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INTERACTIONS OF MICROFIBRILLATED CELLULOSE AND CELLULOSIC FINES WITH CATIONIC POLYELECTROLYTES

Doctoral Dissertation

Tero Taipale

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Abstract

The overall aim of this work was to produce and characterize different types of cellulosic fines and microfibrillated cellulose; to study their interactions with high molar mass cationic polyelectrolytes; and to demonstrate novel examples of their utilization. The work was performed, and its results discussed mainly from papermaking point of view, but the results are also well applicable in other fields of industry.

Cellulosic fines are an essential component of papermaking fiber suspension. Microfibrillated cellulose can be considered as a sub fraction of cellulosic fines, produced by disintegration and dispergation of wood fibers to fibrillar level. High molar mass cationic polyelectrolytes are commonly used to improve fines retention in consolidating fiber network. Thus, their interactions with fines have a significant role in modern papermaking. As the different fractions obviously have unique characteristics, it can be surmised that their interactions with polyelectrolytes are dissimilar.

Four fines fractions, three fiber fractions and four microfibrillated cellulose fractions were produced. Their physical and chemical characteristics were determined among others by X-ray photoelectron spectrometry, atomic force microscopy, cryogenic transmission electron microscopy, ultracentrifugation and turbidimetry were used. Six different cationic polyacrylamides and one cationic starch were used as flocculants. The adsorption of the polyelectrolytes on the cellulosic fractions was measured by polyelectrolyte titration method. The flocculation behavior of these components was studied with multiple light scattering apparatus and focused beam reflectance measurement device.

This work shows that, since the different fines fractions have specific properties, they have individual flocculation and adsorption behaviors with high molar mass cationic polyelectrolytes. It was also shown that the retention and adsorption of clay particles is dependent on the properties of the fiber fraction. In addition, by optimum combination microfibrillar cellulose and cationic starch it is possible to enhance the strength properties of paper without simultaneously deteriorating the drainability of the pulp suspension.

Keywords adsorption, fines, flocculation, MFC, microfibrillated cellulose, polyelectrolyte

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Tekijä Tero Taipale

Väitöskirjan nimi
Mikrofibrilloidun selluloosan ja selluloosaperäisen hienoaineen vuorovaikutukset kationisten polyeletrolyyttien kanssa

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Työn ohjaaja	FT Susanna Holappa

Tiivistelmä

Työn tavoitteena oli tuottaa ja karakterisoida erityyppisiä selluloosaperäisiä hienoaineita ja mikrofibrilloituja selluloosia; tutkia niiden vuorovaikutuksia korkeamoolimassaisten polyelektrolyyttien kanssa; ja lisäksi esittää uusia esimerkkejä niiden hyödyntämiseen. Työ suoritettiin ja sen tuloksia tulkittiin paperinvalmistuksen näkökulmasta, mutta tuloksia voidaan soveltaa muillakin teollisuuden aloilla.

Selluloosaperäinen hienoaine on paperinvalmistuksen olennainen komponentti. Mikrofibrilloitu selluloosa voidaan käsittää hienoaineen alatyypiksi joka on tuotettu hajottamalla ja dispergoimalla puukuituja fibrillitasolle. Korkeamoolimassaisia kationisia polyelektrolyyttejä käytetään yleisesti paperinvalmistuksessa parantamaan hienoaineen sitoutumista sakeutuvassa kuituverkostossa. Täten polyelektrolyyttien ja hienoaineen väliset vuorovaikutukset ovat merkittävässä roolissa modernissa paperinvalmistuksessa. Koska erityyppisillä hienoaineilla on oletettavasti erilaiset ominaisuudet, voidaan otaksua että ne myös vuorovaikuttavat eri tavoin polyelektrolyyttien kanssa.

Työssä tuotettiin neljää hienoainetta, kolmea kuitujaetta ja neljää mikrofibrilloitua selluloosaa. Niiden fysikaaliset ja kemialliset ominaisuudet määritettiin käyttäen muun muassa röntgenfotoelektronispektroskopiaa, atomivoimamikroskopiaa, kryogeeninsta transmissioelektronimikroskopiaa, ultrasentrifugointia ja turbidimetriaa. Flokkulantteina käytettiin kuutta erilaista kationista polyakryyliamidia ja yhtä kationista tärkkelystä. Polyelektrolyyttien adsorptiota kuitufraktioihin mitattiin polyelektrolyyttititrauksella. Näiden komponenttien flokkulaatiota tutkittiin sekä kerrannaista valonsirontaa että kohdistetun valonsäteen takaisinheijastusta hyödyntävillä mittalaitteilla.

Työssä osoitettiin, että erilaiset ominaisuudet omaavilla hienoainejakeilla on ominaiset flokkulaatio- ja adsorptiokäyttäytymiset korkeamoolimassaisten kationisten polyelektrolyyttien kanssa. Työssä osoitettiin myös, että kaoliinipartikkelien retentio ja adsorptio riippuvat kuitufraktion ominaisuuksista. Lisäksi havaittiin, että sopivaa mikrofibrilloidun selluloosan ja kationisen tärkin yhdistelmää käyttäen voidaan paperin lujuusominaisuuksia parantaa, kuitenkaan samalla huonontamatta massasuspension vedenpoistoa.

Asiasanat adsorptio, hienoaine, flokkulaatio, MFC, mikrofibrillaarinen selluloosa, polyelektrolyytti

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PREFACE

This study was carried out at the Aalto University School of Science and Technology, Faculty of Chemistry and Materials Sciences, Department of Forest Products Technology during 2004-2010. The work was performed as a part of three consecutive research projects: KIHA (Kiintoaineen hallinta), ECP3 (Embedded Chemistry Project 3) and Nanosellu I.

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Espoo, September 14th, 2010

Tero Taipale

LIST OF PUBLICATIONS

This thesis is mainly based on the results presented in five publications which are referred as Roman numerals in the text.

Paper I	Taipale, T., Holappa, S. and Laine, J. (2010). Isolation and characterization of cellulosic pulp fines and their interactions with cationic polyacrylamides. *Journal of Dispersion Science and Technology*. Accepted for publication.
Paper II	Liimatainen, H., Taipale, T., Haapala, A. and Niinimäki, J. (2008). Influence of mechanical pulp fines on clay retention. *Tappi Journal*, 7(12), 10-16.
Paper III	Taipale, T., Holappa, S., Ahlgren, J., Cecchini, J. and Laine, J. (2010). Interactions of thermo mechanical pulp fractions with high molar mass cationic polyacrylamides: Part 1. Adsorption. *Nordic Pulp and Paper Research Journal*, 25(3).
Paper IV	Taipale, T., Holappa, S., Ahlgren, J., Cecchini, J. and Laine, J. (2010). Interactions of thermo mechanical pulp fractions with high molar mass cationic polyacrylamides: Part 2. Flocculation. *Nordic Pulp and Paper Research Journal*, 25(3).
Paper V	Taipale, T., Österberg, M., Nykänen, A., Ruokolainen, J. and Laine, J. (2010). Effect of microfibrillated cellulose and fines on the drainage of kraft pulp suspension and paper strength. *Cellulose. DOI: 10.1007/s10570-010-9431-9.*

Author's contribution to the appended joint publications:

I, III-V	Tero Taipale was responsible for the experimental design, performed the main part of the experimental work, analyzed the corresponding results, and wrote the manuscripts as corresponding author.
II	Tero Taipale participated in defining the research plan, analyzing the results and writing the manuscript with the co-authors, and prepared the fiber and fines samples. The first author was the corresponding author of this paper.

LIST OF ABBREVIATIONS

AFM	atomic force microscope
BET	Brunauer-Emmet-Teller nitrogen adsorption method
BKP	bleached kraft pulp
CD	charge density
CMMFCF4	microfibrillated cellulose made of carboxymethylated pulp, fluidizated four times
C-PAM	cationically modified polyacrylamide
Cryo-TEM	cryo-transmission electron microscope
CS	cationic starch
CSF	Canadian standard freeness drainage rate
DDA	dynamic drainage analyzer
DP	degree of polymerization
DS	degree of substitution
ECF	elementary chlorine free
FBRM	focused beam reflective measurement device
FESEM	field emission scanning electron microscope
HC	high charge density
HCl	hydrochloric acid
HMW	high molar mass
LC	low charge density
LF	long fraction of thermo mechanical pulp
LMW	low molar mass
mesh	mesh count; threads per inch
MFC	microfibrillated cellulose; microfibrillar cellulose
MFCF10	microfibrillated cellulose, fluidizated ten times
MFCF4	microfibrillated cellulose, fluidizated four times
NaCl	sodium chloride
$NaHCO_3$	sodium hydrogen carbonate, sodium bicarbonate
NaOH	sodium hydroxide
NFC	nanofibrillar cellulose
PDADMAC	poly(diallyldimethylammonium)chloride
PesNa	sodium polyethylensulphonate
pKa	acid dissociation constant
RMP	refiner mechanical pulp
SEM	scanning electron microscope
SF	short fraction of thermo mechanical pulp
SR	Shopper-Riegler drainability
SSV	specific sedimentation volume
TMP	thermo mechanical pulp
UBKP	unbleached kraft pulp
XPS	X-ray photoelectron spectrometer

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1 INTRODUCTION, AIMS AND OUTLINE OF THE STUDY

Introduction. The principal raw material of papermaking is typically a wood-based lignocellulosic fiber suspension. The suspended wood fibers have a complex layered structure, consisting of cellulose fibrils surrounded by hemicelluloses, lignin and extractives. Generally all papermaking pulp suspensions contain small-sized particles (fines); either purposely produced, or alternatively, generated as by-product of pulping and stock preparation. The expression "fines" is determined as the fraction of papermaking pulp suspension able to pass through a 76 µm aperture. However, as wood fibers are disintegrated and additionally dispersed to fibrillar level, the suspension is called microfibrillated cellulose (MFC). Without additional treatments and fractionation both fines and MFC are usually very heterogeneous colloidal dispersions. Different types of fines and MFCs may be produced depending on the raw materials, fibrillation and isolation methods, as well as conditions used. Their physical and chemical characteristics differ significantly from those of the long fiber fraction.

In the papermaking process the fines play a significant role in the behavior of fiber networks, whereby the physical properties and quality of paper are strongly affected by their presence. Typically fines are referred in context with the challenges of papermaking, such as detrimental substances, pitch problems, accumulation of substances, diminished retention or drainage. In industrial scale papermaking the fines material is commonly treated as one single fraction, which is infrequently isolated, classified and treated separately from the whole pulp. Thus, its papermaking potential is obviously not fully exploited, even though its utilization has also been reported to give beneficial influence.

Papermakers commonly use high molar mass polyelectrolytes to improve retention of different particles such as inorganic fillers and cellulosic fines, and also to enhance the physical properties of paper. Starch derivatives and acrylamide copolymers are the most commonly used additives, and they are typically used in cationic form. The ability of these polymers to attach particles to fibers depends on the physical and chemical properties of the components, such as accessible surface area, surface chemical composition of the surface and its charge density. In addition, the prevailing process conditions affect significantly to the interactions between these components.

Research problem. As the different types of fines and MFCs obviously have specific characteristics, it can be surmised that their adsorption and flocculation behavior are dissimilar. Consequently, it is assumed to be beneficial to separate the fines fraction and optimize the polyelectrolyte dosing strategy individually for the long and the short fractions. Besides the flocculation and retention of fines, the polyelectrolyte addition affects multiple wet end parameters of paper machine and the properties of the final paper. Good control of these variables is a demanding optimization task, which strongly affect the cost-effectiveness of the papermaking process. Thus, some hidden papermaking potential may be gained by more specific treatment and utilization of fines.

By constantly developing particle technology, even finer fiber fractions could be produced and utilized in papermaking, and more detailed fractionations and dosing strategies could be evolved to gain sophisticated and novel product specific results. However these predicted benefits have not been studied extensively by comparing the properties and behavior of different isolated fines or MFC fractions. Nor are the assumed advantages of these fractions systematically used in papermaking. This is mainly because cellulosic fines and MFC are difficult to examine and utilize due to their laborious fibrillation and isolation processes.

Objective. The aim of this research work was to produce and isolate various types of fines and MFCs from mill pulps, and further to describe their characteristics as well as their interactions with high molar mass cationic polyelectrolytes. A secondary objective was to find novel examples how specific utilization of fines and MFCs together with high molar mass cationic polyelectrolytes would benefit papermaking.

Scope of the research. The work was performed under three consecutive research projects. In the first project, different kinds of wood-based cellulosic fines were produced and their physical and chemical characteristics were described. In addition, their interactions with various types of cationically modified polyacrylamides (C-PAM) and clay fillers were studied (**Papers I and II**). The interactions between different thermo mechanical pulp fractions with different C-PAMs were studied in the second project (**Papers III and IV**). In the third project, different types of wood-based MFCs were produced and characterized, and the effect of their addition into the papermaking pulp suspension was studied with respect to pulp dewatering and paper strength (**Paper V**).

In this thesis the experiments were performed under controlled chemical and physical laboratory environment so that the number of simultaneous variables in each test point was minimized. The contents of pulp fractions (of total pulp), dosages of polyelectrolytes, hydrodynamics, salt concentration and pH were altered individually. However, the prevailing conditions are referred to those present in industrial papermaking systems. This methodology enabled the interpretation of each individual process parameter and their interrelationships. This work was designed and is further discussed mainly from the papermaking point of view, but the results are also well applicable in other fields of industry.

Contribution. This work shows that the properties of fines and MFCs, isolated form various raw materials by different methods, alter significantly from each other. They have individual flocculation and adsorption behavior with high molar mass cationic polyelectrolytes. It was found that the mechanism of clay filler retention is dependent on the properties of the pulp fraction. In addition, by optimum selection of fines, MFCs and process conditions, it is possible to enhance the strength properties of paper without simultaneously deteriorating the drainability of the pulp suspension.

2 BACKGROUND

2.1 Cellulosic fines and microfibrillated cellulose

2.1.1 Definition of fines and microfibrillated cellulose

Cellulose is a linear homopolysaccharide consisting of β-(1,4)-D-glucopyranosyl units. The degree of polymerization (DP) of natural cellulose may be as high as 15000 (cotton), giving a molecular mass of 2.4 Mg and a contour length of 7.7 µm (Alén 2000; Somerville et al. 2004). A typical kraft pulp cellulose has a DP of 500 - 2000 (Alén 2000). It has been proposed that in higher plants the smallest cellulosic structure is an elementary fibril, consisting of 36 parallel aligned and hydrogen bonded cellulose molecules in amorphous and crystalline regions, and having a lateral dimension of approximately 2 - 4 nm (Jakob et al. 1995; Davies and Harris 2003; Somerville et al 2004; Ding and Himmel 2006). As cellulose elementary fibril is joined or coated with other wood constituents, such as hemicelluloses, proteins, pectin or lignin, a microfibril is formed (Somerville et al 2004; Ding and Himmel 2006). A molecular structural model of a microfibril is shown in Figure 1. The lateral dimension of a single microfibril is estimated to be 3 - 20 nm, depending on the source of cellulose and the method of analysis (Alén 2000; Davies and Harris 2003; Pääkkö et al. 2007 and 2008; Ahola et al. 2008b; Wågberg et al. 2008). The microfibrils form lamellas or bundles (aggregates), sometimes also called macrofibrils, which are the primary components of wood fiber walls.

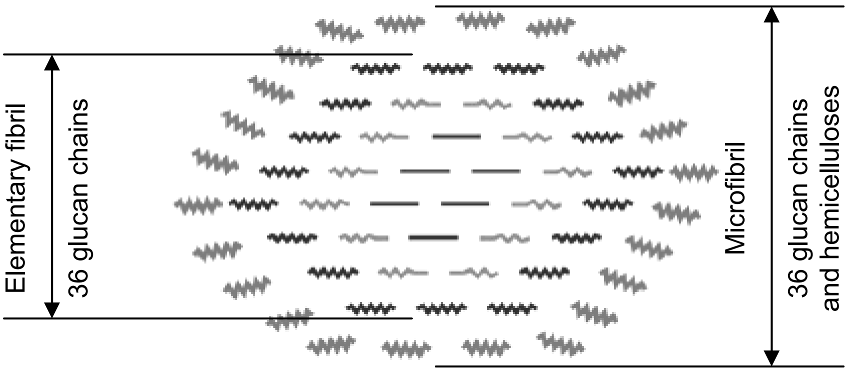

__Figure 1.__ Molecular structural model (cross section) of a microfibril containing the 36-chain elementary fibril. Layers from inside out: 6 true crystalline glucan chains, 12 subcrystalline glucan chains, 18 subcrystalline or noncrystalline glucan chains, and outer coating with 24 hemicellulose chains. (Ding and Himmel 2006; text and arrows added)

As wood fibers are disintegrated, and additionally dispersed to fibrillar level, the suspension is called microfibrillar cellulose, or microfibrillated cellulose, both abbreviated as "MFC" (Turbak et al. 1983; Wågberg et al. 2008). Sometimes the terms nanofibrillar cellulose (NFC) or nanocellulose are used as well. However, these two terms are generally reserved for well-defined, homogeneous micro- or elementary fibril dispersions where all the fibrils have nanoscale thickness (Cranston and Gray 2006; Ahola 2008; Myllytie 2009; Eichhorn et al. 2010). The medium or high aspect ratio and highly chrystalline cellulose "whiskers", produced by strong acid hydrolysis assisted by mechanical shear (e.g. sonication), are sometimes named as nanowhiskers, colloidal cellulose, cellulose micelles, cellulose nanorods, (rod-like) cellulose nanocrystals, or nanocrystalline cellulose (NCC) (Pääkkö et al. 2007; Siró and Plackett 2010). In fact, as also discussed in the review by Siró and Plackett (2010), the terminology around this subject is neither exactly defined nor generally agreed upon, and the usage of all these terms varies in literature. On the other hand, microcrystalline cellulose (MCC) is an established term for a commercially available product consisting of micrometer-sized very low aspect ratio clusters of highly crystalline and, very high purity cellulose (i.e. whisker aggregates) (Levis and Deasy 2001; Berglund 2005; Siró and Plackett 2010). It is produced typically from wood or cotton fibers by acid hydrolysis, followed by neutralization and spray drying (Levis and Deasy 2001). The crystalline MCC and whisker materials are, however, not considered within this work.

Fines is a commonly used general term in papermaking. Broadly interpreted it refers to all particles smaller than wood fibers present in the papermaking pulp suspension (Krogerus et al. 2002). According to this definition fines may contain various particles such as parts of wood cells, inorganic pigments and fillers, colloidal resins and latex, salt crystals, precipitates, deposits, et al. However, a narrower but more commonly used interpretation delimits the fines as the cellulosic fiber fraction which is able to pass through a 76 µm (200 mesh) aperture in a solid-liquid separation process (Tappi T261 cm-00; SCAN-M 6:69). For this reason the fines are sometimes named the P200 or the -200 fraction. Due to the mechanical classification method, even this definition allows a wide range of particles included within the fines. Without additional treatments and fractionation, MFC is as well a very heterogeneous colloidal dispersion (Figure 2); thus, certain fractions of fines and MFC may be very much alike. In other words, both the NFC and the MFC may be considered as subtypes in the category of fines.

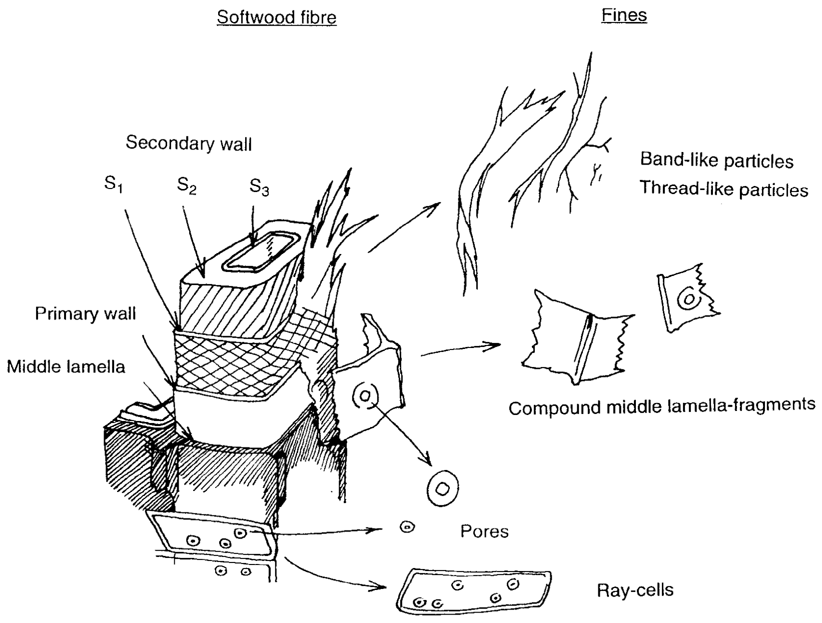

Figure 2. *The appearance and origins of softwood TMP fines. (Rundlöf 1996)*

The physical and chemical properties of different types of fines and MFCs have been widely characterized, and they differ significantly from those of the whole pulp or the long fiber fraction. In comparison to fibers, typical special characteristics for fines and MFCs are as follows: high particle population, large specific surface area, increased accessibility to other materials, high water retention capacity, high aggregation and networking tendency, thixotropicity, high bulk cellulose content and high aspect ratio (length/diameter).

2.1.2 Mechanical pulp fines

In earlier studies, the mechanical pulp fines fraction has been determined to contain a broad selection of different types of particles. Comprehensive literature review have been published e.g. by Honkasalo et al. (1983) and Retulainen et al. (1993b). Brecht and Holl (1939) defined the mechanical pulp fines into two different fractions – fibrillar fines (Schleimstoff, slime stuff) and flake fines (Mehlstoff, flour stuff). It was stated that the defibrillation perpendicular to the fiber orientation favored formation of flake-like fines, while defibrillation parallel to the fiber orientation favored fibrillar fines. This division was very descriptive and it is still very usable. However, due to its heterogeneity, the fines fraction may be further divided into numerous subfractions, as shown earlier (Krogerus et al. 2002; Sundberg et al. 2003) and further discussed below. By their microscopic analysis

Ruck-Florjančič and Ruck (1961) found that the flake fines, having high lignin content, originated from the middle lamella, and the fibrillar fines consisted of swollen fibrils originated from the secondary layers of fiber wall. This is also suggested by Sundberg et al. (2003). Examples of two different types of mechanical pulp fines are shown in Figure 3.

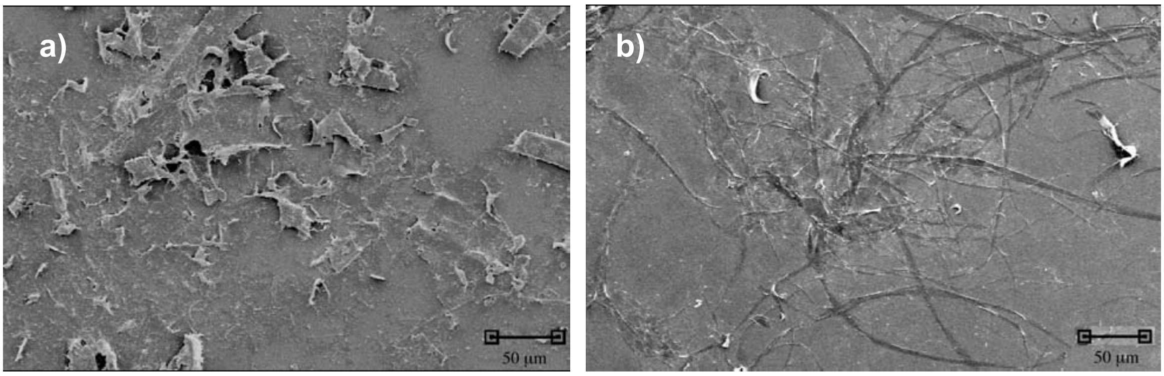

Figure 3. *SEM images of thermo mechanical pulp fines isolated after a) first refining stage (flake fines), and b) fourth refining stage (fibril fines). Scale bar 50 µm. (Mosbye et al. 2002)*

Forgacs (1963) observed different types of mechanical pulp fractions and calculated their hydrodynamic specific surface areas, being 12.6 - 24.5 m^2/g for the fines fractions and 0.5 - 1.24 m^2/g for the long fiber fractions. Gavelin et al. (1975) estimated the outer surface area of mechanical pulp fines to be 12 - 14 m^2/g, and Wood and Karnis (1996) 13 m^2/g. Forgacs (1963) stated that the fibrillar fines have better bonding ability, and further concluded that the proportion of flake fines (chunks) and fibrillar fines (ribbons) should provide an index of the bonding potential of mechanical pulps. Luukko et al. (1997) studied the properties of different types of mechanical pulp fines by image analysis, dividing the particles into fibrillar and non-fibrillar (flake) fraction. The fibrillar material content of the different mechanical pulp fines fractions varied in their work between 14.5 - 36.8 % (w/w), and in the subsequent work by Luukko and Paulapuro 1999 between 29.2 - 79.8 % (w/w). Kangas (2007) reported fibril contents of 53 - 86 % (w/w) for different types of enriched fibril fines and 8 - 42 % (w/w) for enriched flake fines. Both of these experiments showed as well that the physical properties of the fines fractions play an important role in defining their papermaking potential.

Mechanical pulp contains still most of the original constituents of wood in their original proportions. As well, the bulk chemical composition of mechanical pulp fines fraction mainly follows the bulk composition of the initial pulp suspension. However, the degree of refining defines from which layer of cell wall the fines are originating; thus, it affects their lignin-carbohydrate ratio. Typically the fibrillar fines, which originate from the secondary walls, have higher bulk carbohydrate content and lower bulk lignin, pectin and xylan contents than the flake fines originating from the middle lamella and primary wall (Boutelje and Eriksson 1984; Heikkurinen and Hattula 1993; Koljonen et al. 1997; Luukko et al. 1999; Sundberg et al. 2003; Kangas and Kleen 2004). Lignin and extractives are found to be enriched on the surfaces of fines: however, the difference between the surface compositions of fibril and flake fines is not as large as between their bulk compositions (Luukko et al. 1999; Krogerus et al. 2002; Mosbye et al. 2002; Kangas 2007). However, it has been stated that the fibrils generated from the primary wall may have high surface coverage of extractives (Kangas and Kleen 2004). The experiments by Kangas (2007) showed also that the surface chemical compositions of mechanical pulp fines varied depending on the fibrillation method used.

2.1.3 Chemical pulp fines

In contrast to mechanical pulping, a major portion of wood components, such as cellulose, lignin, extractives and hemicelluloses are removed, diminished or altered in chemical pulping processes (Salmén et al. 1998). This gives chemical pulp fines less diverse chemical composition with high cellulose content; e.g. 75.7 - 82.8 % (w/w) by Retulainen et al. (2002). The fundamental properties of chemical pulp fines have not been investigated as extensively as are those of mechanical pulp fines. A majority of works discuss the fines properties through their influence on the papermaking process or on the properties of paper (Aaltio 1962; Lobben 1978; Marton 1980; Retulainen 1993b; Ferreira et al. 2000; Xu and Pelton 2005; Tao and Mousa 2006; Lin et al. 2007). Chemical pulp fines are generally divided into two groups: coarser ray-cell rich primary fines, generated in the pulping process; and finer fibril rich secondary fines, produced during the further refining stages (Retulainen et al. 1993b; Hejnesson et al. 1995; Krogerus et al. 2002; Xu and Pelton 2005). An example of chemical pulp fibrillar fines is shown in Figure 4.

The properties of chemical pulp fines are primarily defined by the types of raw material and pulping process used. Secondarily their properties are impacted by further chemical modifications as well as by the method and intensity of fibrillation (Retulainen et al. 1993b; Ferreira et al. 2000; Krogerus et al. 2002). The proportion of flake fines is typically very low, since the middle lamella and primary cell wall are mostly removed during the pulping process. Thus, chemical pulp fines have typically a fibrillar form with high aspect ratio (length vs. diameter). For example, a fibrillar content of 85 % (w/w) was measured by Luukko and Paulapuro (1999). However, Krogerus et al. (2002) reported that the ray-cell content may be even 45 % (w/w) in hardwood kraft pulp primary fines, while being only 16 % (w/w) in softwood secondary fines. Chemical pulp fines have an increased tendency for water retention and network formation, both of which affect its applicability in papermaking applications. These phenomena are typically characterized by measuring the specific sedimentation volume (SSV); e.g. 890 cm^3/g by Luukko and Paulapuro (1999), and 300 - 600 cm^3/g and 70 - 450 cm^3/g (depending of raw material and fibrillar content) by Krogerus et al. (2002). Kang and Paulapuro 2006 concluded that the finer the fines fraction, the slower the settling and drainage, and the higher the viscosity. The tendency of lignin and extractives to be enriched on surfaces of chemical pulp particles is even stronger than that on mechanical pulp fines. For example, Luukko and Paulapuro (1999) measured bulk lignin content of 1 % (w/w) and the corresponding surface lignin coverage of 37.6 %, and Retulainen et al. (2002) 0.9 - 3.8 % (w/w) and 33.3 - 54.2 %, respectively. The different light scattering properties of mechanical and chemical pulp fines are also an important subject (Retulainen et al. 1993b). Typically the mechanical pulp fines influence the light scattering coefficient of paper more than the chemical pulp fines.

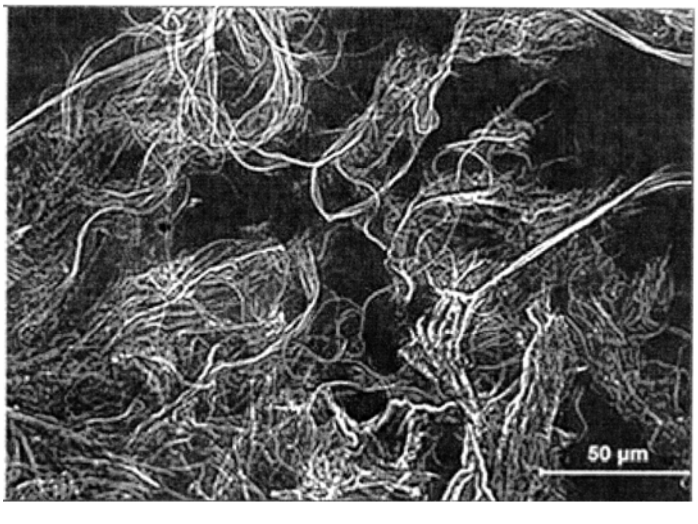

Figure 4. An example of chemical pulp fines. Polarized light mode microscopic image. (Kang and Paulapuro 2006)

2.1.4 Microfibrillated cellulose

As in the case of fines, the physical and chemical properties of MFCs can vary significantly depending on the source of raw material and the methods of production. There are several comprehensive and topical reviews written on this subject (Hamad 2006; Ahola 2008; Gardner et al. 2008; Hubbe et al. 2008; Eichorn et al. 2010; Siró and Plackett 2010).

Microfibrillated cellulose may be isolated from practically any cellulose source such as wood, non-wood plants, crops, fruits, bacteria (e.g. *Acetobacter xylinum*), Chromalveolata microorganisms (e.g. water molds within class Oomycota), tunicates (e.g. sea squirts) or algae (e.g. *Vallonia ventricosa*) (Lennholm and Henriksson 2007; Siró and Plackett 2010). As specified above, the present work considers only wood-based MFC. The function of cellulose in wood is primarily the mechanical strengthening of the composite matrix, and unlike some of the other sources, it occurs closely related with hemicelluloses and lignin, both of which bind the cellulose fibrils together (Lennholm and Henriksson 2007; Siró and Plackett 2010). In order to facilitate the disintegration of wood into its fibrillar level, the wood material is typically first purified by means of chemical pulping process. Hence, a common raw material source for wood-based MFC is bleached kraft pulp.

The cellulosic fibers are fibrillated by mechanical shearing and impact forces, or alternatively by chemical treatments. The main mechanical methods are: refining (Aaltio 1962; Iwamoto et al. 2005), grinding (Taniguchi and Okamura 1998; Iwamoto et al. 2005; Eriksen et al. 2008), fluidization (homogenization) (Turbak 1983; Herrick et al. 1983; Nagakaito and Yano 2005; Eriksen et al. 2008), cryocrushing (Bhatnagar and Sain 2005; Chakraborty et al. 2005; Alemdar and Sain 2008), and ultrasonic treatments (Tatsumi et al. 2002). The most common chemical treatments are: acid hydrolysis (Rånby 1952), alkali treatment (Wang and Sain 2007), partial carboxymethylation (Walecka 1956; Borsa et al. 2000; Wågberg 2008), TEMPO-oxidation (Saito et al. 2006) and enzymatic treatment (Pääkkö et al. 2007; Henriksson et al. 2008). All different methods give specific characteristics for the NFC (an example is given in Figure 5). The acid treatment yields rod-like cellulose whiskers having high degree of crystallinity and low aspect ratio. The mechanical fibrillation methods preserve the amorphous sections of the cellulose and do not chemically degrade the cellulose molecules, though some cutting of microfibrils may occur. However, the mechanical methods consume a remarkable amount of energy. Hence, different combinations of these methods are typically used to decrease energy consumption and to stabilize the process as well as to obtain desired MFC properties.

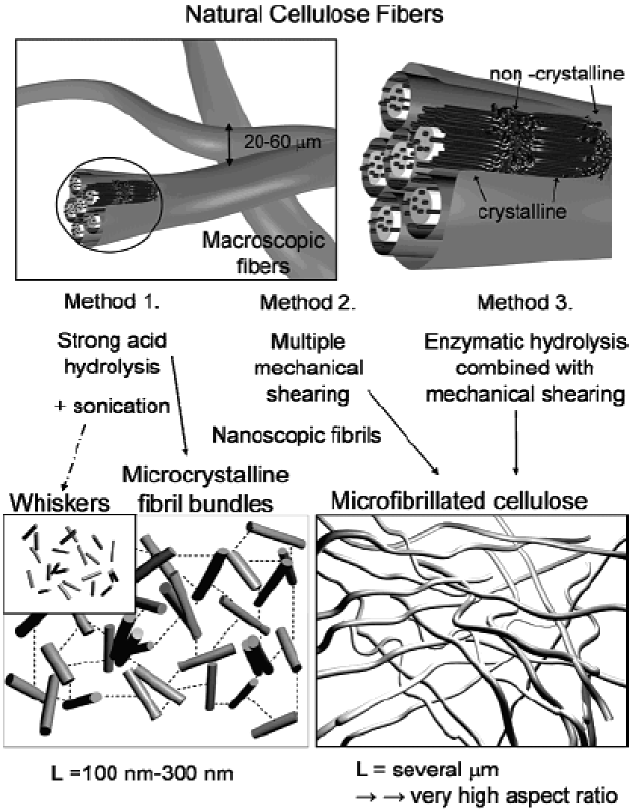

Figure 5. *Schematic presentation of three methods to disintegrate macroscopic cellulosic fibers into nanoscale microfibrils. (Pääkkö et al. 2007)*

The individual microfibrils are ca. 3 - 20 nm in diameter and their lengths vary over a broad range from 100 nm to several micrometers. The small size leads to high particle population and large surface area. By a simple calculation, a microfibril having size of 6 nm in diameter and 1 μm in length, results in 2.3×10^{16} particles/g with a specific surface area of 431 m^2/g. The corresponding properties for typical wood fibers are in the range of about 10^6 particles/g and about 1 m^2/g. These properties of MFC create a high sensitivity to physical and chemical surface activity. Through their high networking tendency and water retention capacity, an aqueous MFC suspension is usually a high viscosity thixotropic gel already at concentrations above 1 % (w/w) (Herrick et al. 1983; Tatsumi et al. 2002; Pääkkö et al. 2007). A well fibrillated and dispersed MFC gel is almost transparent. However, typical MFC suspensions contain not only individual microfibrils but also broader microfibril lamellae and bundles, which might as well have a branched or clustered structure. The polydisperse suspensions may be homogenized by prolonged fibrillation by the mechanical and chemical methods mentioned above. The suspension may as well be fractionated into more homogeneous fractions of different coarseness, e.g. by ultracentrifugation (Ahola et al. 2008).

2.1.5 Ionic charge of cellulosic particles

An essential subject within the behavior of fines and MFCs is their specific charge properties, which affect their swelling as well as their interactions with other charged particles, such as polyelectrolytes and fillers. There are no carboxyl groups present in pure native cellulose molecules, thus the charges in the pulp fractions in the neutral pH regime originate mainly from hemicelluloses, such as 4-O-methylglucuronic acids in xylans and galacturonic acids in pectins (Sjöström 1989; Holmbom and Stenius 2000; Stenius 2000; Mosbye et al. 2002). Also some charges may originate from lignin, containing ionizable phenolic hydroxyl groups and minor amounts of carboxylic groups (Sjöström 1989). Other sources of carboxyl groups are fatty and resin acids in extractives (Sjöström 1989).

Kraft pulping decreases the carboxyl content of wood due to the dissolution of polysaccharides, lignin and extractives, but introduces some new carboxyl groups on lignin (Sjöström 1989). It also converts a significant proportion of 4-O-methylglucuronic acid groups in xylans to hexenuronic acid groups (Teleman et al. 1995). Therefore, the primary sources of charge in unbleached softwood kraft pulps are hexenuronic acid groups (Buchert et al. 1995). Delignification, bleaching and washing processes, performed in favorable conditions, decrease the charges of kraft and mechanical pulps, partly by the removal of the residual lignin and extractives, but also by the degradation of hexenuronic acid groups (Teleman et al. 1995). Thus the main sources of charge in ECF bleached softwood kraft pulps are 4-O-methylglucuronic acid groups. Mechanical pulping does not essentially generate any new carboxyl groups, but some carboxyl groups are removed with dissolved hemicelluloses (Sjöström 1989; Mosbye et al. 2002; Koljonen et al. 2004). On the other hand, new charged groups can be formed by peroxide bleaching in which the alkaline conditions cause demethylation of pectins (Sundberg et al. 1996; Holmbom and Pranovich 1998). Peroxide may as well increase the charge by oxidation of lignin (Gellerstedt et al. 1980).

Although the pKa value of carboxylic groups is around 3 - 5.5 (Sjöström 1989; Laine et al. 1994b) it is known that, in the presence of electrolytes, much higher apparent pKa values are observed if ionic groups are present in films or gel structures (Grignon and Scallan 1980; Lindström 1992; Laine et al. 1994b). The ionization of alcoholic hydroxyl groups (pKa 13 - 17) and phenolic hydroxyl groups (pKa 7 - 11) begins above the neutral regime (Sjöström 1989) and may also further shift the charge formation towards higher pH values. Phenolic groups are present only in lignin and some extractives, both having negligible concentrations in bleached kraft pulp. However, as discussed above lignin and extractives may enrich on the surfaces of fines particles and, thus, may in a minor way increase their charge at elevated pH.

Several authors have measured the total charge density of different fines (Luukko and Maloney 1999; Mosbye et al. 2002; Retulainen et al. 2002 Sundberg et al. 2003; Liimatainen et al. 2009). Typically mechanical pulp flake fines have 117 - 210 µeq/g and mechanical pulp fibrillar fines 86 - 170 µeq/g. Chemical pulp fines are shown to have lower charge densities, 50 - 150 µeq/g, presumably due to their lower hemicellulose, extractives and lignin contents. However, chemical pulp primary fines have been reported to have higher charge densities, 202 - 290 µeq/g (Xu and Pelton 2005; Bäckström et al. 2008. Also the surface charges of fines have been measured earlier, and reported being lower than the total charges (Mosbye et al. 2002; Liimatainen et al. 2009). However, these results should be compared with caution, since titration conditions and properties of the cationic polyelectrolytes used by different authors differ significantly. Due to their anionic charge, small size and high aspect ratio, the fibrillar cellulosic particles are polyelectrolytic in nature, i.e. aqueous fines and MFC suspensions behave like a polyelectrolyte gel. If the small-sized cellulosic particles form a strong network, it could also be considered as a mesoporous solid structure. Still, it is the physical topographies of particles and particle networks which define the accessibility of their charges for adsorbing polyelectrolytes (Wu et al. 2009).

2.2 Adsorption of high molar mass cationic polyelectrolytes on cellulosic particles and their flocculation

The most typically used retention-, drainage- and strength-improving additives in papermaking are cationic starch (CS) and cationic polyacrylamide (C-PAM) (Gregory 1989; Eklund and Lindström 1991; Rojas and Hubbe 2004). Both of these have a high adsorption and flocculation tendency with particles having an anionic charge in water suspensions. These additives are commonly used as well in dual- or multicomponent retention and flocculation systems, together with e.g. anionic polyacrylamide, anionic colloidal silica, anionic colloidal aluminum hydroxide or alkaline activated bentonite (Lindström 1989; Eklund and Lindström 1991; Swerin and Ödberg 1997). However, these multicomponent systems are not included in the scope of this work.

C-PAMs are synthetic macromolecules and available in branched and linear forms, the latter being the most typically used in papermaking. The polyacrylamide is cationized either by copolymerization of a cationic monomer with the acrylamide, or by modification of the initial polyacrylamide chain (Eklund and Lindström 1991). Typically high molar mass (10^5 - 10^7 g/mol) C-PAMs with low or intermediate degree of substitution ($DS < 0.5$) are used to promote bridging flocculation (Lindström 1989; Eklund and Lindström 1991; Laine 2007). The hydrodynamic radii of these polyelectrolytes vary in the range 280–800 nm (Mabire et al. 1984).

Starch, which is one of the oldest and the most widely used dry-strength additive in papermaking (Reynolds 1980; Eklund and Lindström 1991; Ketola and Andersson 1999), is commonly cationized using quaternary ammonium salt which is cationic over a broad pH-interval (Eklund and Lindström 1991; Krogerus 2007). Besides the enhancement of strength, cationic starch acts also as a retention aid by retaining small particles within the fiber network (Reynolds 1980; Ketola and Andersson 1999). Starch has a highly branched cluster-like molecular structure, containing both amylose and amylopectin, the latter being the major constituent (ca. 80 %) in the typical potato starch used in papermaking (Manners 1989; Eklund and Lindström 1991; Van de Steeg 1992). The molar mass of amylopectin varies typically in the range of 10^5 - 10^9 g/mol (Shirazi et al. 2003a and 2003b; Van de Steeg 1992; Buléon et al. 1998, Vermeylen et al. 2004), and its hydrodynamic radius varies in the range of 100-200 nm (Buléon et al. 1998; Shirazi et al. 2003b). Typically the degree of substitution of CS is low, below 0.1 (Krogerus 2007).

The adsorption of high molar mass cationic polyelectrolyte, such as C-PAM or CS, on a porous anionic cellulosic surface in water under hydrodynamic shear is primarily a time-dependent electrokinetic process (Lindström 1989). It involves several consecutive and concurrent phenomena as a sequence of processes (Fleer et al. 1993; Gregory 1989; Horvath et al. 2008). The components must be transported close enough to each other, so that the electrical double layers cross and attractive electrostatic forces can interact. This may take place either perikinetically by Brownian motion, orthokinetically by fluid motion, or by differential settling e.g. by the gravitational field. Diffusion by Brownian motion is very slow; thus, in practical papermaking conditions the dominant mechanism is orthokinetic collisions by turbulent flow (Gregory 1989; Swerin and Ödberg 1997). However, it must be noted that the ratio between perikinetic and orthokinetic collisions increases to the third power with decreasing particle radius, thus, being thousand-fold for particles of 0.1 μm in radius than those of 1 μm (Lindström 1989).

As well as electrokinetics, also solvent interaction and hydrodynamic forces are simultaneously present in the adsorption phenomenon of high molar mass polyelectrolytes on porous cellulosic surfaces (Fleer et al. 1993, Horvath et al. 2008). At short range, Van der Waals forces also influence and attach the particles more strongly together. After the initial adsorption (Figure 6a), the polyelectrolyte chains continue to reconform and rearrange towards their equilibrium state (Figure 6b) (Saarinen et al. 2009; Wågberg et al 1988; Falk et al. 1989; Aksberg and Ödberg 1990). The molecules must change their conformation in order to minimize the free energy. At porous surfaces, such as fibers, some penetration of polyelectrolytes into the finely porous structure of fiber will also occur (Figure 6c) (Wågberg 2000; Wågberg et al. 1988; Falk et al. 1989; van de Ven 2000; Horvath et al. 2008; Saarinen et al. 2009). In the presence of high hydrodynamic shear forces polyelectrolyte detachment, chain breaking and redistribution may as well take place (Tanaka et al. 1993; Ödberg et al. 1993, Swerin and Ödberg 1997).

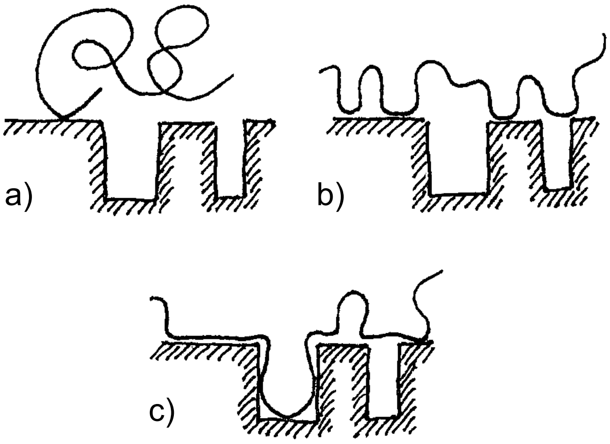

Figure 6. Schematic illustration of a) adsorption, b) reconformation, and c) penetration of a polymer on a cellulosic fiber. Redrawn from Ödberg et al. (1993)

Another important factor that may influence the adsorption of polyelectrolytes on a cellulosic substrate is the accessibility of polyelectrolyte chains into the porous structure of particles (Winter et al. 1986; Shirazi et al. 2003b; Horvath et al. 2008; Wu et al. 2009). The hydrodynamic radius of a linear polyelectrolyte molecule coil depends on its chemical structure, chain length, concentration and charge density, as well as the physicochemical conditions (Fleer 1993; Stenius 2000). In dilute and low salt conditions the polyelectrolyte chains expand strongly into the solution due to the osmotic pressure caused by the counter-ions. A highly charged polyelectrolyte has an extended conformation while a low charged polyelectrolyte retains a more coiled form. During the initial adsorption the polyelectrolyte mainly retains its conformation, but begins immediately its reconformation and penetration towards an equilibrium state (Wågberg et al. 1988; Lindström 1989; Eklund and Lindström 1991; Laine 2007; Wu et al. 2009).

Penetration is a complex process, and assumed to take place due to both enthalpy and entropy reasons. The internal charges are neutralized by the polyelectrolyte molecules and simultaneously, electrolyte ions are released from the pores, thus lowering the free energy of the system. Earlier studies have shown that high molar mass cationic polyelectrolytes may penetrate into the fiber micropores that are smaller than the C-PAM radius of gyration (Wågberg et al. 1988; Van de Ven 2000). Recently, it has also been shown that high charge density cationic polyelectrolytes adsorb strongly on the outermost surfaces of wood fibers and may block the penetration of molecules into the fiber pore structure, but low charge density polyelectrolyte molecules may penetrate into the fiber cell wall despite their molar mass (Horvath et al. 2008). Thus, electrostatic interactions may both promote and hinder the diffusion of polyelectrolytes into cellulosic structures (Wågberg et al. 1988; Fleer et al. 1993; Van de Ven 2000; Horvath et al. 2008).

High molar mass polyelectrolytes that adsorb loosely to cellulosic surfaces with long dangling tails and loops may give rise to particle flocculation (aggregation) by bridging mechanism (Lindström 1989; Swerin and Ödberg 1997). This involves interactions of the protruding ends of the polyelectrolyte with other particles so that loose flocs are formed. An example of cellulosic fines flocculated with high molar mass cationic polyelectrolyte is given in Figure 7. Similar type of images, showing the long polymer bridges and the extending networks, has been presented also earlier by McNeal et al. (2005). Polyelectrolyte-induced flocculation under hydrodynamic conditions is initially a very rapid process. It has been shown that the initial flocculation in papermaking suspensions takes place in hundreds of milliseconds, continuing thereafter for several minutes, or even for hours (Wågberg and Lindström 1987a and 1987b; Falk et al. 1989; Swerin and Ödberg 1997).

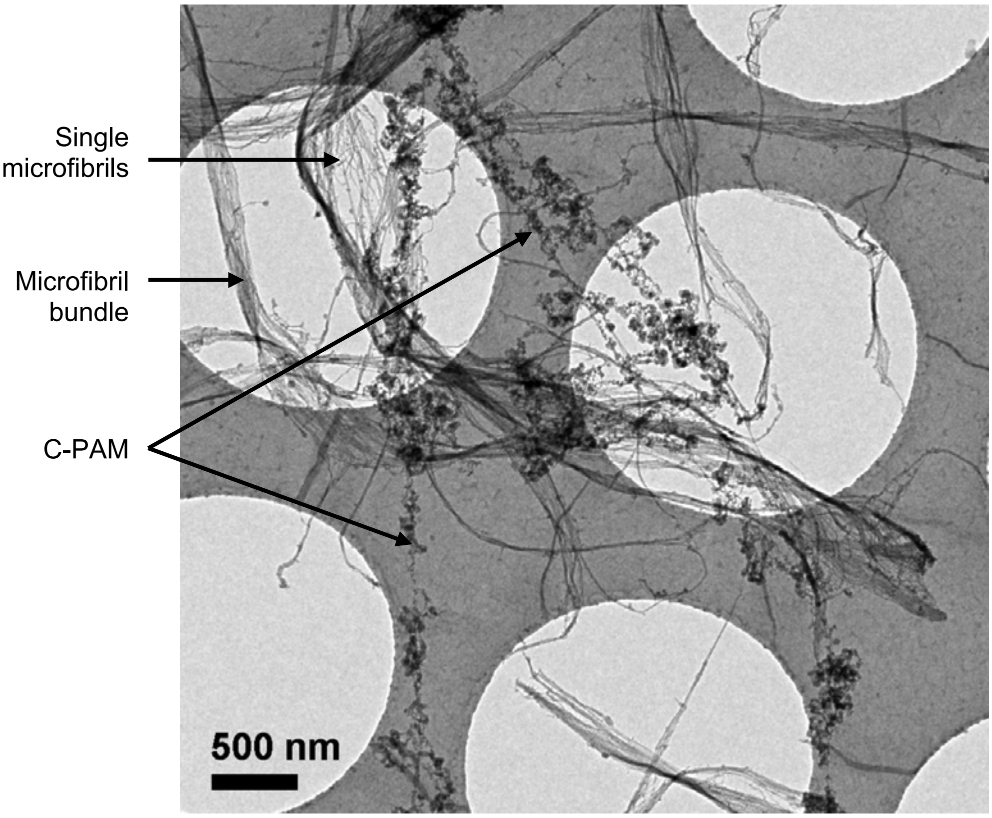

Figure 7. *Cryo-TEM image of a floc formed by the adsorption of HMW-LC C-PAM on thermo mechanical pulp fines (short fraction). C-PAM is marked with anionic colloidal gold spheres, diameter 15 nm (small black dots). The vitrified sample is located on a holey carbon foil. Unpublished work by Taipale, T., Korhonen, M., Nykänen, A., Laaksonen, P. and Holappa, S. (2008).*

The primary colloidal attraction mechanisms which cause flocculation of particles are the electrokinetic interactions, mechanical entanglement, Van der Waals forces and surface tension (Gregory 1989; Ödberg et al. 1993; Asselman and Garnier 2000; Solberg and Wågberg 2003; van de Ven 2005). These attractive forces are at short range, thus, the particles must be at first transported close to each other, as discussed above. Under hydrodynamic papermaking conditions this approach takes place mainly orthokinetically by fluid motion (Lindström 1989; Gregory 1989; Swerin and Ödberg 1997). Under turbulent flow conditions, the floc dimensions increase until a critical size is reached, where the diverging hydrodynamic shear forces equal or overcome the attracting forces. This critical size depends on the physical and chemical state of the system. The deformation and disruption of the floc may give the polyelectrolyte chain more degrees of freedom, more possibilities to change its conformation and to transfer between surfaces, leading to charge reversal and irreversible decreasing of floc size (Lindström 1989; Gregory 1989; Ödberg et al. 1993; Asselman and Garnier 2000; van de Ven 2005).

2.3 Utilization of microfibrillated cellulose and cellulosic fines in papermaking

As the fines fraction is an essential and valuable part of the inhomogeneous pulp suspension, knowledge about interactions between polyelectrolytes and the different fractions is an interesting subject from the papermaker's point of view. Closure of paper mill water circuits, increasing raw material costs and the continuous search for new innovative product properties lead to increasing demands for production efficiency and to higher usage of additives, and further to more complex wet-end chemistry. Some hidden papermaking potential may be gained by more specific treatment and utilization of fines and MFC fractions, which then could compensate for this continuously complicating trend in modern papermaking.

As discussed above, a typical pulp suspension contains a very heterogeneous set of physically and chemically dissimilar particles. Hence, it can be surmised that the adsorption and flocculation kinetics are specific for fractions of different type. Consequently, it may be beneficial to separate the fines fraction and optimize the polyelectrolyte dosing strategy individually for each fraction (Stratton 1989; Retulainen 1993a; Surface et al. 1998; Huovila et al. 1999; Cecchini et al. 2007). By constantly developing particle technology (Ahola 2008; Eriksen et al. 2008; Siró and Plackett 2010), even finer fractions with unique properties could be utilized, and more detailed fractionations and dosing strategies could be evolved to gain sophisticated and focused effects. However, it is interesting subject that fines and MFC particles, unlike fibers, are in the size-class of macromolecules (Figure 7). This fact questions whether the traditional flocculation and adsorption behavior of fibers are any longer applicable with fines fractions of ever decreasing size used in papermaking.

The tensile strength of an individual fiber is much higher than that of an inter-fiber bond (or attraction) between two fibers or the forces required to break the mechanical entanglement of fibers in the network (Campbell 1959). This assumption is mainly tenable with dry fiber networks (dry paper), but also to a certain extent applicable with high consistency fiber networks (wet paper). Thus, the strength of the fiber network can be enhanced by increasing the mechanical entanglement or the number of bonds (Retulainen et al.1993a; Lobben 1978). Fines and MFC, having a small size and a large surface area, may increase the number of bonds and the extent of entanglement, especially if a cationic polyelectrolyte, such as CS or C-PAM, is used to retain them on the anionic fiber. Hypotheses and research results have been presented that MFC could be added into the pulp suspension to enhance the physical properties of paper (Ahola et al. 2008a; Eriksen et al. 2008), or alternatively, MFC may be formed into sheets having high strength properties (Taniguchi and Okamura 1998; Yano and Nakahara 2004; Berglund 2005; Henriksson et al. 2008; Pääkkö et al. 2008; Zimmermann et al. 2010). Retulainen et al. (1993a) has also suggested that starch and fines additions have complementary mechanisms in strengthening fiber-fiber bonding. Furthermore, an interesting finding is that a mixture of MFC and amylopectin (starch) suspensions yields films with excellent strength properties (Dufresne 2000; López-Rubio et al. 2007; Svagan et al. 2007).

Several studies can be found on the interactions between cationic polyacrylamides and different fiber, filler and fines mixtures, or different model surfaces (Honkasalo et al. 1983; Pelton et al. 1980; Wågberg and Lindström 1987a and 1987b; Wågberg and Hägglund 2001; Salmi et al. 2007; Salmi 2009). Less research work has been performed on the interactions between mere pulp fines and high molar cationic polyelectrolytes in well defined simple systems without the presence of other disturbing constituents, such as diverse inorganic salts and filler particles. In addition, the enhancement of paper strength properties achieved with the use of MFC, or NFC, has previously not been evaluated against the drainage properties of the pulp suspension. In industrial applications the strong water retention property of MFC may dominate over the achieved benefits, as is already observed in the use of chemical pulp fines (Lin et al. 2007; Cole et al. 2008). An increase of fines or MFC content increases the total surface area of pulp suspension. It enhances the water retention by hydrogen bonding within the small capillary interstices of the network. The small particles loosely retained in the fiber matrix decrease the available pore area and lengthen and narrow the capillaries available for water flow (Figure 8), as thoroughly reviewed and discussed by Hubbe and Heitmann (2007) and Hubbe et al. (2009).

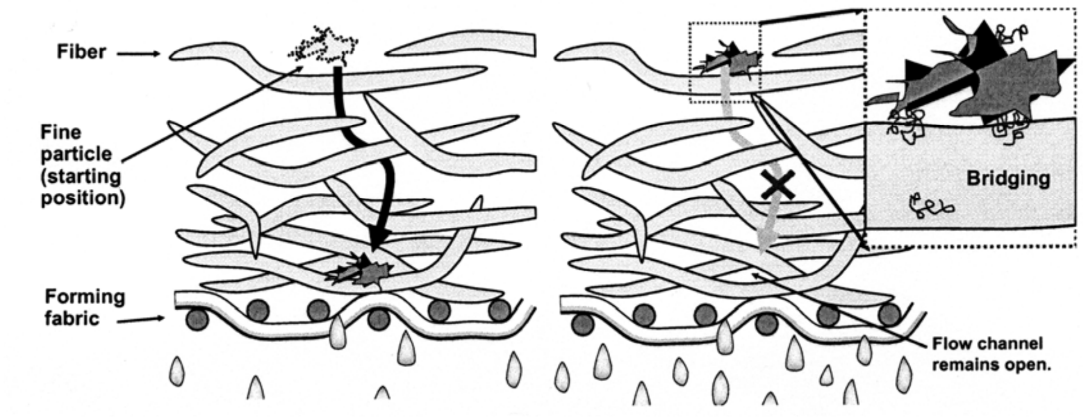

Figure 8. Left: Schematic illustration of "choke-point" mechanism in which unattached fine particles move through drainage channels to vulnerable points at which they block the flow; Right: Proposed effect of bridging polyelectrolytes on defeating choke-point mechanism by keeping fiber fines attached to fiber surfaces. (Hubbe and Heitmann 2007)

However, an optimum dosage of high molar mass low charge density cationic polyelectrolyte may enhance the drainage by binding the fine material on the fibers through charge neutralization and bridging mechanisms (Hubbe and Heitmann 2007; Salmi 2009; Xiao et al. 2009). An example of this is shown in Figure 9. However, it should be taken into account that not only the binding of fine material but the flocculation of fibers might as well promote the drainage. In their review Hubbe and Heitmann (2007) argued that the fines material with high surface area may well entrain small air bubbles, which may further increase the drainage resistance of the pulp suspension. It has also been proposed that NFC may create a nano-network inside the macroscopic fiber web, which may also be a potential mechanism for reduced drainage rate (Salmi 2009). Thus, it is important that the correlation between drainage characteristics and strength enhancement is further investigated to fully facilitate the broad utilization of this very promising biomaterial.

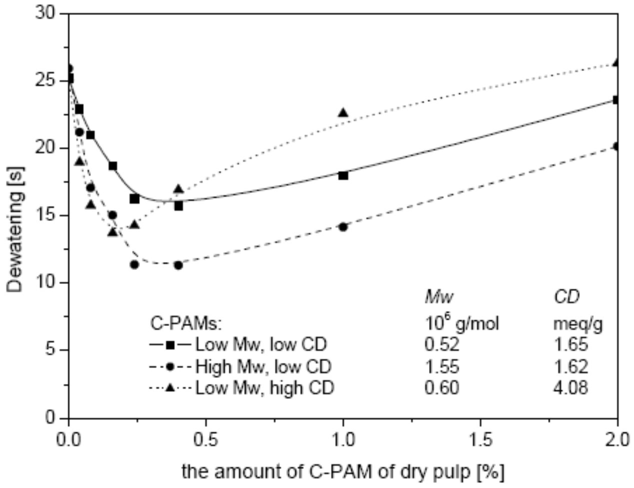

Figure 9. *The effect of different C-PAMs on dewatering time of pulp. (Data from Xiao et al. 2009; Figure adapted from Salmi 2009)*

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 arrangement used.

3.1 Materials

3.1.1 Pulps

Unbleached softwood (*Pinus sylvestris*) kraft pulp, having kappa number κ-24, was acquired from a Finnish pulp mill after the washing stage but prior to the oxygen delignification stage. The consistency of this sample was approximately 20 % (w/w). This pulp was used for the production of fines (Paper I).

ECF (elemental chlorine free) bleached softwood kraft pulp, produced from Scots pine (*Pinus sylvestris*), was provided by a Finnish pulp mill as air-dry sheets. This pulp was used for the hand sheets, water removal testing, and for fines production (Papers I and V).

Unbleached RMP (Refiner Mechanical Pulp) made from Norway spruce (*Picea abies*) was acquired at a consistency of approximately 40 % (w/w) from a Finnish paper mill after the first and the second refining stages. This pulp was used for the production (Paper I) of fibril-rich (RMP fibril fines) and flake-rich fines (RMP flake fines), both used in experiments in Paper I and II. The long fiber fraction (RMP fibers), remaining after the separation of the fibril-rich fines, was used for the experiments in Paper II.

Unbleached TMP (Thermo Mechanical Pulp) made from Norway spruce (*Picea abies*) was acquired from a Finnish paper mill (Papers III and IV). This pulp was used as received (sample REF) and a portion of it was fractionated to long fiber (LF) and short fiber (SF) fractions.

ECF bleached hardwood kraft pulp, produced from Birch (*Betula pendula*), was provided by a Finnish pulp mill as a never-dried suspension at a consistency of approximately 20 % (w/w). This pulp was used for the production of MFCs (Paper V).

3.1.2 Fines

The fines (Papers I, II and V) were produced by refining the bleached and unbleached softwood kraft pulps as well as the unbleached softwood RMP with conventional papermaking refiners. Thereafter the pulp suspensions were fractionated at 1 % (w/w) consistency by mechanical solid-liquid separation with 75 μm opening (230 mesh) wire mesh. The fines-containing filtrates were allowed to settle for 3 days before the supernatant was drained out. The concentrate was thereafter centrifuged for 5 min at 2000 *g* and the supernatant was again poured out. As a result of different production and separation sequences and conditions, described in detail in Paper I, two mechanical pulp fines (RMP flake fines and RMP fibril fines) and two chemical pulp fines (UBKP fines and BKP fines) were produced.

The unbleached softwood TMP suspension was fractionated at 1.3 % (w/w) consistency to long and short fiber fractions with a single stage unpressurised laboratory screen having slot width of 60 μm (Papers III and IV). The reject (long fraction) of the 1st fractionation was diluted and re-fractionated using the same parameters; i.e. the separation procedure was completed in two stages. The long fraction sample (LF) comprised of reject after the 2nd screening. The short fraction sample (SF) was composed of accepts of the 1st and 2nd fractionations, and was paralleled by fines in the discussion.

3.1.3 Microfibrillated celluloses

Two different unmodified, and one modified (carboxymethylated) MFCs were produced (Paper V). ECF bleached hardwood kraft pulp was pre-refined with a double disc laboratory refiner, and was further disintegrated by a high-pressure fluidizer (Microfluidics M700, Microfluidics Int. Co., Newton, MA, USA). A well-dispersed pulp was firstly passed through two serially connected Z-shaped chambers (diameters 500 and 200 μm). Additional passes were processed with a smaller chamber pair (diameters 500 and 100 μm). The consistency of the feed pulp was 1.5 - 2 % (w/w), and an operating pressure of 184 MPa was used. The pulp was passed either four or ten times through the fluidizer unit resulting in two different samples MFCF4 and MFCF10, respectively.

The partial carboxymethylation of hardwood kraft pulp was performed according to the method described by Walecka (1956), and thereafter the sample was fluidizated four times by the method described in Paper V. The carboxymethylation assisted the streaming of the pulp through the fluidizer chambers, so a higher feed consistency of 4–5 % (w/w) was used. This procedure resulted in sample CMMFCF4.

3.1.4 Clay

Kaolin clay filler powder was provided by J.M. Huber, Hamina, Finland. It was supplied as an air-dry powder from which slurry with a solids content of 10 % (w/w) was prepared by addition of deionized water. The main properties of the clay were: mean particle size 1.4 μm (Sedigraph, D_{50}), surface area 12 m^2/g (BET-nitrogen adsorption), and zeta potential -29.0 mV (electrophoretic mobility -2.19 $\mu ms^{-1}/Vcm^{-1}$) (Coulter Delsa 440).

3.1.5 Cationic polyelectrolytes

Poly(1,5-dimethyl-1,5-diazaundecamethylene)bromide (Polybrene) was purchased from Sigma-Aldrich Chemie, GmbH. Cationic poly-(diallyldimethylammonium)chloride (PDADMAC), provided by Ciba Specialty Chemicals Ltd, was used unfractionated and fractionated. Cationically modified potato starch (CS), Raisamyl 50021 was provided by Ciba Specialty Chemicals Ltd, Finland. The CS cationizing agent used was 2,3-epoxypropyltrimethylammonium chloride (EPTAC). Different types of cationically modified linear chain polyacrylamides (C-PAM) were provided by Kemira Oyj, Espoo, Finland. The charged substituent in the C-PAMs was trimethylammoniumethyl acrylate chloride. The properties of the polyelectrolytes and references to experiments in which they are used are described in Table 1.

Table 1. *Properties of cationic polyelectrolytes.*

Polyelectrolyte	Molar mass[a] [Mg/mol]	Charge density[b] [meq/g]	Degree of substitution (DS)[c]	Paper
Polybrene	0.008	5.35[c]	1	I, II
PDADMAC	0.3	5.15; 6.19[c]	1	III, IV, V
PDADMAC	0.1-0.3[d]	6.19[c]	1	I, II
CS	200[c]	0.23	0.035	V
LMW-LC C-PAM	1.5	1.45	0.12	I, V
LMW-HC C-PAM	1.5	4.02	0.44	I, V
HMW-LC C-PAM	7	1.44	0.12	I, II, III, IV
HMW-MC C-PAM	7	3.06	0.30	III, IV
HMW-HC C-PAM	6	3.60	0.37	I, III, IV
HMW-HC C-PAM	4	5.31	0.70	V

a) Average value, given by manufacturer; b) Value determined by polyelectrolyte titration against 2 meq/l sodium polyethylensulphonate (PesNa) solution at pH 8 and 0.1 mM NaCl; c) Theoretical, calculated value; d) Fractionated by ultrafiltration.

3.2 Methods

All sample preparations, characterizations and experiments were performed at room temperature (20 - 24 ºC). Analytical grade NaCl, $NaHCO_3$, HCl and NaOH were used for the adjustment of the salt concentration and pH. De-ionized water was used for dilution and for dissolution throughout the study. Prior to use all the pulp and fines samples (excluding ECF bleached birch kraft pulp and MFCs) were treated with 10 mM HCl solution to remove metal ions, and thereafter washed to their sodium form using 1 mM $NaHCO_3$ solution (Swerin et al. 1990). The salt concentration was adjusted to 9 mM NaCl and 1 mM $NaHCO_3$, and the pH was adjusted to 8.0 unless otherwise stated. Prior to use the MFC and the fines samples used in Paper V were disintegrated with an ultrasonic microtip homogenizer for 120 s at 25 % amplitude setting (Branson Digital Sonifier S-250D, 102C tip, Emerson Electric Co, St Louis MO, USA).

3.2.1 Adsorption of cationic polyelectrolytes on pulp fractions

Adsorption isotherms of cationic polyelectrolytes on pulp fractions (Paper I) were performed by adding a known amount of polyelectrolyte solution into fines suspension having consistency of 4 g/l and being stirred at 400 rpm. Mixing was continued at this speed for 1 min after polyelectrolyte dosage, and then for 14 min at 140 rpm. Subsequent to mixing the samples were centrifuged for 15 min at 800 *g*. The excess polyelectrolyte concentration in the supernatant was analyzed titrimetrically against an anionic (1 meq/l) sodium polyethensulphonate (PesNa) solution. A streaming current detector (Particle Charge Detector, Mütek PCD-03, Germany) was used for point of equivalence indication. The maximum amount of polyelectrolyte adsorbed onto pulp fines was defined by extrapolating the plateau level of the obtained adsorption isotherm to zero equilibrium concentration.

A DDA apparatus (Dynamic Drainage Analyzer, AB Akribi Kemikonsulter, Sweden) was used for adsorption studies in Paper III. Pulp having a consistency of 1 g/l was poured into the DDA and stirred at 1500 rpm. Subsequently, a stirring speed of either 250 or 1500 rpm was applied, and a known amount of a polyelectrolyte was added into the suspension. After a defined contact time the drainage valve of the DDA unit was opened for a period of 5 s. The filtrate was passed through a 38 µm opening (400 mesh) stainless steel wire cloth and was collected into the vacuum vessel of the DDA. Three different contact times (5, 20 and 30 s) were used under high shear conditions (1500 rpm) to represent a fast "dynamic" adsorption, where the adsorption process is in the non-equilibrium state. A long contact time (15 min) was used under the low shear conditions (250 rpm) to represent slow, "static" adsorption, where the adsorption phenomenon is close to its equilibrium state. Finally a sample of the drained filtrate was collected into a glass centrifuge tube and centrifuged and titrated as described above.

3.2.2 Flocculation of pulp fractions

A multiple light scattering apparatus (Turbiscan Online by Formulaction SA, L'Union, France) and a focused beam reflective measurement device (FBRM, Lasentec D600 L, Mettler-Toledo AutoChem Inc., Columbus, OH, USA) were used for the monitoring of the flocculation in Papers I and IV, respectively. Both methods allow fast, instant and direct online-monitoring of the flocculation phenomenon of suspended polydisperse particles under highly turbulent conditions. The conditions used in both the flocculation experiments were the same as those used in the respective adsorption studies (Papers I and III) described above.

The multiple light scattering apparatus (Figure 10a) measures the intensity of light (850 nm LED) transmitted and backscattered from the suspension. In this work (Paper I), a dimensionless flocculation index was calculated from the transmission intensity measurements to indicate the extent of flocculation compared to the initial state of the suspension. The fines suspension was stirred in a glass beaker with a magnetic stirrer at constant speed (400 rpm) and sucked through the measurement cell at a constant flow rate (600 ml/min) by using a peristaltic pump. The measured suspension was re-circulated into the beaker.

In the FBRM (Figure 10b) a 791 nm laser light is focused on the outer surface of the probe sapphire window. The probe optics is rotated and the laser beam scans in a circular path across the suspension. The backscattered light from the particles passing through the focal point is detected, and the duration of each backscattering pulse is multiplied by the scan velocity. This gives the chord length of an individual particle as a result. Typically thousands of chord lengths per second are measured, giving a chord length distribution of the sample, which is a function of the particle size and shape. The particles can be classified into pre-defined size classes and their measured sizes, as well as the particle counts in each class, can be related with the initial state. With the FBRM technique no assumption of the particle shape is necessary. Due to the rotation of the optics and the turbulent flow, the orientation of the particles may be considered as random. In this work the mean chord length was discussed as particle (floc) size. The submersible probe design of the FBRM enabled using both a mixing vessel and an impeller with similar designs to a standard DDA used in the adsorption studies in Paper III. The base of the vessel was made of solid plastic without the wire cloth used in the DDA.

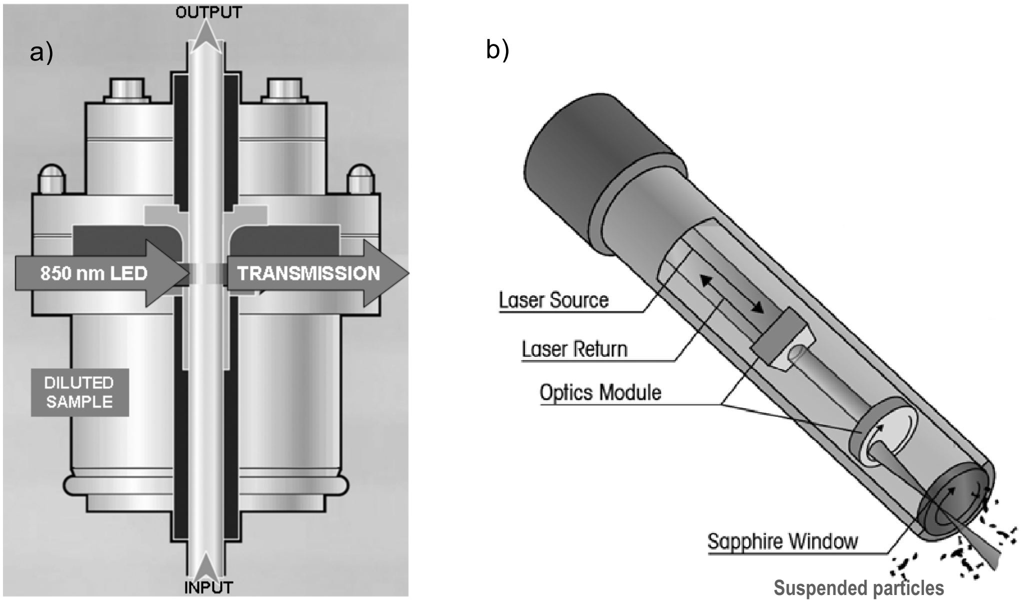

Figure 10. *Equipments used in flocculation experiments. a) Multiple light scattering apparatus (Turbiscan Online), b) Focused beam reflective measurement device (Lasentec).*

3.2.3 Adsorption and retention of clay

Adsorption of clay filler particles onto the RMP fractions was investigated by analyzing the concentration of free clay particles in a stirred beaker (Paper II). A suspension of clay particles, followed by the addition of polyelectrolyte, was added into a pulp suspension under stirring (500 rpm). After a 120 s contact time a portion of the suspension was filtered while stirring by using a screen with cut-off of 5 μm, which retained both the cellulosic material and the clay adsorbed on the pulp, but not the free clay particles. The stirring was continued during the filtration, so that formation of a fiber mat on the screen was restricted (delayed). By means of turbidity measurement (Hach Ratio/XR Turbidimeter, Hach Company, Loveland, CO, USA) of the filtrate, the deposition of clay particles on the pulp fractions was obtained as a function of polyelectrolyte dosage.

In addition, the retention of clay filler (Paper II) into a consolidating pulp suspension was studied by filtering the pulp fraction suspension containing clay filler particles and added polyelectrolyte through a wire mesh (50 µm, 270 mesh) under a constant pressure difference (10 kPa) and stirring halted prior to filtering. The retention of clay was monitored by measuring the turbidity and ash content of the filtrate after a constant cumulative amount of filtrate (250 ml of total 1000 ml) was obtained. The concentrations of the suspension components were identical in both the adsorption and the retention experiments: pulp fractions 1 g/l; clay 0.7 g/g pulp; and C-PAM 0 - 3 mg/g pulp.

3.2.4 Hand sheets preparation

Cationic starch (CS) was added into a fiber suspension, and after 15 min mixing at 500 rpm a known amount of MFC or fines was added. After a further 15 min of mixing, hand sheets were formed in a laboratory sheet former without wire water circulation. The target grammage was 60 g/m^2. After forming, the sheets were wet pressed 4 min at 420 kPa and further air dried under restraint for 3 min at 105 °C. The work was performed according to standards SCAN-C 26:76 and SCAN-M 5:76, except for drying. (Paper V)

The dried paper sheets were conditioned according to standard SCAN-P 2:75, and the determined paper properties were: grammage (SCAN-P 6:75), thickness (SCAN-P 7:75), density (grammage/thickness), tensile strength (SCAN-P 38:80), out-of-plane (z-) strength (Scott Bond, Tappi Test Method T 569 pm 00) and air permeability (Bendtsen, SCAN-P 60:87). (Paper V)

3.2.5 Drainage of pulp suspension

The drainage properties of the pulp suspensions containing CS, fines or MFC were determined with a standard DDA apparatus equipped with a 36 µm opening (400 mesh) stainless steel wire cloth (Paper V). The conditions and dosing sequences of CS, fines and MFC were selected similarly to the hand sheet preparation, described above. The pulp was diluted so that the final consistency after MFC or fines addition was 3 g/l. The stirring was stopped simultaneously with the opening of the drainage valve and the vacuum level was kept constant at 0.10 bar.

3.2.6 Other methods used

Several standard and previously described methods were used to characterize the pulp, fines and MFC samples. The methods listed below are described in more detail in Papers I - V.

Chemical characterization

The amount of total lignin content of the mechanical pulp fines was measured according to TAPPI T222om-98 and UM250, and that of the kraft pulp fines was measured according to TAPPI T236cm-85. The obtained kappa number was converted to lignin content (Kyrklund and Strandell 1969). (Paper I)

The amount of total extractives content was determined by using acetone extraction according to standard SCAN-CM 49:93. (Paper I)

The surface chemical compositions (lignin, extractives and carbohydrates) were measured with an X-Ray Photoelectron Spectrometer (XPS). The method (Dorris and Gray 1978a and 1978b), the experimental procedure (Johansson et al. 1999) and the calculation procedure (Ström and Carlsson 1992; Laine et al. 1994a) have been reported earlier, with an exception that in these experiment extractives was removed by acetone extraction (SCAN-CM 49:93). (Papers I and II)

The total and the surface charge were determined by the polyelectrolyte titration method (Wågberg and Ödberg 1989) by using a streaming current detector for point of equivalence indication. Polybrene (Table 1) was used for total charge determination, and PDADMAC (Table 1) for surface charge determination. (Papers I - IV)

Zeta-potential was measured with Coulter Delsa 440 equipment (Beckman Coulter Inc., Brea, CA, USA). The samples were filtered prior to measurements using a 149 µm opening (100 mesh) stainless steel wire cloth to avoid capillary clogging. (Papers II and V)

Physical characterization

The proportions of flake, fibril and ray-cell fines were determined by the image analysis method (Luukko et al. 1997). (Papers I and II)

The total specific surface area was determined by using the Brunauer-Emmet-Teller (BET) nitrogen adsorption method (Brunauer et al 1938; Stone and Scallan 1965). Prior to the measurement the samples were dried by using the H_2O - C_2H_5OH - CO_2 critical point drying method (Lounatmaa and Rantala 1991). (Paper I)

The outer specific surface area was measured by a turbidity method (Wood and Karnis 1996). Polystyrene microparticle beads in two sizes, 5 μm and 10 μm, were used as reference. (Papers I, III and IV)

The specific sedimentation volume (SSV) was measured by a settling technique (Marton and Robie 1969). (Paper I)

The mean particle size was calculated as a Sauter surface mean diameter (i.e. diameter of a sphere that has the same volume/surface area ratio as the particle of interest) from the multiple light scattering apparatus signal (TurbiSoft Online software by Formulaction SA, L'Union, France). (Paper I).

The content of nano-sized material was defined gravimetrically by ultracentrifugation for 45 min at ca. 10000 *g*. (Paper V).

The visual survey of fines was performed using a Field Emission Scanning Electron Microscope (FESEM). Prior to imaging, the samples were dried by using the H_2O - C_2H_5OH - CO_2 critical point drying method (Lounatmaa and Rantala 1991), and thereafter sputter coated with 30 nm of platinum. (Papers I and V)

The dimensions and morphology of the fines and MFC samples were studied by Atomic Force Microscopy (AFM). Prior to imaging the samples were air dried on a Muscovite mica surface. (Paper V).

A Cryogenic Transmission Electron Microscopy (Cryo-TEM) microscope was used for the imaging to characterize the morphology, aggregation, orientation and size of the fines and MFC samples. Prior to imaging the samples were applied on a holey carbon grid and vitrified in 1:1 propane-ethane mixture at -180 ºC, and further cooled to -188 ºC. (Paper V).

The drainage rates of mechanical pulp fractions were determined with a Canadian Standard Freeness (CSF) apparatus according to standard SCAN-C 21:65. The drainability (Schopper-Riegler, °SR) of chemical pulps was measured according to standard ISO 5267-1:1999. (Papers I - V)

The fines contents of mechanical pulp fractions were defined as the mass proportion of particles passing through the 76 μm opening (200 mesh) stainless steel wire cloth. It was measured with a Bauer McNett apparatus according to standard SCAN-M 6:69. (Papers III and IV)

Fines contents of chemical pulps were defined as a proportion of particles in class L(l) 0 - 0.2 mm according to standard ISO 16065-1:2001 (length weighted projectile fiber length). (Paper V)

The length weighted projectile fiber lengths L(l) of the pulp fractions were analyzed according to standard ISO 16065-1:2001. (Papers III - V)

4 RESULTS AND DISCUSSION

This chapter summarizes the most important findings of this thesis work. More detailed and complete results are presented in the attached Papers I - V.

4.1 Properties of fines and microfibrillated celluloses

Different types of fines (Papers I and II), pulp fractions (Papers III and IV) and MFCs (Paper V) were produced from various raw materials by using different methods of fabrication, as described above. The fines were produced by refining and mechanical separation. The TMP pulp was fractionated by mechanical screening. The MFCs were produced by short pre-refining followed by fluidization without any additional fractionation.

4.1.1 Fines

The FESEM images in Figures 11a and 11b show RMP flake and RMP fibril fines. Different types of fiber particles can be seen: parts of middle lamella and primary wall, pieces of wood cells and microfibril bundles. Based on the image analysis, the RMP flake fines had lower fibril content than the RMP fibril fines (Table 2). As expected, the kraft pulp fines (Figures 11c and 11d) contained less flake type particles than the mechanical pulp fines. Also, the microfibril bundles in the kraft pulp fines seemed more curled, branched and disintegrated while the RMP fibril fines had a more ribbon-like shape.

The RMP flake fines had higher total and surface lignin content as well as extractives content than the RMP fibril fines (Table 2). This result is in accordance with earlier results concluding that the flake fines originate from the outer parts of the fiber (middle lamella, primary wall and outer layer of secondary wall), and therefore contain more lignin and extractives than the fibril fines originating from the inner parts of the fiber (Heikkurinen and Hattula 1993; Luukko et al. 1999; Krogerus et al. 2002; Mosbye et al. 2002; Sundberg et al. 2003). As expected, the kraft pulp fines had lower total lignin and extractives contents than the RMP fines, since most of these substances are dissolved from the pulp during the kraft pulping and the bleaching processes. The surface lignin content of kraft pulp fines was significantly higher, showing that the residual lignin may enrich on surfaces, as also shown earlier (Laine et al. 1994; Luukko et al. 1999; Retulainen et al. 2002).

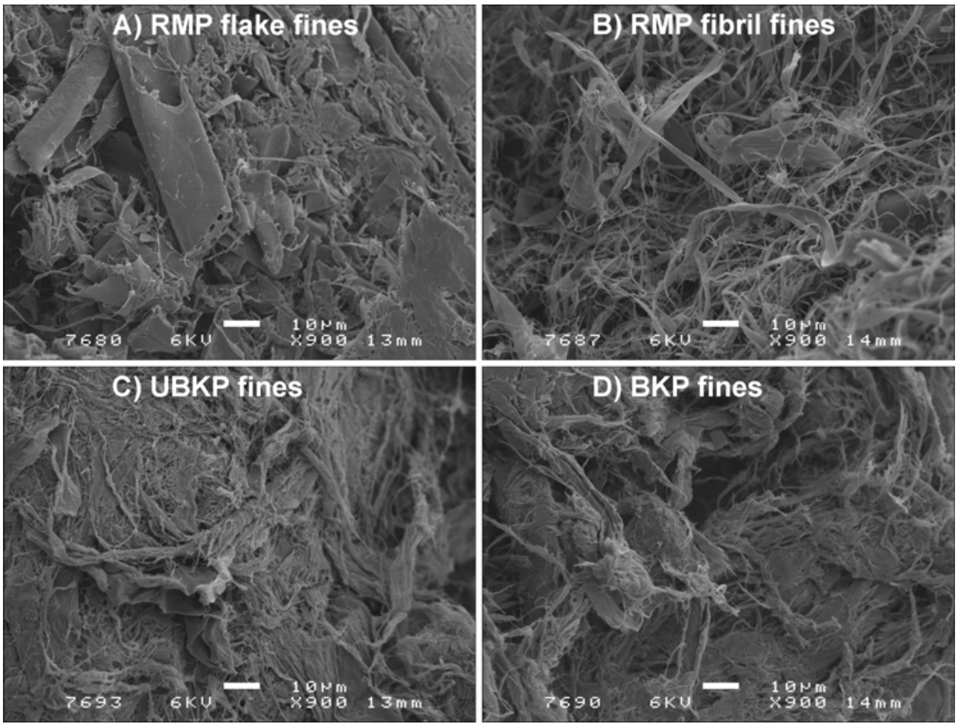

Figure 11. *FESEM images of a) Refiner mechanical pulp flake fines; b) Refiner mechanical pulp fibril fines; c) Unbleached kraft pulp fines; d) Bleached kraft pulp fines. Image size 100 µm × 133 µm. (Paper I)*

Refining and disintegration of the wood to fibers, and further to fines, opens up the cell walls and increases the number of accessible charges. However, the surface area of the particles increases as well, but not necessarily in linear proportion to charges. The total and surface charges (µeq/g) of the BKP fines were lower, but the charge ratio (surface charge per total charge) was higher than those of the other fines (Table 2). The mechanical pulp fines had higher charge densities per unit area (meq/m^2) than the kraft pulp fines, which may arose from the differences in their surface chemical compositions. If the charge ratios are compared, it appears that the mechanical fines and the UBKP fines have relatively less accessible charges on the outer surface than the BKP fines. Partly similar results have been reported also by other authors (Fardim et al. 2002; Koljonen et al. 2004).

The UBKP fines and the BKP fines had higher total specific surface area than either of the RMP fines (Table 2). The higher specific surface area may arise from the lower lignin content, as well as from the higher degree of fibrillation, which both affect the values achieved by the BET method (Stone and Scallan 1965). The lignin and the hemicelluloses hold the microfibril bundles and fibers together and thus block the porous structure of the mechanical pulp fines. The porosity of fibers has been found to increase during the pulping, delignification and fibrillation processes (Stone and Scallan 1965; Gullichsen 2000; Fahlén and Salmén 2005). Presumably the microfibrils in the kraft pulp fines are more separated than in the RMP as the lignin and the hemicelluloses are removed in kraft cooking. Together with the observations from the FESEM images, these results conform that the kraft pulp fines possess a smaller scale porous structure than the mechanical pulp fines. However, it must be taken into account that the nature of porosity in fines is partly different than that in fibers. In fines, the fiber lumen and cell wall layer structures are mainly fragmented to the fibrillar level, and do not contribute to the porosity as such. The main sources of porosity are the interstices between partly dispersed microfibrils and branched microfibril bundles. In addition the fines network, with its fine interstices, may be considered as a porous structure. Thus, it is difficult to distinguish the porosities of fines network and single fines particles. In addition, the surface area and size of fines particles are rather subjective properties due to their partially fragmented fractal structure.

Table 2. *Chemical and physical properties of pulp fines. (Paper I)*

	RMP flake fines	RMP fibril fines	UBKP fines	BKP fines
Total lignin content [%, w/w]	38.2	34.9	4.0	0.6
Total extractive content [%, w/w]	2.2	0.6	0.3	0.2
Total carbohydrate content [%, w/w]	59.7	64.5	95.6	99.2
Surface lignin content [%]	53	41	46	22
Surface extractives content [%]	23	11	1	1
Surface carbohydrate content [%]	24	48	53	77
Total charge [μeq/g]	119	120	141	64
Surface charge [μeq/g]	35	39	38	30
Total charge / Total specific surface area [μeq/m^2]	0.88	0.91	0.35	0.19
Surface charge / Outer specific surface area [μeq/m^2]	8.9	8.4	5.6	6.8
Charge ratio, Surface charge / Total charge	0.29	0.33	0.27	0.47
Total specific surface area, BET [m^2/g]	134	131	399	338
Outer specific surface area [m^2/g]	3.9	4.7	6.8	4.4
Total / outer specific surface area	34	27	59	76
Specific sedimentation volume [cm^3/g]	151	490	163	117
Fibrillar content [%, w/w]	36	46	36	29
Ray-cells, content [%, w/w]	7	5	13	10
Flakes, content [%, w/w]	57	49	51	61
Particle size, mean by volume, Turbiscan [μm]	6.9	7.1	14.5	13.3

In Papers III and IV the fractionation of the TMP (REF) introduced two additional fractions, the short fraction (SF) and the long fraction (LF). The properties of these fractions differed significantly from the initial pulp (Table 3). As expected, the SF had higher fines content, specific surface area and surface charge, but lower fiber length and drainage rate than the REF and LF (Table 2).

Table 3. The characteristics of the TMP fractions. (Paper III and IV)

Sample	Drainage rate, CSF [ml]	Fines content [mass-%]	Fiber length, length weighted average [mm]	Outer specific surface area [m^2/g]	Surface charge [µeq/g]	Surface charge density [$\mu eq/m^2$]
SF	25	65	0.82	4.1	76	19
REF	77	32	1.77	1.4	31	22
LF	218	17	1.91	1.0	18	18

4.1.2 Microfibrillated celluloses

The fibrillation of hardwood kraft pulp at different levels and optional chemical treatment led to three different MFC samples, each having unique properties that are summarized in Table 4 and in Figures 12 and 13. One fines sample (BKP fines) was also examined and further used in the experiments to compare its properties and behavior with the MFCs. According to zeta potential measurements, BKP fines had the lowest, and the partially carboxymethylated MFC (CMMFCF4) the highest amount of charged groups. BKP fines were produced from pine pulp and the other samples from birch pulp, which may explain its minor charge (Laine and Stenius 1997). Evidently the ionizable carboxyl groups formed during the carboxymethylation resulted in an increased anionicity, and this further improved the fibrillation efficiency and the stability of the CMMFCF4 dispersion. An increase in fibrillation efficiency due to increased anionicity, induced by carboxymethylation, has also been previously observed by Walecka (1956).

Table 4. *Properties of MFC and fines samples. (Paper V)*

Sample	Zeta potential [mV]	Nano-sized material content [%, w/w]
BKP fines	-6.2	12.8
MFCF4	-8.3	18.1
MFCF10	-8.1	29.4
CMMFCF4	-16.2	39.9

The BKP fines that had been fibrillated by conventional refining had the lowest nano-sized material content, whereas CMMFCF4 had the highest. The fine structure of the samples was further analyzed by AFM and Cryo-TEM imaging methods (Figures 12 and 13). According to the AFM images, BKP fines consisted of the coarsest fibrils while MFCF10 that had passed 10 times through the fluidizer had finer fibrils and the most homogeneous appearance. The CMMFCF4 had as well very small sized fibrils, already after four passes of fluidization. Presumably, the increased swelling caused by carboxymethylation promoted the fibrillation of fibers. However, some coarser fibrils were still found in this sample.

When comparing the AFM images of air-dried samples (Figure 12) with the Cryo-TEM micrographs of vitrified samples (Figure 13), it can be seen that the large fibrils observed in the AFM images actually consist of numerous microfibrils closely and parallel associated together in bundles. Similar difference between the results obtained by the two microscopy methods has also been observed by Pääkkö et al. (2007). The fibrils in MFCF10 were disintegrated into individual microfibrils or into small sized bundles consisting of only ca. 5 to 20 microfibrils (Figure 13d). In contrast, the microfibrils in MFCF4 and BKP fines are mainly present in larger bundles consisting of tens or hundreds of parallel aligned microfibrils, BKP fines having clearly the broadest bundles (Figures 13a and 13b). However, the distinction between a bundle and single fibrils is rather obscure and subjective.

The carboxymethylation affected the structure of the fibrils in CMMFCF4. The AFM image (Figure 12c) suggested a rather heterogeneous sample, containing both thick and long microfibril bundles as well as a network of very fine irregular fibrils. The Cryo-TEM micrograph of the same sample (Figure 13c) shows short microfibrils ordered in a fluffy bundle and having more kinks than in the other samples. In comparison to the other samples, the conformation of CMMFCF4 microfibrils and microfibril bundles was clearly different. Saito et al. (2006) observed similar kinks in their experiments, and further proposed those to be due to damage from the mechanical treatment. Similar orientation and structure of carboxymethylated microfibrils can be seen in the AFM images by Ahola et al. (2008a) and the TEM image by Wågberg et al. (2008), as well. These characteristics may be due to partial chemical degradation of cellulose by carboxymethylation. The fluidization may well have caused increased mechanical cutting of the partially carboxymethylated microfibrils. However, the degree of polymerization of the NFC samples was not analyzed in this work.

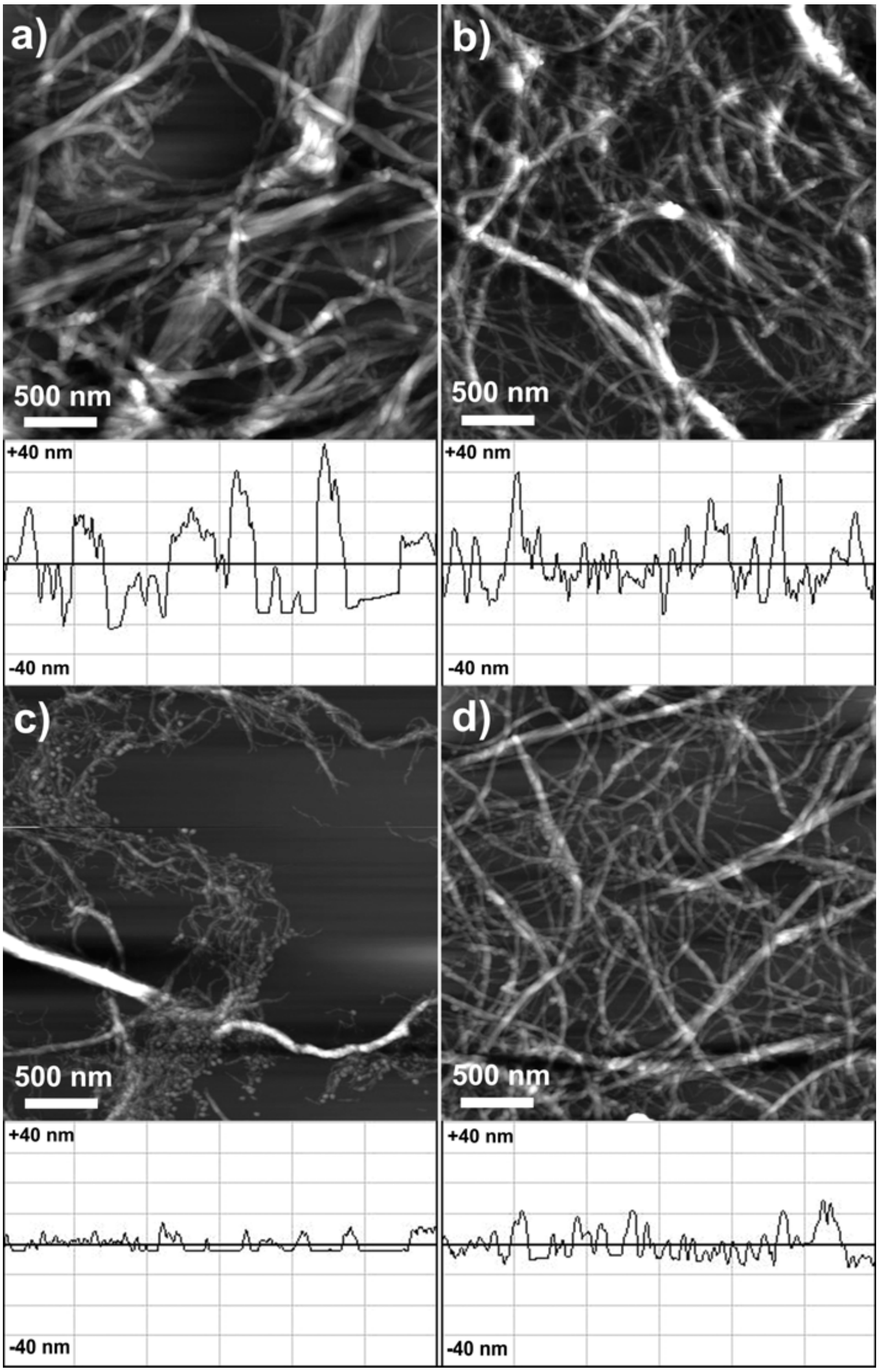

Figure 12. *AFM height images of a) BKP fines, b) MFCF4, c) CMMFCF4, d) MFCF10. The color scale range in the height images is from black to white a) 150 nm, b) 80 nm, c) 40 nm, d) 80 nm. The Z-profile graphs are taken across the images from arbitrary horizontal lines. Image size 3 µm × 3 µm. (Paper V)*

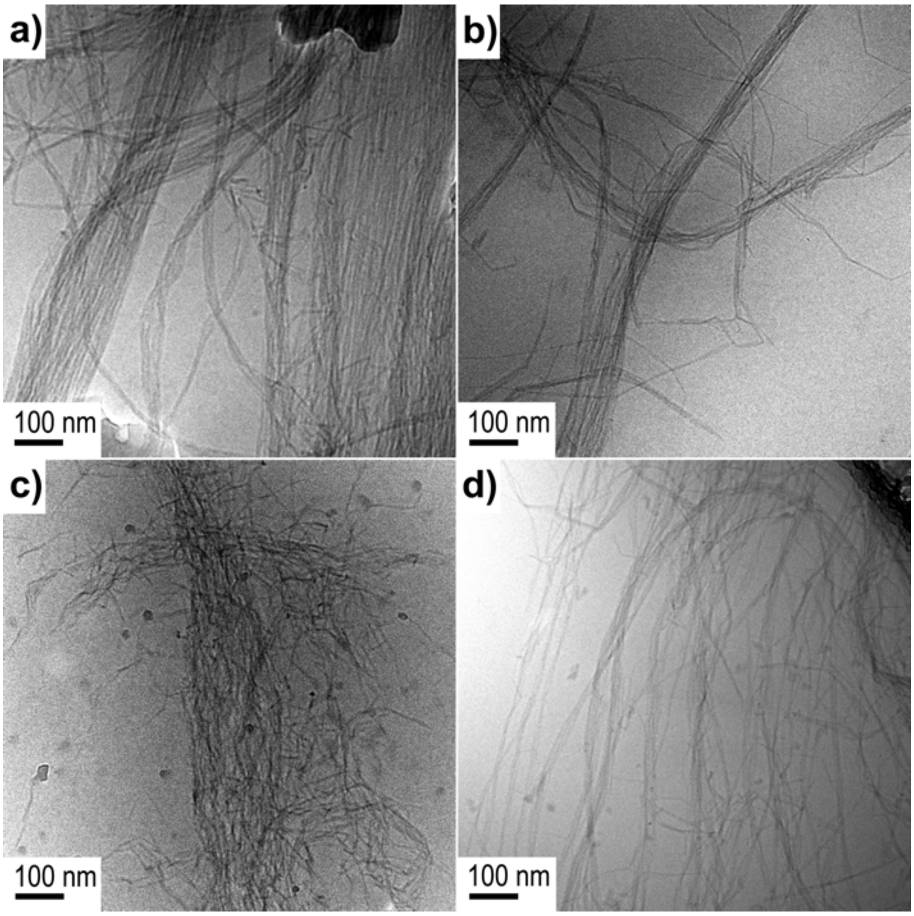

Figure 13. *Cryo-TEM micrographs of a) BKP fines, b) MFCF4, c) CMMFCF4, d) MFCF10. Image size 0.9 µm × 0.9 µm. (Paper V)*

The widths (lateral size) of single microfibrils were measured from Cryo-TEM micrographs to be ca. 6 nm, and from AFM images ca. 11 nm. The AFM Z-profiles suggest a height of ca. 5 nm for an individual microfibril. It should be noted that the differences in sample preparations (vitrification vs. air drying), as well as the exaggeration of lateral dimensions by AFM tip convolution, may lead to differences in the obtained results by these two microscopy methods. Nevertheless, the measured dimensions of microfibrils are in good accordance with earlier reports (Alén 2000; Davies and Harris 2003; Pääkkö et al. 2007 and 2008; Ahola et al. 2008a; Wågberg et al. 2008).

According to the characterization results of the samples, it was predicted that their behaviors with high molar mass cationic polyelectrolytes in aqueous suspensions differ significantly. In addition, their influence in the papermaking process was supposed to vary with respect to their properties.

4.2 Adsorption of cationic polyelectrolytes on fines

4.2.1 Effect of molar mass and charge density

The adsorption of different types of C-PAMs on four different types of fines was studied in Paper I. The polyelectrolytes (Table 1) were chosen so that the influence of both the molar mass and the charge density could be observed in the experiments. The maximum adsorptions of the various C-PAMs on the different fines are summarized in Figure 14. The adsorption was typically the highest on the RMP fibril fines and the lowest on the BKP fines. In addition to the different adsorption behavior of the different fines, the typical effects of the polyelectrolytes (Lindström 1989; Eklund and Lindström 1991; Van de Ven 2000; Wågberg 2000) were also seen. Hence, due to better accessibility, the adsorption of low molar mass C-PAMs was higher than that of high molar mass C-PAMs. Furthermore, a higher charge density of C-PAMs led to lower adsorption, with the exception of the adsorption of high molar mass C-PAMs on kraft pulp fines where the adsorption of HMW-HC C-PAM exceeded that of the HMW-LC C-PAM.

The strongest increase of C-PAM adsorption with decreasing molar mass was recorded on the UBKP and the BKP fines when low charge density C-PAMs were used. Apparently this arises from the different porous structures of the fines (Table 2); the kraft pulp fines exhibit a larger total specific surface area as well as a higher total/outer specific surface area ratio than the mechanical pulp fines.

The maximum adsorption decreased on all fines as the charge density of the low molar mass C-PAM was increased (Figure 14). LMW-HC C-PAM adsorbs in a more extended (flat) conformation than LMW-LC C-PAM. As a consequence, the adsorbed polyelectrolyte layer was evidently thinner and the adsorbed amount lower with LMW-HC than LMW-LC C-PAM. The surface charges (µeq/g) of the fines (Table 2), correlated directly with the adsorbed amount of LMW-HC C-PAM (RMP fibril > UBKP > RMP flake > BKP). Thus, the charge density of the fines appeared to be the most significant factor in the adsorption of low molar mass C-PAMs on fines.

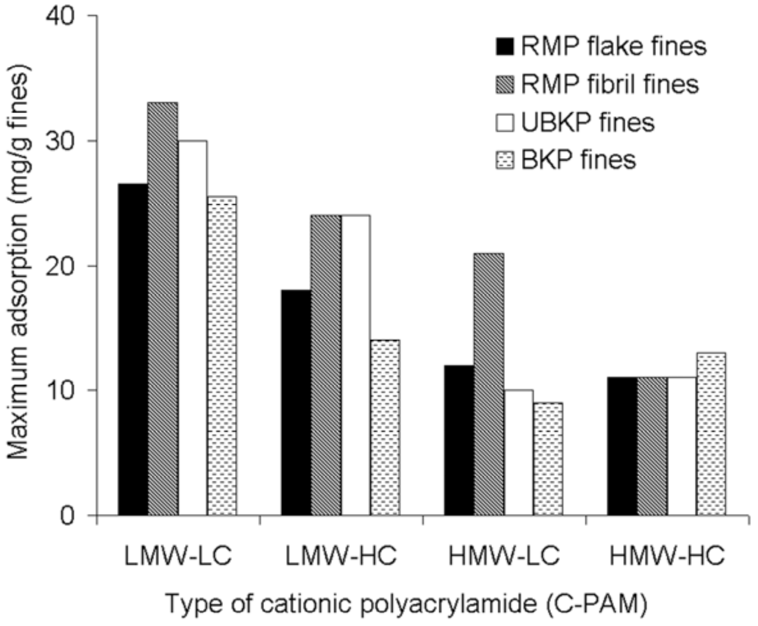

Figure 14. *Adsorption of various C-PAMs on different types of fines. Stirring speed 400 rpm for 1 min and 140 rpm for 14 min. (Paper I)*

With the increasing charge density of high molar mass C-PAM, the maximum adsorption decreased with the RMP fibril fines and the RMP flake fines, and conversely, increased with the UBKP fines and the BKP fines. The RMP fibril fines have a high surface charge combined with a stiff structure and a less porous surface, which then together allow the HMW-LC C-PAM to form a thick protruding layer. The HMW-LC C-PAM cannot penetrate very well into the porous structure, and for this reason, it adsorbs mainly on the outer surface of the fines. The flocs of flexible kraft pulp fines and the small sized RMP flake fines can be collapsed or fully covered already at low polymer concentrations, and subsequently have reduced accessible surface area for further HMW-LC C-PAM adsorption. Thus, the adsorption of HMW-LC C-PAM is significantly higher on the RMP fibril than on the other types of fines. In contrast to the HMW-LC C-PAM, the HMW-HC C-PAM can relatively better utilize the porous microstructure of the kraft pulp fines than the mechanical pulp fines. Partly similar conclusions have also been proposed by Van de Ven (2000) and Horvath et al. (2008). In this context, as well a noteworthy subject is that the maximum adsorption of the HMW-HC C-PAM was almost equal on different fines (Figure 14); however, their flocculation behaviors were not similar (Figure 18).

A comparison of the adsorbed amounts of the LMW-LC and the HMW-HC C-PAMs reveals again the importance of the accessibility of the active surfaces (Van de Ven 2000;

Horvath et al. 2008). The LMW-LC C-PAM can better utilize the internal surface area of the BKP fines than the HMW-HC C-PAM, due to its lower molar mass and larger reconformation tendency. It appears that in addition to the differences in C-PAM conformation, the different structures of the fines strongly influence the adsorption of high molar mass C-PAMs. This conclusion is supported by the fact that the differences in the adsorbed amounts of HMW-HC and HMW-LC C-PAMs were largest on the BKP and the RMP fibril fines which had the most and the least porous structures and the lowest and highest specific sedimentation volumes, respectively (Table 2).

4.2.2 Effect of hydrodynamic shear and contact time

The adsorption of high molar mass cationic polyelectrolytes on porous cellulosic surfaces was further studied in Papers III and IV. These experiments were performed under low shear (static) conditions with a long contact time, and under high shear (dynamic) conditions using various short contact times. The adsorption of three high molar mass C-PAMs with different charge densities was adsorbed on different fractions of TMP (REF, SF and LF). In addition, adsorption isotherms of PDADMAC were used, to have a reference adsorption behavior in comparison to those of C-PAMs.

As expected, the amount of PDADMAC adsorbed on the SF was more than two times higher than that on the LF (Figure 15a). However, when the adsorbed amount (mg/g) was divided by the outer specific surface areas (m^2/g) of each pulp fraction (Table 3), the adsorption per unit area (mg/m^2) at zero equilibrium concentration was nearly equal for each fraction (Figure 15b). Once the surface charge densities ($\mu eq/m^2$) of the different pulp fractions were almost equal, it means that the adsorption differences are mainly due to variations in surface area, rather than the chemical composition of the surface.

The adsorption isotherm of low molar mass (in comparison to the C-PAMs used), high charge density PDADMAC under the low shear conditions (Figure 15a and 15b) was clearly of the Langmuir type (Langmuir 1918; Barnes and Gentle 2005) denoting high affinity adsorption by ion exchange process, as also suggested by Wågberg and Hägglund (2001). The low shear adsorption isotherms of high molar mass C-PAMs showed high affinity at low polyelectrolyte dosages when no excess polyelectrolyte was present, however, no plateau level of adsorption was found within the dosages used (Paper III). An example of this is shown in Figures 16a and 16b (HMW-HC C-PAM). The more rounded low-affinity type adsorption isotherms of C-PAM indicate a non-stoichiometric process with a thick layer of protruding polyelectrolyte chains undergoing conformational changes due to competition for surface charges and due to the increase of excess polymer concentration (Wågberg et al. 1988; Wågberg and Ödberg 1989; Barnes and Gentle 2005).

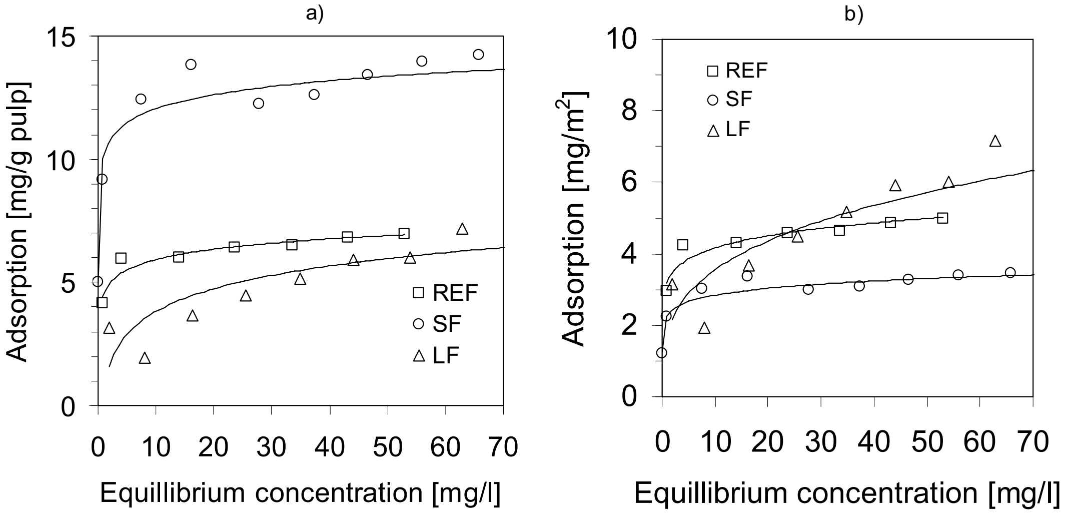

Figure 15. *Adsorption of PDADMAC on different pulp fractions. Stirring speed 250 rpm and contact time 15 min. Adsorption given in a) mg/g pulp; b) mg/m^2.*
REF - unfractionated TMP pulp; SF - TMP short fraction, LF - TMP long fraction.
(Paper III)

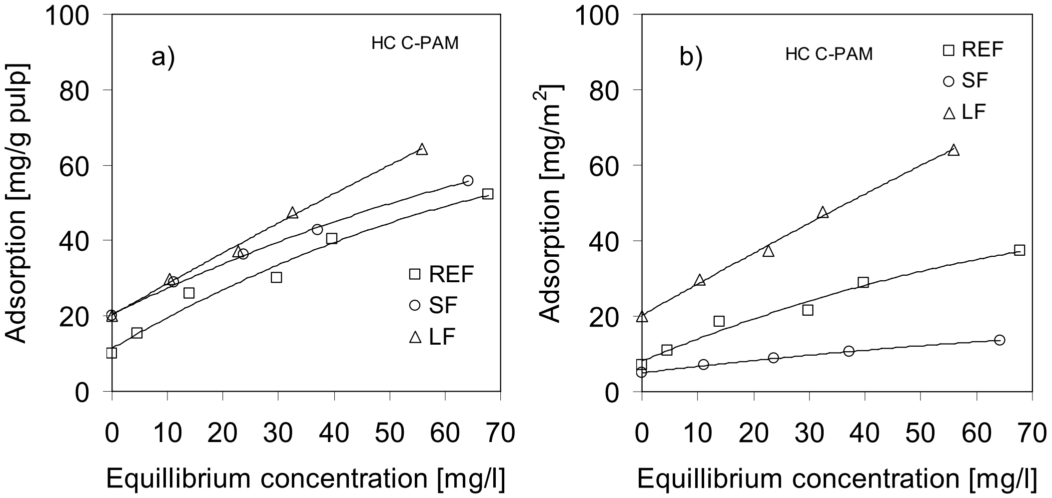

Figure 16. *Adsorption of HMW-HC C-PAM on different pulp fractions. Stirring speed 250 rpm and contact time 15 min. Adsorption given in a) mg/g pulp; b) mg/m2.*
REF - unfractionated TMP pulp; SF - TMP short fraction, LF - TMP long fraction.
(Paper III)

In Figure 16a the adsorption is presented in mg/g, whereas in Figure 16b it is presented in mg/m^2. The highest adsorption amounts per mass or per surface area were both recorded on the LF. The least adsorption per mass was recorded on the REF, and least adsorption per surface area on the SF. When no excess polyelectrolyte was present, the amount of C-PAM adsorption was independent of the charge density of the polyelectrolyte but instead, depended on the type of pulp fraction, being about 20 mg/m^2 on the LF, about 7 mg/m^2 on the REF, and about 5 mg/m^2 on the SF. Given that the surface charge densities (μeq/m^2) for these fractions and the molar masses of the polyelectrolytes were substantially equal, it can be assumed that it was the structural differences of the TMP fractions which defined the primary adsorption of high molar mass C-PAM under low shear conditions. The reason for this is not fully clear, but some suggestions have been presented.

Several authors (Wågberg et al 1988; Falk et al. 1989; van de Ven 2000; Horvath et al. 2008, Saarinen et al. 2009) have suggested that even the high molar mass polyelectrolytes, or parts of the molecules, could penetrate, or reptate (De Gennes 1979), into porous cellulosic surfaces (fibers). Even though this is a slow process in comparison to the initial adsorption phenomenon, it is still possible in the time scale of this experiment (15 min). Seeing that the more easily available fiber lumen exists in fibers, most present in the LF, but not in the fines (SF), this estimate may be reasonable. The polydispersity of the C-PAMs used may as well lead to dissimilar adsorption behaviors on the different TMP fractions. A third proposal is the above described collapse, or full polymer coverage, of the flocs of small sized flexible particles (SF). Thus, the high molar mass C-PAM cannot fully utilize the surface area of the SF that might be accessible to smaller size molecules. On the other hand, the less fibrillated and more open surface area of stiff LF particles (fibers) allows high molar mass C-PAMs, especially HMW-LC C-PAM, to form a thick protruding layer.

The time-dependence of adsorption under high shear conditions was studied by taking filtrate samples from the DDA unit at 5 s and at 30 s after polyelectrolyte dosage, and analyzing the concentration of free C-PAM in the filtrate by means of polyelectrolyte titration. Differences were found between the different combinations of polyelectrolytes and pulp fractions. The adsorption rate and amount of HMW-HC C-PAM was almost equal on the fractions SF and LF under high shear conditions; and no significant time-dependent behavior was found (Figure 17a). Presumably the initial adsorption of HMW-HC C-PAM reached its maximum rapidly, faster than 5 s, which was the shortest sampling time used in this study. On the other hand, when HMW-MC C-PAM was used, a strong time-dependence was found on the SF and the LF (Figure 17b). The slow adsorption of HMW-MC C-PAM on LF (Figure 17b) was considered to be due to formation of voluminous flocs followed by rupture and cleavage of polymer chains, as well as further adsorption of degraded polyelectrolyte fractions. In addition, some minor time-dependence was also observed when HMW-LC C-PAM was adsorbed on the SF and the LF (Figure 17c). The high shear stresses restrict the adsorption rate and amount of HMW-LC C-PAM having a low electrostatic affinity towards the cellulosic surfaces (Figure 17c). In addition, the high hydrodynamic shear supposedly causes desorption and cleavage of the HMW-LC C-PAM chains which are adsorbed only at few contact points, thus, yielding a lower amount of adsorption. On the contrary, HMW-HC C-PAM seems to yield denser and more shear-resistant flocs due to its adsorption in a flatter conformation, caused by its higher electrostatic affinity.

Similar time-dependent adsorption of polyelectrolytes has also earlier been found by other authors. Wågberg et al. (1988) showed that both the amount and the stoichiometry of C-PAM adsorption on cellulosic fibers developed several minutes, even the initial adsorption occurred within seconds. Falk et al. (1989) continued the study and reported that a constant adsorption level was established under turbulent conditions in less than one second. They also suggested that the subsequent change from the initial state towards an equilibrium situation probably depends on the rate of reconformation and penetration processes. Aksberg and Ödberg (1990) found in their experiments that the amount of adsorbed anionic polyelectrolyte (A-PAM) on cellulosic fibers changes in time, thus, depends on the conformation of the pre-adsorbed cationic polymer (C-PAM). Saarinen et al. (2009) reported that the adsorption of C-PAM was instant on silica but continued for several minutes on cellulose model surface.

It has also been reported that even small concentrations of high molar mass polyelectrolytes may reduce the drag, and damp the energy bursts of a highly turbulent solution (Lindström 1989). This may lead to the decreasing of disruptive forces and increase adsorption with respect to excess polyelectrolyte concentration. As the conformation and the coil size of a polyelectrolyte in an aqueous solution are dependent on its charge density, it may therefore also influence its dampening effect, and thus the rate of adsorption. In addition, high shear forces may cause fragmentation of polymer chains which further leads to increased adsorption by enhanced accessibility. The extent of fragmentation may as well be dependent on the polymer chain conformation. These assumptions may partially explain the differences in the slopes of the adsorption isotherms shown in Figures 17a - c. However, both of these assumptions are rather conjectural and can not be confirmed within the extent of this work.

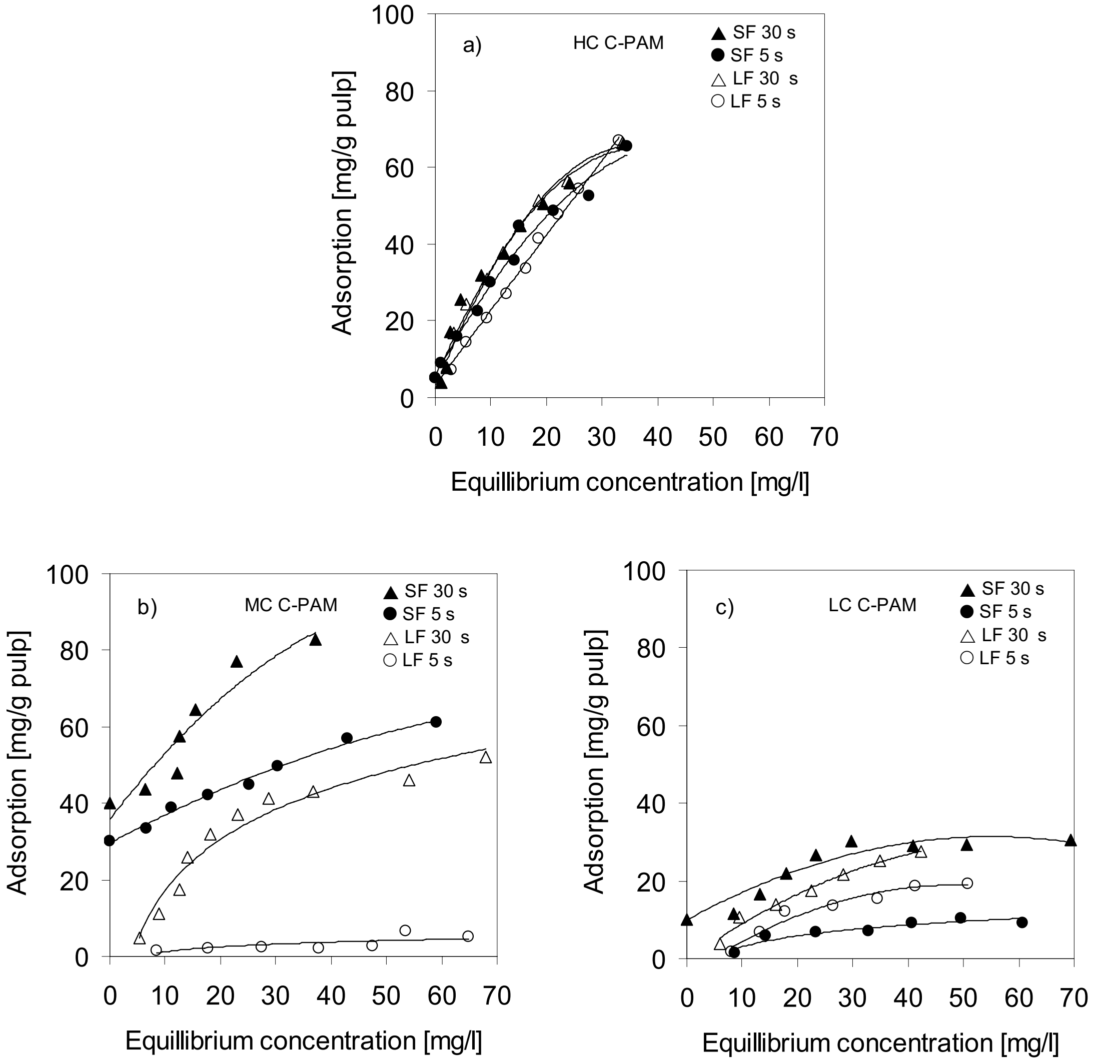

***Figure 17.** Adsorption of C-PAMs on different pulp fractions. Stirring speed 1500 rpm. Contact time 5 s and 30 s. a) HMW-HC C-PAM; b) HMW-MC C-PAM; c) HMW-LC C-PAM. REF - unfractionated TMP pulp; SF - TMP short fraction, LF - TMP long fraction. (Paper III)*

4.3 Flocculation of fines by cationic polyelectrolytes

4.3.1 Effect of properties of polyelectrolytes and fines

Figures 18a - d show the flocculation of different types of fines with various C-PAMs as a function of polyelectrolyte dosage. In general, the higher the molar mass, or the lower the charge density of a C-PAM, the higher the flocculation index was. These phenomena are typical behavior for bridging type flocculation, as longer protruding polyelectrolyte chain parts enhance flocculation (Wågberg and Lindström 1987b; Gregory 1989; Lindström 1989; Eklund and Lindström 1991; Wågberg 2000). A high molar mass polyelectrolyte chain tends to extend out from the surface, and high charge density flattens the conformation of adsorbed polyelectrolyte.

However, not only the C-PAM properties, but also the properties of fines affected the flocculation. The flocculation index increases in the order BKP < UBKP < RMP fibril < RMP flake. The highest flocculation index was achieved with the HMW-LC C-PAM on the RMP flake fines, and the lowest with the LMW-HC C-PAM on the BKP fines. When comparing the RMP fibril fines and the RMP flake fines, it can be assumed that the most pronounced flocculation of the RMP flake fines is due to a lower degree of penetration of C-PAMs into the flat and smooth surfaces of the flakes (Table 2). This induces the availability of the C-PAMs for flocculation. Also the small-sized RMP flake fines can form more compact flocs which may be seen as higher transmission intensity (higher flocculation index) in the flocculation experiments, thus, giving a higher flocculation index.

There was also a large difference in the required C-PAM dosages between the different fines types (Figure 18). At low C-PAM dosages (< 5 mg/g) the flocculation indices increase faster with the mechanical pulp fines than with the kraft pulp fines. For instance, up to a tenfold dosage was necessary to reach the same flocculation index with the BKP fines as with the RMP flake fines. As described above, the polyelectrolytes are evidently adsorbed more on the surfaces of the mechanical pulp fines, whereas they penetrate into the porous structure of the kraft pulp fines. The other important factor is the higher surface charge per surface area (µeq/m^2) of the RMP fines (Table 2), meaning that their charges are more easily accessible for high molar mass polyelectrolytes. The partial penetration and conformation change processes consume charges of polyelectrolytes, decrease their degrees of freedom, and also reduce the protruding polyelectrolyte layer thickness, thus causing diminished flocculation of kraft pulp fines. In addition, when Figures 14 and 18 are compared, neither the maximum flocculation index nor the dosage required to reach it may not be universally evaluated from the maximum polyelectrolyte adsorption values. The effect of molar mass was the only strong correlation found between the adsorption and flocculation experiments.

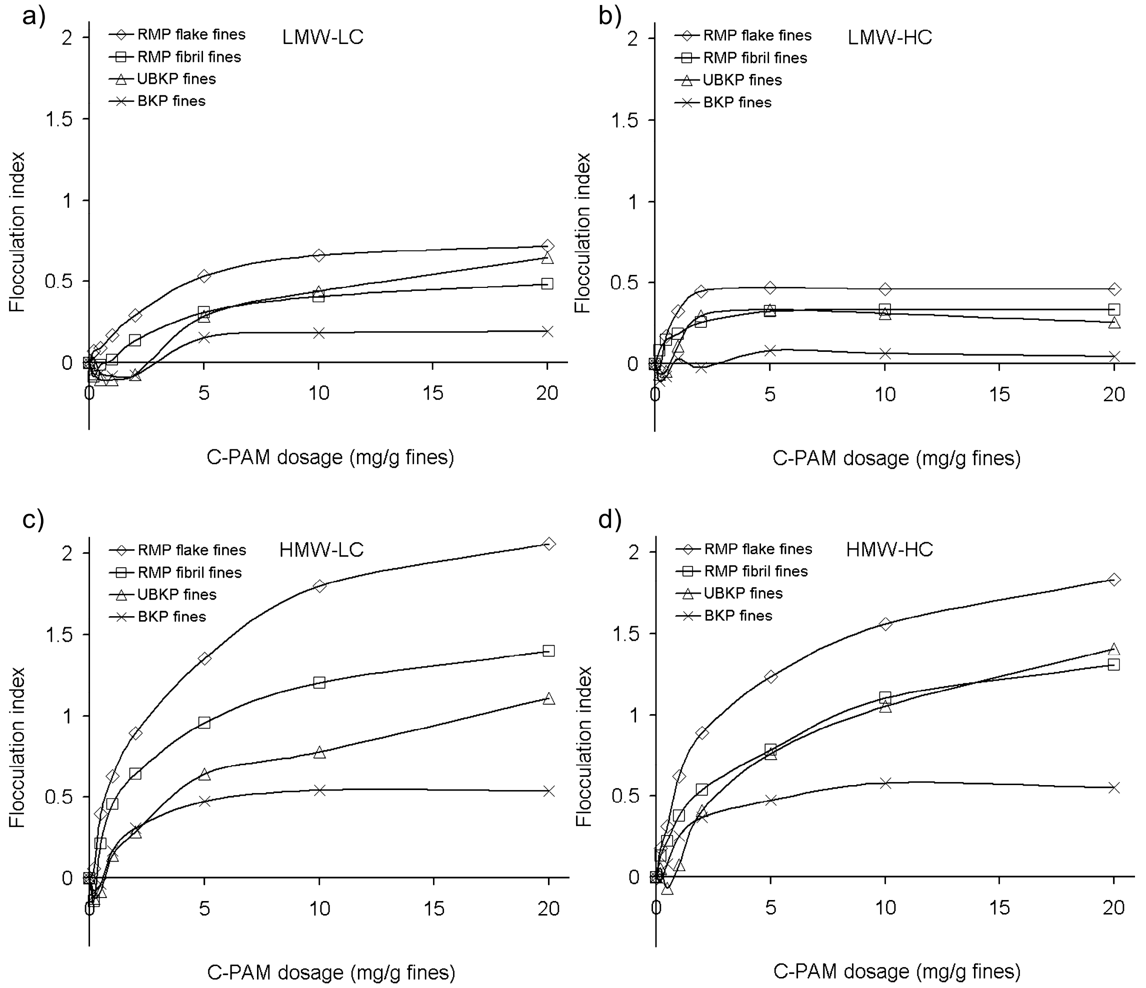

Figure 18. *Flocculation of different types of fines with various C-PAMs.*

a) LMW-LC C-PAM; b) LMW-HC C-PAM; c) HMW-LC C-PAM; d) HMW-HC C-PAM.

◊ RMP flake fines; □ RMP fibril fines; Δ UBKP fines; × BKP fines. Stirring speed 400 rpm. (Paper I)

4.3.2 Effect of shear, contact time and pulp fraction

The flocculation phenomena were further studied by adding high molar mass C-PAMs into suspensions of different TMP fractions under sheared conditions (Paper IV). The increase of particle size was recorded with respect to time and polyelectrolyte dosage.

The relative mean particle size of the suspensions developed differently depending on the pulp fraction, shear level and polyelectrolyte dosage used. As an example of this, Figures 19a and 19b show the effect of HMW-LC C-PAM dosage under high shear conditions on the development of the relative mean particle sizes of SF and of LF, respectively. As expected, flocculation and deflocculation occurred rapidly. After the local maximum was reached, the relative mean particle size decreased, representing disintegration or compaction of the flocs. Neither the pulp fraction type nor the polyelectrolyte charge density significantly affected this time response under high shear conditions.

It can be supposed that under high shear conditions the initial adsorption of C-PAM on TMP fractions occurs rapidly but only at a few tenacious contact points. The thick layer of protruding polyelectrolyte chains efficiently promotes bridging flocculation and the formation of large flocs. For example Gregory (1989) and Auber and Cannell (1986) have proposed that slow aggregation yields compact flocs, whereas rapidly formed flocs are initially more open and restructure further towards a denser form. However, the flocs formed may not completely endure the high hydrodynamic shear; desorption, transfer and cleavage of polyelectrolyte chains, as well as rupture of pulp particles, may occur (Gregory 1989, Ödberg 1993, Asselman and Garnier 2000, Solberg and Wågberg 2003, van de Ven 2005). Under high shear conditions, this process breaks up the flocs and allows further continuation of polyelectrolyte reconformation which both leads to a decrease of floc size with respect to time (Figures 19a and 19b).

However, the rate of this floc size decrease was inversely proportional to the amount of C-PAM used. One possible explanation is that the excess polyelectrolyte, in its extended conformation, retards the disintegration and compaction process of the flocs under high shear conditions. It has also been suggested earlier (Lindström 1989) that high molar mass polyelectrolytes may reduce the viscous drag and damp the energy bursts of a highly turbulent solution, thus leading to a decrease of disruptive forces and increased adsorption.

However, a more reasonable explanation is that a higher C-PAM dosage enables creation of more contact points, thus, leading up to more shear-resistant flocs.

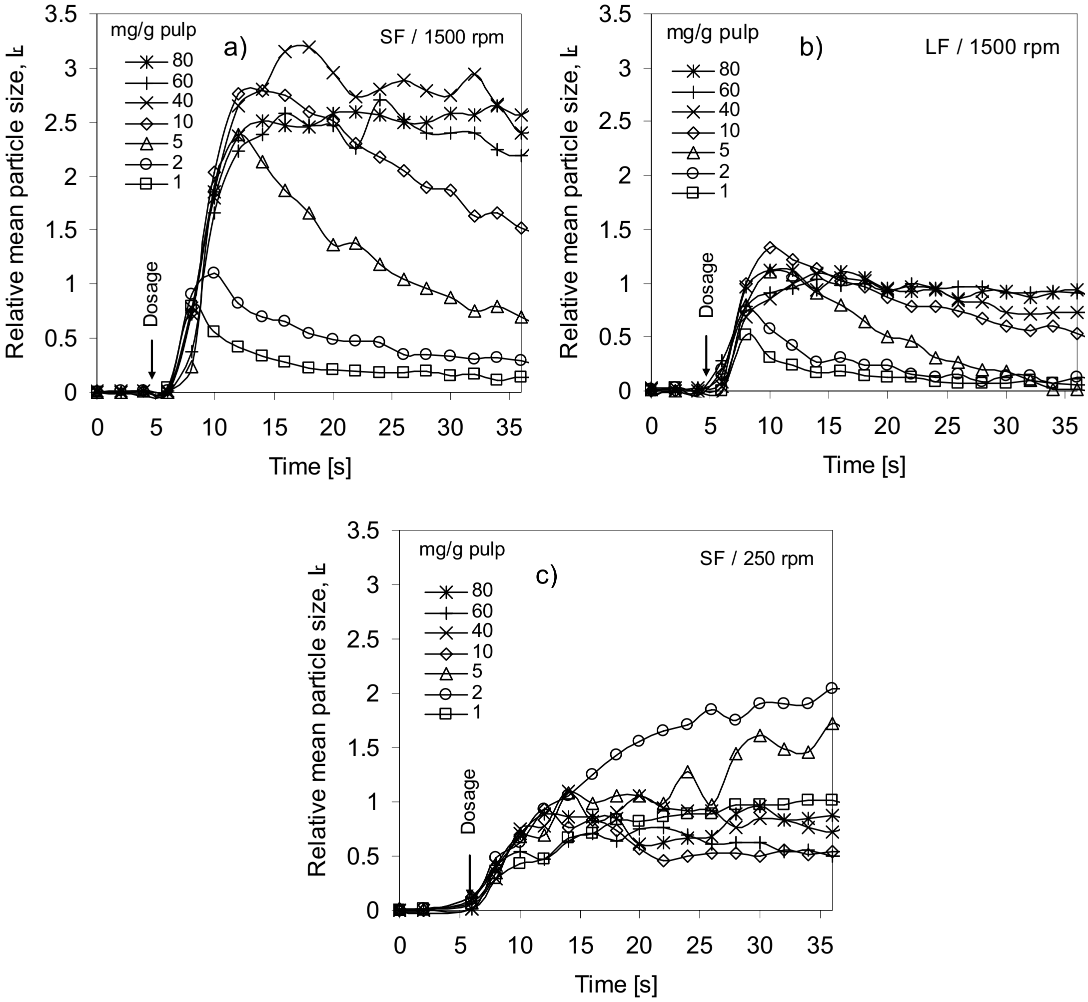

Figure 19. Flocculation of SF (TMP short fraction) and LF (TMP long fraction) with HMW-LC C-PAM. Stirring speed a) 1500 rpm, b) 1500 rpm, and c) 250 rpm. (Paper IV)

In contrast, under low shear conditions (Figure 19c) the relative mean particle size increased slowly towards its maximum value and the maximum flocculation was reached with a lower polyelectrolyte dosage than under high shear conditions (Figures 19a and 19b). Furthermore, the particle size remained constant near its attained maximum value and the degradation of flocs was scarcely detectable under low shear conditions within the 5 min measuring period (in Figure 19c only the first 35 s is shown). The prevailing shear forces seem not to be able to disintegrate the flocs. However, the hydrodynamic effect of low shear mixing may still be sufficient for pulling flocculated particles apart (without breaking the flocs), hence, limiting the ability of polyelectrolyte chains in the flocs to reconform towards a lower free energy state. This may prevent the compaction of the formed flocs and maintain the steady state of large flocs formed under low shear conditions (Figure 19c).

The effects of pulp fraction, C-PAM charge density, and shear level on particle size, contact time, and C-PAM dosage are summarized in Figures 20a - c. Neither the charge density of C-PAM nor the shear rate substantially affected the mean particle sizes achieved (Figure 20a). But the differences in particle sizes mainly arose from the properties and behavior of the different fractions used. Typically, the relative mean particle size increased the most with SF and least with REF, where the maximum values were slightly lower than with the LF.

It can be seen that the maximum mean particle size was reached under high shear conditions within 10 to 30 s after the polyelectrolyte dosage (Figure 20b). The response time was not significantly dependent on the type of pulp fraction, whereas it was observed that a HMW-HC C-PAM introduced slightly faster flocculation than the other C-PAMs. On the other hand, under low shear conditions the development rate of the mean particle size was more dependent on the properties of the pulp fraction. Thus, reaching the maximum floc size required most time with SF and least with REF. This time-dependency is also an indication of the continuation of the flocculation phenomena and the polyelectrolyte reconformation process under low shear conditions.

When comparing Figures 20b and 20c, the requirements for C-PAM contact time and dosage required to reach the maximum floc size of SF and REF were reversed as the applied shear conditions was altered. The occurrence of this was not found with LF. Hence, it seems that at high shear LF is more sensitive to overdose of C-PAM than SF and REF. However, if the specific surface areas of the fractions (Table 2) are taken into account, it leads to a result that at low shear conditions LF requires a higher C-PAM dosage than SF and REF. This finding is in good accordance with the adsorption experiments in this work (Paper III) that under low shear conditions the adsorption of C-PAM (g/m2) is greater on LF than on SF and REF (an example shown in Figure 16b). Hence, it can be assumed that this phenomenon arises from the differences in microstructure and accessibility of the different pulp fractions.

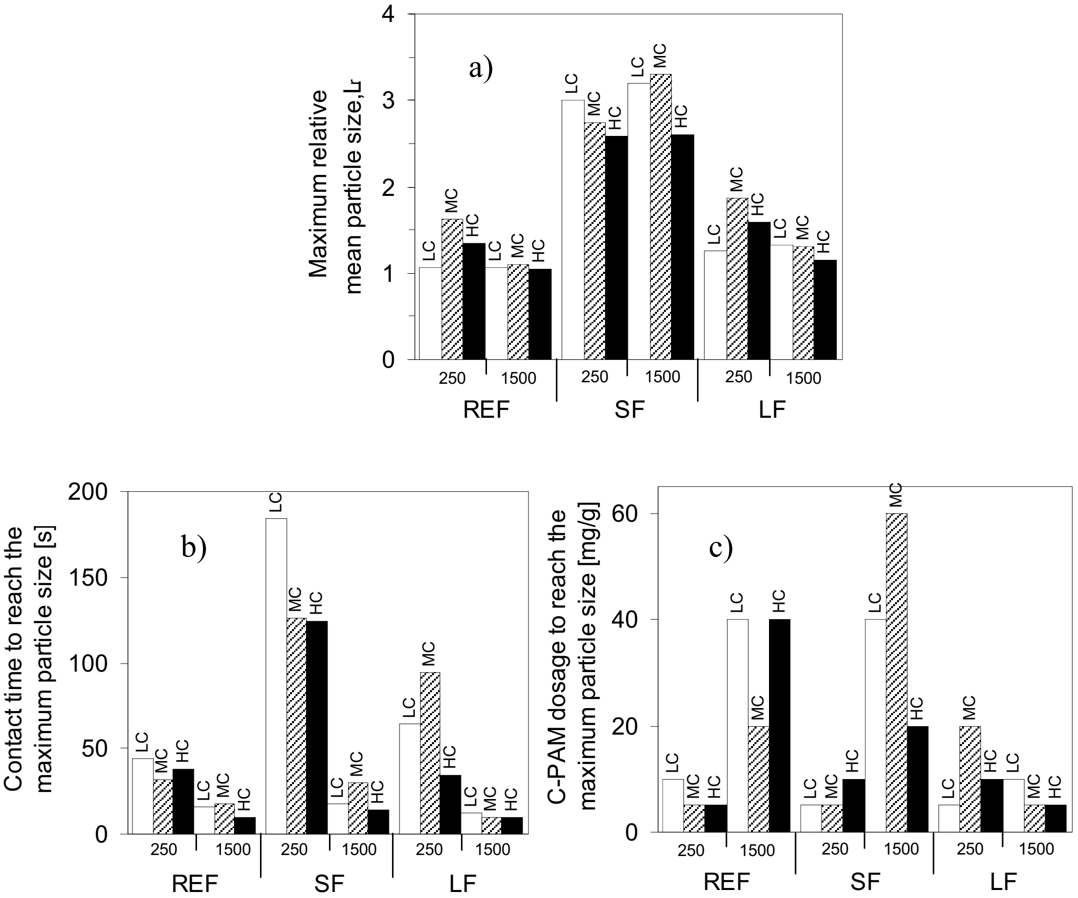

Figure 20. Effect of pulp fraction (REF, SF, LF), C-PAM charge density (LC, MC, HC) and shear level (250 rpm, 1500 rpm) on a) particle size; b) contact time; and c) C-PAM dosage. (Paper IV)

It is well known that there is an optimum polyelectrolyte dosage to reach the maximum flocculation of pulp suspensions (Swerin et al. 1996, Solberg and Wågberg 2003). This optimum was also found in these experiments, and its location was dependent on the shear force applied (Figure 21). Generally, the maximum relative particle size decreased strongly if higher polyelectrolyte dosages than the amount required for the maximum flocculation were used under low shear conditions. Presumably, it indicates steric stabilization of the pulp particles as well as C-PAM conformational changes due to the increased polyelectrolyte concentration and/or effects of hydrodynamic shear. Under high shear conditions, the maximum flocculation was observed at higher C-PAM dosages and only a slight decrease of particle size was detected when higher than optimum dosages were added into pulp suspension. In other words, strong flocculation was attained with a broader dosage range under high shear conditions than under low shear conditions. This effect was not found in the flocculation experiments described above (Paper I), where the maximum polyelectrolyte dosages were lower (max. 20 mg/g) and the applied stirring speeds higher (400 rpm).

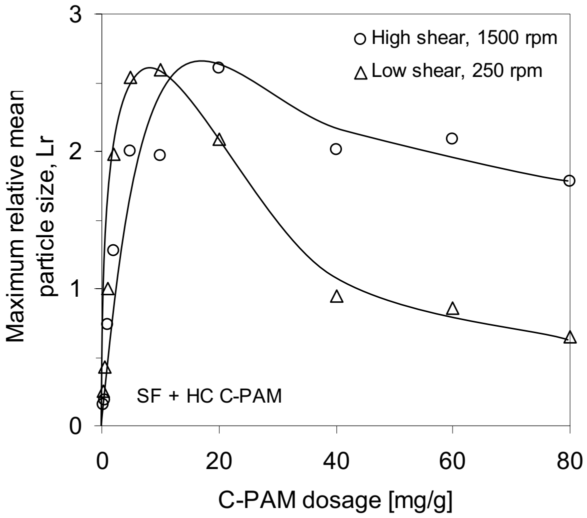

Figure 21. *Effect of shear level on the flocculation of SF (TMP short fraction) with HMW-HC C-PAM. (Paper IV)*

4.4 Effects of fines and microfibrillated cellulose on papermaking

As the fines and MFCs are an essential part of a pulp suspension, some of their influences on papermaking were studied in this work. The influence of RMP pulp suspension components on the adsorption and retention of clay filler was studied in Paper II. The effect of MFC dosage to the drainage of kraft pulp suspension and to the strength properties of paper was investigated in Paper V.

4.4.1 Effect of mechanical pulp fines on the adsorption and retention of clay filler

The influence of different RMP fractions (fibril fines, flake fines, fibers) on the adsorption of clay particles was studied by using HMW-LC C-PAM as fixative (Paper II). The concentration of free clay particles in a stirred beaker was detected by turbidimetrically analyzing the filtrate passing through a screen having a cut-off of 5 µm. In this study the stirring was continued during the filtration, so that formation of a fiber mat on the screen was restricted (delayed). Expectedly, the cationic polyelectrolyte promoted the deposition of clay particles on the RMP fractions. Assuming that a mutual flocculation of clay particles was the preferred retention mechanism; the retention would have been independent of the pulp properties. However, the results for the suspensions containing

C-PAM demonstrated that at polymer dosages above 1 mg/g both fines fractions adsorbed more filler than did the fiber fraction (Figure 22). At high C-PAM dosages the amount of clay adsorbed onto RMP flake fines was nearly twofold with relation to the state when RMP fiber fraction was used.

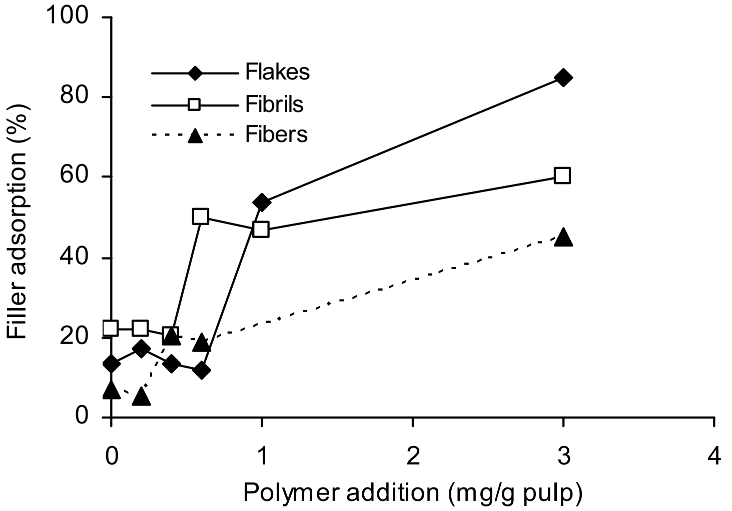

Figure 22. *Adsorption of clay filler particles on pulp fractions as a function of HMW-LC C-PAM dosage. Pulp consistency 1 g/l. Clay dosage 0.7 g/g pulp. (▲) Refiner mechanical pulp long fiber fraction; (♦) Refiner mechanical pulp flake fines; (□) Refiner mechanical pulp fibril fines. (Paper II)*

Presumably, more clay was adsorbed onto the fines fractions than onto the fibers in the presence of C-PAM, since the both fines have larger external surface areas than the fiber fraction. It was also shown that the RMP flake fines adsorbed higher amount of clay than the RMP fibril fines. Probably this was due to the differences in their surface charge densities (μeq/m^2, Table 2), mainly arisen from their dislike surface chemical compositions (Table I in Paper II). Another possible explanation is the hydrodynamic avoidance effect which has more influence between unequal-sized particles (Van de Ven 1981), and thus favors the collisions of flaky clay particles with RMP flake fines rather than with RMP fibril fines and fibers (REF). In other words, in addition to electrostatic interactions, the size and geometry of pulp fractions may as well affect the adsorption of clay. Partly similar findings have been presented earlier by Marton (1980) in their studies with fibers, fines, clays and cationic starch. He concluded that fines played a determining role in the surface interactions of papermaking additives. In addition to the accessible surface area, the surface structure and charge properties of the particles was described being an important factor in these interactions. Even if, he used materials slightly different than the ones in the current work, these two experiments are complementary and supportive.

The retention of clay particles into a consolidating pulp suspension was studied by filtering the different pulp fractions with added clay and HMW-LC C-PAM (Paper II). The filtering was performed under low shear conditions, so that a filter cake was allowed to form on the filter media. The clay retention was based on the above described physical and electrostatic interactions of the fillers and pulp fractions, and as well on the mechanical entrapment of the filler into the filter cake formed. The results presented previously by Solberg and Wågberg (2002) showed that filtration or sieving has only a minor effect on the retention of ground calcium carbonate (GCC) filler particles, and they proposed also, that adsorption prior filter cake formation is the predominant mechanism for GCC retention. In contrast, Davison (1982) concluded that filtration is the primary mechanism of fine particle retention due to the entrapment of self-agglomerated flocs of single particles into the filter cake. These contradictory standpoints are discussed also in a review by Hubbe and Heitmann (2007).

The above shown results (Figure 22) of our clay adsorption experiments indicate that, in the presence of C-PAM, RMP fines adsorb more clay particles than RMP fibers. On the contrary, in our filtration experiments (Figure 23) the retention of clay by RMP fines was lower than by RMP fibers, especially at low C-PAM dosages. In this work the plate-like shape of the clay particles and the low shear conditions may have promoted clay retention during filtration. Under low shear conditions, that fines require a substantially longer contact time for maximum flocculation than the long fiber fraction may be a noteworthy subject (Paper IV). Nonetheless, it can be suggested that the mechanism of clay retention is highly dependent on the properties of the suspension components and their mutual interaction. Specifically targeted utilization of fines gives a possibility to affect the adsorption and the retention of filler particles in papermaking pulp suspensions.

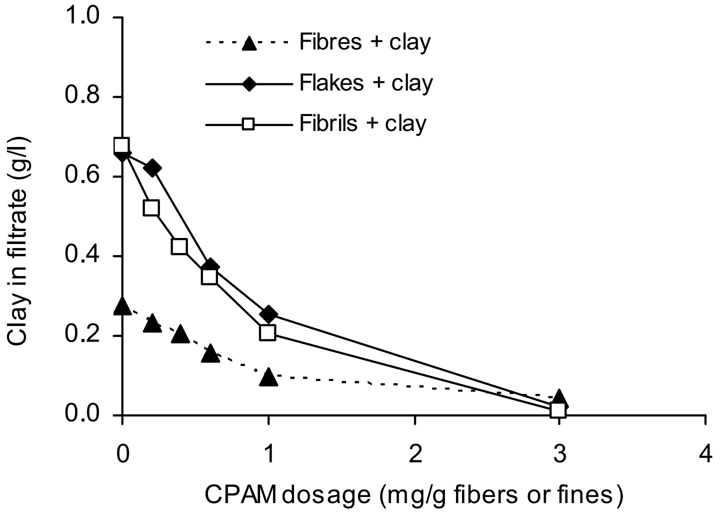

Figure 23. *Retention of clay filler particles in filtration as a function of HMW-LC C-PAM dosage. Pulp consistency 1 g/l. Clay dosage 0.7 g/g pulp. (▲) Refiner mechanical pulp long fiber fraction and clay; (♦) Refiner mechanical pulp flake fines and clay; (□) Refiner mechanical pulp fibril fines and clay. (Paper II)*

4.4.2 Effect of MFC on the relation between pulp drainage and paper strength

It has been already discussed above that cationic starch (CS) has been widely used as retention and strengthening agent in papermaking. In addition, MFC has been used successfully to enhance the strength properties of starch and amylopectin biocomposite films (Dufresne 2000; López-Rubio et al. 2007; Svagan et al. 2007). Hence, it was interesting to examine their combined utilization in papermaking pulp suspensions. In Paper V it was shown that the drainage rate of a pulp suspension decelerated linearly with increasing MFC content. In addition, the dosage of MFC significantly increased the strength properties of paper through increased bonding (Paper V). These findings are in accordance with previous findings by other authors for addition of fines or MFC (Taniguchi and Okamura 1998; Krogerus et al. 2002; Retulainen et al. 2002; Yano and Nakahara 2004; Berglund 2005; Ahola et al. 2008a; Henriksson et al. 2008; Pääkkö et al. 2008; Zimmermann et al. 2009).

In this work, a linear relation between tensile strength paper and drainage time of pulp suspension was found, since, both of these properties increased almost linearly with the increasing MFC content (Figure 24a). However, the out-of-plane strength was found not to increase linearly, even though the drainage time increased (Figure 24b). A possible reason for this may be a layering of fibers and MFC during the drainage process, which further promotes delamination of the paper structure under out-of-plane strength testing. According to these results, the optimum MFC content could be considered as ca. 30 mg/g pulp (3 % w/w); even though the drainage rate continuously increased. At this concentration a significant improvement in paper strength was observed without severe loss in drainage rate: whereas a further increased addition of MFC led to a strong increase of drainage time. Nevertheless, this optimum concentration is a system specific value, and depends on the degree of beating, properties of MFC, type of polyelectrolyte, as well as on the physical and chemical process conditions.

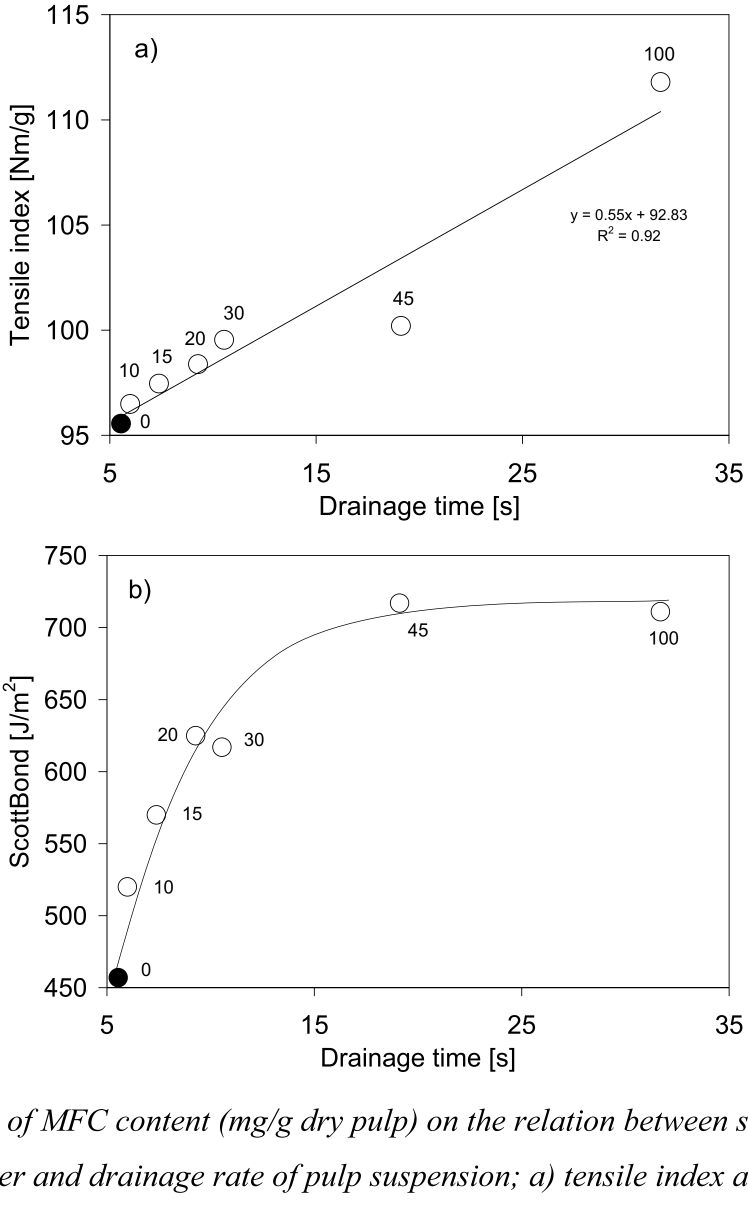

Figure 24. *Effect of MFC content (mg/g dry pulp) on the relation between strength properties of paper and drainage rate of pulp suspension; a) tensile index and b) out-of-plane strength (ScottBond). 30 min beaten pulp was used, and 15 mg/g dry pulp of cationic starch was added to retain the MFC. Sample MFCF10. (Paper V)*

The properties of different MFCs have been discussed above, and it was now also stated that the addition of CS and MFC enhances the paper strength but simultaneously impair the drainage properties of the pulp suspension. Because the properties of the produced fines and MFCs were highly dissimilar, the effects of the different MFCs on the drainage and strength properties were further studied using the optimum dosages of MFC and CS discovered in Paper V. In order to gain some additional perspective, the results were compared against the results achieved by only beating the kraft pulp fibers.

Generally, as MFC was added without CS, the results substantially followed the ones obtained with beating (Paper V). The addition of CS prior to MFC addition into the kraft pulp suspension increased paper strength properties well above the results achieved by beating (Figures 25a and 25b). The strength properties and the drainage rate of 10 min beaten pulp were both dependent on the type of MFC used. The addition of carboxymethylated MFC (CMMFCF4) yielded superior strength and drainage properties, whereas MFCF4 generated the slowest drainage and BKP fines the least increase in strength. The effect of CMMFCF4 addition to a 10 min beaten pulp, with CS used as fixative, introduced an exceptional result. The tensile strength doubled and the out-of-plane strength quadrupled without any simultaneous decrease in drainage rate.

Significant improvements of paper strength using partially carboxymethylated fibers (Walecka 1956; Fors 2000) or NFC (Ahola et al. 2008a; Henriksson et al. 2008) have been reported earlier. Retulainen et al. (1993a) has also suggested that CS and fines additions have complementary mechanisms for strengthening fiber bonding, especially if CS is added prior to fines in the long fiber fraction. They stated that the fines not only have the capability to strengthen the peripheral areas of fiber bonds but also form new interfiber connections. Fines primarily exercise a structural influence while CS contributes more by chemical effects. It was also stated that a small part, not all, of the effect is due to the higher retention of fines caused by CS addition. In addition, the combination of MFC with amylopectin (starch) suspension has been found to improve the mechanical properties of films made thereof (Dufresne 2000; López-Rubio et al. 2007; Svagan et al. 2007). However, it is a novel and surprising finding that paper strength can be improved without significant loss in the drainage efficiency of the suspension.

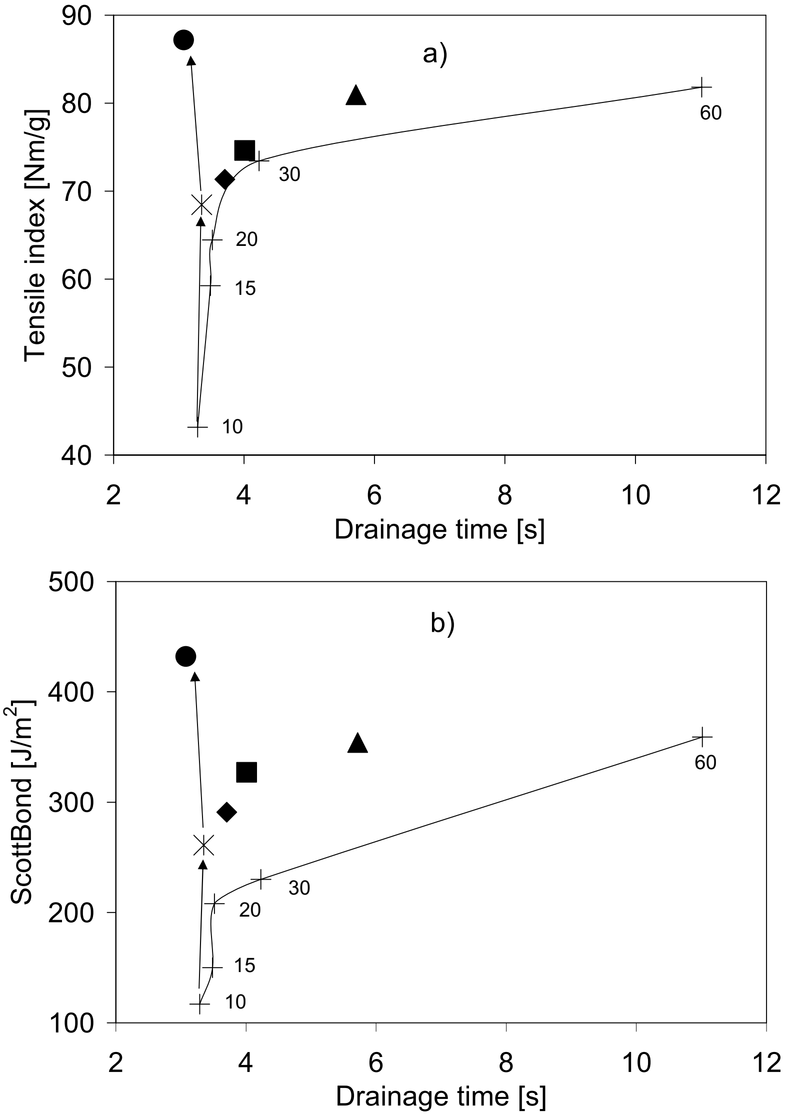

Figure 25. *The relation between strength properties of paper and drainage rate of pulp suspension; a) tensile index and b) out-of-plane strength (ScottBond). The addition of different MFCs and cationic starch (CS) compared to the beating of pulp. The initial pulp was beaten 10 min. Different types of MFCs were added with CS as fixative. Additives: (✳) CS only, (●) CS+CMMFCF4, (■) CS+MFCF10, (▲) CS+MFCF4, (♦) CS+BKP fines. CS dosage was 15 mg/g dry pulp and MFC and fines content 30 mg/g dry pulp. For comparison the effect of beating alone (without any additives) is also shown for 10, 15, 20, 30 and 60 min beaten pulps (+). (Paper V)*

Some assumptions of the reasons for this exceptional result can be made. As discussed above, CS has extremely branched molecular structure, low degree of substitution and a small radius of gyration in comparison to C-PAM. Hence it adsorbs in a thin layer on the surfaces of fibers. In addition, the microfibrils and microfibril bundles of CMMFCF4 were presumably shortened during the carboxymethylation and fluidization processes. The small size, together with the high charge, allows a thin MFC layer to be formed on the adsorbed CS. As a result, the formed nano-network coated the fibers rather than filled the interstices between them. In comparison to the other materials studied, this phenomenon left the pores in the consolidating fiber network less tortuous and more open for free water flow. In addition, the diverse orientation of the CMMFCF4 microfibrils (Figure 13c) may have been beneficial for the development strength properties by their enhanced capability to load distribution in multiple directions. Additionally, as discussed above in chapter 2.3, MFC particles are in the size-class of macromolecules. This leads to an inference that anionic microfibrils and cationic starch molecules may act as polyelectrolyte complexes (PEC) or polymer multilayers (PEM), and thus enable the exceptional result described above. This field has been studied and discussed recently by e.g. Eriksson et al. (2006), Gärdlund et al. (2007), Ahola et al. (2008a) and (2008b), Wågberg et al. (2008), Salmi (2009), Salmi et al. (2009) and Ankerfors et al. (2009).

However, there are still many other parameters and paper properties affected by fines or MFC addition in the papermaking process, and the papermaking systems are each very unique in their raw materials, chemistry and physical conditions. Thus, the results must be carefully considered with respect to each individual process.

Generally speaking, it is interesting to observe that the correlation between strength and drainage is not necessarily constant. It is also noteworthy that the MFC or fines content (w/w-% of total pulp) used in this experiment was only 3 % (w/w), whereas in earlier studies (Aaltio 1962; Retulainen et al. 1993a; 1993b and 2002; Krogerus et al. 2002; Xu and Pelton 2005; Eriksen et al. 2008) higher contents, 4 - 30 % (w/w), have been used. Ahola et al. (2008a) on the other hand used contents of 1 - 10 % (w/w), which are partly closer to contents used in the present work. Retulainen (1993a) highlighted as well the importance of addition sequence (starch and carboxymethyl cellulose were added prior fines into the pulp suspension), which was shown to further improve paper strength. A similar order was also used in this work; CS was allowed to reach almost its equilibrium state prior to MFC addition. This sequence is different from the general practice, where cationic polyelectrolyte is added into the fiber-fines mixture. It reveals again the above discussed subject of optimizing the polyelectrolyte dosing strategy individually for each pulp fraction.

A detailed explanation for the superior properties of the combined use of CS and CMMFCF4 was not found. Hence, work will be continued in this field. Nevertheless, it can be generally concluded that the drainage of the pulp suspension, and the strength properties of the paper made thereof, are strongly influenced by the type of the fines or MFC materials added, as well as by the prevailing conditions. In addition, it was generally important to know that the raw materials and production methods of fines and MFCs have significant influence in their characteristics, which further affect their industrial utilization potential.

5 CONCLUDING REMARKS

It is possible to produce and isolate different types of cellulosic fines and microfibrillated cellulose suspensions having unique physical and chemical characteristics. As high molar mass cationic polyelectrolytes are added into these suspensions, it is the combination of the properties of the polyelectrolytes and the cellulosic fractions which define the adsorption and flocculation phenomena. None of these properties alone can fully describe these phenomena. When multitude molecules are concerned, these two phenomena are parallel but partly independent events. Thus, the flocculation of polydisperse, porous and small-sized cellulosic material should not be directly interpreted only through adsorption studies, nor vice versa.

The fractionation of pulp suspension followed by the optimization of polyelectrolyte type and dosage individually for each fraction opens a novel approach to control the interrelation of forming-, retention-, drainage- and flocculation phenomena in the paper machine environment. This gives new possibilities to enhance the properties of paper and increase the productivity of the papermaking process. For example, the clay filler adsorption and retention in fiber suspensions can be influenced by the properties of the fiber fraction used. In addition, by optimum selection of the process conditions as well as the properties and amount of cationic polyelectrolyte and MFC used, the strength of paper may be increased without deteriorating the drainage properties of the pulp suspension.

It can be also concluded that there is still some hidden papermaking potential which could be gained by more specific treatment and utilization of cellulosic fines materials. For example, different types of fines could be purposely produced and further modified, and thereafter added into different stages of a papermaking process. Alternatively, fines fractions could be isolated from one paper grade, then stored, and added later into another paper grade manufactured in the same (or another) production line. Perhaps, both paper grades could then gain value added. In addition, the productivity and cost-effectiveness of a papermaking process could be enhanced by isolating the fines and long fiber fractions and thereafter treating them separately. The new aspects shown in this work may be utilized not only in papermaking but as well in other fields of industry and science. Thus, even it is not discussed in this work; one can just imagine what kind of possible applications specific cellulosic fines and MFCs would have e.g. in the food-, pharmaceutical-, cosmetic-, construction-, or electronics industry. Also in those fields, the properties of the cellulosic fractions and their interactions with polyelectrolytes are relevant topics.

Due to the rapidly advancing materials and methods in the field of nanotechnology, there is a broad field open for further experimental studies. If the number of different raw materials, production and modification methods, and conditions are considered, the terms "fines" and "microfibrillated cellulose" are not specific enough to differentiate the multiple grades possible to produce. The properties of these particles should be defined and characterized in more detail, as has been already taken place with fiber materials in the field of traditional pulp- and papermaking. For this reason, there is a further demand for new characterization methods as well as for development of the current methods to further promote the utilization of these small-sized biomaterial particles.

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