systems in this thesis are water-swollen, repulsive hydration forces may also contribute to the force profile. While these forces are usually very short-ranged, the situation is slightly different when water molecules are bound to polymer structure. Here, hydration forces may be present between protruding chains as well as within the swollen gel and hence they may affect the force curve also at longer distances. However, these forces without doubt can not be separated from the steric effects based on our results.

The above mentioned theories have been equilibrium theories, but equilibrium is most likely not achieved during force measurements in polymeric systems due to long-lasting relaxation procedures of polymers layers, when surface are approaching each other. First, the solvent has to flow out through the polymer layer, second, the polymer layer must reorder as they become compressed, third, new binding sites and bridges have to be formed, and fourth, a certain fraction of polymer molecules may enter or leave the gap. Entanglement of polymer molecules slow down these processes substantially and it can take days to reach true equilibrium. In the case of an adsorbed polymer, where the structure is more random and the polymer is not anchored to the surface, the measured surface forces depend on the rate of approach and hysteresis is often observed (Klein and Luckham 1984; Luckham and Klein 1990).

2.1.3 Hydrodynamic forces and other water induced forces

Oscillatory structural forces and solvation forces, or *hydration forces* in the case of water molecules, due to step-like removal of trapped solvent or polymer molecules are

usually not observed in cellulosic systems due to a roughness and porosity of the surface and due to steric forces observed at the proximity of the surface. The oscillatory structure of force is evened out. The remaining contribution may be seen as a repulsive hydration force or an attractive hydrophobic force (Marcelja and Radic 1976; Marcelja et al. 1977; Van Olphen 1977; Stanley and Teixeira 1980; Jönsson 1981; Pashley 1982; Horn et al. 1989; Ducker et al. 1992). This is caused by the ordered structure of water molecules at the surface and the affinity difference between surface-water and water-water molecule contacts. The repulsive hydration force decays exponentially and ranges only a few nanometers. It is regulated by ion exchange. The effect of hydration force may be augmented by the polymer layer leading to stronger steric repulsion.

The studied systems are often dynamic systems. This introduces another solvent induced force. When water drains from the gap between two approaching surfaces, a *hydrodynamic force* is produced resulting from viscous dissipation (Chan and Horn 1985; Claesson et al. 2001; Butt 2005). The hydrodynamic force depends on viscosity of solution and velocity of approaching surfaces. An adsorbed polymer layer can increase the viscosity of the solution near the surface, and thus the hydrodynamic effect can increase near the contact (Fredrickson and Pincus 1991).

2.1.4 Observations in cellulosic systems

Cellulose surfaces are relevant e.g. for papermaking because cellulose is one of the main materials in wood fiber. Therefore, the interactions between cellulose surfaces have gained an interest in literature. The features of these interactions are briefly described here. The surface forces between pure cellulose surfaces are repulsive. Two force regions, steric and electrostatic, are usually observed for cellulose II surfaces (Rutland et al. 1997; Carambassis and Rutland 1999; Poptoshev et al. 2000a and 2000b; Zauscher and Klingenberg 2000; Notley et al. 2004; Paananen et al. 2004; Notley and Wågberg 2005; Stiernstedt et al. 2006a and 2006b). Cellulose has a low negative charge. The range of electrostatic repulsion decreases with increasing ionic strength as predicted in DLVO theory. The range of the steric force for cellulose depends on the cellulose used in the experiments, but the range is only a few tens of nanometers with the most surfaces used. The crystallinity of cellulose affects the

nature of interactions (Eriksson 2006; Stiernstedt et al. 2006b). For amorphous cellulose surfaces, mainly steric forces have been observed (Neuman et al. 1993; Holmberg et al. 1997a; Österberg and Claesson 2000; Notley et al. 2004 and 2006; Notley and Wågberg 2005; Eriksson 2006). Increasing pH increases the repulsion between cellulose surfaces (Carambassis and Rutland 1999; Poptoshev et al. 2000a; Österberg and Claesson 2000; Notley et al. 2004; Notley and Wågberg 2005; Eriksson 2006). This is caused by the dissociation of carboxyl groups in cellulose, hence surface charge increases with pH. Also steric repulsion increases due to the more extended form of charged cellulose tails and due to swelling. Generally, the pull-off force between pure cellulose surfaces is quite low in mild salt solution.

When polyelectrolytes are adsorbed on cellulose surfaces, first, the electrostatic repulsion between cellulose surfaces decreases (Holmberg et al. 1997b; Poptoshev et al. 2000b). Close to the charge neutralization point (cnp), attractive forces like van der Waals forces or patch-wise attraction are typically dominating. Further adsorption leads to charge reversal and thus electrostatic repulsion increases again. If the charge density of polyelectrolyte is decreased, the polyelectrolyte adsorbs in a looser conformation containing more loops and tails. These can introduce a repulsive steric contribution to interactions even at large distances. The range of steric interaction can be several hundred nanometers (Zauscher and Klingenberg 2000; Poptoshev and Claesson 2002). Close to charge neutralization, bridging attraction can be seen. This attraction is usually lower, but it ranges further than with high charged polyelectrolytes (Poptoshev 2001) because of the lower affinity of the low charged polyelectrolyte to the surface. On separation, pull-off forces are highest when surfaces are partly covered, i.e. close to cnp (Poptoshev et al. 2000b; Zauscher and Klingenberg 2000; Poptoshev and Claesson 2002). When more polyelectrolyte adsorbs, the pull-off force decreases.

2.2 Colloidal stability in papermaking

Colloidal stability regarding papermaking is only briefly described here. For a more thorough discussion on the subject, books by Stenius (2000) and Laine (2007) and review articles by Lindström (1989), Swerin and Ödberg (1997), Norell et al. (1999),

and Hubbe and Rojas (2008) are recommended. Here, we concentrate on flocculation and retention of fines.

2.2.1 General aspects of stability

The papermaking stock is a heterogeneous mixture of substances originating from the wood as well as additives and electrolytes. Some of them are in the size range from nanometers to millimeters. Hence, papermaking system is often considered to be a colloidal system. In the wet end of a paper machine, different additives adsorb on particles, i.e. cellulosic fibers, fines and fillers, and thus they affect surface forces between these particles, and further the stability of the system. The most important factors in adsorption and surface forces are surface properties of particles, properties of additives, solution properties and hydrodynamic conditions. Prediction of the stability is complex due to the amount of factors affecting to the system.

On high speed machines, behavior of the system is a balance between colloidal interactions and hydrodynamic forces. The collision of particles is limited by the hydrodynamic forces. Two different size particles can not collide without attractive force (or Brownian motion) ranging over the limiting trajectory (van de Ven and Mason 1981; Stenius 2000). The collision rate is determined by shear forces and on the rate of diffusion (Stenius 2000), and affects the kinetics of the flocculation (Norell et al. 1999).

Repulsive forces cause stabilization, whereas flocculation is due to attractive forces. Thereby, the type of stabilization or destabilization can be grouped according to causative surface interactions. System can be electrostatically stabilized, in which case it is possible to destabilize (or flocculate) the system by adding salt, as predicted by DLVO theory. Polymers can be used both for stabilization and destabilization. Stability in this case is a matter of dosage (Stenius 2000). If polymers are used to stabilize system, it is referred to as a steric stabilization. Polymers can also flocculate system, if only low amount of the polymer is added. Flocculation can be due to different mechanisms, which are discussed more detailed in following chapters.

Fibers contain mostly cellulose and the surface of fiber is slightly anionic. The surface of fiber is laminated and fibrillated along the process (Laine 2007; Hubbe and Rojas 2008). Hence, the surface of fibers, and also the surface of fines, behaves like a polyelectrolyte gel in water. Anionic fiber surface swells due to uneven ion distribution between outer and inner phase due to Donnan effect (Donnan 1912; Procter and Wilson 1916). Thus, factors like pH, ionic strength and valence of ions affect the swelling of the fiber surface. When adding polymers into solution, they mix with the microfibrillar surface structure of the fiber, which further complicates the situation.

Water-soluble cationic polymers, i.e. polyelectrolytes, are used as retention chemicals, but also for draining, fixing and increasing paper strength. They adsorb on the negatively charged surface of fibers and fines, and thus they change the surface forces between these particles. Adsorption is mainly electrostatically driven. Adsorption is depending on the properties of polymer (molecular weight, charge density, cross-linking, structural restrictions, branching), solution conditions and the surface properties of the particles (surface area, surface charge, surface chemical composition and porosity). Depending on these factors, polymer may adsorb in different conformations (Fleer et al. 1993; Wågberg 2000; Saarinen 2008). High charged polyelectrolytes tend to adsorb in a flat conformation while low charged polyelectrolytes adsorbs in a loose conformation forming a thick layer containing a lot of loops and tails. Rather high molecular weight polymers are usually used because of the surface structure of fibre and requirement of the process (hydrodynamic forces).

The main rationale for using cationic polymeric retention and drainage aids is that they are thought to bind anionic fine material through charge neutralization and bridging onto the long anionic fibers already in the stock suspension before the fiber mat is formed (Forsberg and Ström et al. 1994; Scott 1996; Norell et al. 1999). To ensure higher retention of fines and fillers with effective dewatering, without a loss of even formation of fiber web due to fiber flocking, and without of a loss of paper quality, the basic mechanism of flocculation needs to be understood in depth.

2.2.2 Single polymer systems

Charge neutralization and patch-wise flocculation are closely related and are hard to distinguish from one another. The charge neutralization mechanism is based on attractive van der Waals forces. When the surface charge of the particles has been neutralized by changing pH or by adding an oppositely charged polymer in solution, or when the range of electrostatic repulsion has been diminished by adding a high amount of salt, attractive van der Waals forces dominate the interactions and the particles flocculate. This is referred to as charge neutralization flocculation. On the other hand, the patch-wise mechanism originates from the electrostatic attraction between oppositely charged areas in two particles, also comparable to hetero-flocculation. The mechanism of the patch-wise flocculation is based on polyelectrolyte addition (Gregory 1973; Borkovec and Papastavrou 2008). An oppositely charged polymer adsorbs on the surface of the particle, partly covers it and, thus, forms charged patches. These charge patches attract the oppositely charged regions of another particle (Miklavic et al. 1994). This leads to flocculation and is referred to as patch-wise flocculation. Polyelectrolytes used in these cases are typically high charged polyelectrolytes. The flocs formed by these mechanisms are dense and break easily under shear (Lindström 1989).

Another mechanism of single polymer induced flocculation is *polymer bridging* (see chapter 2.1.2). In bridging, the polymer adsorbs in an extended conformation with many loops and tails. These loops and tails “adsorb” to another surface forming bridges. Also, a free polymer can form a bridge, if attracted to two bare surfaces simultaneously. Bridging is common for high molecular weight and low charged polyelectrolytes because they tend to adsorb in extended conformations on surfaces (Wågberg and Lindström 1987a; Lindström 1989; Swerin and Ödberg 1997). The flocs formed by bridging are looser than flocs formed by charge neutralization. The flocs formed by bridging resists shear well (Dickinson and Eriksson 1991).

Many retention aids are based on bridging flocculation mechanism, because large extension of polymer is needed in order to achieve a good retention under hydrodynamic conditions. This is best achieved with high molecular weight, low

charged polyelectrolytes, whereas high charged polyelectrolytes are often used for fixing, i.e. capturing disturbing substances (Laine 2007).

Single polymer mechanisms are very sensitive to *polymer dosage* and overdosing of polyelectrolyte leads to stabilization (Stenius 2000). In charge neutralization or patch-wise flocculation, the optimum dosage is at the charge neutralization point, whereas the dosage for flocculation is optimum in the bridging mechanism when half of the surface is covered with polymer. The effect of the polyelectrolyte dosage has been seen in flocculation experiments of a fiber suspension with and without fines (Wågberg and Lindström 1987; Lindström 1989; Swerin et al. 1996; Solberg 2003; Solberg and Wågberg 2003). Flocculation passed through a maximum when the dosage was increased and the charge of suspension was neutralized.

2.2.3 Dual polymer systems

Dual polymer systems can be conventionally formed by adding oppositely charged polyelectrolytes in sequences to increase effectiveness of high speed papermaking. For expense reason, cationic polyelectrolyte with high charge and low molecular weight is added first causing charge reversal. After a shear stage the anionic polyelectrolyte with low charge and high molecular weight acts as a bridging flocculant between the cationic floc fragments forms. In this way, polyelectrolytes form bilayer structures, which resembles the polyelectrolyte multilayer (PEM). In some cases, two cationic polyelectrolytes are used together in similar way. The layer structure can be tuned by changing polyelectrolyte properties or by an adding method. After multiple collisions and the influence of the shear forces, one can assume that the multilayer structure is partly mixed towards the less ordered structure of a complex.

If flocculation is too effective, the paper quality may suffer due to fiber flocculation. The use of *polyelectrolyte complexes (PEC)* is a possible solution to this problem. Even the PECs are not in commercial use yet, they have been found to improve the flocculation and to broaden the optimum concentration range compared to single polyelectrolyte systems (Petzold et al. 1996 and 1998; Buchhammer et al. 1999; Lu et al. 2002; Nyström et al. 2003). PECs has been reported to form more stable flocs than single polymer systems (Petzold et al. 1998; Nyström et al. 2003). In addition,

positive effects of PECs have been reported on paper strength (Gärdlund et al. 2003 and 2005; Torgnysdotter and Wågberg 2006; Vainio et al. 2006; Ankerfors 2008) and on retention (Petzold et al. 1996; Nyström and Rosenholm 2005) without harming sheet formation (Bessonoff et al. 2006). Also, PEMs have been reported to increase paper strength, when compared to single polyelectrolyte systems (Wågberg et al. 2002; Eriksson et al. 2005; Lingström 2006). Dual polyelectrolyte systems are able to increase the polymer amount in the fiber web making the fiber surface smoother, and thus increasing the bonded area between fibers (Lingström 2006). This, however, only partly explains why the paper strength is increased. In addition, PECs have been reported to yield better retention and strength properties than the sequential addition of polymer (Nyström and Rosenholm 2005; Lingström 2006; Ankerfors 2008). Only by increasing the layer number of PEM, i.e. the amount of the polymer, could similar levels of strength be achieved (Ankerfors 2008).

2.2.4 Microparticle-polyelectrolyte systems

A microparticle system deviates only slightly from the dual polymer system. In the microparticle system, one of the polyelectrolytes is replaced by microparticles, usually negatively charged, such as colloidal silica, alumina, or montmorillonite. Polyelectrolyte and microparticle is added in sequence. The role of the microparticles is to provide links between adsorbed polymer layers (Asselman et al. 2000). Microparticles are proposed to form unbranched, short chains called pearl necklace structure (Cabane and Duplessix 1982). The layer structures obtained using microparticles are different compared to dual polymer system, but similar benefits are achieved.

A clearly positive influence on flocculation has been reported when microparticles are added in suspension, compared to the situation where only C-PAM is added (Swerin and Ödeberg 1996). It has been found that the charge density of microparticles determines the addition level necessary to attain the maximum retention (higher charge density gives lower addition level) (Andersson and Lindgren 1996). The microparticle systems differ from other dual retention systems in their ability to reflocculate after floc breakage (Andersson and Lindgren 1996; Swerin and Ödeberg 1996). The dual polymer system gives the largest degree of flocculation and the

largest average floc size, whereas the microparticle system give a much smaller floc size at the same flocculation index (Wågberg and Lindström 1987b). The use of the microparticle system enhances also dewatering because microparticles bind less water than polyelectrolytes (Swerin et al. 1992; Wågberg et al. 1996).

3 EXPERIMENTAL

The materials and methods used in the experiments included in this thesis are described in detail in the attached Papers I-V. Thus, this chapter gives a more general overview of the experimental design and provides some background on the methods used. The methods section focuses on the main instrument used, the atomic force microscope (AFM).

3.1 Materials

3.1.1 Cellulose surfaces

In AFM force measurements, precipitated spheres of cellulose II regenerated via the viscose process (Kanebo Co., Japan) were used as colloidal probes in all surface force measurements, and also as a lower surface in Papers I and II. They were 5–35% crystalline and slightly negatively charged (Carambassis and Rutland 1999). Their radius was 15–30 μm , as determined *in situ* in electrolyte solution by using an optical microscope and a digital camera.

Low charge nanofibrillar cellulose (NFC) was used as a substrate in the quartz crystal microbalance with dissipation monitoring (QCM-D) and atomic force microscope (AFM) measurements in Papers III and IV. In order to remove larger aggregates prior to film formation, the 2% nanofibril gel (Pääkkö et al. 2007) was first diluted to 1.67 g/l and disintegrated with an ultrasonic microtip, a Branson Sonifier S-450 D (Danbury, USA). The microfibril dispersion was then centrifuged. The charge of the low charge nanofibrils were 44.2 $\mu\text{eq/g}$ (Pääkkö et al. 2007). Then the cellulose films were prepared by spin-coating the clear supernatant fluid with the nanofibrillar dispersion onto silica coated QCM-D crystals (Q-Sense AB, Sweden) or onto smooth silica wafers (Oktometic Oy, Finland). 3-aminopropyltrimethoxysilane (APTS) was used as an anchoring substance. The spin-coated surfaces were rinsed with water, dried gently with nitrogen gas, and heat-treated before use. The thickness of the films was about 11 nm (Ahola 2008) and the crystallinity of the surface (of cellulose I) was 70 % (Aulin et al. 2009).

3.1.2 Additives

Polyelectrolytes were used to build different molecular architectures on surfaces. The monomer unit of poly(diallyldimethylammonium chloride)s (PDADMAC) and the building blocks of the cationic and anionic polyacrylamides (C-PAM and A-PAM) copolymers are presented in Figure 3. C-PAMs and A-PAMs (Kemira Chemicals Oy, Finland) with different molecular weights and different charge densities and PDADMAC (Allied Colloids Ltd., England) were used in the surface force measurements. Their properties are presented in the Table 1. For surface force measurements, polyelectrolytes were ultra filtrated with different cut-offs to narrow the molecular weight (M_w) distribution. In Paper II, the polyelectrolyte complexes were formed using C-PAM and A-PAM by mixing either high charged and low molecular weight polymers or low charged and high molecular weight polymers in a mass ratio of 9:1 (C-PAM:A-PAM), which have shown promising results in adsorption studies (Saarinen et al. 2008). Furthermore, the solution properties of the polyelectrolyte complexes and the effect of PECs on dewatering were studied in Paper V. The properties of the polymers used in these studies are presented more detail in Paper V.

Table 1. *The properties of polyelectrolytes and polyelectrolyte complexes (PEC) appearing in force measurements. M_w = molecular weight, CD = charge density.*

		M_w 10^6 g/mol	CD meq/g	Referred as
PDADMAC		0.39	6.1	Low M_w , high CD
C-PAM		1.40	1.8	High M_w , low CD
PEC 1	C-PAM	1.40	1.80	High M_w , low CD
	A-PAM	2.40	1.80	
PEC 2	C-PAM	0.40	3.10	Low M_w , high CD
	A-PAM	0.22	6.30	

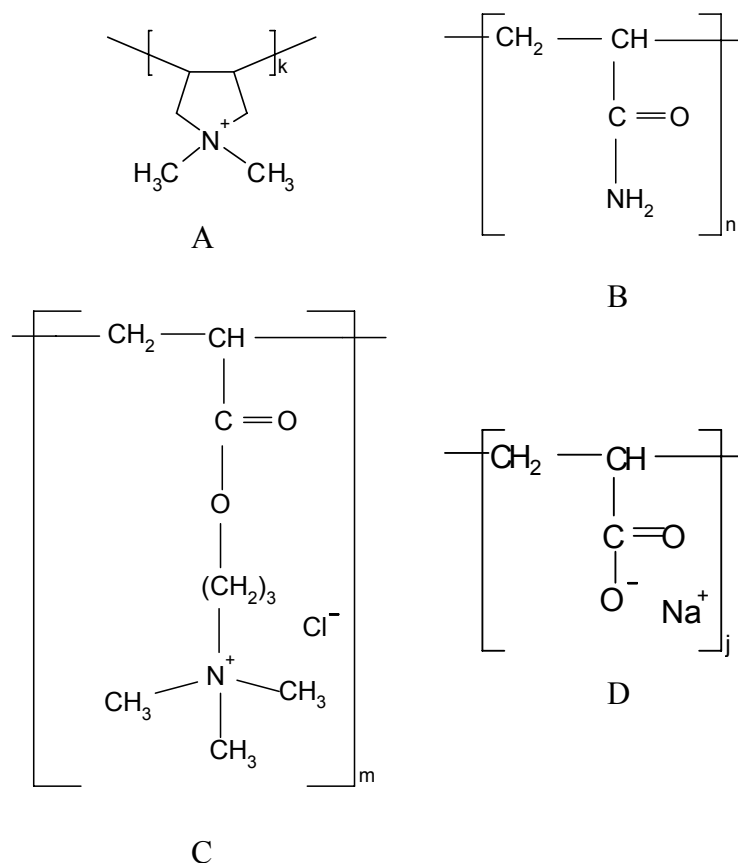


Figure 3. The molecular structures of monomers forming polyelectrolytes. Monomer A forms PDADMAC and the uncharged monomer B forms a copolymer of C-PAM with cationic monomers C or a copolymer of A-PAM with anionic monomers D.

In addition, inorganic *silica nanoparticles* (SNP) and high charged *cellulose nanofibrils* were used to form complexes and multilayers with low charged and high molecular weight C-PAM in Paper IV. The SNP had a surface area of 130 m²/g and a particle size of 25 nm (Bindzil 40/130, Eka Chemicals, Sweden). They were negatively charged with a charge density of 150 µeq/g as determined by polyelectrolyte titration. They were used as received from the supplier. Cellulose nanofibrils with high charge density, received from STFI-packforsk, Stockholm, Sweden, were prepared by performing a carboxymethylation pretreatment for the pulp (Wågberg et al. 2008). The dispersion was prepared similarly to the dispersion of low charged cellulose nanofibrils used for cellulose surface preparation. The charge of the high charged nanofibrils was 515 µeq/g (Wågberg et al. 2008).

Measurements were performed in fresh polymer solutions, varying the concentration of either salt or polyelectrolyte. The solutions were prepared using ultra pure water (Elga UHQ system, UK). NaHCO_3 was used to buffer the pH. The electrolyte concentration was adjusted using analytical grade NaCl. Surfaces were allowed to equilibrate in an electrolyte solution overnight before the measurements. When changing the solution, the system was allowed to stabilize for 1 h.

3.1.3 Pulp

The composition of stock used in dewatering measurements (Paper V) was 50 % bleached thermomechanical pulp (TMP) and 50 % chemical pulp. The TMP was from UPM-Kymmene Oy (Kaipola, Finland). ECF bleached kraft pulp made mainly from spruce was from Metsä-Sellu (Äänekoski, Finland). The bleached mechanical pulp was hot-disintegrated to a freeness of 40 CSF according to SCAN-M 10:77. The chemical pulp was beaten to SR 22 in a Valley Beater according to SCAN-C 25:76, and washed into sodium form according to the procedure described by Swerin et al. (1990).

3.2 Methods

3.2.1 AFM imaging

To characterize the coverage, morphology and roughness of the structures formed, AFM imaging was performed using a Nanoscope IIIa multimode scanning probe microscope (Digital Instruments Inc., Santa Barbara, USA). The atomic force microscope (AFM) was invented in 1986 and since then it has increased its popularity (Binnig et al. 1986; Butt et al. 2007). The basic principle of AFM is shown in Figure 4. The sample interacts with a sharp tip attached to the free end of the cantilever. The radius of curvature of the tip is usually 10 nm. The changes of the interactions due to surface features leads to a bending of the cantilever in contact mode or a change in amplitude (A) of the oscillating cantilever in tapping mode. The motion of the cantilever is detected in a photodetector as a shift of the laser reflecting from the back of the cantilever. The scanner corrects the changes in the bending of the cantilever or

the change in the amplitude, in order to keep the cantilever state constant. It also moves the sample during scanning. This produces a topographical image from the sample (height image) recorded from the scanner movement. Tapping mode is often useful for soft samples because it reduces the tip-sample contact time and can also collect phase data (Zhong et al. 1993). Phase (phase-shift) data is an extension to tapping mode and is recorded simultaneously with height data. It is the phase difference between the oscillation fed to cantilever and the oscillation detected from cantilever. The tapping force transmitted to surface is determined by the free amplitude (A_0) and the set-point amplitude (A_{sp}) (Bar et al. 1997; Magonov et al. 1997; Cleveland et al. 1998; Whangbo et al. 1998). The damping ratio (A_{sp}/A_0) specifies what properties are emphasized in the phase image. The phase image is proposed to be sensitive to stiffness at moderate tapping ($A_{sp}/A_0 = 0.4-0.7$) and to capillary forces and adhesion between the tip and the sample at light tapping ($A_{sp}/A_0 = 0.8-0.9$), indicating the chemistry of the sample. At hard tapping ($A_{sp}/A_0 < 0.3$), the phase image is reversed compared to moderate tapping and indicates the domination of the tip-sample contact area. In the first place, the free amplitude needs to be large enough, i.e. tapping force is high enough, to go through a water or contamination layer on the sample. In addition, the edges of surface features are highlighted in the phase image due to the delay in the response in AFM device.

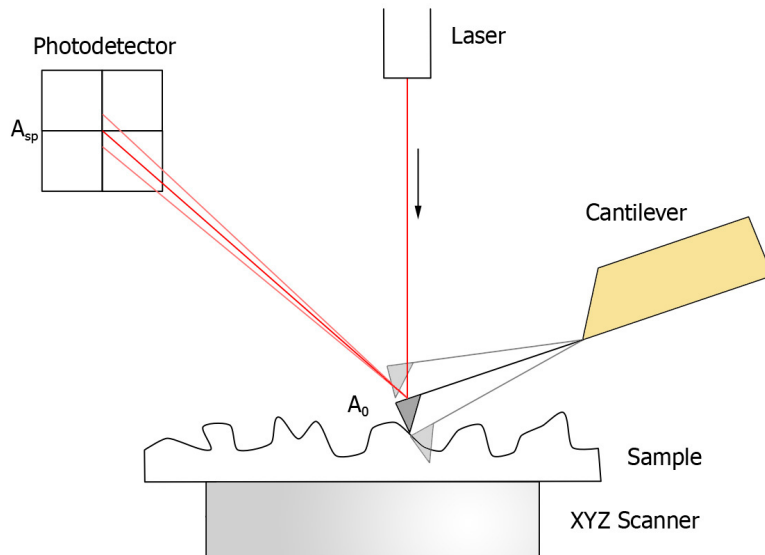


Figure 4. The basic principle of AFM in tapping mode.

The images in this thesis were scanned in tapping mode in air (i.e. samples were dried after force measurements and before imaging) using silicon cantilevers (NSC15/AIBS) delivered by MicroMasch, Estonia. The drive frequency of the cantilever was 310–350 kHz. No image processing except flattening was made. The imaging was performed at 30–40% relative humidity at 25 °C. A Scanning Probe Image Processor (SPIP, Image Metrology, Denmark) was used to analyze RMS roughness (ISO standard 4287/1) and to perform grain analysis to analyze surface features. When analyzing the surface features, the influence of the shape and size of the tip was paid attention to. In addition, scanner hysteresis, creep and drift as well as tip contamination are possible source of error, but these are rather easy to detect and to avoid.

3.2.2 AFM force measurements

AFM was also used to measure surface forces between cellulose surfaces using the colloidal probe technique in solution, represented in Figure 5 (Butt 1991; Ducker et al. 1991). A cellulose sphere was glued to the tipless end of the AFM cantilever with a reported spring constant of 0.06 N/m (Veeco Instruments, USA). The surface forces between the colloidal probe and the surface is detected from the deflection of the cantilever (Δz), while scanner is moving sample toward or away from the tip. The deflection is converted to surface force using Hooke's law (3.1) where the cantilever acting like a spring with a spring constant, k .

$$F = k\Delta z \quad (3.1)$$

Repulsion, denoted as a positive force in force curves, bends the cantilever upward, whereas attraction, negative force, bends tip downward. Both approaching and retraction curves are recorded. The force observed on retraction is referred to as the pull-off force indicating the force needed to separate surfaces. The separation between surfaces is calculated from contact point, scanner movement and deflection. The contact point at zero separation, is the beginning of the constant compliance region, where the deflection is only caused by scanner movement, i.e. the probe is in contact with the surface. Further, the slope of the constant compliance region (the sensitivity parameter) is used to determine the sensitivity of the system to convert the unit of the

deflection to nanometers. A more detailed description about the setup of surface force measurements and the conversion of force curves can be found elsewhere (Claesson et al. 1996 and 2001; Senden 2001; Butt et al. 2005; Ralston et al. 2005).

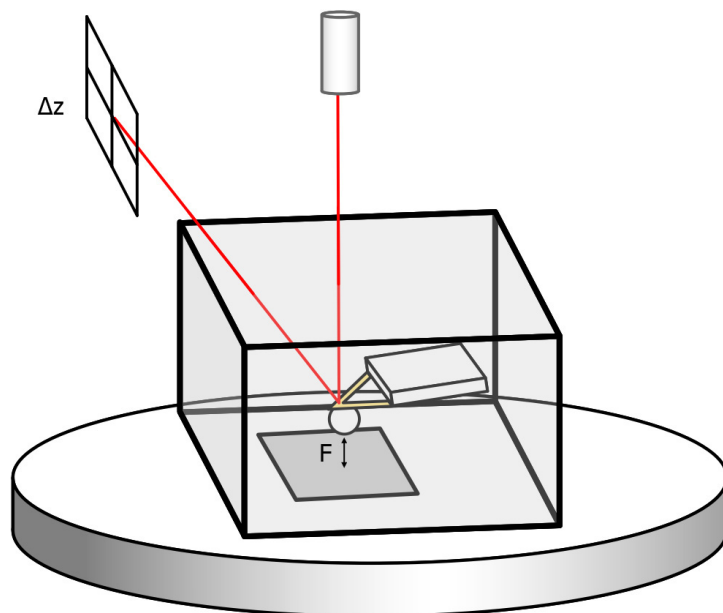


Figure 5. A schematic drawing of the force measurement setup. Colloidal probe method of AFM.

In practice, the raw data (cantilever deflection vs. piezo movement) were converted into force curves (force vs. separation) using the SPIP. The curves were further handled within the Origin software package (OriginLab Co., USA). The spring constants of the cantilevers were determined by the thermal noise method, and the result was controlled by the reference spring method (Hutter and Bechhöfer 1993; Torii et al. 1996; Tortonese and Kirk 1997). To facilitate a comparison to other studies, the forces in this study were normalized to the radii of the interacting cellulose spheres. The results were fitted to the interactions predicted by the DLVO theory using the linearized Poisson-Boltzmann equation for constant charge and constant potential, which are valid at distances larger than the Debye length and provided the surface potential of cellulose surfaces is low (< 25 mV) (Chapter 2.1.1). In the van der Waals part of the DLVO theory, a Hamaker constant of $0.8 \cdot 10^{-20}$ J was used for cellulose in water (Bergström et al. 1999). For fitting, the plane of charge

was fixed to zero separation. The surface potential was a variable, whereas Debye length was a constant depending on the ionic strength of the solution. One should remember that the quantification of the surface potentials were also affected by the possible experimental errors in the spring constant, sphere radius, and the apparent zero separation.

The hydrodynamic forces were not included in the predictions, but measures were taken to minimize their influence on the experimental results. Thus, the approach velocity of the cellulose beads to each other was kept fairly low. Typical approach velocities were between 100 and 500 nm/s. We did not observe any effect of velocity on the interactions at the two approach velocities used, and 200 nm/s has previously been reported to be sufficiently low for hydrodynamic forces between cellulose surfaces to be negligible (Stiernstedt et al. 2006a). However, nanofibrillar cellulose and polymers tended to form gel-like layer, and thus we can not rule out a dynamic effect due to an increase in viscosity near the surface, but no such effect was observed.

A clear constant compliance region could not be reached for the all systems due to compressibility of the layers. This may lead to erroneous result, if it is not taken into account (Rutland et al. 2004). In these cases, raw data (deflection versus piezo movement) was transferred to force curves by using the sensitivity value obtained for cellulose-cellulose contact. For cellulose-cellulose contact, a constant compliance regime was attained due to the low spring constant of the cantilevers used in the experiments. Compressibility (load/indentation, $\mu\text{N/m}$) of such surfaces was also analyzed from the force curve. Owing to the same reasons, exact separation between cellulose surfaces was not known. Some of the polymer was always pressed and trapped between the surfaces, when AFM senses the surfaces to be in contact. Hence, the range of the surface force does not represent the layer thickness of the polymer. This should be borne in mind when interpreting results. However, the analysis of the compressibility provides a tool to estimate this effect. The concept of the surface and of the contact is determined relatively to compress force, and is thus comparable between measurements.

3.2.3 Other methods used

Quartz crystal microbalance with dissipation monitoring (QCM-D, Q-Sense, Gothenburg, Sweden) measures the mass adsorbed on a quartz crystal by measuring the change in frequency of a quartz crystal resonator (Rodahl et al. 1995; Höök 1998). By measuring several frequencies (overtones) and the dissipation, i.e. the energy loss of the crystal movement in water solution, it becomes possible to determine whether the adsorbed film is rigid or water-rich (soft). QCM-D was used for studying the swelling of the NFC surfaces in Paper III and the adsorption of C-PAM, SNP and NFC in Paper IV. The QCM-D data comprised valuable information for surface force measurements by providing more information about surface structure and the development of adsorption.

Solution properties of polyelectrolyte complexes and the complexes of the nanoparticles and polyelectrolyte were in supporting role by giving information of the structure of the complexes in Papers II, IV and V. The average size of the complexes was measured by the means of dynamic light scattering using a N4 and N5 Submicron Particle Size Analyzer (Beckman Coulter Inc., USA). Electrophoretic mobility was measured by Laser-Doppler electrophoresis (Coulter Delsa 440SX, Coulter Electronics Ltd., UK) in order to determine the charge of the complexes.

A dynamic drainage analyzer (DDA) was used for recording the dewatering time in Paper V. The standard deviation of the method is about 9 %. Turbidity of the filtrate after dewatering was measured with an Analite Nephelometer and was taken as an indicator of fines retention. The remaining charge in the supernatant fluid was determined by polyelectrolyte titration (Koljonen et al. 2004).

4 RESULTS AND DISCUSSION

This chapter summarises the most important findings of this work. More detailed results can be found in the attached Papers I-V.

4.1 Surface forces between different cellulose surfaces without added polyelectrolyte

The surface type is highly relevant in force measurements. It affects surface forces as well as adsorption. In this study, different cellulose surfaces have been used. In surface force measurements, the colloidal probe was a mostly amorphous cellulose bead having crystalline cellulose II regions. The substrate, however, varied between Papers I-IV. In Paper I and II, the cellulose sphere was acting also as a substrate, whereas a new native cellulose substrate was developed in Paper III and it was then used in Paper IV. The new substrate contained both amorphous and crystalline cellulose I regions and was prepared by spin-coating aqueous cellulose nanofibril dispersions onto silica. The crystallinity of the surface was approximately 70 % (Aulin et al. 2009). These films differ from previous model cellulose films both in crystallinity, chemical composition (including the residual portion of hemicelluloses) and fibrillar structure. Since both their morphology as well as crystal form resembled the structure of native cellulose, they serve as excellent models for the pulp fiber surface. The morphology of the spin-coated film is presented in Figure 6. Low charged fibrils formed a fully covered but porous network structure. A highly charged nanofibrillar cellulose surface was also developed from carboxymethylated cellulose in Paper III, but here we will concentrate on the low charged nanofibrillar cellulose as they are in native cellulose fiber. More throughout discussion about cellulose model surfaces and interactions between cellulose surfaces can be found in publications by Kontturi et al. (2006) and Ahola (2008).

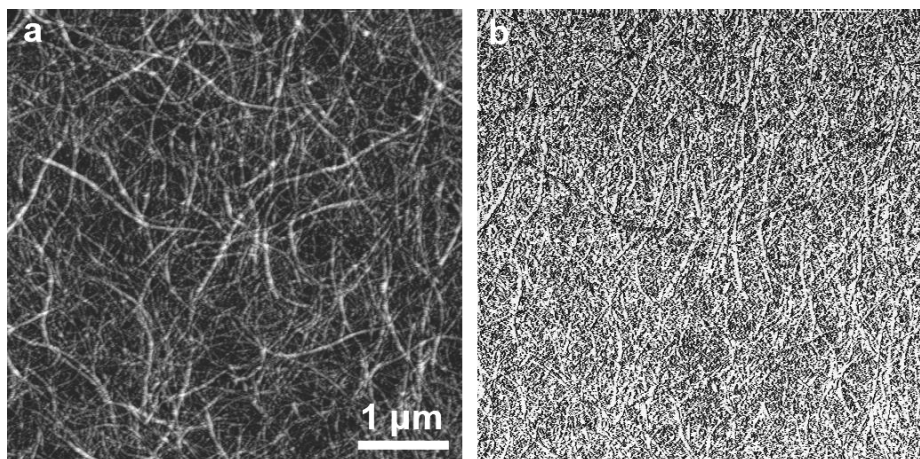


Figure 6. AFM height image (a) and phase image (b) of NFC. Size of images is 5x5 μm and height scales are a. 40 nm and b. 100°. RMS roughness for surface was 3.5 nm. (Paper III)

The effect of salt and pH on the surface forces is well known in cellulosic systems, and the effect of salt is treated only cursorily here (more details in Paper III). The surface forces on approach between a cellulose sphere and a low charged nanofibrillar cellulose film were repulsive in all measured electrolyte solutions (Figure 7). At low electrolyte concentration, the forces at long distances were rather well explained by DLVO theory. This implies that the origin of the interactions was mainly double-layer repulsion due to accumulation of counter-ions close to the charges on cellulose. The obtained surface potentials indicated a low surface charge, which has been observed in Paper I and II and reported earlier for cellulose spheres (e.g. Rutland et al. 1997; Carambassis and Rutland 1999). However, increasing the electrolyte concentration did not result in a decrease in decay length of the forces as would be expected for purely electrostatic interactions. Hence, steric forces also affected the interactions between the cellulose surfaces, although these were dominated by the double-layer repulsion at low electrolyte concentration. The range of steric forces is usually very short between two spheres of the kind we used (Paper I and II, Chapter 2.1.4). Thus, it can be concluded that the observed electrosteric forces were due to the cellulose nanofibrils. In addition, the crystallinity of cellulose as well as the roughness of the surface affects the nature of interactions (Notley et al. 2004 and 2006; Stiernstedt et al. 2006b). The NFC surface, in this thesis, was highly crystalline and rather smooth. Because the nanofibril films are water-swollen, repulsive hydration forces may also contribute to the force profile. Here, hydration forces may be present between

protruding chains as well as within the swollen gel, and hence may affect the force curve also at longer distances. However, these forces can not be separated from the steric effects. Furthermore, the swelling of the surface shatters the plane of charge, which affects the accuracy of the fittings, and hence the observed surface potentials. Overall, the surface forces agreed well with changes in swelling measured with QCM-D. The swelling increased the contribution of steric repulsion.

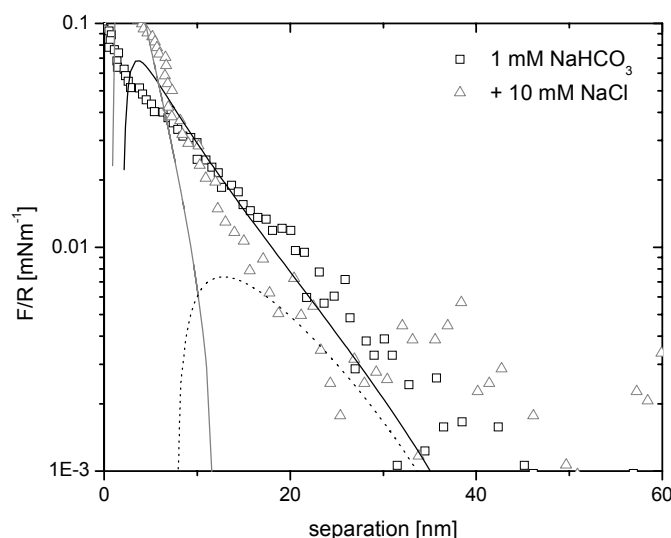


Figure 7. The effect of electrolyte concentration on surfaces forces between a cellulose sphere and a nanofibrillar cellulose surface with low charge. The lines are the best fits according to DLVO theory assuming constant charge (solid line) and constant potential (dotted line) in the respective electrolyte concentrations. The surface potentials for the cellulose surfaces giving the best fits were -9 mV for 1 mM NaHCO_3 and -15 mV for 1 mM $\text{NaHCO}_3 + 10$ mM NaCl . (Paper III)

4.2 The effect of a single cationic polyelectrolyte on surface forces

The effect of polyelectrolyte addition was studied using PDADMAC and C-PAMs with different charge densities and different molecular weights (Paper I). It was observed that the repulsion between the cellulose spheres decreased initially when a small amount of cationic polyelectrolyte was added. Near the charge neutralization point (cnp), an attractive contribution to the surface forces was observed (Figure 8A).

Further addition of polyelectrolyte led to charge reversal. When the concentration of polyelectrolyte was high, surface forces at large distances were well explained by the DLVO theory in the case of highly charged, low molecular weight polyelectrolyte, implying that the origin of repulsive interactions at large distances was mainly electrostatic; however, when a low charged, high molecular weight polyelectrolyte was added to the solution, a mainly electrostatic behavior turned into steric repulsion at high polymer concentrations. The range of steric repulsion was about 300-400 nm, indicating a thick and loose layer of polyelectrolyte, which is typical for low CD, high M_w polyelectrolytes. This steric repulsion is still affected by salt concentration because charges in the polymer layer are affected by changes in electrostatic double-layer (Paper I), and thus the repulsive force can be considered electrosteric repulsion (Chapter 2.1.2). The observed range was consistent with the results obtained by other research groups on low charged polyelectrolytes (Zauscher and Klingenberg 2000; Poptoshev and Claesson 2002) and the range is reasonable when considering the hydrodynamic radius of similar C-PAMs in solution (420 nm for degree of substitution 20% and M_w 1.4 million, Mabire et al. 1984).

The forces on separation were also depended on the properties of polyelectrolyte (Figure 8B). While a sharp minimum was found in the presence of a polyelectrolyte with high charge density and low molecular weight, the detachment was gradual with attractive forces observed at separation of hundreds of nanometers for a polyelectrolyte with low charge density and high molecular weight (Figure 8B). The pull-off force, i.e. attractive force on retraction, was at its largest near the charge neutralization point, where the surfaces were only partially covered and the polyelectrolyte was able to effectively bind the surfaces together. The pull-off force in C-PAM solutions was long ranged and the detachment of the surfaces was gradual. Similar findings have been reported by Poptoshev et al. (2000a), Zauscher and Klingenberg (2000) and Poptoshev and Claesson (2002), using low charged cationic polyelectrolyte. Joints formed via bridges can be assumed to be long ranged and flexible, which leads to a gradual detachment of surfaces keeping them connected at large separation. In contrast, a sharp minimum in pull-off force was found in the presence of highly charged polyelectrolyte, in agreement with the observation by Poptoshev et al. (2000b). The range of pull-off force, as well as the attractive contribution between approaching surfaces, of highly charged PE was unaffected by

molecular weight. This was due to the flat conformation of the adsorbed polyelectrolyte enabling only the formation of short bridges. In both cases, the pull-off force was weaker at high polymer concentration and mainly due to entangled polymer molecules.

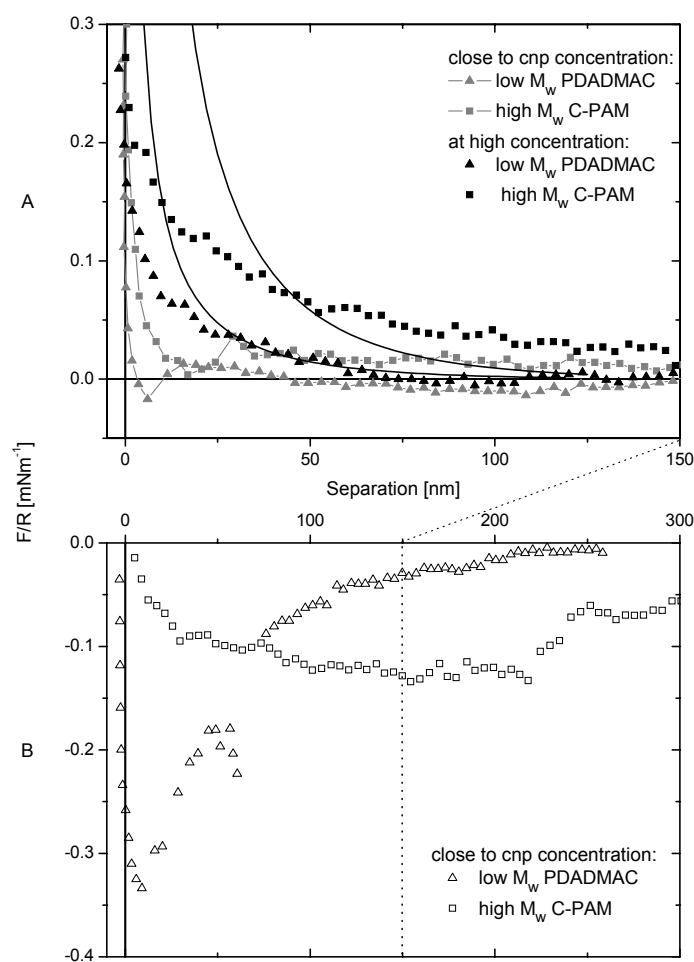


Figure 8. The effect of highly charged, low molecular weight PDADMAC (\blacktriangle) and low charged, high molecular weight C-PAM (\blacksquare) on surface forces between cellulose spheres presented close to the charge neutralization point (cnp) concentration and at high concentration. Closed symbols are for forces measured on approach (A) and open symbols are for pull-off force, forces measured on retraction (B). In image A, The points are connected for clarity close to cnp concentration. Solid lines represent DLVO fitting results at high concentration of polyelectrolyte. Note that the scales differ between images A and B. (Paper I)

The effect of different C-PAMs on *dewatering* of the pulp suspension is compared in Figure 9 (Paper V). In all cases, dewatering goes through a minimum as a function of C-PAM dosage. The fastest drainage coincides with the dosage that renders the residual particles in the filtrate neutral. In the presence of C-PAM, the negative fines are nearly neutralized, the double-layer forces are reduced and the fines start to flocculate due to attractive van der Waals force or due to the attractive bridging force as was seen in force measurements. Thus, at least under the conditions used in this investigation, the charge neutralisation of surface and polymer bridging seems to be important factors in the formation of an easily drainable sheet. The best dewatering was achieved using high molecular weight, low charged C-PAM. The ability to form longer and more flexible bridges seems to be the key factor for good dewatering. In addition, long ranged attractive forces due to the long bridges more easily overcome the repulsive hydrodynamic barrier in the presence of shear. The importance of bridging is emphasized when surfaces are withdrawing. This is easy to understand in the light of the observed pull-off forces why particles connected with long and flexible polyelectrolyte bridges stay together even in shear (Dickinson and Eriksson 1991). On the other hand, at C-PAM dosages higher than the optimum dosage, the surface charge of fibers and fines is reversed due to the adsorption of excess polymer. This leads to electrostatic repulsion in the case of low M_w , high charged polyelectrolytes and to steric repulsion in the case of high M_w , low charged polyelectrolytes, which restabilizes the fine material, reduces fines retention and slows down dewatering. The effect of high charged C-PAM on dewatering is weaker than the effect of the low charged C-PAM. The high charged polymer adsorbs in a flatter configuration on the surface of particles, which has a negative effect on bridging force on separation and thus on bridging flocculation (Abson and Brooks 1985).

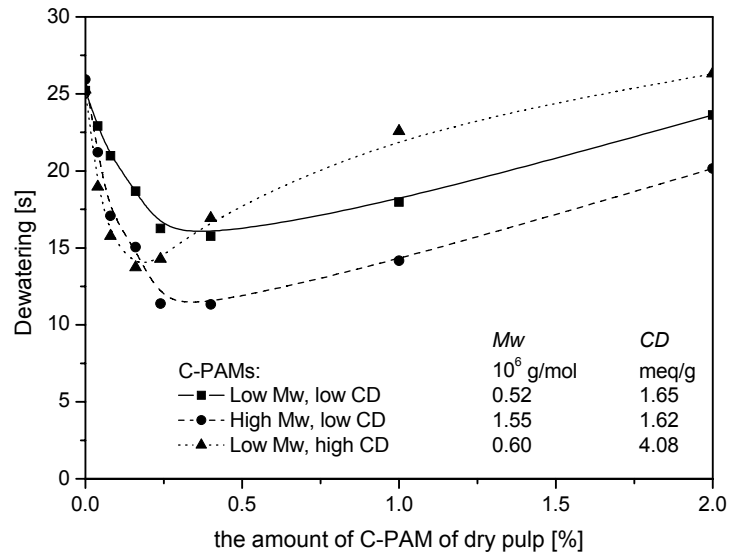


Figure 9. The effect of different C-PAMs on dewatering time of pulp. Note that the properties of C-PAMs differ slightly from ones used in surface force measurements (see Table 1). (Paper V)

Our results indicated that the main mechanism in flocculation was bridging irrespective of which cationic polyelectrolyte was used. Bridging is schematically illustrated in Figure 2B. Patchwise attraction is often presented as a parallel mechanism with bridging. Patchwise flocculation mechanisms can be seen as an intermediate of heteroflocculation and charge neutralization. It's a matter of the size of the patches. However, it should be noted that the possibility to detect patchwise attraction in the force measurements has been criticized, because the measurement system used is static, not freely rotating, and surfaces are macroscopic (Poptoshev 2001). Furthermore, no repulsive contribution was observed in the surface force measurement near the charge neutralization point, which should statistically be a consequence of the static setup of force measurements in the patch-wise mechanism. Patch-wise flocculation may have a minor role in some specific cases during flocculation, but the force holding the flocs together is due to bridging, and this is more important in the flocculation of the system under shear.

4.3 The effect of PEC on surface forces

The adsorption of polyelectrolyte complexes on a negatively charged cellulose surface had a strong influence on the interactions between the surfaces, and the forces were clearly different as compared to single polymer systems (Figure 10 and Paper II). The interactions between the adsorbed polyelectrolyte complex layers were mainly steric and repulsive, even at low polymer concentrations. The comparison between two polyelectrolyte complexes (mixing ratio of 1:9 = A-PAM:C-PAM) showed that the complex formed by high molecular weight and low charged polyelectrolytes induced a steric force ranging farther than the steric force induced by the complex of low molecular weight (M_w) and high charge density (CD) polyelectrolytes. The steric force ranged over 1.0 μm in the 100 mg/l PEC solution formed by high M_w , low CD components, whereas the range was below 300 nm in the PEC solution formed by low M_w , high CD polymers. For comparison, the range of steric repulsion in high M_w , low CD C-PAM was only ca. 200 nm at 1.0 mM NaHCO_3 . The explanation is that high molecular weight, low charged polyelectrolytes form larger complexes in solution than low M_w , high CD polyelectrolytes (Paper V). In addition, large M_w , low CD PECs have been shown to form a looser and thicker layer in adsorption experiments (Saarinen et al. 2008). The electrolyte concentration did not affect the surface forces significantly in the case of the large PEC. PECs are reported to contain a large amount of water, even close to 90 % (Gärdlund et al. 2007; Ankerfors 2008). Hence, one may assume that trapped water also affects the surface forces and hence the repulsion could also be due to a hydration-steric force.

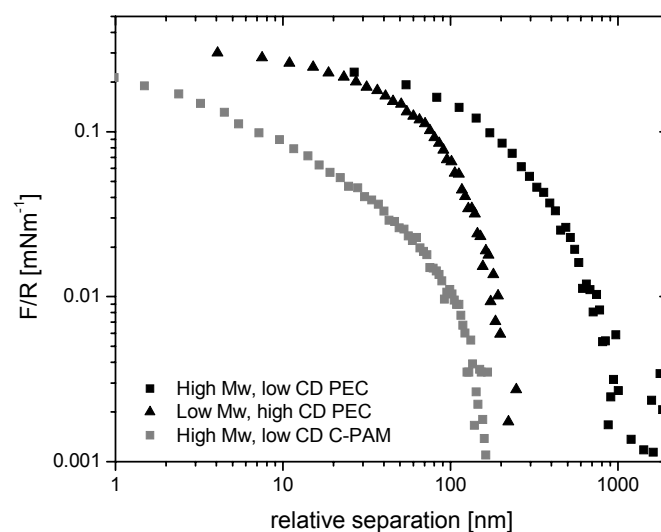


Figure 10. The effect of PEC properties on surface interaction between approaching cellulose surfaces at high polymer concentration and at 1.0 mM NaHCO₃. Note logarithmic scale in both axes. (Paper II)

When recording the force curves between PEC layers on withdrawal, it was observed that also the *pull-off forces* was extremely long ranged for the large PEC (Figure 11). The magnitude of the pull-off force was, however, rather low and the curve had three minima. In contrast, the shape of the pull-off force curve in the case of PEC formed by low M_w , high CD C-PAMs was clearly different. It was sharper and only one force minimum was found at much smaller separation. The shape difference in pull-off force curve indicated that PECs from high M_w , low CD polyelectrolytes are flexible, whereas molecules in PECs from by low M_w , high CD polyelectrolytes are binding and stiff (Gong et al. 2005). The flexibility of the larger PEC is further supported by adsorption measurements that showed that high M_w , low CD PEC is able to rearrange during the adsorption (Saarinen et al. 2008). In addition, it was observed that the PEC from high M_w polyelectrolytes had a larger optimum range of the maximal pull-off force than the PEC of low M_w components. Compared to one component C-PAM, two observations can be made. Although the magnitude of the pull-off force was approximately the same, the range of the pull-off force increased from a few hundred nanometers for the single component system to microns for the PEC system, containing only one tenth of A-PAM. Another difference was that the maximum pull-off force was reached near the charge neutralization point for one component system

while the pull-off force between PEC layers was observed also at high surface coverage.

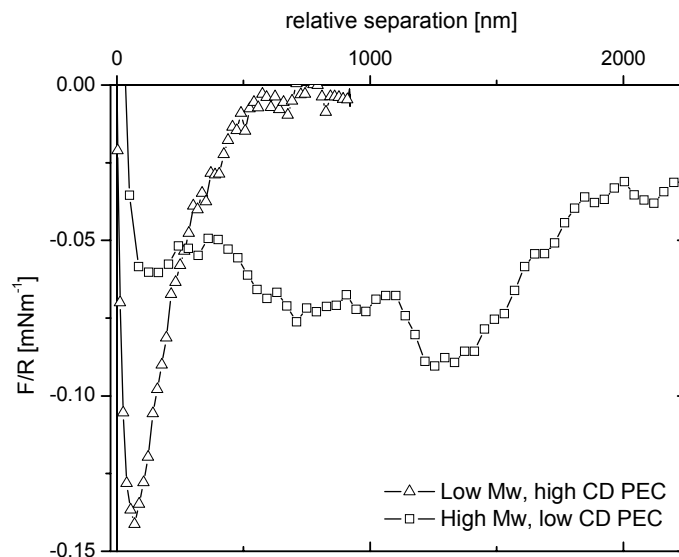


Figure 11. The effect of PEC properties on pull-off force at high polymer concentration. The concentration of NaHCO_3 was 0.1 mM for high M_w , low CD PEC and 1.0 mM for low M_w , high CD PEC. (Paper II)

The comparison of phase data in Figures 12 and 6 indicates that PEC formed by high M_w , low CD C-PAMs is almost fully covering the surface, although the structure beneath the PEC layer is seen through in Figure 12. This together with long ranged repulsion and long ranged, gradual pull-off force indicated that pull-off force is based on *A-PAM linking* rather than complex bridging at high polymer concentration. In complex bridging, the PEC forms bridges between two cellulose surfaces, whereas in *A-PAM linking*, the A-PAM molecules act as a link between C-PAM molecules. These mechanisms differ from each other most clearly in regard to the optimal surface coverage. *A-PAM linking* is possible between fully covered surfaces, whereas the complex bridging is favorable between partially covered surfaces. The three minima in the pull-off force correspond to the detaching of links between C-PAM and A-PAM. C-PAM and A-PAM attracts electrostatically each other forming the link, and detaching them from proximity to each other requires work observed as the minimum in the pull-off force curve. In other words, when the complex layers are overlapping, it is favorable for A-PAM molecule to be in the proximity of the C-PAM molecule in

the opposite complex layer (Decher and Schlenoff 2003). A-PAM and C-PAM can even undergo complexation reaction forming a new temporary complex. This is possible only when the complex layers are loose. A potential and speculative mechanism for the A-PAM linking between PEC covered surfaces is proposed in Figure 13 (only one complex is illustrated for the sake of the clarity). The detachments indicate the bonding of the A-PAM molecule to the C-PAM molecule of the opposite complex layer in a different level of the layer. The first detachment is due to detachment of A-PAM from the C-PAM close to the cellulose surface. The second minimum is due to break off of the link between C-PAM on the side of A-PAM and topside A-PAM, when the complexes are slightly offset. The third detachment is between the end of the strands of C-PAM and A-PAM. The A-PAM linking is possible due to flexible nature of the complex enabling the mixing of layers and due to the low A-PAM content regulated by the use of complexes. However, to verify this model, one should investigate the complex layers more detailed.

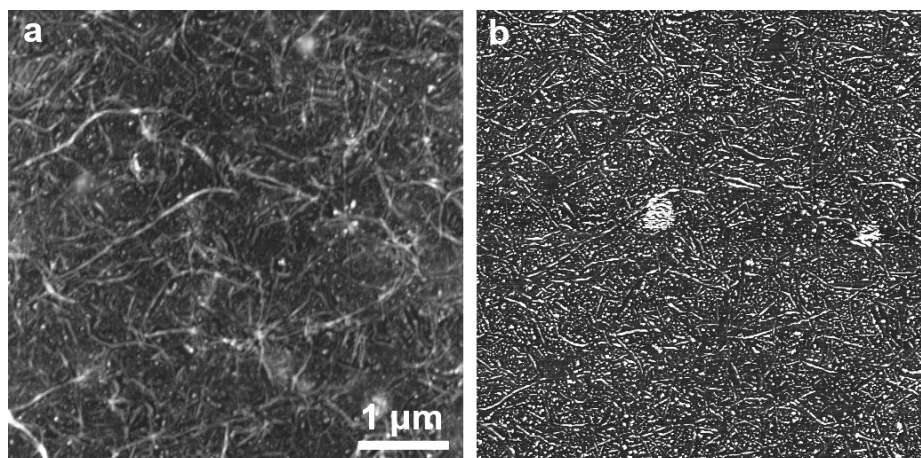


Figure 12. AFM height image (a) and phase image (b) show the layer structures of the adsorbed PECs formed by high molecular weight, low charged C-PAM and A-PAM (at mass ratio of 9:1). Size of images is 5x5 μm and Z scales are a. 30 nm and b. 100°. Samples were rinsed and dried before imaging, and imaged in air. RMS roughness was 2.7 nm. (Unpublished result)

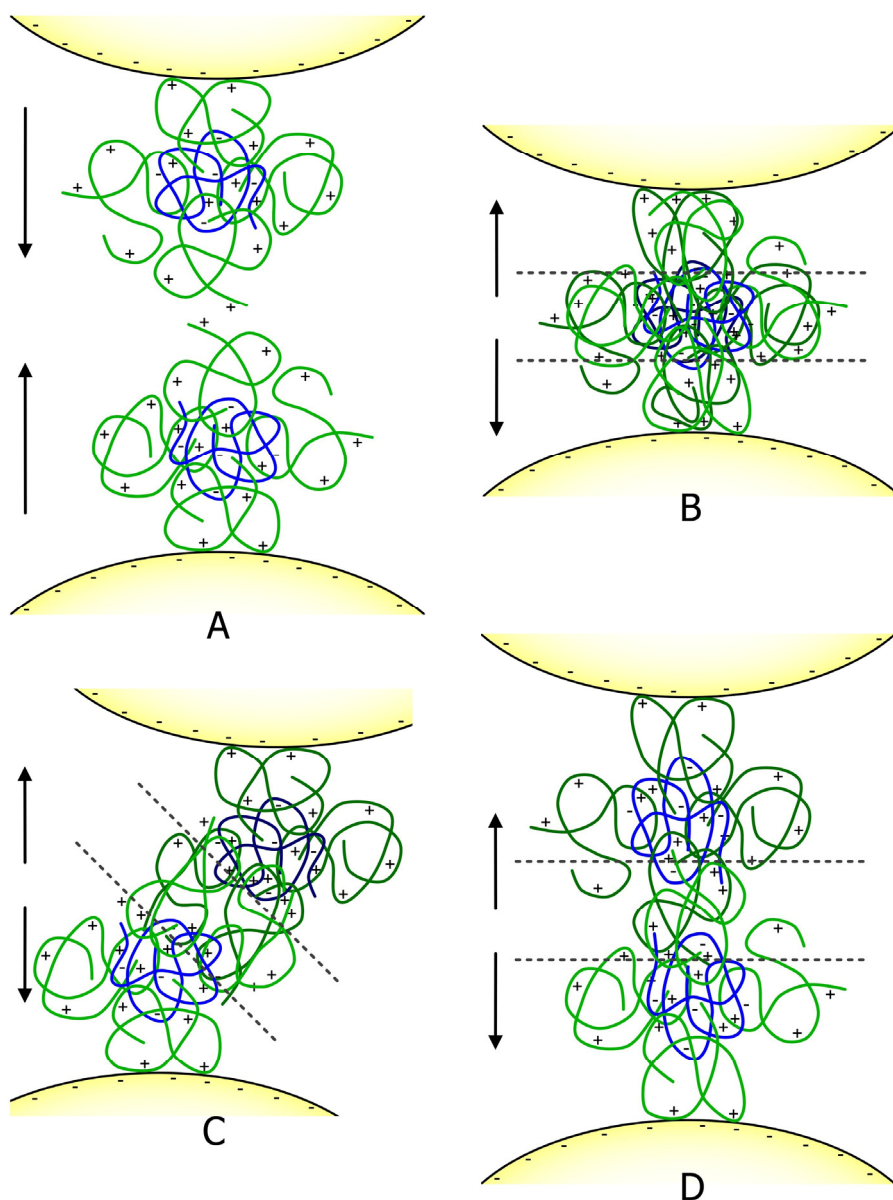


Figure 13. A schematic drawing of A-PAM linking mechanism. Image A represents the approaching surfaces covered with PECs (only one complex is shown). Images B-D represent the stages of break-off of A-PAM links while surfaces are separating, simulating the minima in pull-off force. Dotted lines demonstrate the locations of the break-off. B. The full-overlap of layers and first detachment between A-PAM and C-PAM closest to the cellulose surface. C. Second detachment, when the PECs are at slight offset. D. Third break-off of A-PAM link between A-PAM and topmost C-PAM.

The fact that the interaction forces are totally different using polymer complexes as compared to single polymer systems can have a drastic effect on e.g. water removal efficiency, as well as flocculation during the formation of the paper web. In fact, it

was shown in Paper V that the use of PECs as drainage and retention aids enhanced the drainability of papermaking stock compared to C-PAM alone (Figure 14), or to the sequentially added polymer system (see Figure 16). *Dewatering* studies of different polyelectrolyte complexes revealed that the most effective drainage aid was the largest PEC containing the largest M_w , low CD polyelectrolytes (Figure 15), and that a small amount of A-PAM was enough to reach optimum influence. In addition, the optimum concentration range of the dewatering effect induced by A-PAM/C-PAM complexes was broader than that of single C-PAM. The decrease in dewatering time at low additions of PEC was probably mainly caused by the formation of complex bridges, which presumably was further promoted by A-PAM molecules acting as a link between C-PAM molecules in the complex. The deviations between the dewatering times of C-PAM and PEC at higher amounts of polyelectrolytes may be a sign of changing from complex-induced bridging to an A-PAM promoted linking of complex layers when the complexes are fully covering the surfaces.

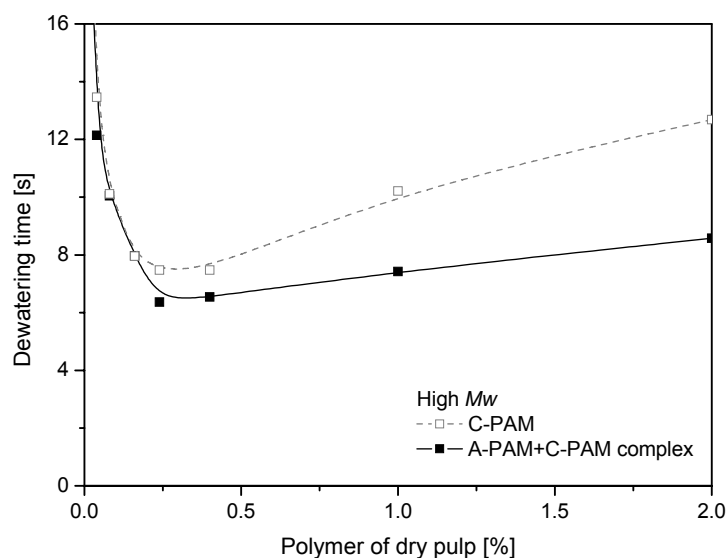


Figure 14. The comparison of the dewatering times between high molecular weight C-PAM and PEC. A-PAM : C-PAM charge ratio in the complex was 0.28:1. The polymers are the same as in Figure 15. (Paper V)

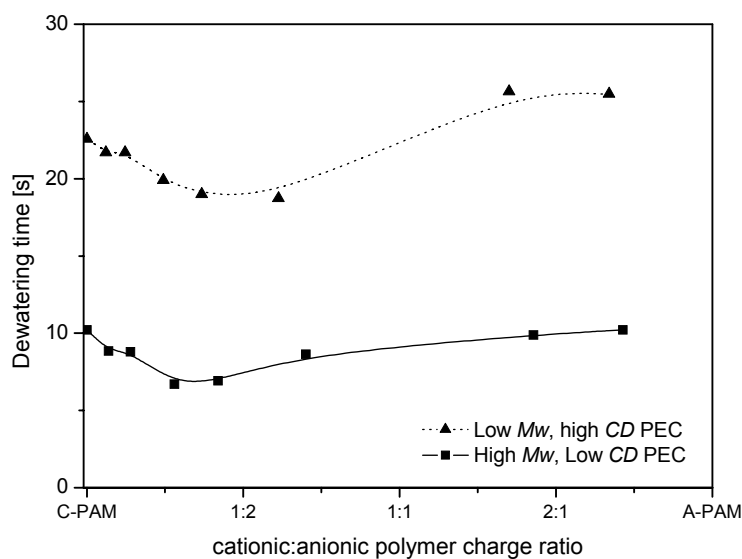


Figure 15. The effect of complex composition on dewatering time. Low M_w , high CD PEC (\blacktriangle) contains C-PAM with M_w of $0.60 \cdot 10^6$ g/mol and CD of 4.1 meq/g and A-PAM with M_w of $0.77 \cdot 10^6$ g/mol and CD of 6.3 meq/g, whereas high M_w , low CD PEC (\blacksquare) is formed by C-PAM with M_w of $6.0 \cdot 10^6$ g/mol and CD of 1.0 meq/g and A-PAM with M_w of $1.67 \cdot 10^6$ g/mol and CD of 1.8 meq/g. (Paper V)

The large size of the PEC is beneficial for two reasons. First, it can attract the opposite surface from far away and thus overcome the barrier of hydrodynamic repulsion due to shear. Second, the attraction has to be stronger than the shear forces present for the flocs to be stable. The fact that the pull-off forces are weak but very long ranged implies that the flocs formed by these PECs would be rather flexible. This means that to detach two particles completely, the particles have to be drawn more than one μm apart, whereas the pull-off forces in single cationic polyelectrolyte systems were stronger, but shorter than in PEC systems. This could be a reason for the unique behavior of the polyelectrolyte complexes where flocculation may be increased without affecting the strength and the formation negatively (Chapter 2.2.3).

A more conventional way to add polyelectrolytes in dual polymer system is to add them sequentially. In *polyelectrolyte multilayer* systems, the surface forces are determined mainly by the outermost layer of the system (Lowack and Helm 1998; Blomberg et al. 2004; Kulcsar et al. 2004 and 2005; Gong et al. 2005). The outermost layer affects also the multilayer structure (Lösche et al. 1998; Decher and Schlenoff

2003; Eriksson et al. 2005; Notley et al. 2005; Saarinen et al. 2008). Although PEMs has been reported to increase the pull-off force between mineral surfaces (Lowack and Helm 1998; Blomberg et al. 2004; Kulcsar et al. 2004; Gong et al. 2005; Notley et al. 2005), the smaller effect on dewatering (Figure 16) and retention (Nyström and Rosenholm 2005) is probably caused by their more ordered structure, compared to PECs, weakening the linking ability of the anionic polyelectrolyte. The structure of the layer seems to be a crucial factor. In congruence with the observation in PEC systems, a flexible PEM structure is beneficial for paper strength (Wågberg et al. 2002; Eriksson et al. 2005; Hubbe et al. 2005; Notley et al. 2005; Enarsson and Wågberg 2007). Sequential addition is capable of introducing more polymer into the system, increasing the number of the layers, and thus become more effective than PEC systems; however, the benefits of using PECs compared to PEMs in an industrial setting are ease of use (only one addition step), the low amounts of polymer needed and a wide optimum concentration range.

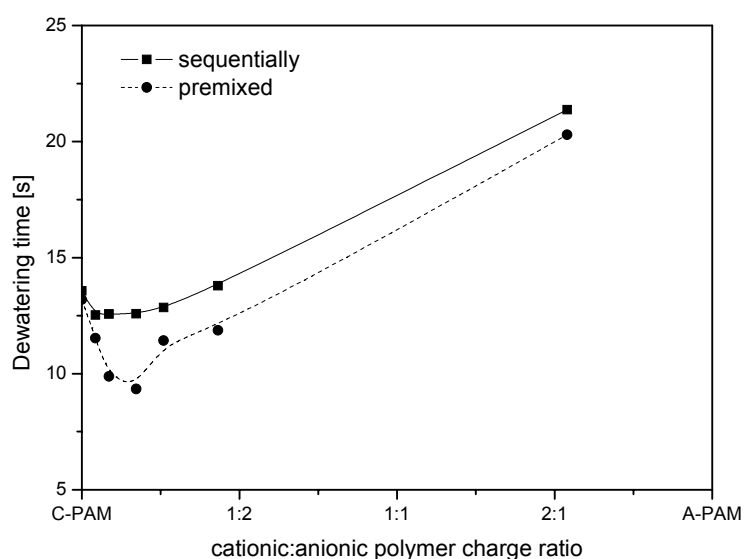


Figure 16. The effect of addition strategies of C-PAM and A-PAM on dewatering. The C-PAM concentration was kept constant at 1 % of pulp. The M_w of C-PAM is $1.6 \cdot 10^6$ g/mol and CD is 1.6 meq/g. The M_w of A-PAM is $0.5 \cdot 10^6$ g/mol and CD is 2 meq/g. (unpublished result)

4.4 The effect of the multilayer and complex of nanoparticles and polyelectrolyte on surface forces

The effect of nanoparticles on surface forces was studied in Paper IV. Two different nanoparticles were used together with high molecular weight, low charged C-PAM, which showed most promising results in polyelectrolyte and polyelectrolyte complex systems. Inorganic silica nanoparticles (SNP) represent the conventional nanoparticle used in papermaking (Chapter 4.4.1) while nanofibrillar cellulose (NFC) is a rather new innovation (Chapter 4.4.2), and thus there are a lot of expectations for its exploitation in industry.

4.4.1 Silica nanoparticles and C-PAM

The formation of polyelectrolyte-nanoparticle layers was studied using silica nanoparticles (SNP) and cellulose nanofibrils together with C-PAM. The results were compared to the surface structure of the complexes. The plot of the QCM-D results in Figure 17 shows the decrease in Δf upon the stepwise adsorption of C-PAM and SNPs. A rather high amount of SNP was adsorbed on C-PAM, although the dissipation change was not outstandingly high. After the addition of a second layer of C-PAM, the dissipation decreased slightly, indicating that the layer became denser. This suggests that silica nanoparticles are able to penetrate into the C-PAM layer and replace bound water in the layer. Further analysis of the QCM-D data revealed, in Paper IV, that the good correlation among the 3rd, 5th and 7th overtone data indicated that the layer is behaving quite uniformly (Johannsmann et al. 2008).

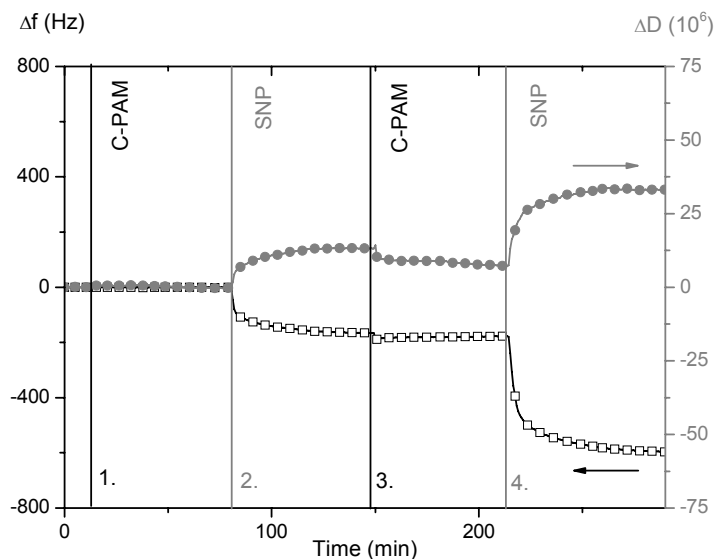


Figure 17. QCM-D results (3^{rd} overtone) during C-PAM-SNP layer formation showed the changes in frequency (open square) and in dissipation (grey filled circles) when C-PAM and SNP are adsorbed on nanofibrillar cellulose surface at 1 mM NaHCO_3 . After each layer the system were rinsed with buffer solution. (Paper IV)

The build-up of the C-PAM – silica nanoparticle – C-PAM layers affected surface forces between the cellulose sphere and the low charged nanofibrillar cellulose film. Surface forces during multilayer formation are shown in Figure 18. Repulsion increased step by step as layer formation progressed. Cationic C-PAM adsorbed onto cellulose and overcompensated the negative charge of the surface. Further, negatively charged nanoparticles adsorbed on the C-PAM layer. This increased repulsion only slightly. Again, C-PAM adsorbed on the C-PAM – silica nanoparticle layer, which is assumed to be neutral or negative charged. Repulsion in any solution did not follow the DLVO theory. Thus, the repulsion was concluded to be mainly of steric origin due to the overlapping of the layers.

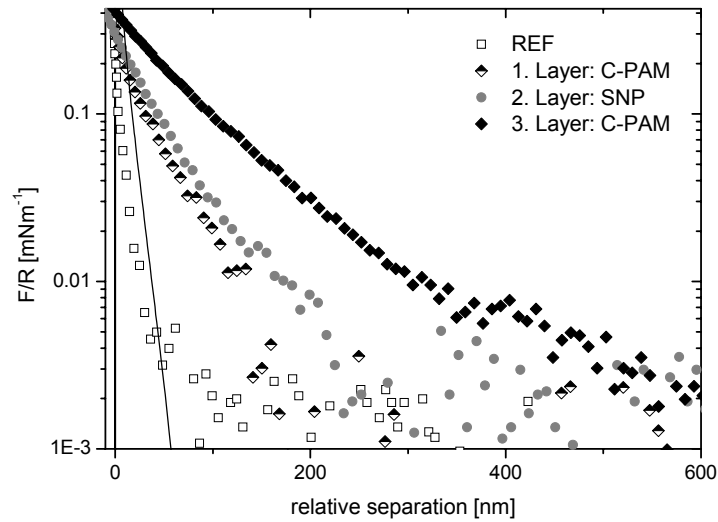


Figure 18. Surface forces between cellulose sphere and nanofibrillar cellulose film measured in the formation of the layer structure C-PAM – silica NP – C-PAM at 1 mM NaHCO₃. The solid line represents the fitting of DLVO forces with a constant charge assumption, resulting in a surface potential of 24 mV. In each step, the concentration of solution was 100 mg/l of C-PAM or of silica nanoparticles. (Paper IV)

AFM images showed that a fully covered surface was observed in the multilayer formation (Figure 19a). When C-PAM and silica nanoparticles were complexed in solution (in a mass ratio of 1:1) and then added, the surface became only partially covered, revealing the nanofibrillar cellulose structure underneath. In addition, AFM images showed that both structures were formed from similar granules, which were further organized into larger clusters. This indicated that the addition of SNP caused the C-PAM molecules to associate tightly together with nanoparticles. Because the size of the clusters were close in size to the complexes in solution, it is probable that the clusters formed by the smaller granules correspond with the complexes. Therefore, the complex of C-PAM and SNP can be seen as a collapsed pearl necklace structure on the surface (Cabane and Duplessix 1982).

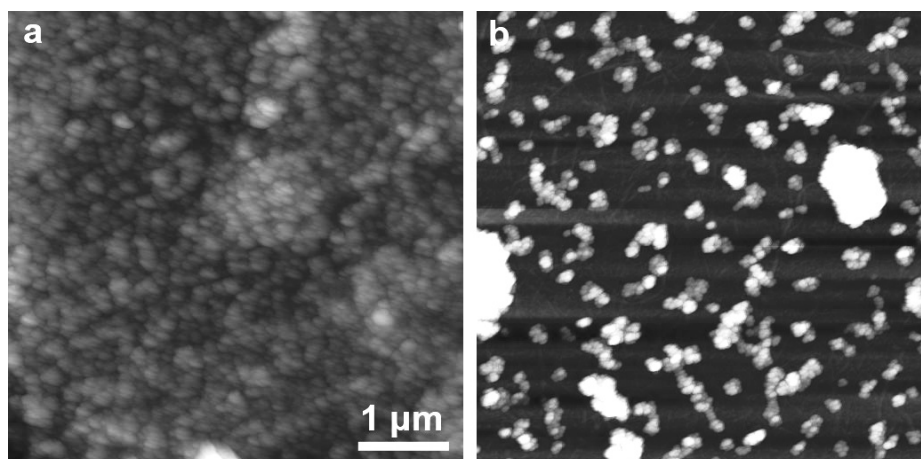


Figure 19. AFM height images: a. the layer structures of C-PAM – SNP – C-PAM and b. the complexes (at mass ratio of 1:1) of SNP and C-PAM. Size of images are $5 \times 5 \mu\text{m}$ and height scales are a. 400 nm and b. 150 nm. Samples were rinsed and dried after force measurements, and imaged in air. RMS roughness were a. 24 nm and b. 17 nm. (Paper IV)

When C-PAM and silica nanoparticles were added together in solution as a complex, it was observed that surface force and pull-off force strongly depended on the location where the measurement was made. This was expected from the AFM results, where only partial coverage of the surface was observed (Figure 19b). Interactions between partly complex-covered cellulose surfaces did not follow DLVO forces, indicating the presence of steric repulsion (Paper IV). The surface interactions with the complex structures differed clearly from the layered structures in the matter of pull-off force. The range and magnitude of pull-off force between complex layers increased, when complex concentration increased (Figure 20). Logically, the pull-off force of the complex originates from the partial coverage, whereas the absence of pull-off force in the layered structure was likely due to a fully covered surface and the structure of the layer. Complexes were able to attach to both surfaces forming complex bridges when the surfaces were pressed together. Thereupon when surfaces were withdrawn, complex bridges stretched and detached slowly from the surface. SNPs and C-PAM formed a rather dense complex, whereas A-PAM and C-PAM formed a flexible PEC. This explains the difference between the complexes. A-PAM is able to link the layers together in the PEC systems, but the SNP-C-PAM complex bridges the surfaces together.

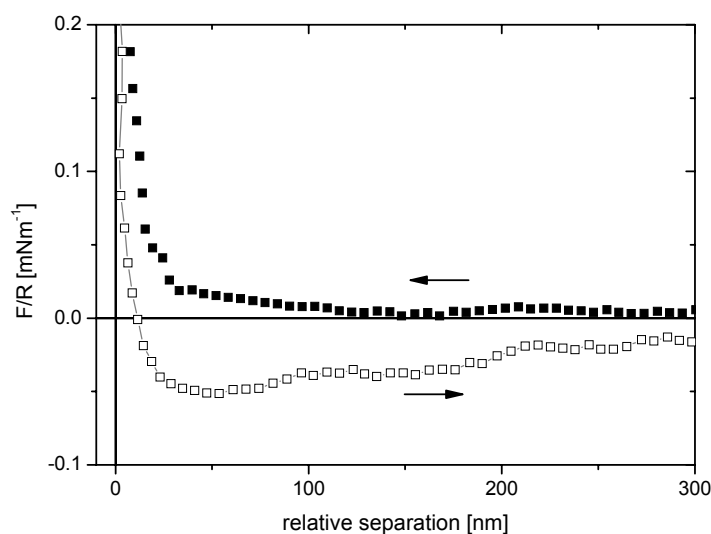


Figure 20. Pull-off force (open symbols) in 100 mg/l complex of C-PAM and SNP (in mass ratio of 1:1) solution at 11 mM electrolyte concentration. Filled symbols are for approaching data. (Paper IV)

From the observations above, the uniform layer structure, the high amount of adsorbed SNP and the similarities in AFM images, it was concluded that nanoparticles are able to penetrate inside the polyelectrolyte layer due to their small size. We propose the hypothesis for the behavior of silica nanoparticles with loose polyelectrolyte layer schematically in Figure 21A. At high salt concentration, the charges of polyelectrolyte are more randomly located due to screening of the charges. Hence, negatively charged nanoparticles are located all over the layer. This leads to strong repulsion between segments, which for its part leads to an increase in a layer thickness and repulsion after addition of SNP (Paper IV). At low salt concentration, the charges of the polyelectrolyte layer were located only very close to the cellulose surface, instead. Therefore, nanoparticles tend to adsorb near the cellulose surface, where the charges of C-PAM are. This keeps the outermost polymer layer fairly unchanged, which was seen in the range and magnitude of repulsion (Figure 19). All together, silica nanoparticles are able to move freely inside layer and thus they are forming quite similar layers with C-PAM compared to complex layer, which were freely forming in solution before adsorption.

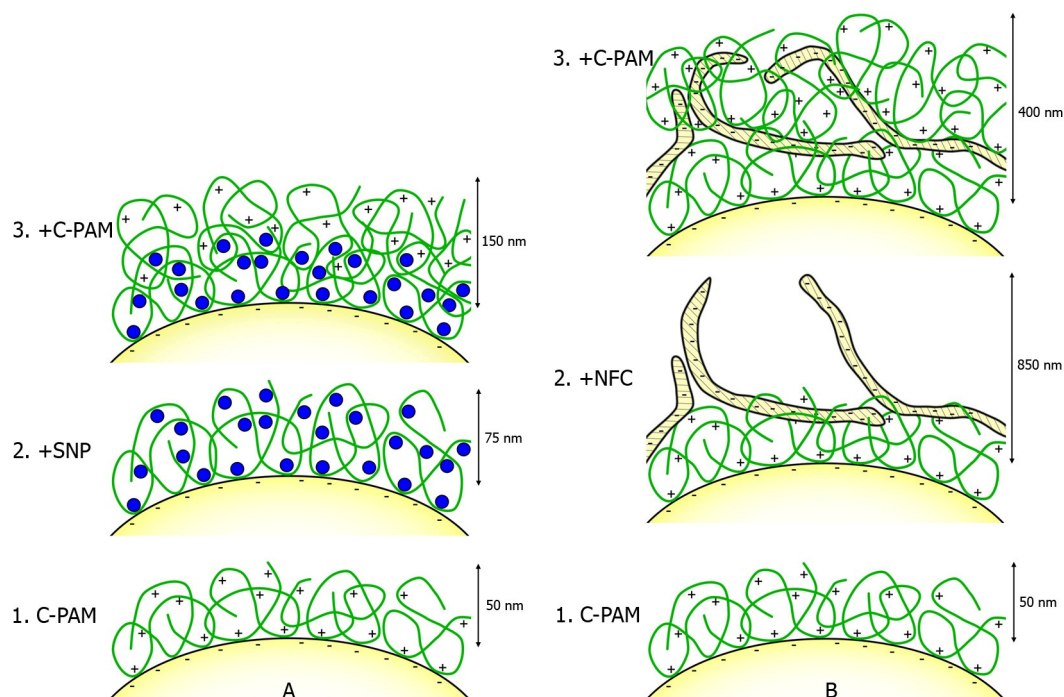


Figure 21. A schematic image of A. C-PAM-SNP-C-PAM layer growth and B. C-PAM-NFC-C-PAM layer growth at high salt concentration. The indicated scale given for each layer is based on the range of repulsion in force measurements at 11 mM electrolyte solution. However, the exact layer thickness is unknown due to uncertainty at zero separation.

Freely moving, charged silica nanoparticles tend to act as a binding site between charges. Earlier Jiang et al. (2008) suggested that nanoparticles act as physical cross-link points. This idea definitely supports the observations that nanoparticle-polyelectrolyte systems have shown a better re-flocculation ability than dual polymer systems (Andersson and Lindgren 1996; Swerin and Ödeberg 1996). Freely moving, binding nanoparticles may re-organize the layer structure of nanoparticles and polyelectrolytes, and thus broken flocs may reflocculate.

4.4.2 Cellulose nanofibrils and C-PAM

In order to evaluate the effect of nanoparticle type on interactions, adsorption and surface forces were also studied in a solution of cellulose nanofibrils with C-PAM. These results were compared to the interactions of C-PAM in the presence of

inorganic silica nanoparticles. The size, shape and chemistry are totally different in these two cases. The adsorption of nanofibrils forms an extremely loose and viscoelastic layer which can be seen as a dramatic increase in dissipation observed with QCM-D (Figure 22). Similar behavior has earlier been seen by Ahola et al. (2008a) and Aulin et al. (2008). This behavior is most probably due to the very high water binding capacity of the cellulose nanofibrils. In addition, QCM-D studies based on the differences in the data recorded with the different overtones indicated that the layers were only partially mixing (Paper IV; Johannsmann et al. 2008). This is easy to understand, when considering that the large size and the network forming ability of nanofibrillar cellulose (NFC) prevent the penetration of the nanofibrils freely into C-PAM layer. Furthermore, the AFM image shows that the layers of C-PAM and NFC covered the cellulose surface fully and evenly, and that the layer structure was well-organized and similar to a NFC surface without any added layers (Figure 23, compare to Figure 6).

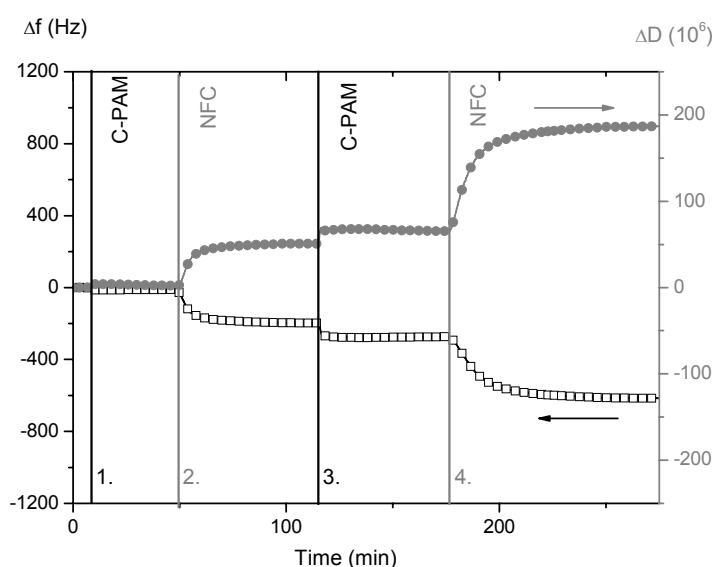


Figure 22. The QCM-D results (3rd overtone) during C-PAM-NFC layer formation shows the changes in frequency (open square) and in dissipation (grey filled circles) when C-PAM and NFC are adsorbed sequentially on a nanofibrillar cellulose surface at 11 mM electrolyte concentration. After each layer the system was rinsed with buffer solution. (Paper IV)

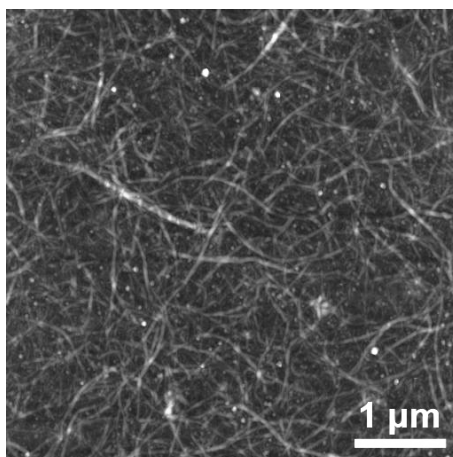


Figure 23. AFM height image of the layer structures of C-PAM – NFC – C-PAM. Size of images is 5x5 μm and height scale is 50 nm. Sample was rinsed with water and dried after force measurements, and imaged in air. RMS roughness was 2.6 nm. (Paper IV)

The normalized surface force between the cellulose sphere and the low charged nanofibrillar cellulose surface are presented as a function of the relative separation during layer formation of high molecular weight C-PAM and highly charged cellulose nanofibrils in Figure 24. Repulsion increased substantially when highly charged nanofibrils were added into solution after a C-PAM step. The range of repulsion was more than 1500 nm. Evidently, NFC forms a very thick and loose layer structure. This introduced long ranged repulsion between cellulose surfaces. Interestingly, repulsion decreased clearly, when C-PAM solution was added for the second time, although QCM-D data indicated opposite. This indicates that the adsorption of C-PAM collapsed the topmost part of the highly charged nanofibrillar cellulose layer and possibly released water molecules. A schematic representation of the layer build-up is shown in Figure 21B. Surface forces during layer formation did not follow DLVO theory, and thus it may be concluded that the interactions are mainly influenced by steric forces. NFC systems are known to contain much water (Ahola 2008b; Aulin et al. 2008), and thus this repulsion can also be called hydration-steric force.

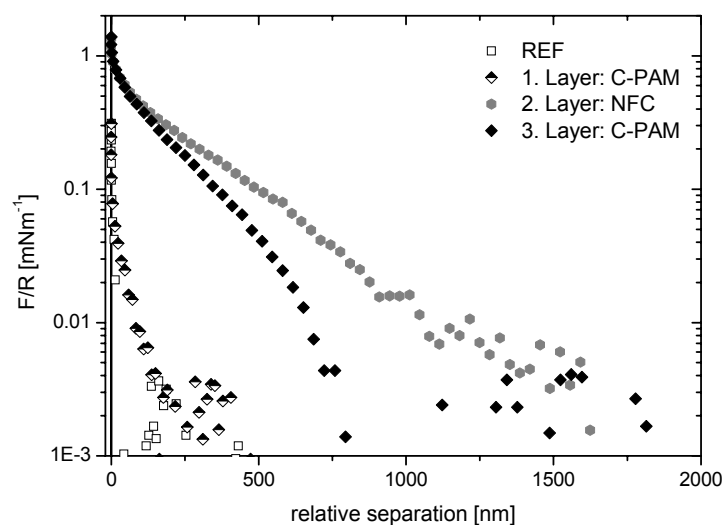


Figure 24. Surface forces between cellulose surfaces measured in the formation of the trilayer structure C-PAM – high charged NFC – C-PAM at 1 mM NaHCO₃ + 10 mM NaCl. In each step, the concentration was 100 mg/l of C-PAM or NFC. (Paper IV)

Cellulose nanofibrils are long and, in addition, they tend to form networks. Nanofibrillar cellulose builds a loose and open network with long-range interactions, which stretch even farther than on the PEC covered surface. It is plausible that NFC is able to create a nanonetwork inside the macroscopic fiber web. This opens possibilities to use the NFC forming network structure as a strength or flocculation additive. In matter of fact, a positive effect on paper strength has been reported (Ahola et al. 2008a). The flocculation mechanism could be similar to network flocculation (Stenius 2000).

5 CONCLUDING REMARKS

Surface force measurements are able to deepen our knowledge about the molecular level mechanisms of flocculation. The measured surface forces correlate well with practical observations of e.g. dewatering of fiber suspensions, illustrating that the surface layer structure has a great influence on the behavior of particles. Even slight changes in the properties of additives or of solution may lead to a different layer structure, and further, to a different behavior of the system. Polyelectrolyte systems were considered from the aspect of papermaking in this thesis, but the molecular level observation of the flocculation mechanisms can be adapted to any similar colloidal suspension.

The key observation in single cationic polyelectrolyte system was that the optimum concentration for flocculation was narrow and near the charge neutralization point. This led to the appearance of pull-off force and a decrease in repulsion. Large molecular weight and low charged polyelectrolytes were able to form longer bridges, and thus hold floc together better than highly charged polyelectrolytes.

Experiments with polyelectrolyte complex systems showed that PECs have a large optimum concentration with respect to dewatering due to A-PAM's linking ability. The mechanism of flocculation changes from complex introduced bridging to A-PAM linking with increasing polymer concentration. The size and flexibility of PECs were crucial for A-PAM linking, and further for dewatering efficiency. The best results in polyelectrolyte linking and dewatering were achieved when the complex was formed by high molecular weight, low charged polyelectrolytes. In addition, the low amount of anionic component favors A-PAM linking due to the self-regulation of the amount of the linking agent. PECs act as flexible "glue" in the fiber web. When once attached, the system stayed well together, but a bonding PEC layer remained formable and elastic under shear and mechanical forces. Due to their flexibility, PECs are capable of increasing flocculation and paper strength without harming sheet formation.

When studying the layer formed by nanoparticles and polyelectrolytes, NPs were observed to be able to penetrate into the layer structure, if their size was small enough

and the polyelectrolyte layer was loose. Nanoparticles bound the polyelectrolyte molecules together, and the layer structure covered the whole surface. Meanwhile, the self-regulation of complex adsorption left the surface only partially covered, leading to complex bridging. This might improve flocculation. Furthermore, nanoparticles act as links for the polyelectrolyte and thus favors reflocculation.

Nanofibrillar cellulose was long and tends to form a network structure, and hence, formed its own layer. The size and networking prevented it penetrating inside the polyelectrolyte layer as silica nanoparticles do. Nanofibrillar cellulose showed a large repulsion and thick layer structure. NFC could be seen as a potential agent for network flocculation or for paper strength.

The knowledge of the surface structure and its influence on surface forces is essential for controlling system behavior, such as flocculation. Based on these results, some concepts for a future flocculant can be drawn. The long reaching and networking ability of nanofibrillar cellulose provides an opportunity for a good flocculant, if it is combined with a linking polyelectrolyte or nanoparticle. The proportion of the linking polyelectrolyte in an adsorbed layer might be useful to control using complex addition. The high water content of NFC layer may, however, lead to trouble in dewatering, but this can be diminished by using linking polyelectrolyte or nanoparticles which are also able to remove water from the layer.

Regardless of the many answers gained about the flocculation mechanisms and the layers structure, some questions remained open for the future. AFM force measurements and QCM-D are not capable to determine the exact layer thickness. The determination of the layer thickness could provide new and important information regarding the layer structures. Surface force apparatus (SFA), ellipsometry and surface plasmon resonance (SPR) could illuminate the structure further. Moreover the transmission electron microscope using cryofixation, cryo-TEM, could be used to analyse the detailed structure of the layer. Also, the existing data could be analysed with the theories of the steric forces and of the viscoelastic properties of the layer to clarify the details of the physical structure of the layer, if theoretical models are developed onwards. In addition, the precise mechanism and the principle of the A-

PAM linking would need more research with different types of PECs to verify the proposed mechanism and details.

6 REFERENCES

- Abson, D. and Brooks, D.F. (1985). Wet-end behavior of dry strength additives, *Tappi J.* 68(1), 76-78.
- Ahola, S. (2008): *Properties and interfacial behaviour of cellulose nanofibrils*, Doctoral Thesis, TKK, Espoo, Finland.
- Ahola, S., Österberg, M. and Laine, J. (2008a). Cellulose nanofibrils – adsorption with poly(amideamine) epichlorohydrin studied by QCM-D and application as a paper strength additive, *Cellulose* 15, 303-314.
- Ahola, S., Myllytie, P., Österberg, M. and Laine, J. (2008b). The effect of polymer adsorption on cellulose nanofibril water binding capacity and aggregation, *BioResources*, 3(4), 1315-1328.
- Almog, Y. and Klein, J. (1985). Interactions between mica surfaces in a polystyrene-cyclopentane solution near the θ -temperature, *J. Colloid Interface Sci.* 106(1), 33-44.
- Andersson, K. and Lindgren, E (1996). Important properties of colloidal silica in microparticulate systems, *Nord. Pulp Paper Res. J.* 11(1), 15-21.
- Ankerfors, C. (2008). *Polyelectrolyte complexes: Their preparation, adsorption behaviour, and effect on paper properties*, Licentiate Thesis, KTH, Stockholm, Sweden.
- Asselman, T., Alince, B., Garnier, G. and Van de Ven, T.G.M. (2000). Mechanism of polyacrylamide-bentonite microparticulate retention aids, *Nord. Pulp Paper Res. J.* 15(5), 515-519.
- Aulin, C., Varga, I., Claesson, P.M., Wågberg, L., and Lindström, T. (2008). Build-up of Polyelectrolyte Multilayers of Polyethyleneimine and Microfibrillated Cellulose

Studied by in Situ Dual-Polarization Interferometry and Quartz Crystal Microbalance with Dissipation, *Langmuir* 24(6), 2509-2518.

Aulin, C., Ahola, S., Josefsson, P., Nishino, T., Hirose, Y., Österberg, M. and Wågberg, L. (2009). Nanoscale cellulose films with different crystallinity – Their surface properties and interaction with water, *Langmuir*, submitted.

Bar, G., Thomann, Y., Brandsch, R., Cantow, H.-J. and Whangbo, M.-H. (1997). Factors affecting the height and phase images in tapping mode atomic force microscopy. Study of phase-separated polymer blends of poly(ethene-co-styrene) and poly(2,6-dimethyl-1,4-phenylene oxide), *Langmuir* 13(14), 3807-3812.

Bergström, L., Stemme, S., Dahlfors, T., Arwin, H. and Ödberg, L. (1999). Spectroscopic ellipsometry characterization and estimation of the Hamaker constant of cellulose, *Cellulose* 6(1), 1-13.

Bessonoff, M., Paltakari, J., Laine, J. and Paulapuro, H. (2006). Effects of A-PAM/C-PAM complexes on retention, formation and dewatering of papermaking pulp, 92nd Annual meeting of PAPTAC, Montreal, Canada, 7-9. Feb., 2006, Book A, pp. A117-A121.

Biggs, S. (1995). Steric and bridging forces between surfaces bearing adsorbed polymer: an atomic force microscopy study, *Langmuir* 11(1), 156-162.

Binnig, G., Quate, CF and Gerber C. (1986). Atomic force microscope, *Phys. Rev. Lett.* 56(9), 930-933.

Blomberg, E., Poptoshev, E., Claesson, P.M. and Caruso, F. (2004). Surface Interactions during Polyelectrolyte Multilayer Build-up. 1. Interactions and Layer Structure in Dilute Electrolyte Solutions, *Langmuir* 20(13), 5432-5438

Borkovec, M. and Papastavrou, G. (2008). Interactions between solid surfaces with adsorbed polyelectrolytes of opposite charge, *Curr. Opin. Colloid Interface Sci.* 13(6), 429–437.

Buchhammer, H.-M., Petzold, G. and Lunkwitz, K. (1999). Salt effect on formation and properties of interpolyelectrolyte complexes and their interactions with silica particles, *Langmuir* 15(12), 4306-4310.

Butt, H.-J. (1991). Measuring electrostatic, van der Waals, and hydration forces in electrolyte solutions with an atomic force microscope, *Biophys. J.* 60(6), 1438-1444.

Butt, H.-J., Cappella, B., and Kappl, M. (2005). Force measurements with the atomic force microscope: Technique, interpretation and applications, *Surf. Sci. Rep.* 59(1-6), 1-152.

Butt, H.-J., Berger, R., Bonaccorso, E., Chen, Y. and Wang, J. (2007). Impact of atomic force microscopy on interface and colloid science, *Adv. Colloid Interface Sci.* 133(2), 91-104.

Cabane, B. and Duplessix, R. (1982). Organization of surfactant micelles adsorbed on a polymer molecule in water: a neutron scattering study, *Journal de Physique (Paris)* 43(10), 1529-1542.

Carambassis, A. and Rutland, M.W. (1999). Interactions of cellulose surfaces: effect of electrolyte, *Langmuir* 15(17), 5584-5590.

Chan, D.Y.C., Pashley, R.M. and White, L.R. (1980). A simple algorithm for the calculation of the electrostatic repulsion between identical charged surfaces in electrolyte, *J. Colloid Interface Sci.* 77(1), 283-5.

Chan, D.Y.C. and Horn, R.G. (1985). The drainage of thin liquid films between solid surfaces, *J. Chem. Phys.* 83(10), 5311-5324.

Claesson, P.M., Ederth, T., Bergeron, V. and Rutland, M.W. (1996). Techniques for measuring surface forces, *Adv. Colloid Interface Sci.* 67, 119-183.

Claesson, P.M., Blomberg, E. and Poptoshev, E. (2001). Surface forces and emulsion stability, in *Encyclopedic Handbook of Emulsion Technology*, Ed. Sjöblom J, Marcel Dekker Inc, New York, pp. 305-326.

Claesson, P.M., Poptoshev, E., Blomberg, E. and Dedinaite, A. (2005). Polyelectrolyte-mediated surface interactions, *Adv. Colloid Interface Sci.* 114–115, 173.

Cleveland, J.P., Anczykowski, B., Schmid, A.E. and Elings, V.B. (1998). Energy dissipation in tapping-mode atomic force microscopy, *Appl. Phys. Lett.* 72(20), 2613-2615.

Decher, G. and Schlenoff, J.B. (2003). Multilayer Thin Films: Sequential Assembly of Nanocomposite Materials, Wiley-VCH, Weinheim.

Derjaguin, B. (1934): Untersuchungen über die Reibung und Adhäsion, *Kolloid-Zeit.* 69, 155.

Derjaguin, B.V., Churaev, N.V. and Muller, V.M. (1987). Surface Forces, Consultants Bureau, New York.

Derjaguin, B.V. and Landau, L. (1941). Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solution of electrolytes, *Acta Physicochim. URSS* 14, 633-662.

Dickinson, E. and Eriksson, L. (1991): Particle flocculation by adsorbing polymers, *Adv. Colloid Interface Sci.* 34, 1-29.

Dolan A.K. and Edwards S.F (1974). Theory of the stabilization of colloids by adsorbed polymer, *Proc. R. Soc. London A* 337(1611), 509-516.

Donnan, F. G. (1912). The theory of membrane equilibrium in the presence of a non-dialyzable electrolyte, *Z. Elektrochem.* 17, 572.

Ducker, W., Senden, T. and Pashley, R. (1991). Direct measurement of colloidal forces using an atomic force microscope, *Nature* 353(6341), 239-241.

Ducker, W.A., Senden, T.J. and Pashley, R.M. (1992). Measurement of Forces in Liquids Using a Force Microscope, *Langmuir* 8(7), 1831-1836.

Enarsson, L.-E. and Wågberg, L. (2007). Kinetics of sequential adsorption of polyelectrolyte multilayers on pulp fibres and their effect on paper strength, *Nord. Pulp Paper Res. J.* 22(2), 258–266.

Eriksson, M., Notley, S.M. and Wågberg L. (2005). The influence on paper strength properties when building multilayers of weak polyelectrolytes onto wood fibers, *J. Colloid Interface Sci.* 292(1), 38-45.

Eriksson, M. (2006). *The Influence of Molecular Adhesion on Paper Strength*, Doctoral thesis, KTH, Stockholm.

Fleer, G.J, Cohen Stuart, M.A., Scheutjens, J.M.H.M., Cosgrove, T. and Vincent, B. (1993). *Polymers at interfaces*, Chapman&Hall, University Press, Cambridge.

Forsberg, S. and Ström, G. (1994). The effect of contact time between cationic polymers and furnish on retention and drainage, *J. Pulp Paper Sci.* 20(3), 71-76.

Fredrickson, G.H. and Pincus, P. (1991). Drainage of compressed polymer layers: Dynamics of a “squeezed sponge”, *Langmuir* 7(4), 786-795.

De Gennes, P.-G. (1979). *Scaling concepts in polymer physics*, Cornell University press, Ithaca, NY.

De Gennes, P.-G. (1987). Polymers at an interface; a simplified view, *Adv. Colloid Interface Sci.* 27(3-4), 189-209.

De Gennes, P.-G. (1982). Polymers at an interface. 2. Interaction between two plates carrying adsorbed polymer layers, *Macromolecules* 15(2), 492-500.

Gong, H., Garcia-Turiel, J., Vasilev, K., Vinogradova, O.I.. (2005). Interaction and Adhesion Properties of Polyelectrolyte Multilayers, *Langmuir* 21(16), 7545-7550.

Gregory, J. (1973). Rates of flocculation of latex particles by cationic polymers, *J. Colloid Interface Sci.* 42(2), 448–456.

Gärdlund, L., Wågberg, L. and Gernandt, R. (2003). Polyelectrolyte complexes for surface modification of wood fibres. II. Influence of complexes on wet and dry strength of paper, *Colloids Surf. A* 218(1-3), 137-149.

Gärdlund, L., Forsström, J., Andreasson, B. and Wågberg L. (2005). Influence of polyelectrolyte complexes on the strength properties of papers from unbleached kraft pulps with different yields, *Nord. Pulp Paper Res. J.* 20(1), 36–42.

Gärdlund, L., Wågberg, L. and Norgren, M. (2007). New insights into the structure of polyelectrolyte complexes, *J. Colloid Interface Sci.* 312(2), 237-246.

Hamaker, H.C. (1937). The London-van der Waals attraction between spherical particles, *Physica* 4, 1058-1072.

Hartley, P.G. (1999). Measurement of colloidal interactions using atomic force microscope, in *Colloid-Polymer Interactions From Fundamentals to Practice*, Farinato, R.S. and Dubin P.L. (ed.), John Wiley & Sons Inc., New York, pp. 253-286.

Hiemenz, P.C. and Rajagopalan, R. (1997). *Principles of Colloid and Surface Chemistry*, 3. ed., Dekker, New York.

Hodges, C.S. (2002). Measuring forces with the AFM: polymeric surfaces in liquids, *Adv. Colloid Interface Sci.* 99(1), 13-75.

Holmberg, M., Berg, J., Stemme, S., Ödberg, L., Rasmusson, J. and Claesson, P. (1997a). Surface force studies of Langmuir-Blodgett cellulose films, *J. Colloid Interface Sci.* 186(2), 369-381.

Holmberg, M., Wigren, R., Erlandsson, R. and Claesson, P.M. (1997b), Interactions between cellulose and colloidal silica in the presence of polyelectrolytes, *Colloids Surf. A* 129-130, 175-183.

Horn, R.G., Smith, D.T. and Haller, W. (1989). Surface Forces and Viscosity of Water Measured between Silica Sheets, *Chem. Phys. Lett.* 162(4-5), 404-408.

Hubbe, M.A., Moore, S.M. and Lee, S.Y. (2005). Effects of charge ratios and cationic polymer nature on polyelectrolyte complex deposition onto cellulose, *Ind. Eng. Chem. Res.* 44(9), 3068–3074.

Hubbe, M.A. and Rojas, O.J. (2008). Colloidal stability and aggregation of lignocellulosic materials in aqueous suspension: A review, *BioRes.* 3(4), 1419-1491.

Hutter, J.L. and Bechhöfer, J. (1993). Calibration of atomic-force microscope tips, *Rev. Sci. Instrum.* 64(7), 1868-1873.

Höök, F., Rodahl, M., Brzezinski, P. and Kasemo, B. (1998). Energy Dissipation Kinetics for Protein and Antibody-Antigen Adsorption under Shear Oscillation on a Quartz Crystal Microbalance, *Langmuir* 14(4), 729-734.

Israelachvili, J. (1992). *Intermolecular and Surface Forces*; 2nd Ed., Academic Press, San Diego.

Ji, H., Hone, D., Pincus, P.A. and Rossi, G. (1991). Polymer bridging between two parallel plates, *Macromolecules* 23(3), 698-707.

Jiang, Y., Shen, Y. and Wu, P. (2008). Self-assembly of multilayer films containing gold nanoparticles via hydrogen bonding, *J. Colloid Interface Sci.* 319(2), 398-405.

Johannsmann, D., Reviakine, I., Rojas, E. and Gallego, M. (2008). Effect of Sample Heterogeneity on the Interpretation of QCM(-D) Data: Comparison of Combined

Quartz Crystal Microbalance/Atomic Force Microscopy Measurements with Finite Elemental Method Modeling, *Anal. Chem.* 80(23), 8891-8899.

Jönsson, B. (1981). Monte Carlo simulations of liquid water between two rigid walls, *Chem. Phys. Lett.* 82(3), 520-525.

Klein, J. and Luckham, P. (1984). Forces between two adsorbed poly(ethylene oxide) layers in a good aqueous solvent in the range 0-150 nm, *Macromolecules* 17(5), 1041-1048.

Koljonen, K., Muistranta, A. and Stenius, P. (2004). Surface characterisation of mechanical pulps by polyelectrolyte adsorption and titration, *Nord. Pulp Paper Res. J.* 19(4), 495-505.

Kontturi, E., Tammelin, T. and Österberg, M. (2006). Cellulose--model films and the fundamental approach, *Chem. Soc. Rev.* 35(12), 1287-1304.

Kulcsar, A., Voegel, J.-C., Schaaf, P. and Kekicheff, P. (2005). Glassy state of polystyrene sulfonate/polyallylamine polyelectrolyte multilayers revealed by the surface force apparatus, *Langmuir* 21(4), 1166-1170.

Kulcsar, A., Lavallo, P., Voegel, J.-C., Schaaf, P. and Kekicheff P. (2004). Interactions between Two Polyelectrolyte Multilayers Investigated by the Surface Force Apparatus, *Langmuir* 20(2), 282-286.

Laine, J. (2007). General aspects of papermaking chemistry, In *Papermaking Chemistry*, Alén, R. (Ed.), 2nd ed., Fapet OY, Helsinki, pp. 27-53.

Lifshitz, E.M. (1956). The theory of molecular attractive forces between solids, *Sov. Phys. JETP* 2, 73-83.

Lindström, T. (1989). Some fundamental chemical aspects on paper forming, in *Fundamentals of papermaking*, Baker, C.F. and Punton, V.W. (ed.), Mechanical Engineering Publications Ltd, London, Vol. 1, pp. 309-412.

Lingström, R. (2006). *Formation and properties of polyelectrolyte multilayers on wood fibres: Influence on paper strength and fibre wettability*, Licentiate Thesis, KTH, Stockholm.

Lowack, K. and Helm, C.A. (1998). Molecular Mechanisms Controlling the Self-Assembly Process of Polyelectrolyte Multilayers, *Macromolecules* 31(3), 823-833.

Lu, C., Pelton, R., Valliant, J., Bothwell S. and Stephenson. K. (2002). Colloidal Flocculation with Poly(ethylene oxide)/Polypeptide Complexes, *Langmuir* 18(11), 4536-4538.

Luckham, P.F. and Klein, J. (1990). Forces between mica surfaces bearing adsorbed homopolymers in good solvents, *J. Chem. Soc. Faraday Trans.* 86(9), 1363-1368.

Lösche, M., Schmitt, J., Decher, G., Bouwman, W.G. and Kjaer, K. (1998). Detailed structure of molecularly thin polyelectrolytemultilayer films on solid substrates as revealed by neutron reflectometry, *Macromolecules* 31(25), 8893–8906.

Mabire, F., Audebert, R. and Quivoron, C. (1984). Synthesis and solution properties of water soluble copolymers based on acrylamide and quaternary ammonium acrylic comonomer, *Polymer* 25(9), 1317-1322.

Magonov, S.N., Elings V. and Whangbo M.-H (1997). Phase imaging and stiffness in tapping-mode atomic force microscopy, *Surf. Sci.* 375(2/3), L385-L391.

Marcelja, S. and Radic, N. (1976). Repulsion of interfaces due to boundary water, *Chem. Phys. Lett.* 42(1), 129-130.

Marcelja, S, Mitchell, D.J., Ninham, B.W. and Sculley, M.J. (1977). Role of solvent structure in solution theory, *J. Chem. Soc. Faraday Trans. 2* 73(5), 630-648.

La Mer, V.K. and Healy, T.W. (1963). Adsorption-flocculation reactions of macromolecules at the solid–liquid interface, *Rev. Pure Appl. Chem.* 13,112–33

Miklavic, S.J., Woodward, C.E., Jönsson, B. and Åkesson, T. (1990). The interaction of charged surfaces with grafted polyelectrolytes: a Poisson-Boltzmann and Monte Carlo study, *Macromolecules* 23(18), 4149-4157.

Miklavic, S.J., Chan, D.Y.C., White, L.R. and Healy, T.W. (1994). Double layer forces between heterogeneous charged surfaces, *J. Phys. Chem.* 98(36), 9022-9032.

Milner, S.T., Witten, T.A. and Cates, M.E. (1988). A parabolic density profile for grafted polymers, *Europhys. Lett.* 5(5), 413-418.

Neuman, R.D., Berg, J.M. and Claesson, P.M. (1993). Direct measurement of surface forces in papermaking and paper coating systems. *Nord. Pulp Paper Res. J.* 8(1), 96-104.

Ninham, B.W. and Parsegian, V.A. (1971). Electrostatic potential between surfaces bearing ionizable groups in ionic equilibrium with physiologic saline solution, *J. Theor. Biol.* 31(3), 405-428.

Norell, M., Johansson, K. and Persson, M. (1999). Retention and drainage, in *Papermaking Science and technology, Part 4, Papermaking Chemistry*, Neimo, L. (ed.), Fapet Oy, Helsinki, Finland, pp. 42-81.

Notley, S.M., Pettersson, B. and Wågberg, L. (2004). Direct measurement of attractive van der Waals' forces between regenerated cellulose surfaces in an aqueous environment, *J. Am. Chem. Soc.* 126(43), 13930-13931.

Notley, S.M. and Wågberg, L. (2005). Morphology of modified regenerated model cellulose II surfaces studied by atomic force microscopy: Effect of carboxymethylation and heat treatment, *Biomacromolecules* 6(3), 1586-1591.

Notley, S.M., Eriksson, M. and Wågberg, L. (2005). Visco-elastic and adhesive properties of adsorbed polyelectrolyte multilayers determined in situ with QCM-D and AFM measurements, *J. Colloid Interface Sci.* 292(1), 29-37

Notley, S., Eriksson, M., Wågberg, L., Beck, S. and Gray, D. (2006). Surface Forces Measurements of Spin-Coated Cellulose Thin Films with Different Crystallinity, *Langmuir* 22(7), 3154-3160.

Nyström, R.S., Rosenholm, J.B. and Nurmi, K. (2003). Flocculation of semidilute calcite dispersions induced by anionic sodium polyacrylate–cationic starch complexes, *Langmuir* 19(9), 3981–3986.

Nyström, R. and Rosenholm, J.B. (2005). Highly cationic starch and "anionic trash" for optimal filler retention and paper strength? *Colloids Surf. A* 252(2-3), 135-141.

Van Olphen, H (1977). *An introduction to clay colloid chemistry*, 2nd ed., John Wiley & Sons, New York, Chapter 10.

Paananen, A., Österberg, M., Rutland, M., Tammelin, T., Saarinen, T., Tappura, K. and Stenius, P. (2004). Interaction between cellulose and xylan: An atomic force microscope and quartz crystal microbalance study, *ACS Symp. Ser.* 864, 269-290.

Paananen, A. (2007). *On the Interactions and interfacial behaviour of biopolymers. An AFM study*, Doctoral Thesis, Åbo Akademi University, Turku, Finland.

Pashley, R.M. (1982). Hydration forces between mica surfaces in electrolyte solutions, *Adv. Colloid Interface Sci* 16, 57-62.

Petzold, G., Buchhammer, H.-M. and Lunkwitz, K. (1996): The use of oppositely charged polyelectrolytes as flocculants and retention aids, *Colloids Surf. A* 119(1), 87-92.

Petzold, G., Nebel, A., Buchhammer, H.-M. and Lunkwitz, K. (1998). Preparation and characterization of different polyelectrolyte complexes and their application as flocculants, *Colloid Polym. Sci.* 276(2), 125–130.

Pincus, P. (1991). Colloid stabilization with grafted polyelectrolytes, *Macromolecules* 24(10), 2912-2919.

Poptoshev, E., Carambassis, A., Österberg, M., Claesson, P.M. and Rutland M.W. (2000a). Comparison of model surfaces for cellulose interactions: elevated pH, *Prog. Colloid Polym. Sci.* 116, 79-83.

Poptoshev, E., Rutland, M.W. and Claesson, P.M. (2000b). Surface Forces in Aqueous Polyvinylamine Solutions. 2. Interactions between Glass and Cellulose, *Langmuir* 16(4), 1987-1992

Poptoshev, E. (2001). *Polyelectrolyte Moderated Interactions between Glass and Cellulose Surfaces*, Ph.D. Thesis, Royal Institute of Technology, Stockholm, Sweden.

Poptoshev, E. and Claesson, P.M. (2002). Weakly charged polyelectrolyte adsorption to glass and cellulose studied by surface force technique, *Langmuir* 18(4), 1184-1189.

Procter, H.R. and Wilson, J.A. (1916). The acid-gelatin equilibria, *J. Chem. Soc.* 109, 1307-1319.

Pääkkö, M., Ankerfors, M., Kosonen, H., Nykänen, A., Ahola, S., Österberg, M., Ruokolainen, J., Laine, J., Larsson, P.T., Ikkala, O. and Lindström, T. (2007). Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels, *Biomacromolecules* 8(6), 1934-1941.

Ralston, J., Larson, I., Rutland, M.W., Feiler, A.A., and Kleijn, M. (2005). Atomic force microscopy and direct surface force measurements (IUPAC Technical Report), *Pure Appl. Chem.* 77(12), 2149-2170.

Rand, R.P., Fuller, N.L. and Lis, L.J. (1979). Myelin Swelling and Measurement of Forces between Myelin Membranes, *Nature* 279(5710), 258-260.

Rodahl, M., Höök, F., Krozer, A., Brzezinski, P. and Kasemo, B. (1995). Quartz crystal microbalance setup for frequency and Q-factor measurements in gaseous and liquid environments, *Rev. Sci. Instrum.* 66(7), 3924-3930.

Rutland, M.W. and Christenson, H.K. (1990). The effect of nonionic surfactant on ion adsorption and hydration forces, *Langmuir* 6(6), 1083–1087.

Rutland, M.W., Carambassis, A., Willing, G.A. and Neuman, R.D. (1997). Surface force measurements between cellulose surfaces using scanning probe microscopy, *Colloids Surf. A* 123-124, 369-374.

Rutland, M.W., Tyrrell, J.W.G. and Attard, P. (2004). Analysis of atomic force microscopy data for deformable materials, *J. Adhesion Sci. Technol.* 18(10), 1199-1215.

Saarinen, T. (2008). *Adsorption studies of polyelectrolytes and enzymes on lignocellulosic model surfaces*, Doctoral Thesis, TKK, Espoo, Finland.

Saarinen, T., Österberg, M. and Laine, J. (2008). Adsorption of polyelectrolyte multilayers and complexes on silica and cellulose surfaces studied by QCM-D, *Colloids Surf. A* 330(2-3), 134-142.

Scott, W.E. (1996). *Principles of Wet-End Chemistry*, Tappi Press, Atlanta, GA, USA.

Senden, T.J. (2001). Force microscopy and surface interactions, *Curr. Opin. Colloid Interface Sci.* 6(2), 95-101.

Sennerfors, T., Fröberg, J.C. and Tiberg, F. (2000). Adsorption of Polyelectrolyte-Nanoparticle Systems on Silica: Influence on Interaction Forces, *J. Colloid Interface Sci.* 228(1), 127-134.

Solberg, D. (2003). *Adsorption kinetics of cationic polyacrylamides on cellulose fibres and its influence on fibre flocculation*, Licentiate thesis, KTH, Stockholm, Sweden.

Solberg, D. and Wågberg, L. (2003). On the mechanism of cationic-polyacrylamide-induced flocculation and re-dispersion of a pulp fiber dispersion, *Nord. Pulp Paper Res. J.* 18(1), 51-55.

Sonntag, H., Ehmke, B., Miller, R. and Knapschinski, L. (1982). Steric stabilization of poly(vinyl alcohol) adsorbed on silica/water and water/oil interfaces, *Adv. Colloid Interface Sci.* 16, 381-390.

Stanley, H.E. and Teixeira, J. (1980). Interpretation of the unusual behavior of water and heavy water at low temperatures: tests of a percolation model, *J. Chem. Phys.* 73(7), 3404-22. .

Stenius, P. (2000). Macromolecular, surface and colloid chemistry, In *Forest Products Chemistry*, Stenius, P. (ed.), Fapet OY, Helsinki, pp. 173-278.

Stiernstedt, J., Brumer, H. III, Zhou, Q., Teeri, T.T. and Rutland, M.W. (2006a). Friction between cellulose surfaces and the effect of and xyloglucan Adsorption, *Biomacromolecules* 7(7), 2147-2153.

Stiernstedt, J., Nordgren, N., Wågberg, L., Brumer, H., Gray, D.G. and Rutland, M.W. (2006b). Friction and forces between cellulose model surfaces: A comparison, *J. Colloid Interface Sci.* 303(1), 117-123.

Swerin, A., Ödberg, L. and Lindström, T. (1990). Deswelling of hardwood kraft pulp fibers by cationic polymers: the effect on wet pressing and sheet properties, *Nord. Pulp Paper Res. J.* 5(4), 188-196.

Swerin, A., Ödberg, L. and Sjödin, U. (1992). Flocculation - microparticle retention aid systems, *Paper Technology* 33(12), 28-29.

Swerin, A. and Ödberg, L. (1996). Flocculation of cellulosic fiber suspensions by a microparticulate retention aid system consisting of cationic polyacrylamide and

anionic montmorillonite. Effect of contact time, shear level and electrolyte concentration, *Nord. Pulp Paper Res. J.* 11(1), 22-29.

Swerin, A., Risinger, G. and Ödberg, L. (1996). Shear strength in papermaking suspensions flocculated by retention aid systems, *Nord. Pulp Paper Res. J.* 11(1), 30-35.

Swerin, A. and Ödeberg, L. (1997). Some aspects of retention aids. In *Fundamentals of Papermaking Materials*, Trans. of the 11th Fundamental Research Symposium, Baker, C.F. (Ed.), Cambridge, UK, Vol. 1, 265-350.

Torgnysdotter, A. and Wågberg, L. (2006). Tailoring of fibre/fibre joints in order to avoid the negative impacts of drying on paper properties, *Nord. Pulp Paper Res. J.* 21(3), 411-418.

Torii, A., Sasaki, M., Hane, K. and Okuma, S. (1996). A method for determining the spring constant of cantilevers for atomic force microscopy, *Meas. Sci. Technol.* 7(2), 179-184.

Tortonesi, M. and Kirk, M. (1997). Characterization of application specific probes for SPMs, *Proceedings of SPIE - The International Society for Optical Engineering* 3009(Micromachining and Imaging), 53-60.

Vainio, A., Paulapuro, H., Koljonen, K. and Laine, J. (2006). The effect of drying stress and polyelectrolyte complexes on the strength properties of paper, *J. Pulp Paper Sci.* 32(1), 9–13.

Van de Ven, T.G.M. and Mason, S.G. (1981). Comparison of hydrodynamic and colloidal forces in paper machine headboxes, *Tappi* 64(9), 171-175.

Verwey, E.J.W. and Overbeek, J.Th.G. (1948). *Theory and Stability of Lyophobic Colloids: the interactions of sol particles having an electric double layer*, Elsevier, New York.

Whangbo, M.H., Bar, G. and Brandsch, R. (1998). Qualitative relationships describing height and phase images of tapping mode atomic force microscopy. An application to micro-contact-printed patterned self-assembled monolayers, *Appl. Phys. A* 66, S1267-S1270.

Wågberg, L. and Lindström, T. (1987a). Flocculation of cellulosic fibers by cationic polyacrylamides with different charge densities, *Nord. Pulp Paper Res. J.* 2(4), 152-160.

Wågberg, L. and Lindström, T. (1987b). Some fundamental aspects on dual component retention aid systems, *Nord. Pulp Paper Res. J.* 2(2), 49-55.

Wågberg, L., Björklund, M., Åsell, I. and Swerin, A. (1996). On the mechanism of flocculation by microparticle retention-aid systems, *Tappi J.* 79(6), 157-164.

Wågberg, L. (2000). Polyelectrolyte adsorption onto cellulose fibers - a review, *Nord. Pulp Paper Res. J.* 15(5), 586-597.

Wågberg, L., Forsberg, S., Johansson, A. and Juntti, P. (2002). Engineering of fibre surface properties by application of the polyelectrolyte multilayer concept. Part I. Modification of paper strength, *J. Pulp Paper Sci.* 28(7), 222-228.

Wågberg, L., Decher, G., Norgren, M., Lindström, T., Ankerfors, M. and Axnäs, K. (2008). The build-up of polyelectrolyte multilayers of microfibrillated cellulose and cationic polyelectrolytes, *Langmuir* 24(3), 784-795.

Zauscher, S. and Klingenberg, D.J. (2000). Normal Forces between Cellulose Surfaces Measured with Colloidal Probe Microscopy, *J. Colloid Interface Sci.* 229(2), 497-510.

Zhong, Q., Inniss, D., Kjoller, K. and Elings, V.B. (1993). Fractured polymer/silica fiber surface studied by tapping mode atomic force microscopy, *Surf. Sci.* 290(1-2), L688-L692.

Åkesson, T., Woodward, C., and Jönsson, B. (1989). Electric Double-Layer Forces in the Presence of Poly-Electrolytes, *J. Chem. Phys.* 91(4), 2461-2469.

Österberg, M. and Claesson, P.M. (2000). Interactions between cellulose surfaces: effect of solution pH, *J. Adhes. Sci. Technol.* 14(5), 603-618.