MODIFICATION OF CELLULOSIC FIBERS BY CARBOXYMETHYL CELLULOSE - EFFECTS ON FIBER AND SHEET PROPERTIES
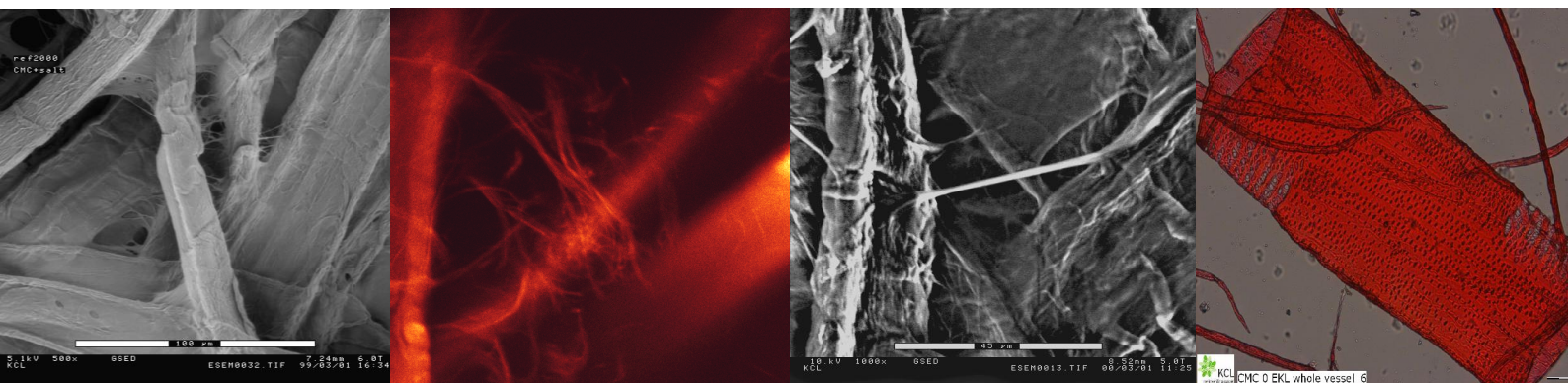
Minna Blomstedt

MODIFICATION OF CELLULOSIC FIBERS BY CARBOXYMETHYL CELLULOSE - EFFECTS ON FIBER AND SHEET PROPERTIES

Minna Blomstedt

Dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the Department of Forest Products Technology for public examination and debate in Auditorium AS1 at Helsinki University of Technology (Espoo, Finland) on the 30th of November, 2007, at 12 noon.

Author   Minna Blomstedt

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Modification of cellulosic fibers by carboxymethyl cellulose - effects on fiber and sheet properties

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Abstract
The main purpose of this study was to determine whether fiber and sheet properties can be improved by modifying the surface of ECF-bleached softwood and hardwood pulps with carboxymethyl cellulose (CMC).
The main objectives of the study were to evaluate;
- the effect of CMC modification and modification conditions on handsheet and fiber properties
- the combined effect of CMC and surfactant modification on softwood handsheet properties
- the effect of different drying techniques (freely/restrained) on the handsheets properties of hardwood pulp
- the effect of fiber morphology on CMC modification of hardwood pulp
- the effect of fines and beating on CMC-modified pulps

Fiber properties were investigated by fiber analysis, measurement of water retention values (WRV) and confocal laser scanning microscopy (CLSM). Sheet properties were studied by testing the sheets and by imaging the CMC-modified sheets with environmental scanning electron microscopy (ESEM). The role of fines was studied by fractionating hardwood pulps before and after CMC modification. All CMC treatments were made for both beaten and unbeaten pulps, in order to examine the significance of beating.

In general, the sorption degree of CMC on pulp increased with more extensive beating whereas it decreased with a higher degree of substitution of CMC. After CMC modification the water retention value (WRV) increased for both hardwood pulps and especially for softwood pulps, which accounted for a significant improvement in the internal and tensile strength properties of the handsheets. A unique feature in these experiments was that tensile properties improved remarkably for the CMC-modified hardwood handsheets when dried under restraint, which is considered closer to the drying process in real papermaking conditions. The addition of CMC and surfactant increased the internal and tensile strength properties further. Specific microfibril bonds on the surface of the handsheets revealed by electron microscopy could partly explain the improved strength properties of the CMC-modified softwood sheets. As the sorption conditions used in this study were similar to those in a commercial papermaking system, the surface modification method may be useful in practice, for example, after the refining stage. Preliminary results show that also the vessel picking tendency of eucalyptus pulp could be significantly reduced through CMC modification.

Keywords   Chemical pulp, surface modification, CMC, ESEM, fractionation, sheet and fiber properties

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Työn ohjaaja	Ph.D. Eero Kontturi

Tiivistelmä

Työn päämääränä oli määrittää, kuinka ECF-valkaistun havu- ja lehtipuusellun ominaisuuksia voidaan parantaa muokkaamalla kuitujen pintaa karboksimetyyliselluloosalla (CMC).

Tutkimuksen pääasialliset tavoitteet:
- kartoittaa CMC-muokkauksen ja muokkaus-olosuhteiden vaikutuksia kuitujen ja käsiarkkien ominaisuuksiin
- tutkia CMC:n ja pinta-aktiivisten aineiden yhteisvaikutusta havupuusellusta valmistettujen käsiarkkien ominaisuuksiin
- selvittää erilaisten kuivaustapojen (vapaa/rajattu) vaikutus lehtipuusellusta valmistettujen käsiarkkien ominaisuuksiin
- löytää yhteys kuitumorfologian ja CMC-muokatun lehtipuusellun välillä
- määrittää hienoaineen ja jauhatuksen vaikutus CMC-muokattuun selluun

Kuituominaisuuksia tutkittiin kuituanalyysillä, mittaamalla kuitujen vedenpidätyskykyä (WRV) ja konfokaali laserpyyhkäisymikroskoopilla (CLSM). Käsiarkkien ominaisuuksia selvitettiin tavallisilla arkintestausmenetelmillä ja kuvaamalla arkkeja pyyhkäisyelektronimikroskoopilla (ESEM). Hienoaineen vaikutusta tutkittiin fraktioimalla lehtipuusellu ennen ja jälkeen CMC-muokkausta. Kaikki CMC-käsittelyt tehtiin jauhetulle ja jauhamattomalle massalle, jotta jauhatuksen merkitystä voitaisiin paremmin arvioida.

Kiinnittyneen CMC:n määrä yleisesti ottaen nousi lisääntyvän jauhatuksen funktiona ja laski lisääntyvän CMC:n substituutioasteen funktiona. Lehtipuusellun ja etenkin havupuusellun CMC-muokkaus nosti kuitujen vedenpidätyskykyä (WRV), mikä paransi huomattavasti kuiduista valmistettujen käsiarkkien sisäistä lujuutta ja vetolujuutta. Yksi tutkimuksen tärkeimmistä tuloksista oli, että CMC-käsittely paransi merkittävästi käsiarkkien lujuusominaisuuksia, kun arkit kuivattiin siten, että niitä ei päästetty kutistumaan. Tällainen rajattu kuivaus on lähempänä todellisia paperinvalmistusolosuhteita. Pinta-aktiivisen aineen ja CMC:n käsittely paransi edelleen kuituverkoston sisäistä lujuutta ja vetolujuutta. Erityiset mikrofibrillisidokset kuitujen välillä voivat osaltaan selittää CMC-muokatun havupuusellun paremmat lujuusominaisuudet. CMC-muokkauksen olosuhteet olivat siis sellaisia, jotka voi helposti sisällyttää kaupalliseen paperinvalmistusprosessiin, esimerkiksi jauhatusvaiheen jälkeen. Alustavat tulokset osoittivat myös, että putkilosolujen haitalliset vaikutukset paperin painatusvaiheessa (nk. "vessel picking") vähenivät selvästi kuitujen CMC-muokkauksen vaikutuksesta.

Asiasanat   Kemiallinen massa, pinta muokkaus, CMC, ESEM, fraktioni, kuitu- ja arkkiominaisuudet

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To Fredde

I have little patience with scientists who take a board of wood, look for its thinnest part, and drill a great number of holes where drilling is easy.
-- Albert Einstein --

PREFACE

Most of the work described in this thesis was carried out in the Laboratory of Forest Products Chemistry at Helsinki University of Technology during 1999-2001 and 2004-2006. A part was carried out in the laboratory of M-real's Technology Centre in Örnsköldsvik, Sweden, in 2001. Financial support from the Fibre Engineering (FINE) Forest Cluster Programme WOOD WISDOM conducted by TEKES (1998-2001), the Sustainpack project (6th Framework program of European Union, 2004->) and from Andritz, Myllykoski Paper, Metso, M-real, Stora-Enso and UPM-Kymmene is gratefully acknowledged.

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Espoo, 20th of June 2007
Minna Blomstedt

LIST OF PUBLICATIONS

The thesis is based on the following five manuscripts, which are referred to in the text by their Roman numerals (I-V). Some new results are also included regarding the vessel picking tendency of eucalyptus pulp sheets.

I. Blomstedt, M., Mitikka-Eklund, M. and Vuorinen, T. (2007) Simplified modification of bleached softwood pulp with carboxymethyl cellulose. *Appita **60**(4): 309-314.*

II. Blomstedt, M. and Vuorinen, T. (2007) Modification of softwood kraft pulp with carboxymethyl cellulose and cationic surfactants. *J. Wood Sci. **53**(3): 223-228*.

III. Blomstedt, M. and Vuorinen, T. (2006) Fractionation of CMC-modified hardwood pulp. *Appita* **59**(1): 44-49.

IV. Blomstedt, M., Kontturi, E. and Vuorinen, T. (2007) Optimising CMC sorption in order to improve tensile stiffness of hardwood pulp sheets. *Nord. Pulp Pap. Res. J. **22**(3): 336-342.*

V. Blomstedt, M., Kontturi, E. and Vuorinen, T. (2007) Surface modification of eucalyptus pulp by carboxymethyl cellulose: effect of fiber properties and paper strength properties. *O Papel (6): 51-63.*

AUTHOR´S CONTRIBUTION

I   Minna Blomstedt defined the research plan together with the co-author, performed or supervised the experimental work in part, interpreted the results, and wrote the manuscript.

II-V Minna Blomstedt defined the research plan together with the co-author, performed or supervised the experimental work, interpreted the results, and wrote the manuscript.

SUPPORTING PUBLICATIONS AND PROCEEDINGS

Mitikka-Eklund, M., Halttunen, M., Melander, M., Ruuttunen, K. and Vuorinen, T. (1999) Fibre engineering. *10th International Symposium on Wood and Pulping Chemistry*, June 7-10, Yokohama, Japan, pp. 432-439.

Melander, M., Mitikka-Eklund, M. and Vuorinen, T. (2000) Sorption of carboxymethylcellulose on cellulose fibers, *Paper and Coating Chemistry Symposium,* June 6-8, Stockholm, Sweden, pp. 23.

Melander, M. and Vuorinen, T. (2000) A new approach to determining the degree of polymerisation of CMC by SEC. *Sixth European Workshop on Lignocellulosics and Pulp (EWLP),* September 3-6, Bordeaux, France, pp. 453-456.

Melander, M. and Vuorinen, T. (2001) Determination of the degree of polymerisation of carboxymethyl cellulose by size exclusion chromatography. *Carbohydrate Polymers*, **46** (3): 227-233.

Blomstedt, M., Mitikka-Eklund, M., Kontturi, E. and Vuorinen, T. (2007) Chemical modification of cellulosic fibers. *14th International Symposium in Wood Fibre and Pulping Chemsitry (ISWFPC)*, June 25-28, Durban, South Africa, 9 p.

Blomstedt, M., Panula-Ontto, S., Kontturi, E. and Vuorinen, T. (2007) A novel method to reduce vessel picking of eucalyptus pulp sheets by carboxymethyl cellulose modification ? *Submitted to O Papel.*

LIST OF SYMBOLS AND ABBREVIATIONS

ECF   elemental chlorine free
DS   degree of substitution
DP   degree of polymerization
Mw   molecular weight
ML   middle lamella in fiber wall
ML+P   compound middle lamella includes middle lamella and primary wall
S1   outer layer of secondary cell wall
S2   middle layer of secondary cell wall
S3   inner layer of secondary cell wall
PAE   polyamide(amine)epichlorohydrin
CTMP   chemi-thermomechanical pulp
PFI   Papirindustriens Forskningsinstitutt (Norway)
rev.   revolutions
SRE   specific refining energy
$C_{10}TAB$ decyltrimethylammonium bromide, $C_{10}H_{21}N(CH_3)_3Br$
$C_{12}TAB$ dodecyltrimethylammonium bromide, $C_{12}H_{25}N(CH_3)_3Br$
$C_{14}TAB$ tetradecyltrimethylammonium bromide, $C_{14}H_{29}N(CH_3)_3Br$
$C_{16}TAB$ hexadecyltrimethylammonium bromide, $C_{16}H_{33}N(CH_3)_3Br$
GC   gas chromatography
DDJ   dynamic drainage jar
ESEM   environmental scanning electron microscopy
GSED   gaseous secondary electron detetor
SR   scopper-riegler number
WRV   water retention value
CLSM   confocal laser scanning microscopy
CMF   cellulose microfibrils
MD   machine direction
REF   reference (untreated) pulp
CMC   carboxymethyl cellulose-treated pulp
U   unbeaten pulp
B   beaten pulp
HW   hardwood pulp
SW   softwood pulp
drum   drum-dried sheets
plate   plate-dried sheets

CONTENTS

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1 INTRODUCTION

A recent trend in papermaking is toward "weaker" paper sheets. This is a result of several factors: lower basis weights and increasing use of hardwood pulp, recycled fibers and minerals. Despite these changes, papermakers would like to maintain or even enhance the strength of paper. To accomplish this, papermakers increasingly use chemical strength aids, which are rather expensive. Various strength aids, for example cationic starch products, can be used to promote inter-fiber bonding and to improve the dry strength of paper. Chapter 3 reviews and discusses the fiber and paper strength properties in more detail.

The goal of this study was to find a new approach to modify chemically the properties of fibers as a means to improve fiber quality. In principle, the modification can be directed either to the internal or external cell wall structure of the fibers. Because the internal surface area of the cell wall is so large, a huge amount of chemicals would be needed to change the properties of the internal surface significantly. For this simple reason, it was decided to modify the external surface of the fibers instead of the internal surface. In addition, a polymer, carboxymethyl cellulose (CMC) was chosen for the chemical modification. It has a chain conformation similar to that of cellulose and a high degree of polymerization which prevents penetration into the cell wall. The character of CMC and the effect of CMC modification on pulp and paper properties are discussed in more detail in the background section (Chapter 3.4).

The experimental scheme, including materials and methods used in this study, are described in Chapter 4 and the results of the work are presented and discussed in Chapter 5. In Chapter 5.1, the sorption degree of CMC on softwood and hardwood pulps is evaluated. To gain a broader understanding of the effects of CMC modification on different pulps, sorption experiments were performed on both softwood (spruce) and hardwood pulps (birch, eucalyptus). The effect of

beating was evaluated by modifying unbeaten and beaten pulps. The fiber properties, water retention value (WRV), morphological properties and fiber surface properties, of CMC-modified pulps are discussed in Chapter 5.2. Finally, the sheet properties of softwood and hardwood pulps are presented in Chapter 5.3, which are summarized in the last section. To gain a deeper understanding of the effect of drying the sheets, experiments with restrained drying, which is considered closer to real papermaking, were performed. Additional results concerning the effect of CMC modification on the vessel picking tendency were added (Chapter 5.3.2) in order to explain the decreased vessel content in CMC-modified eucalyptus pulps (Chapter 5.2.3). Finally, Chapter 6 gives the overall conclusions and some suggestions for further research.

2 AIMS AND OUTLINE OF THE STUDY

The overall aim of this thesis was to evaluate if fiber and sheet properties can be improved by CMC modification of hardwood and softwood fibers. A significant improvement in strength properties would make it possible to produce lighter paper products.

The first experiments performed during this work were aimed at finding the suitable sorption conditions of CMC on softwood fibers **(Paper I).** The role of beating of pulp, pH value, degree of substitution (DS) and electrolyte concentration was investigated as a function of the sorbed amount of CMC. The effect of higher electrolyte concentration was examined in order to study the effect of mill closure and increasing electrolyte concentrations on the sorbed amount of CMC. The hypothesis was that the attachment of CMC on the external cellulose surface could be controlled by choosing the appropriate degree of polymerization (DP) and degree of substitution (DS) of CMC. Furthermore, because CMC has a similar chain conformation with cellulose it was assumed that CMC could increase the charged groups on the fiber surface and enabling

association with cellulose microfibrils, which would theoretically lead to better strength properties.

After the factors affecting the sorption conditions had been investigated, the study continued by studying the combined effect of CMC and cationic surfactants on paper properties **(Paper II).** In order to obtain a deeper understanding of the behavior of different fibers, CMC experiments were also performed on hardwood pulp **(Paper III, IV, V).** In addition, the role of fiber morphology (fiber length, curl, vessel and fines content) was studied by fractionating hardwood pulps before **(Paper III)** and after CMC modification **(Paper IV).** The main purpose of the fractionation experiments was to get more information on whether CMC is sorbed on fibers or fines and how other morphological properties of the fibers are affected after the CMC modification.

Different drying conditions of paper sheets have shown to have significant effect on the final strength properties of paper. Therefore, the effects of different dying techniques were studied by drying hardwood sheets freely in a drum dryer or under restraint by using drying plates **(Paper IV, V).** The main aims of these experiments were to perform the experiments closer to the real papermaking conditions. All CMC treatments were made for both beaten and unbeaten pulps, in order to examine the significance of beating.

Generally, the fiber properties were investigated by fiber analysis **(Paper III, IV, V),** measurement of water retention values **(Paper I, IV, V)** and confocal laser scanning microscopy. Sheet properties were studied by testing the sheets **(Paper I-V)** and by imaging the CMC-modified sheets with environmental scanning electron microscopy **(Paper I, II).**

All sorption conditions were chosen to be similar to those in a commercial papermaking system, since this surface modification method presented in this thesis may be useful in practice, for example, after the refining stage.

3 BACKGROUND

3.1 Some features of fibers

Wood fiber properties can be divided into 1) *chemical properties (*chemical composition and structure) 2) *structural properties* (S2 fibril angle etc.) and 3) *morphological properties* (cell wall thickness, fiber width and fiber length). For example the morphological properties have been shown to be responsible for 70% to 90% of paper property variations (Paavilainen 2002). In the next Chapters, the properties mentioned above are explained in more detail.

3.1.1 Chemical composition of wood

The wood cell consists of cellulose, hemicellulose and lignin but also of small amounts of extractives *(Table 1, Figure 2a).* A simplified picture is that the main component cellulose forms a skeleton which is surrounded by other substances functioning as matrix (hemicelluloses and lignin) and encrusting (lignin) materials (Sjöström 1993). *Cellulose* is a linear polymer (homopolysaccharide) composed of D-glucose units joined together by β-1,4 glycosidic bonds and has a DP of up to 10000 (Goring et al. 1962) (after chemical pulping around 500-2000, (de Choudens et al. 1999)). The smallest building element in the cellulose skeleton is often considered to be a microfibril (size 3-5 nm) (Beck-Candanedo et al. 2005), which consists of 30-40 parallell cellulose chains. When the microfibrils are further aggregated they form fibrils (20 nm) or lamellae. In other words, cellulose forms the inner building blocks of the microfibrils and they can exist in either amorphous or crystalline form within the microfibrils *(Figure 1c).* Amorphous hemicelluloses and lignin are located in the spaces between the microfibrils.

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Table 1. *Natural composition of pine and birch and the kraft pulps derived from them (Roberts 1996).*

Component	Wood component		Kraft pulp component	
	Pine (%)	Birch (%)	Pine (%)	Birch (%)
Cellulose	39	40	73	64
Hemicellulose	30	37	19	32
Lignin	27	20	6	4
Extractives	4	3	1	1

Hemicelluloses constitute about 25% to 40% of the wood material and are a group of branched polysaccharide polymers (heteropolysaccharide) built of xylan, glucomannan, galactoglucomannan, arabinogalactan and galactan, with low molecular weight (DP 50-300) (Paavilainen 2002). The main group of hemicellulose in softwood is galactoglucomannan and in hardwood glucuronoxylan. Because hemicelluloses exist in amorphous form, these polymers are chemically not as stabile as cellulose, and thus partly dissolve in both acid and alkaline pulping conditions (Gullichsen 2000b, Meller 1965). It is widely recognized that hemicelluloses, due to increased bonding within or between fibers, are beneficial for pulp and paper properties (Hannuksela et al. 2004, Mitikka-Eklund 1996, Roberts et al. 1983). However, hemicellulose can also function as a physical barrier for diffusion of residual lignin from the fibers (Kantelinen et al. 1993). In contrast, the higher hemicellulose content of kraft pulps may also lead to a more porous surface of kraft fibers (Duchesne et al. 2001).

About 15% to 30% of wood fibers are composed of *lignin.* Lignin, the glue of wood, which binds the wood cells together and, together with hemicellulose, controls the water content within the cell wall. In addition, lignin is a very complex three-dimensional network polymer with hydroxyl phenylpropane groups as the basic units. The concentration of lignin is highest in the middle lamella, although

most of the lignin is found in the cell wall itself. Softwood and hardwood lignin differ in their methoxyl content (Sjöström et al. 1999). Since lignin is responsible for most of the color in the papermaking fiber, it is beneficial to remove as much as possible of the lignin, for example by chemical pulping. Ander et al. have recently shown that delignification does not affect the tensile stiffness of fibers, whereas it does affect their tensile strength, probably due to formation of discontinuities in cooking (Ander et al. 2003).

Wood also contains small quantities of *extractives,* mainly resin and fatty acids and esters, waxes, terpenes and phenolic components, which can relatively easily be removed in alkaline conditions (Roberts 1996). It is beneficial to remove extractives because large amounts of extractives in pulp can disturb the bleaching process and cause quality problems in the end product.

In general, hardwood pulps contain less lignin (17-25%) and more hemicellulose (28-42%) than softwood *(Table 1).* The cellulose content in hardwoods (40-48%) is similar to that of softwoods. After kraft pulping the cellulose content increases for both softwood and hardwood pulps, while hemicellulose, lignin and extractive contents decrease.

3.1.2 Structure of cell wall

The cell walls consist of several layers, namely, the middle lamella (ML), primary cell wall (P), secondary cell wall (S1, S2, S3) (*Figure 1)* and warty layer (W). These layers differ from one another in terms of their structure and chemical composition (Sjöström 1993). The cell wall consists of cellulose microfibrils (Chapter 3.1.1) which are embedded in an amorphous matrix of hemicellulose and lignin. *Figure 1b* illustrates how cellulose and hemicellulose may be distributed between the microfibrils in the secondary cell wall. The microfibrils

wind around the cell axis in different directions either to the right (Z helix) or to the left (S helix).
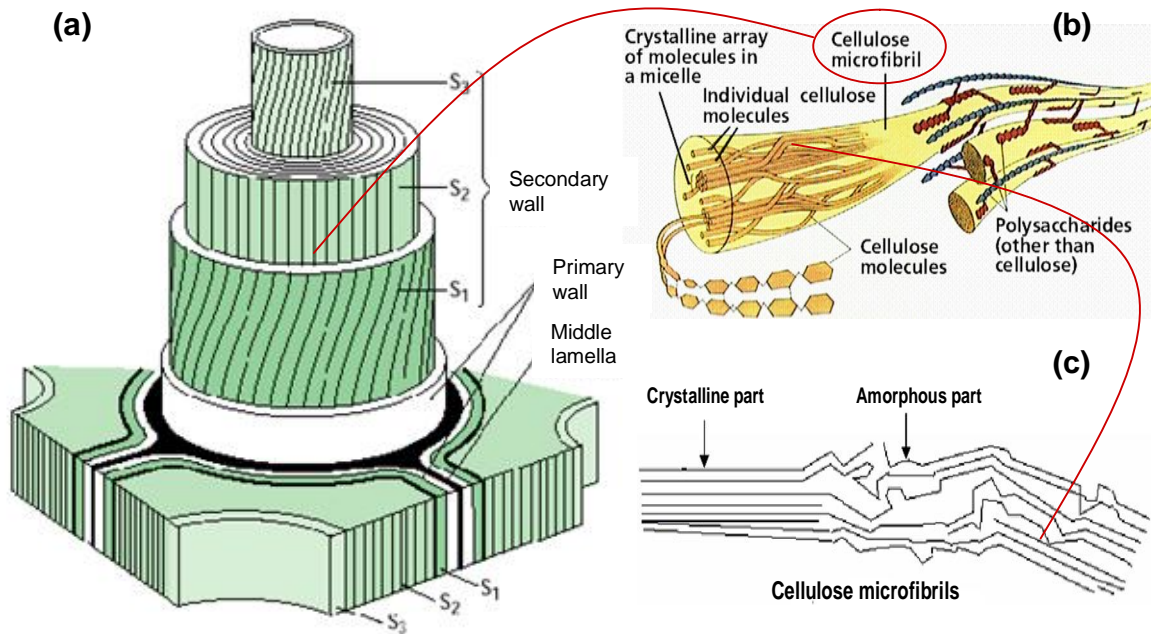
Figure 1. (a) *Simplified composition of the wood cell wall. The cell wall is divided into a primary (P) and secondary (S1, S2, S3) cell wall. The lines in the secondary cell wall represent the microfibrillar alignment (adapted from Taiz et al. 2002).* **(b)** *A schematic representation of the cellulosic microfibrils. Amporphous hemicellulose and some lignin are located between the crystalline cellulose microfibrils.* **(c)** *Scematics of a cellulose microfibril.*

The outermost amorphous and lignin-rich layer, called *middle lamella (ML),* glues the cells together and also gives structural support to and imposes swelling restrictions on the fiber (Salmén 1985). The *primary cell wall (P)* is a thin layer, consisting of cellulose, hemicellulose, pectin, and protein completely embedded in lignin (Sjöström 1993). The microfibrils in the middle lamella form an irregular network (Paavilainen 2002). During refining the primary layer is normally removed completely. The middle lamella, together with the primary cell walls on both sides, is often referred to as the compound middle lamella (ML+P).

The thicker *secondary wall* consists of three layers: a thin outer (S1) and inner layer (S3) and a thick middle (S2) layer. The fibrils in each layer are built up of cellulose microfibrils in which the cellulose chain axis is arranged parallel to the axis of the micrifibrils, thus having a high reinforcing effect in its length direction (Salmén 1985). The *outer layer (S1)* contains 3-4 lamellae where the microfibrils form either a Z helix or an S helix. The microfibril angle of the crossed fibrillar network varies between 50° and 70° in relation to the fiber axis (Sjöström 1993) *(Figure 2b).*

(a)

(b)

Layer	Thickness (µm)	Angle (°)
ML	0.2-1.0	-
P	0.1-0.2	Irregular
S1	0.2-0.3	50-70
S2	1-5	0-30
S3	~1	50-90
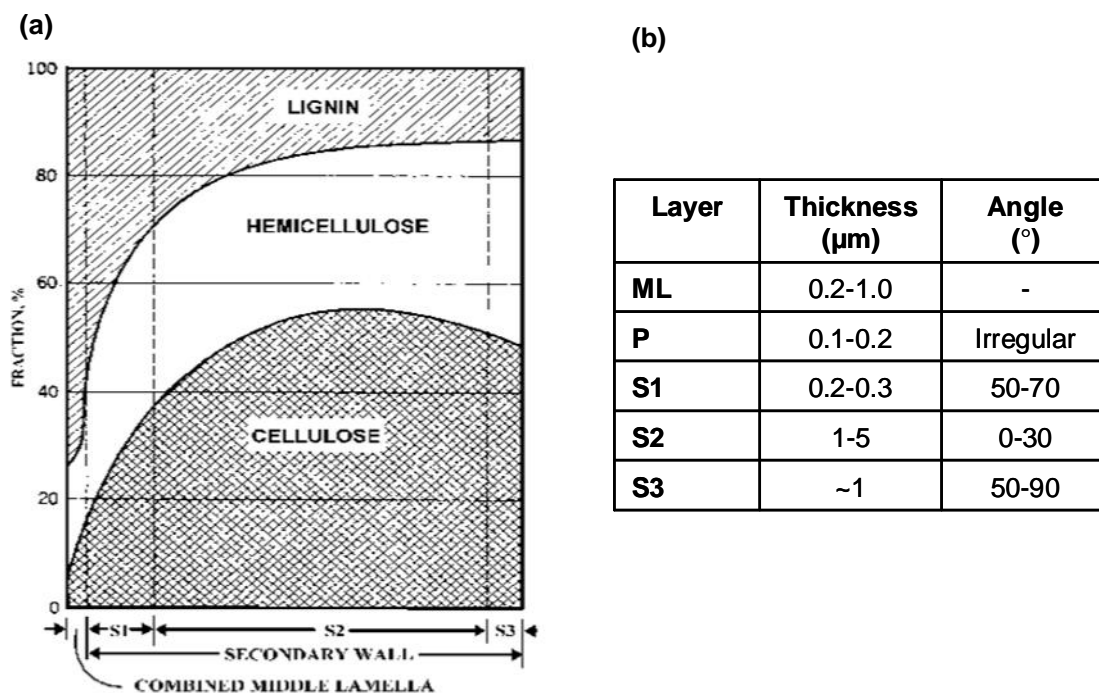
Figure 2. (a) Chemical composition of the cell layer (adapted from Panshin et al. 1970) and (b) the average layer thickness of the cell layers (ML, P, S1, S2, S3) and the microfibril angles (Sjöström 1993).

The *middle layer (S2)* forms the main part of the cell wall and contains from three to more than 150 lamellae. The S2 layer is a right-handed helix (Paavilainen 2002). The microfibrillar angle varies between 5° and 10° for latewood and 20°

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and 30° for earlywood *(Figure 2b).* Since the S2 layer constitutes most of the fiber and has the largest amount of cellulose, the fibril angle of the S2 layer principally determines the stiffness and strength of the fibers (Courchene et al. 2006, Paavilainen 2002). A smaller fibril angle is beneficial for paper strength. But also the internal and external fibrillation of the S2 layer during refining is important for the papermaking properties of the fibers (Giertz 1980). However, the other layers can also contribute to fiber strength (Mark 2002). The *inner layer (S3)* is a thin layer consisting of several lamellae which contain microfibrils in both Z helices and S helices (50-90°) (Sjöström 1993).

The *warty layer (W)* is a thin amorphous membrane located in the inner surface of the cell wall in all softwoods and in some hardwoods, containing warty deposits of still unknown composition (Sjöström 1993).

3.1.3 Cell types

The wood substance in *softwoods* is composed of two types of cell: long tracheids or fibers (90-95%) and a small number (less than 10%) of ray cells (Sjöström 1993). The ray cells are narrow and short cells (< 0.2 mm in length) which are often lost in screening of chemical pulps (Roberts 1996) and therefore softwood tracheids form the basis of papermaking fibers. The thin-walled fibers formed at the beginning of the growing season are called earlywood or springwood, and the thick-walled fibers formed later during the growing period are known as latewood or summerwood fibers (Paavilainen 2002). The softwood cellwall thickness is typically 2 to 4 µm for earlywood and 4 to 8 µm for latewood, though values vary between wood species and even within the same tree (Sjöström 1993). The average fiber length of Scandinavian softwood tracheids is 2 to 4 mm*)* and the width in the tangential direction 20 to 40 µm (Sjöström 1993).

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The structure of *hardwood* is much more varied and complex than that of softwood. Hardwoods contain several cell types: fiber tracheids and libriform fibers (30-70%), vessels (15-40%) and parenchyma cells (5-30%). Hardwood contains a significant portion of short (0.3-0.6 mm), large-diameter cells (30-130 µm) called vessel elements through which sap is transported (Paavilainen 2002). The size and number of vessels vary strongly from species to species. The large vessel elements can cause vessel picking problems in papermaking (Gopichand et al. 1990). Ray and parenchyma cells are also present in hardwoods, as they are in softwoods, although they are more abundant and exhibit a greater variety in form. The number of parenchyma cells in hardwoods is, on an average, higher than in softwoods (Alén 2000). In general, hardwood fibers are shorter and narrower and have smaller pits compared to softwoods (Gullichsen 2000b). The dimensions of hardwood fibers used in papermaking are, on average, the following: length 0.7 to 1.7 mm, width 14 to 40 µm and cell wall thickness 3 to 4 µm (Paavilainen 2002). In general, the composition of the main cell types is not far from the overall composition of wood (see Chapter 3.2.1), although small differences have been reported (Sjöström et al. 1999).

3.2 Chemical pulp production and pretreatment

In 2004, approximately 175 million tons (Finland ~12.6 million tons) of wood pulp was produced worldwide, with chemical pulp accounting for 73% of the total (Peltola 2006). The pulp making process starts when the trees are debarked mechanically, cut into chips and screened before chemical treatment under strictly controlled conditions. Chemical wood pulp fibers are manufactured by dissolving chemically the components (mainly lignin) that keep the wood cells together to form the original wood structure. The quality of the fibers or tracheids produced depends on their chemical composition and morphology which, in turn, depend on the wood species. There are two major types of fibers for the production of paper and board: long softwood fibers which give the required

strength, and short hardwood fibers which give good printability and stiffness (Paavilainen 2002).

The chemical pulping process, aiming at effective removal of lignin while preserving the carbohydrates, takes place at high pressure and temperature under aqueous alkaline, neutral or acidic conditions (Roberts 1996). The dominant process is the strongly alkaline kraft process, in which the active components are the hydroxide (OH^-) ion and the hydrosulfide (HS^-) ion. Alkaline delignifying processes produce strong and flexible but brown fibers, while fibers made in acidic processes are weaker, stiff and brittle, but much lighter in color (Gullichsen 2000a). The carboxyl or charged group content decreases during kraft pulping as a result of dissolution of acidic polysaccharides, xylans and kraft lignins (Sjöström 1993). When lignin is removed the wet fibers become porous and flexible.

After pulping the pulps are usually washed and screened before bleaching. Bleaching is a purification process in which colored substances (mainly residual lignin) are modified so that they either lose their light absorption ability or dissolve (Gullichsen 2000a). The most common bleaching chemicals include oxygen, chlorine dioxide and hydrogen peroxide. Bleaching of chemical pulps decreases the total charge of pulps due to dissolution of lignin and hemicellulose.

After bleaching and before entering the paper mill, the pulps are usually beaten (i.e. refined) *(Figure 3)*. In beating, pulps are mechanically treated with metallic bars in the presence of water, which cut and shorten the fibers but also make the fiber surface larger by external fibrillation or partial removal of the fiber wall. Furthermore, also internal changes in the wall structure (internal fibrillation), curling or straightening of fibers or fines production are promoted by beating (Page 1989). In other words, beating or refining improves the bonding ability of fibers in the papermaking process (Lumiainen 2000).

After beating the pulp enters the paper mill where the web is pressed and dried under controlled conditions to produce the final paper, with each end product setting its own requirements for the pulp properties. A simplified presentation of the kraft pulp production process is shown in *Figure 3.*
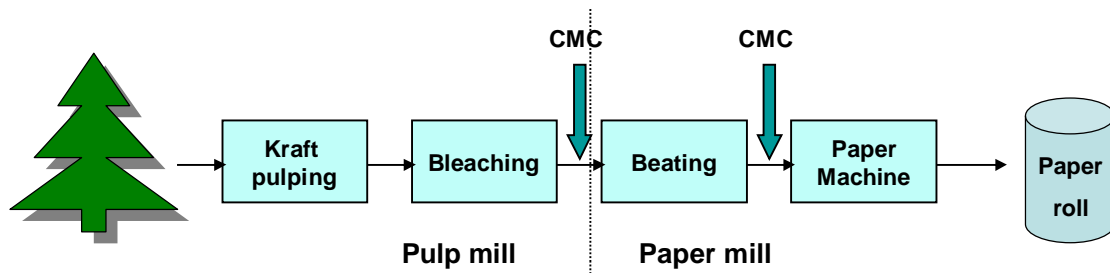
Figure 3. *Simplified presentation of kraft pulp production, from wood to paper. The most favorable CMC addition points for the method presented in this thesis are shown in the figure.*

3.3 Paper strength

3.3.1 General

Paper is a bonded, more or less randomly formed network of fibers making up an extremely complicated structure. In the papermaking process and during the subsequent pressing and drying of the sheet, the aim is to develop fiber-to-fiber bonding to gain strength. Water plays an important role in bond development, because water brings the fibers into close contact, resulting in fiber-to-fiber bonding. Increased bonding is essentially achieved by increasing the bonded area either by forcing the surfaces together as in wet pressing or more importantly by increasing the flexibility and specific surface area of fibers by beating. The increased density due to fibrillation and fines generation in beating results in improved tensile strength and tensile stiffness (Salmén 1985).

The hemicellulose present in fibers promotes swelling and leads to more bonding between fibers and improved strength properties (Spiegelberg 1966). In addition, fiber strength is also important for paper strength. The main fiber strength defining factors are cellulose fibrils, microfibrillar angle and fiber deformation (Wathén 2006). Fiber deformation is important because straight fibers, due to their higher fiber segment activation, have been found to have better tensile strength and elastic properties than deformed fibers (Giertz et al. 1979, Joutsimo et al. 2005). In addition to the factors described in the foregoing, the properties of paper are also dramatically affected when the shrinkage and stretching of the fiber web are varied during the drying process (Wahlström et al. 2000b). If the paper is stretched or shrinkage reduced, the tensile strength of the sheet increases, whereas the strain to break and bonding strength decrease (Chance 1992, Vainio et al. 2005, Wahlström et al. 2000b).

Thus the most important factors affecting paper strength are the following;

- ***properties of fibers*** (fiber strength, fiber deformation and fiber dimensions, chemical composition of fibers, cellulose microfibril angle, charge of fibers and fiber wall porosity etc.)
- ***extent of fiber-to-fiber bonding*** (beating, wet pressing etc.)
- ***fiber orientation and distribution*** (machine direction, sheet formation, density etc.)
- ***shrinkage restrictions during drying*** (residual stresses, restraint drying etc.)

However, also other factors may affect the strength properties of paper, such as the moisture content (Wahlström et al. 2000b). Some of the properties affecting the strength properties of paper are discussed in more detail in the results and discussion section (Paper IV and V).

3.3.2 Testing paper strength

Paper responds differently to stresses applied in different ways, so it is clear that there is no single measure or definition of paper strength (Page et al. 1992). The classical equation for tensile strength formulated by Page has been a useful tool in understanding the relationship between sheet properties and fiber properties *(Figure 4)*. Page's equation describes the ability of paper to resist failure by considering the strengths of individual fibers and the bonds between those fibers (Page 1969, Page et al. 1988). Tensile strength can be used to determine the effect of fiber orientation (Levlin 1999)*,* but also *elastic modulus or tensile stiffness* can be determined from the slope of the primary part of the load-elongation curve of paper illustrated in *Figure 4* (Lobben 1975, Page et al. 1979). The main factors affecting the elastic modulus of paper are the elastic modulus of fibers, the degree of bonding between fibers, the drying conditions (Giertz et al. 1979, Lobben 1975) and the presence of curl, kinks, crimps and microcompressions in the fibers (Page et al. 1985, Seth 2006). There is a problem with this approach, namely, how to actually measure the fiber-to-fiber bond properties (Niskanen et al. 1998). However, with kraft fibers it has been shown that the tensile strength of paper can be approximately modeled according to the Page equation (Page 1969).

Another important test method is the test of sheet brittleness, which is generally measured as the work done to tear a unit length of the sheet, as in the Elmendorf tear test (Page 1994, Page et al. 1992). The *tearing strength* of paper depends on at least the following factors: fiber length, fiber strength, degree of bonding between fibers and degree or orientation of fibers in the paper (Levlin 1999). Generally, the greater the fiber length and fiber strength, the better the tear strength (Page 1994, Seth et al. 1988).
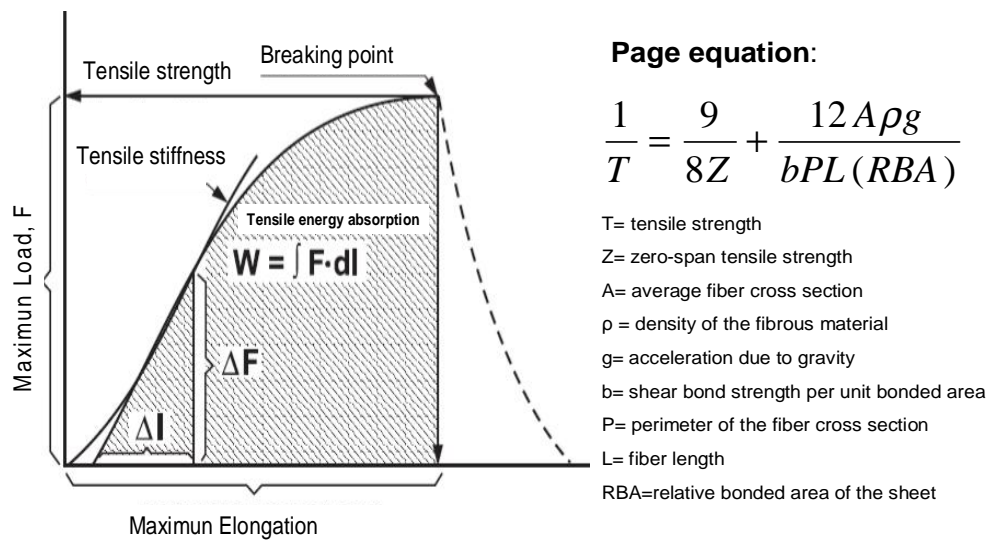
Page equation:

$$\frac{1}{T} = \frac{9}{8Z} + \frac{12A\rho g}{bPL(RBA)}$$

T= tensile strength
Z= zero-span tensile strength
A= average fiber cross section
ρ = density of the fibrous material
g= acceleration due to gravity
b= shear bond strength per unit bonded area
P= perimeter of the fiber cross section
L= fiber length
RBA=relative bonded area of the sheet

Figure 4. *Measuring tensile strength and elastic properties of paper* (Levlin 1999) *and Page's equation (Page 1969).*

Other strength measurements are, for example, zero-span tensile strength and z-directional strength. The *zero-span tensile strength* is a good indicator of the average strength of individual fibers but also of fiber defects (Mohlin et al. 1996, Wathén 2006). The *z-directional strength* refers to the ability of a paper or board to resist tensile loading in a direction perpendicular to the plane of paper (z-direction). More methods to test paper can be found in (Gullichsen et al. 1999).

3.3.3 Effect of fiber charge on paper strength

The fiber charge is of great importance for the properties of paper as well as for the behavior of fibers in the papermaking process. Charged fibers may affect the swelling and flexibilization of fibers or affect the fiber bonding or specific bond strength, as discussed by Barzyk (1997a and b). It has been suggested that the importance of charged groups for paper properties is due to increased specific bond strength, while the role of swelling and fiber flexibilization is only of secondary importance (Laine et al. 2003b).

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Different approaches to increase the amount of charged groups on the fibers have been used, such as carboxymethylation (Nelson et al. 1964), sulfonation (Allan et al. 1971, Allan et al. 1975) or oxidation (Saito et al. 2005). *Carboxymethylation* as a method for introduction of charges and increasing the swelling of fibers and, subsequently, the strength of paper has been demonstrated many times over a period of years (Fors 2000, Nelson et al. 1964, Walecka 1956). This aspect has been investigated for kraft pulps (Fors 2000, Saito et al. 2005) and mechanical pulps (Ampulski 1985, Zhang et al. 1994). In addition, Barzyk and coworkers (1997a, 1997b) carboxymethylated fibers under non-swelling conditions and showed that by introducing carboxyl groups on the surface of fibers the internal and tensile strengths improved, which they attributed to an increase in fiber-to-fiber specific bond strength. The beneficial role of the surface charge for the bonding properties of fibers and for the properties of paper have been widely investigated (Ampulski 1985, Fors 2000, Saito et al. 2005, Zhang et al. 1994). Previous studies in this laboratory have shown that carboxymethyl cellulose (Mitikka-Eklund et al. 1999) and wood xylans (Mitikka-Eklund 1996) can be sorbed onto cellulosic fibers and as a consequence the surface charge of fibers increases. A disadvantage is that more swollen fibers (more charged fibers) are generally more difficult to dewater (Lindström 1992).

3.4 Carboxymethyl cellulose in fiber modification

3.4.1 Carboxymethyl cellulose

CMC or sodium carboxylmethyl cellulose is a water-soluble anionic polymer achieved by introducing carboxymethyl groups along the cellulose chain *(Figure 5)*. CMC is usually synthesized by the alkali-catalyzed reaction of cellulose with chloroacetic acid (Kloow 2000). The functional properties of CMC depend on the degree of substitution of the cellulose structure (i.e., how many of the hydroxyl groups have taken part in the substitution reaction), and also on the chain length

of the cellulose backbone. The degree of substitution (DS) of CMC is usually in the range 0.6 to 0.95 derivatives per monomer unit. CMC is generally considered a water-soluble polymer down to DS 0.3 (Horsey 1947, Liu et al. 1997).

(a)

Cellulose

(b)

Carboxymethyl cellulose

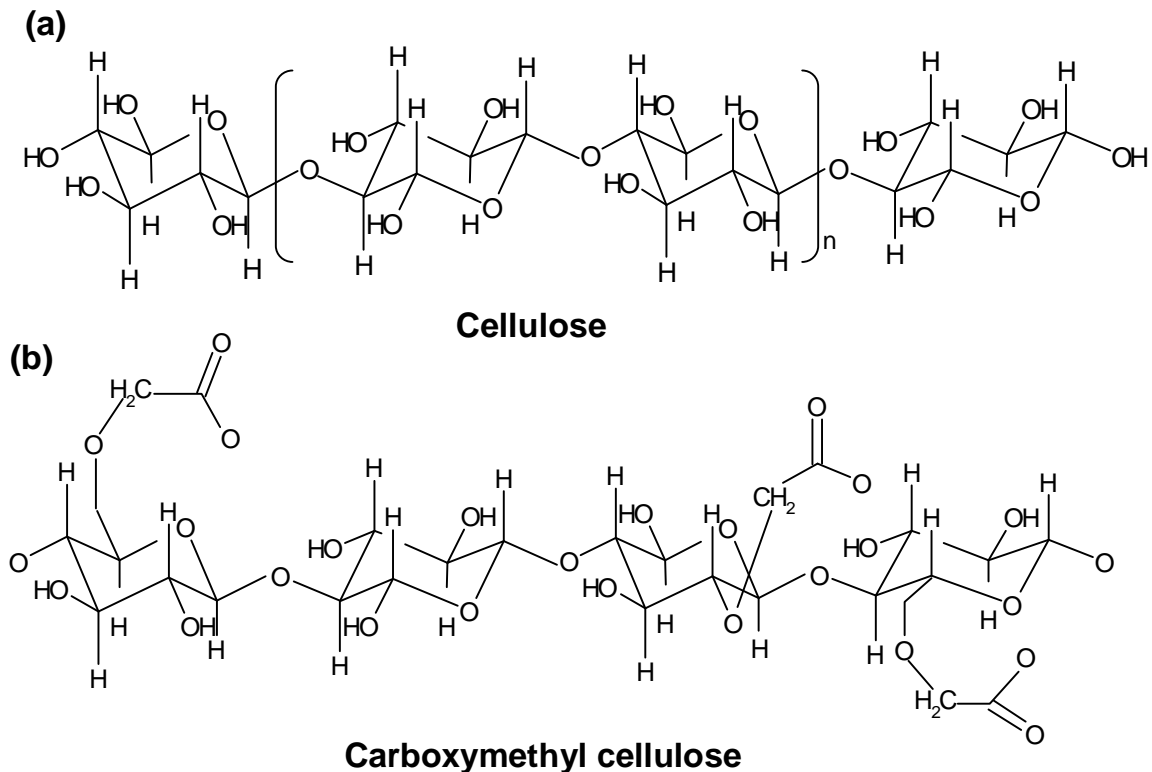*Figure 5. Structure of (a) cellulose and (b) carboxymethyl cellulose.*

3.4.2 Carboxymethyl cellulose sorption

Adsorption of polymers, usually cationic polyelectrolytes, on cellulosic fibers has been studied comprehensively (Wågberg 2000, Wågberg et al. 1989). Anionic polyelectrolytes, such as CMC, do not generally attach on cellulosic fibers because of the electrostatic repulsion between the negatively charged cellulosic

surface and the anionic polyelectrolyte (Laurell 1952, Wiebe et al. 1957). Traditionally, to retain anionic polymers efficiently in cellulosic fibers it is necessary to add something cationic to the system, usually alum (Horsey 1947, Laurell 1952).

Recently an alternative approach has been presented in which fibers are treated with CMC in the absence of a cationic additive. Mitikka-Eklund and co-workers (1999) have shown that CMC with a low degree of substitution can be permanently sorbed on the external surface of ECF-bleached softwood pulp under specified sorption conditions (1h, 60°C, pH 12.5). The strength and topology of the sorption of CMC on cellulose could be controlled by the degree of substitution (DS) and polymerization (DP) of the CMC. The molecular weight of CMC was high because only polyelectrolytes with high DP do not penetrate inside the cell wall (Allan et al. 1975). Since cellulosic fibers are porous in nature, it is obvious that the molecular mass of the polyelectrolyte will have a large impact on the sorbed amount (Wågberg 2000).

More recently it was found that a high level of CMC (DS 0.4-0.8) can be sorbed onto the fiber surface by prolonged heating (120°C, 2h) in the presence of 0.05 M calcium chloride (Fors 2000, Laine et al. 2000, Laine et al. 2001, Laine et al. 2002). The function of the high electrolyte concentration was simply to screen the charge interactions between the negatively charged CMC and the anionic cellulose surface so that the CMC molecule can absorb to the fiber surface (Laine et al. 2000). This CMC treatment was found to increase fiber swelling and surface charge. Generally, the lower the degree of substitution and molecular weight of CMC, the higher the CMC attachment (Laine et al. 2002). According to Fors (2000), sorption of carboxymethyl cellulose on cellulosic fibers is thought to take place through cooperative hydrogen bonding between the free cellulose segments on the CMC backbone and the cellulosic fiber surfaces on the fiber *(Figure 5)*. In other words, the similarity in the backbones is considered to be the main reason for carboxymethyl cellulose to be sorbed onto the cellulosic fibers, in

a similar way as hemicellulose is sorbed onto cellulose (Clayton et al. 1965, Hubbe 2006, Mitikka-Eklund 1996). However, it is still not fully understood how the CMC sorption takes place.

3.4.3 Effect of CMC on pulp and paper properties

Because of its excellent film-forming and water retention properties CMC has been used as a surface sizing agent, coating binder and wet end additive in the paper industry for many years (Beghello et al. 1997). CMC is also widely used in the food and textile industries.

CMC as a dry strength additive

Various polyelectrolytes, including cationic starch, CMC and copolymers of acrylamide, are used by papermakers to promote inter-fiber bonding and to increase the dry strength of paper (Ketola et al. 1999). Dry-strength additives need to be adsorbed efficiently onto the fibers and should have a hydrophilic character and a sufficiently high molecular mass. In that way it is possible to achieve superior strength gains, which are usually achieved by addition of oppositely charged polyelectrolytes or by polyelectrolyte complexes sorbed onto the fiber or fiber surface (Hubbe 2006). According to Pelton (2004), the degree of cationic charge, the molecular weight and the presence of reactive groups on the dry strength polymer do not directly influence the dry paper strength. On the other hand, polymer hydrophobicity/hydrophilicity seems to be a predictor of efficacy - the more hydrophilic, the stronger the paper. A more detailed description of the functions of dry strength additives is presented in the articles by Hubbe (2006) and Pelton (2004).

Beghello and coworkers (1997) have successfully used CMC as a wet-end additive to improve paperboard properties. When a small amount of CMC (0.2-0.5%) was added to the top and bottom layers of board the tensile and tear strength properties were increased, whereas the roughness was decreased. The internal strength increased the most when CMC was added to the middle layer. The brightness was also improved after CMC treatment, due to improved retention of the optical brightening agent on the sheet. Watanabe and coworkers (2004) have shown that CMC-treated fibers achieve large gains in strength upon subsequent addition of strength additives in the presence of alum. According to Watanabe's research, by treating pulp with CMC papermakers could reduce the dosage level of wet-end additives, resulting in a cleaner mill system, improved quality, and increased economic efficiency.

Polyelectrolyte complexes of cationic and anionic polymers have also been introduced as a means to enhance paper strength (Gärdlund et al. 2003, Stratton 1989). Stratton (1989) reported wet and dry paper properties of PAE (polyamide(amine)epichlorohydrin) and CMC combinations. The main conclusions of Stratton's research were that the selective adsorption of long fibers gave stronger paper than adsorption of the whole furnish, that wet-end fiber treatment gave stronger paper than impregnation, and that the combination of PAE and CMC produced greater strength than PAE alone.

CMC modification and paper properties

The different approach to sorb CMC on fibers, as described above, has been used in several studies to increase the charge (swelling) on the fiber surface and further to improve the strength properties of paper (Fors 2000, Laine et al. 2001, Laine et al. 2002, Mitikka-Eklund et al. 1999). This kind of treatment increases the water retention value, but since the water held by CMC is mainly on the surface of fibers it can be easily removed by pressing (Laine et al. 2003b). Laine

and coworkers (2002) have shown that CMC modification of softwood kraft pulp results in substantial improvements in tensile strength, strain to failure and tensile energy adsorption, whereas the elastic properties are less affected.

Another area of interest are polyelectrolyte multilayers which are created by repeated adsorption of cationic and anionic polymers. Wågberg and coworkers (2002) have recently shown that multilayers can be created on fiber surfaces and that the multilayers produce significant improvements in paper strength. For example, Petterson et al. (2006a, 2006b) have used polyelectrolyte multilayers of cationic starch and CMC to enhance the strength properties of chemical pulp and CTMP.

4 EXPERIMENTAL

4.1 General experimental plan

An overview over the experiments made in this work is shown in *Figure 6.* In the next Chapters the experiments and the results obtained are presented in more detail.
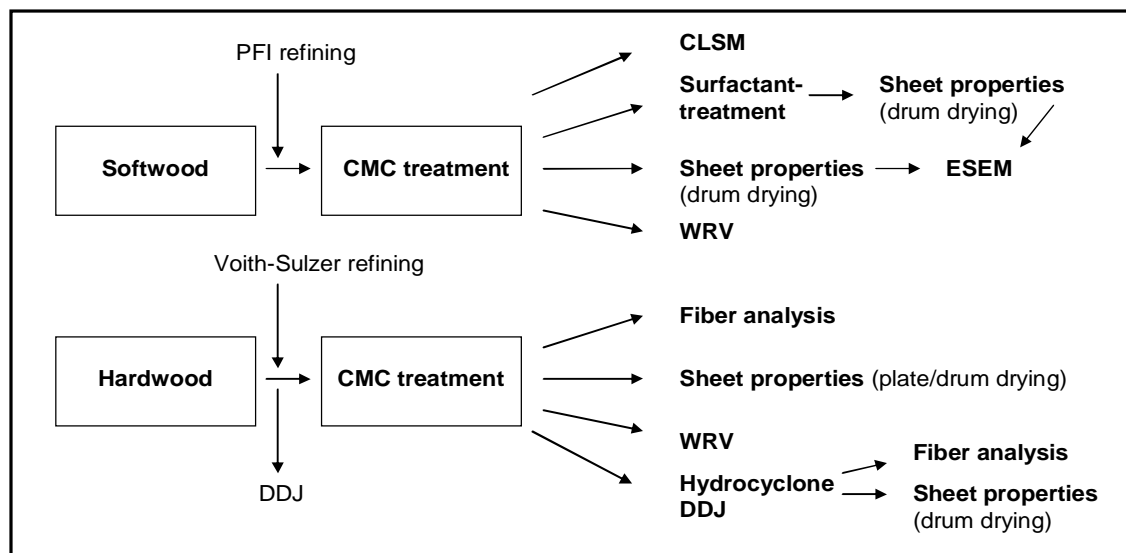
Figure 6. General plan of experimental work.

4.2 Materials

4.2.1 Softwood pulps

The softwood experiments (Paper I, II) were carried out with industrial ECF-bleached *spruce* (*Picea abies*) and pine kraft pulp *(Table 2).* The softwood pulp was delivered as dry pulp sheets. The pulp was soaked in water and disintegrated prior to use (ISO 5263-1). The pulp was refined for 0, 1000, 2000, 4000 or 7000 revolutions with a PFI mill (ISO 5264-2).

4.2.2 Hardwood pulps

The hardwood experiments (Paper IV) were carried out with a mixture of industrial ECF- bleached *birch* and aspen kraft pulp or an ECF-bleached *eucalyptus* kraft pulp (Paper V) *(Table 2).* The hardwood pulp was refined in a Voith Sulzer LR1 research refiner, with the 2/3-1.4-40D blade. The refining consistency was 4%, with a specific edge load of 0.5 Ws/m for birch pulp and 0.3 Ws/m for eucalyptus pulp. The specific refining energy (SRE) levels were 0 and 30 kWh/t.

The hydrocyclone fractionation experiments (Paper III) were carried out with an industrial ECF-bleached *birch* kraft pulp *(Betula pendula)* and refined with a Voith Sulzer refiner as described above *(Table 2).*

Table 2. Notation and properties of the pulps. Fiber length and coarseness values were analyzed with the KajaaniFiberLab.

Notation	Composition	Fiber length (mm)	Coarseness (mg/m)
Spruce (Paper I, II)	83% spruce, 13% pine, 4%hardwood	2.20[a]	0.15[a]
Birch I (Paper III)	birch	0.88	0.10
Birch II (Paper IV)	95% birch, 5% aspen	0.99	0.09
Euca (Paper V)	eucalyptus	0.86	0.07

[a](Zhang 2004), analyzed with Kajaani FS-100

4.2.3 Carboxymethyl cellulose

The commercial *(CMC) samples*, Nymcel ZSB-16 and Nymcel ZSB-10, were obtained from Noviant (now CP Kelco) *(Table 3).* The hardwood (Paper III, IV, V) and surfactant (Paper II) experiments were carried out with Nymcel ZSB-16 and

the softwood experiments (Paper I) with Nymcel ZSB-10. The degree of substitution of CMC was changed according to the procedure presented in Paper I and III.

Table 3. Properties of the CMCs used to modify the softwood and hardwood pulps.

Trade name	Degree of polymerization (DP_v)	Degree of substitution (DS)
Nymcel ZSB-10	750	0.20
		0.31
		0.43
Nymcel ZSB-16	700	0.32
		0.51

4.2.4 Surfactants

The surfactants used in the experiments (Paper II) were *alkyltrimethylammonium bromides* ($C_nH_{2n+1}N(CH_3)_3Br$, n=10, 12, 14 and 16, denotes $C_{10}TAB$, $C_{12}TAB$, $C_{14}TAB$ and $C_{16}TAB$, respectively) from Fluka.

4.3 Methods

4.3.1 Sorption experiments

Sorption of CMC on pulp

The sorption experiments were made as follows *(Figure 7)*. First, the CMC solution (< 10g/L) was prepared in 2.5 M sodium hydroxide. The disintegrated or refined pulp was then mixed with water and the stock CMC solution to obtain a final pulp consistency of 2.5% or 5% and an initial CMC concentration of 0.5% (Paper III) or 1% on pulp (Mitikka-Eklund et al. 1999). The softwood, surfactant

and hydrocyclone hardwood experiments (Paper I, II, III) were carried out in 5% consistency and the other hardwood experiments (Paper IV, V) in 2.5% consistency. The sorptions (pH 7-12.5) were carried out in glass beakers under mixing. The temperature was raised to 60°C in 30 minutes. After 60 minutes, the pulp samples were cooled, filtered and washed with deionized water. Reference treatments were also carried out under similar conditions but without the addition of CMC.

Samples of the liquid phase were withdrawn after the sorption, centrifuged for 30 minutes (Paper IV, V) or filtered with 0.02 or 0.2µm membranes (Paper I, II, III) and then analyzed for dissolved carbohydrates by the phenol-sulfuric acid test (Dubois et al. 1956) or acid methanolysis combined with gas chromatography (GC) (Sundberg et al. 1996).
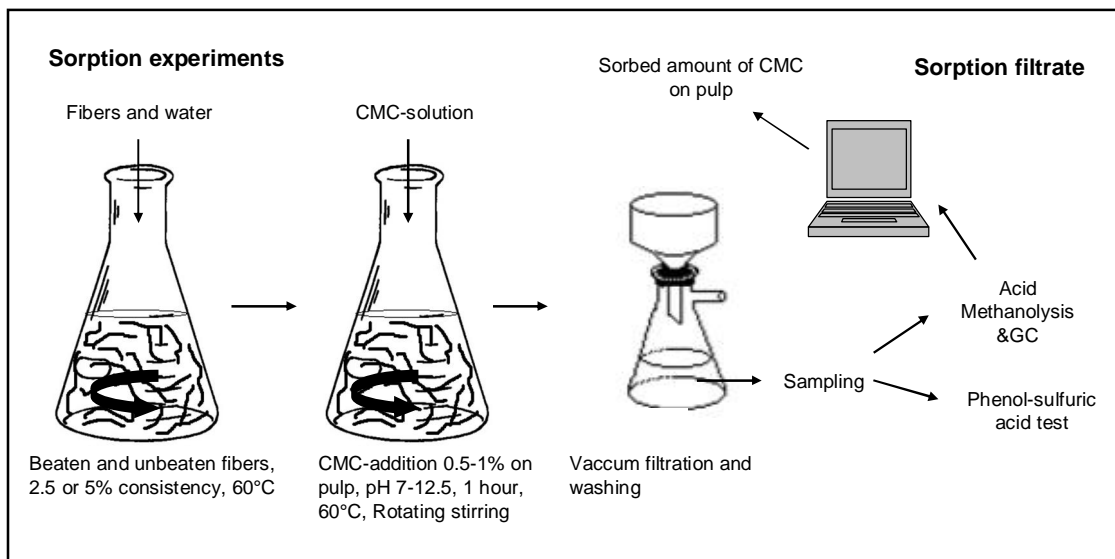

Figure 7. *Simplified scheme of the sorption experiments.*

Sorption of CMC and surfactant on pulp

The softwood pulp was CMC-modified as described above. The surfactants (alkyltrimethylammonium bromides) were added to the diluted pulp suspension before sheet making at a concentration of 0.02% to 0.2% on pulp (Paper II). A trend in papermaking is toward increased recycling of drainage waters; hence, there is growing interest in knowing what effects the higher (accumulated) electrolyte concentrations have on paper properties. Therefore, the effect of an electrolyte on the sheet formation was investigated by preparing the laboratory sheets in dilute solution of sodium chloride (0.05 M NaCl). After electrolyte and surfactant addition, the pulp was allowed to stabilize for one hour under mixing before the sheets were prepared.

4.3.2 Fiber analyses

Fiber analyses can be used to determine morphological properties such as fiber length, fiber width and cell wall thickness. These properties vary a lot between wood species (Chapter 3.1.3), within annual growth rings, different stem parts and depending on the growing conditions of the tree (Paavilainen 2002). There are several commercial image analyzers available to analyze these properties for example KajaaniFiberLab (Mörseburg et al. 1999, Richardson et al. 2003, Tiikkaja 2000), Kajaani FS-200 (Bichard et al. 1988, Turunen et al. 2005) and STFI Fibermaster (Karlsson et al. 1999). The KajaaniFiberLab analyzer is described in more detail, since it has been mainly used in this study (Paper III, IV, V).

The main components of the *KajaaniFiberLab* are the analyzer and the sample units *(Figure 8a)* (Turunen et al. 2005). Fibers flow thorough a narrow capillary at low consistency, and a laser light source in the capillary is used to control the two CCD cameras which capture images of the fibers. When the fiber reaches the

centre of the optics section, a flashing Xenon lamp enables both the cross-sectional and length CCD cameras to capture an image of the fiber (Richardson et al. 2003). The images are processed by the KajaaniFiberLab software to provide several fiber measurements: projected fiber length (resolution 50µm), fines content, fiber width (resolution 1 µm) and cell wall thickness (resolution 1µm). Calculated values are curl index, coarseness, cross sectional area and volume index (KajaaniFiberLab operating manual). Furthermore, KajaaniFiberlab also gives information about the extent of single fiber fibrillation, vessel and kink content of the fibers analyzed. Several studies have compared different analyzers with each other (Richardson et al. 2003, Tiikkaja 2000, Turunen et al. 2005). In general, the analyzers seem to be good and rapid tools for measuring fiber properties, with good correlation in trends between the analyzers, even though absolute values may sometimes be different.
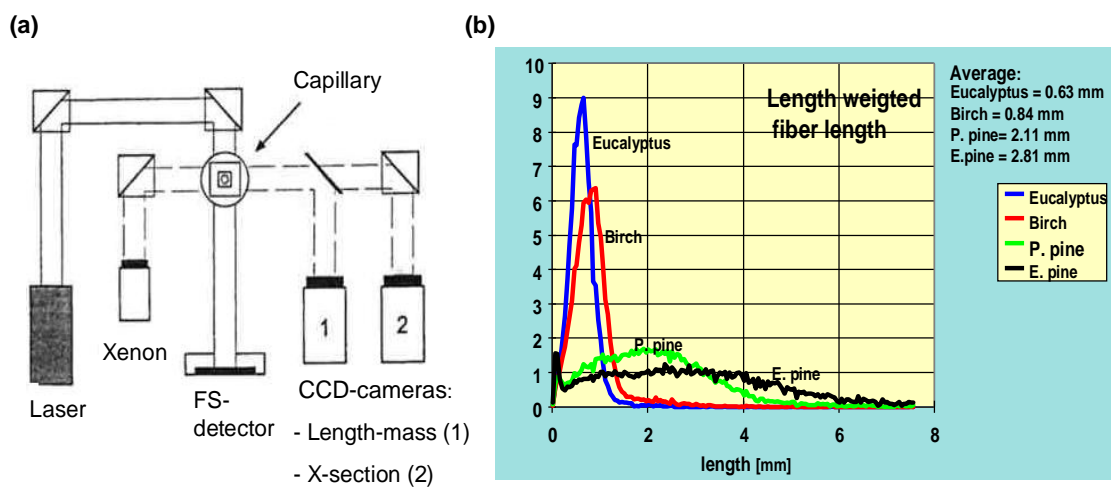

Figure 8. (a) *KajaaniFiberLab measurement platform and* **(b)** *the distribution of length weighted fiber length in softwood and hardwood pulps (KajaaniFiberLab operating manual).*

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In this study, the fiber dimensions and deformations were analyzed with a Metso Automation (Finland) KajaaniFiberLab apparatus (Paper III, IV, V). Samples were prepared according to the manufacturers' recommendations (KCL standard 225:89). The stock consistency used to calculate the coarseness values was determined by the standard method SCAN-C 17:64 and the fiber length according to TAPPI T271. Fiber fibrillation, kink and vessel content were also determined for eucalyptus pulp (Paper V).

4.3.3 Fractionation of hardwood pulps

To be able to meet customers' demands for product quality and performance, as well as environmental demands such as minimizing the use of raw material, the raw material has to be managed for optimal use. One way to utilize the fiber material is to use the right fiber in the right place in the product. A tool to achieve this is fiber fractionation, which separates the fibers into two or more fractions with different properties (Karnis 1997). Many different fractionation techniques are available, for example, screens, hydrocyclones, a plate atomizing wheel, the Johnson apparatus etc. (Rewatkar et al. 1996). Generally, screens and the Johnson apparatus fractionate according to fiber length and flexibility, while hydrocyclones and the plate atomizing wheel fractionate according to the specific surface area (size and shape) of the fibers (Karnis 1997). Since in this study the hydrocyclone has been used for fractionation, a more detailed description of the apparatus is shown below *(Figure 9a).*
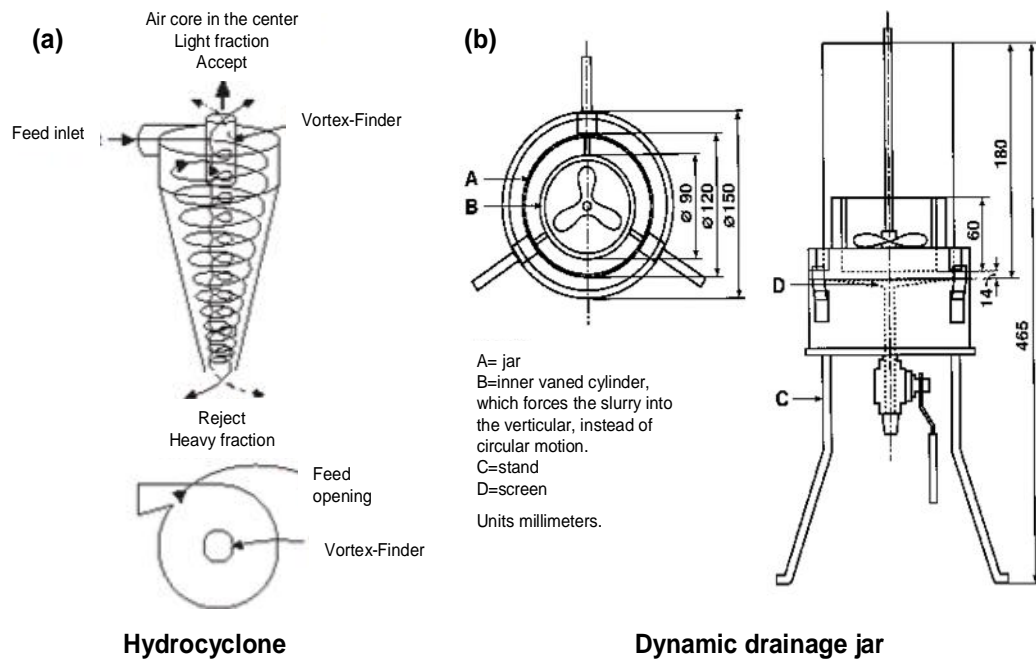
Hydrocyclone   **Dynamic drainage jar**

Figure 9. (a) A hydrocyclone of common design, with a core of air or gas traveling in the center of the cyclone (Hautala et al. 1999) *and (b) KCL's version of the Dynamic Drainage Jar (Krogerus 1999).*

In the pulp and paper industry *hydrocyclones* are generally used to remove dirt particles, plastic contaminants, vessel elements (Ohsawa 1988), shives and ink from recycled pulp (Rewatkar et al. 1996). The hydrocyclone separation of fibers is a result of the interplay between mainly two forces, the centrifugal force moving fibers outwards and the hydrodynamic drag causing the fibers to move inward (Karnis 1997). Dense particles under the influence of the centrifugal force move toward the wall of the hydrocyclone and finally leave through a conical tip as a reject stream. The less dense particles move inward and finally leave with the accept stream flow (Rewatkar et al. 1996). ("Reject" and "accept" are interchangeable terms. If the denser particles form the desired species, the "accept" consists of the heavy fraction.) Several studies have shown that particle separation proceeds on the basis of apparent density (Li et al. 1999) and surface area (Wood et al. 1979, Wood et al. 1991), but also separation according to cell

wall thickness (Panula-Ontto 2003), fiber swelling (Demuner 1999) and coarseness (Karnis 1997) has been reported.

Hydrocyclones have been found to give high separation efficiency, concentrating the thick-walled summerwood (coarse) in the reject fraction and the thin-walled springwood in the accept fraction (Jones et al. 1966, Kure K-A et al. 1999, Paavilainen 1992). The accept fraction has been found to have high tensile and bonding strength (Jones et al. 1966, Li et al. 1999, Paavilainen 1992), higher density and higher fines content (Panula-Ontto 2003), whereas the reject fraction usually has higher tearing resistance (Jones et al. 1966, Paavilainen 1992) and curlier fibers (Panula-Ontto 2003). However, opposite results concerning tear index have been reported (Li et al. 1999, Rehmat et al. 1995). The fractionation of hardwood pulp fibers is exceptionally demanding due to the relatively small variations in their dimensions *(Figure 8b).* Therefore, only a few attempts have been made to fractionate hardwood pulps (Demuner 1999, Johnston et al. 1997, Li et al. 1999). Recently, Jokinen and coworkers (2006) have shown that modification of softwood pulp fibers with CMC increases the differences in specific surface area between fibers and as a consequence enhances pressure screen and hydrocyclone fractionation through increased capacity or fractionation efficiency.

In the present study, hydrocyclone fractionation was carried out on CMC-modified hardwood pulp (birch I) in order to get more information about whether CMC is sorbed onto fibers or fines. In Paper III, an ECF-bleached hardwood pulp (birch I) was modified with CMC and then fractionated with an Alfa laval (Sweden) hydrocyclone (10mm diameter). Appoximately 145g of pulp was added to the hydrocyclone at a concisentcy of 0.3%. The under flow pressure was 1 bar, inlet pressure 5 to 6 bar and feed flow 240 L/h. After fractionation, the reject fraction was filtered (200 mesh) and the accept fraction was sedimented. The fines contents in the accept and reject fractions were further determined by using a Dynamic drainage jar (DDJ) as described in Paper III. Furthermore, in Paper

IV, fines were removed from a hardwood pulp (birch II) using KCL's Super DDJ before CMC modification of the pulp. The Super DDJ is composed of a wire tank with a 200-mesh wire and a mixer *(Figure 9b).*

4.3.4 Environmental scanning electron microscopy

A simplified description of the scanning electron microscopy (SEM) apparatus is that the sample is bombarded with an electron gun and then the scattered electrons are detected. Two types of detector can be used in *environmental scanning electron microscopy (ESEM)*: 1) an environmental secondary electron detector or 2) a back scattered electron detector (Danilatos 1993, De Silveria et al. 1995). ESEM is basically a low-vaccum SEM, where the relative humidity over the sample can be controlled by controlling the pressure and the stage temperature. Because of the low vacuum in the microscope chamber the specimen needs no coating or surface treatment prior to examinantion (Forsberg et al. 1994). A disadvantage is that when working with, for example, wet kraft pulp, care should be taken not to burn the sample. The irradiation damage can be minimized or avoided by using lower accelerating voltages and higher condenser lens settings (De Silveria et al. 1995, Forsberg et al. 1994). A more detailed description of the principle of ESEM is given by Danilatos (1993).

In the present work, ESEM was applied to illustrate how refined pulp fibers form different bonds on the fiber surface during drying of the paper sheet (Paper I, II). The ESEM images were taken with an ElectroScan ESEM 2020 instrument (USA) in the ESEM mode with a gaseous secondary electron detector at a temperature of approximately 23°C. Low acceleration voltage (about 5-10 kV) was used to prevent degradation of cellulose (Forsberg et al. 1994). The pressure in the chamber was 5 to 6 torr, the condenser lens setting 40% and magnification 500 to 1000 times.

4.3.5 Other methods

The *Schopper-Riegler (SR)* numbers of the pulp samples were determined according to the standard method ISO 5267-1 (Paper IV, V).

Water retention values (WRV) of pulps were measured in accordance with the proposed standard SCAN-C 62:00 with a Jouan GR 4 22 centrifuge (Paper I, IV, V). WRVs were also determined for pulps immersed in aqueous solutions of sodium chloride (2.5-10mM NaCl) (Paper I).

The *laboratory sheets* were prepared in deionized water by the standard method ISO 5269-1, with the exception of wet pressing at 490±20 kPa (4 min 20 s) and drying in a *drum dryer* at 60°C for 2 h. Softwood handsheets were also prepared in dilute solution of sodium chloride (0.05 M NaCl) (Paper I). When *drying plates* (Paper IV, V) were used, the wet pressing was carried out in two steps. The first pressing was at 400±10 kPa (5 min 30 s) and then the blotters were removed and replaced before the second wet pressing at 400±10 kPa (2 min 20 s).

The *density* of the sheets was determined by standard method ISO 534. The *tensile strength* and *tensile stiffness* of the laboratory sheets were measured with a tensile testing machine (MTS 400M) by standard method SCAN-P 38:80. Bonding ability *(Scott Bond or internal strength)* was determined according to Tappi 833 pm-94.

Confocal laser scanning microscopy (CLSM) images of wet pulp fibers stained with a fluorescent dye were taken with a CLSM (Leica TCS SP2, Germany) equipped with an argon-ion laser (Ylikoski 1992).

The *vessel picking tendency (number of picks, picked area)* of the eucalyptus sheets prepared using water circulation were analyzed with a new method developed at KCL (Panula-Ontto et al. 2007).

5 RESULTS AND DISCUSSION

5.1 Sorption of CMC onto pulp

5.1.1 Sorption of CMC onto softwood pulp

The amount of sorbed CMC on softwood pulp was estimated by analyzing the sorption filtrate with the phenol-sulfuric acid test (Paper I). Unbeaten softwood pulp sorbed 52% high-molecular weight CMC (DS 0.2), whereas highly beaten pulp led to almost quantitative sorption of CMC at 1% addition of CMC *(Figure 10b).* The sorbed CMC was located mainly on the external fiber surface and the sorption was irreversible (Mitikka-Eklund et al. 1999). Comparable studies have shown that a similar quantitative sorption of CMC (DS 0.5) with a higher degree of substitution requires high temperature (120°C) and addition of an electrolyte (Laine et al. 2000). Therefore, the sorption conditions presented here are more applicable for the actual papermaking process because the sorption conditions and temperature are closer to the conditions in a paper mill.
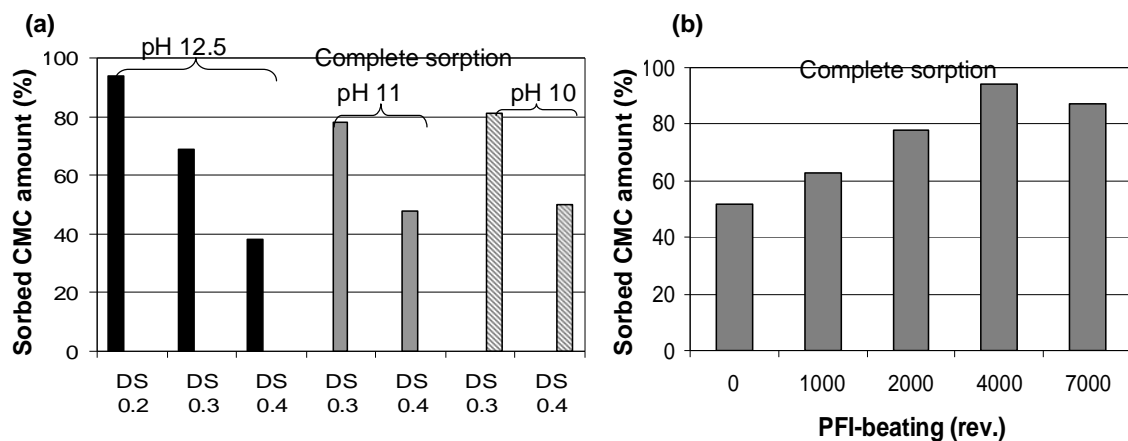

Figure 10. (a) *Effect of the degree of substitution (DS), pH and **(b)** beating on the sorption degree of CMC on softwood pulp (Paper I).*

The amount of sorbed CMC depended strongly on the degree of substitution of CMC *(Figure 10a)*, since the sorbed amount of CMC on pulp decreased with increasing DS (Paper I). In the method used in the present study, the DS of CMC is small, so the electrostatic repulsion between cellulose and CMC is small. Furthermore, when the DS of CMC is small, the solubility of CMC is poor which means that the CMC is preferably sorbed onto the cellulose surface instead of remaining in the solution (Fleer et al. 1993). Thus, it may well be that the CMC sorption here is driven by the conformational similarity between CMC and cellulose in the microfibrils on the fiber surface (Mitikka-Eklund et al. 1999). However, further fundamental research studies are needed to fully understand the mechanism behind the CMC sorption. The sorption of alkali-soluble CMCs could be enhanced to some extent by lowering the pH *(Figure 10a)*.

5.1.2 Sorption of CMC onto hardwood pulp

The sorbed amount of CMC on hardwood pulp was evaluated by determining the content of CMC in the sorption liquid with the phenol-sulfuric acid test and acid methanolysis combined with GC. Two methods were used to determine a reliable sorption degree of CMC, because the small fine particles in the sorption liquid were found to disturb the phenol-sulfuric test results.

Unbeaten birch II pulp sorbed 25% to 40% of high-molecular-weight CMC, whereas eucalyptus pulp sorbed 30% to 40% *(Figure 11)*. When the pulps were beaten (30 kWh/t) the sorption degree varied from 60% to 80% for eucalyptus (Paper V) and 50% to 60% for birch II pulp (Paper IV) and 90% for birch I pulp (Paper III). After DDJ-fractionation of birch II pulp the sorption degree of CMC increased by approximately 20% for both unbeaten and beaten pulp (Paper IV).
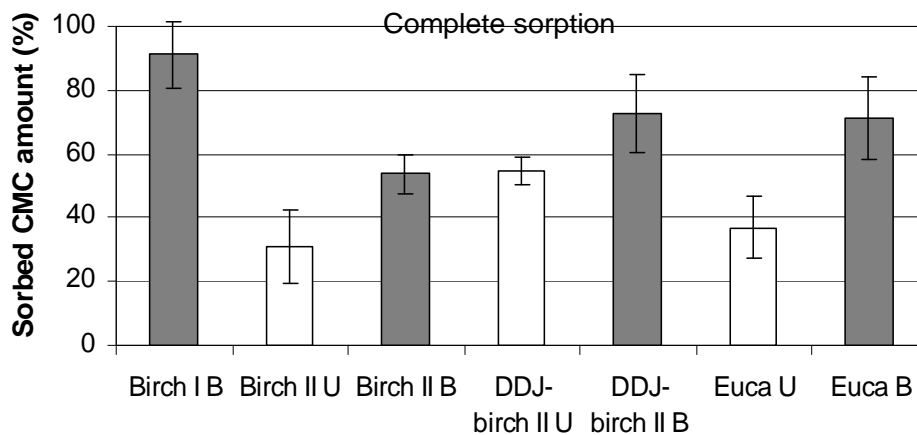
Figure 11. Sorbed amount of CMC on unbeaten (U) and beaten (B) birch and eucalyptus pulps (Paper III, IV, V). The error bars denote the variations between the two analytical methods used to determine the sorption degree.

5.2 Fiber properties of CMC-modified pulps

5.2.1 Water retention value

The water retention value (WRV) is used to determine the swelling capacity of pulps, and introduction of charged groups generally results in higher WRV values (Scallan 1983, Wistara et al. 1999). Accordingly, sorption of anionic CMC on beaten pulps led to a dramatic increase in their WRV values, especially for softwood pulps (Paper I) *(Figure 12).* More extensive beating results in a considerable increase in the WRV values, as could be expected. The WRV has been found to increase more if the charges are localized on the fiber surfaces than if they are distributed within the cell wall (Laine et al. 2003a). However, the high WRV values did not really correlate with the amount of sorbed CMC on the pulp and neither with the increase in total charge of fibers (Mitikka-Eklund et al. 1999). The WRV values of hardwood pulp (Paper IV, V) did not increase as much as the WRV values of softwood pulp (Paper I), probably because the level of sorption was higher in softwood pulp than in hardwood pulp *(Figures 10-11).*

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Another possible explanation is that PFI mills have shown to result in more internal fibrillation and straighter fibers than Voith-Sulzer beaten softwood fibers (Wang et al. 2007). This could partly explain why PFI-beaten softwood pulp displays higher WRV values than Voith-Sulzer beaten hardwood pulp. WRV values of CMC-modified softwood and hardwood pulps are shown in *Figure 12.*
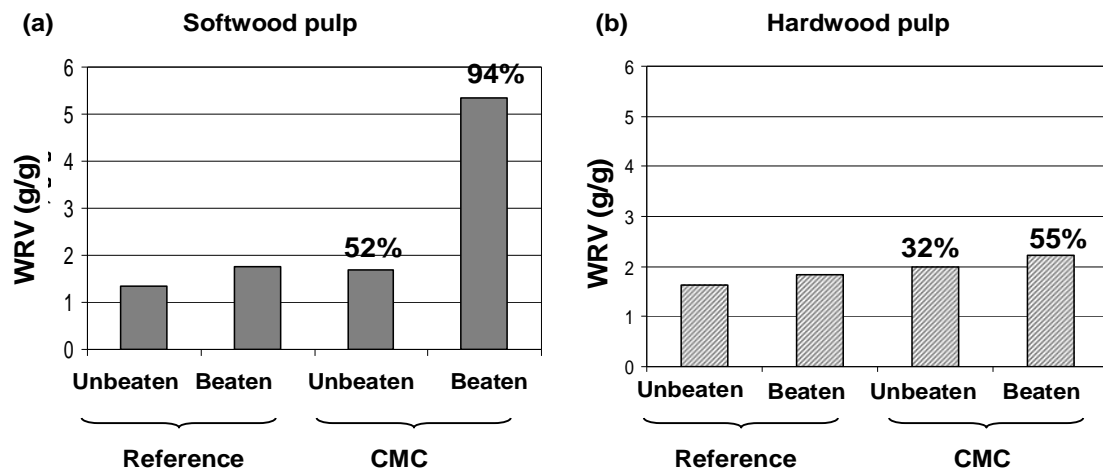

Figure 12. WRV values of CMC-modified (1% on pulp) and reference treated unbeaten and beaten *(a)* spruce (PFI 4000, SR 19, Paper I) and *(b)* birch II (30 kWh/t, SR 23, Paper IV) pulps. The percentages above the columns denote the sorbed amount of CMC on pulp. The standard deviation of the sorption degree varies from 0.02 to 0.001.

The same trends in the WRV values were seen for birch pulps with and without fractionation *(Figure 12b, 13a),* although the fractionated pulps have in general slightly lower WRV values (Paper IV). These results are in agreement with the results presented by Laivins (1996) who showed that fines swell more than fibers and pulp. In addition, eucalyptus pulp (Paper V) shows similar trends in CMC sorption degree and WRV as DDJ-fractionated birch pulp (Paper IV) *(Figure 13).* Comparable studies have shown similar increasing WRV results after CMC modification, especially when the carboxyl groups were in their Na form on the CMC-modified softwood fiber surface (Laine et al. 2002).
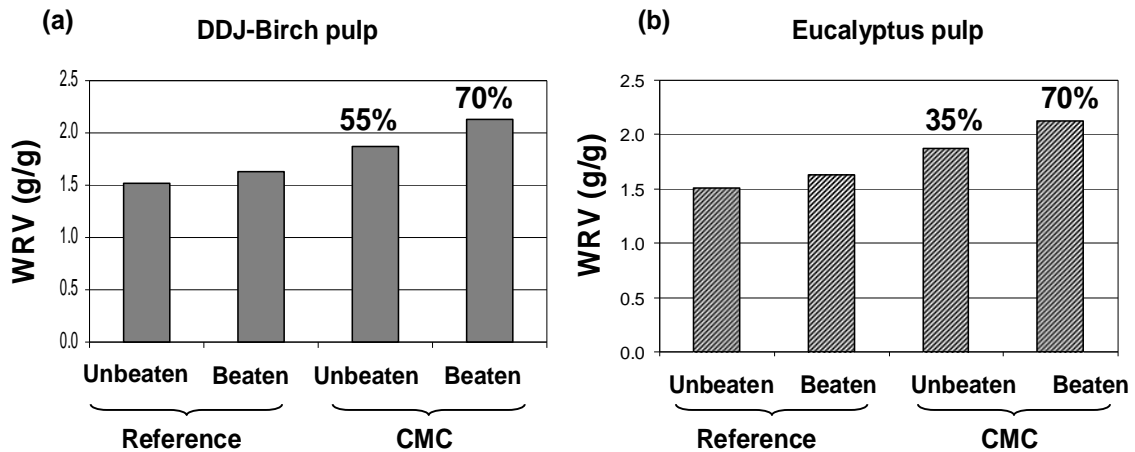
36

(a) DDJ-Birch pulp

(b) Eucalyptus pulp

Figure 13. WRV values of CMC-modified (1% on pulp) and reference treated unbeaten and beaten **(a)** DDJ-fractionated birch II pulp (30kWh/t, SR 13, Paper IV) and **(b)** eucalyptus pulp (30 kWh/t, SR 23, Paper V). The percentages above the columns denote the sorbed amount of CMC on pulp. The standard deviation of the sorption degree varies from 0.01 to 0.001.

When an electrolyte was added before measuring the WRV the swelling was reduced to about half, dropping to the same level as for the reference pulp (Paper I). Collapse of the hydrated structure by electrolytes showed that the cellulose microfibril-water phase may be stabilized by electrostatic interactions (Mitikka-Eklund et al. 1999). Therefore, the difference in WRV values between the pulps in water and in an electrolyte solution illustrates how much water retention is based on osmotic pressure as a consequence of counter ions dissociating from the fiber (Grignon et al. 1980).

5.2.2 Surface properties of CMC-modified softwood pulp

Confocal laser scanning microscopy (CLSM) images were taken in order to get more information about what happens on the surface of fibers when CMC is added. The CLSM images of beaten and CMC-treated softwood pulps showed extensive swelling of bundles of cellulose microfibrils on the fiber surfaces *(Figure 14b).* These extensions were absent in beaten reference pulps which, on

the contrary, contained released bundles of cellulose microfibrils (CMFs) on the fiber surfaces *(Figure 14a).* Thus, visually the main effect of CMC was to disintegrate external bundles of cellulose microfibrils (Mitikka-Eklund et al. 1999). A huge amount of water for the CMC-treated fibers can be bound into this external cellulose microfibril-water gel, which is seen as a dramatic increase in water retention values *(Figure 12a).* Since the water held by CMC is present on the surface, it can be easily removed by pressing (Laine et al. 2003b). It is only water inside the cell wall that is difficult to remove.
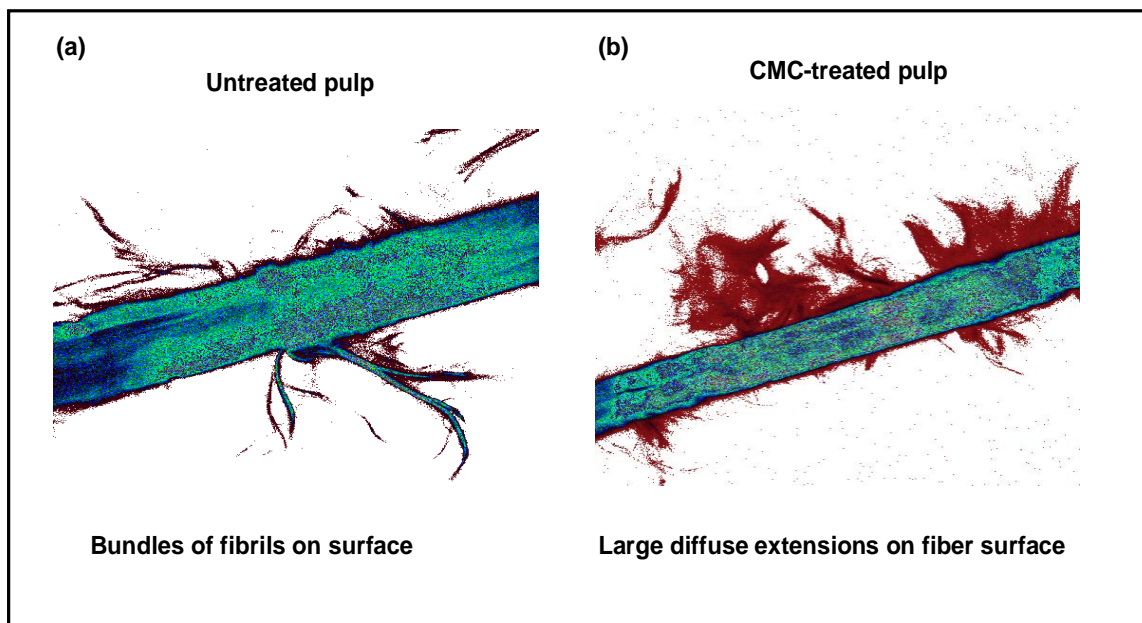
Figure 14. CLSM images of *(a)* a beaten (PFI 7000 rev.) reference softwood pulp and *(b)* a beaten CMC-modified (PFI 7000 rev.) softwood pulp (1% addition of Nymcel ZSB-10, pH 12.5) (Mitikka-Eklund et al. 1999).

5.2.3 Morphological properties of hardwood pulp

Fiber dimensions and deformations were determined with the KajaaniFiberLab as described in the experimental Chapter. The fiber properties for eucalyptus pulp (Paper V) *(Table 4)* and birch pulp (Paper IV), indicate that when the fibers are

beaten more fines are produced and the fibers become straighter. However, eucalyptus pulp produced less fines than birch when refined to the same level, which would theoretically lead to better drainage properties but lower strength properties (Retulainen et al. 1993). The lower curl values presented here *(Table 4)* correlate well with the results presented by Mohlin (1996) and Omholt (1999), who showed that especially PFI mills efficiently reduce fiber curl. One disadvantage of the FiberLab analysis is that the fiber length can be underestimated for curly fibers (Mörseburg et al. 1999). This can be clearly seen in *Table 4:* the curlier unbeaten pulp has lower fiber length than the straighter beaten pulp (Paper V). It should also be kept in mind that the curl values are inadequate because they do not directly measure deformation, only the response of the fiber deformation (Seth 2006). Similar deformation and dimensional trends were seen in all hardwood pulps analyzed with the KajaaniFiberLab (Paper IV, V). But eucalyptus pulps had in general smaller cell wall thickness, fiber length and fiber width compared to birch pulps *(Figure 15),* which is in accordance with earlier publications (Morud 1972, Patt et al. 2006). Furthermore, when birch pulp had been fractionated the fines content was lower and average fiber length higher, as could be expected, when nearly all fines had been removed during DDJ fractionation (Paper IV). Different authors assign different importance to different properties; usually fiber length is considered one of the most important fiber properties but also cell wall thickness has been shown to be important (Paavilainen 1990). Furthermore, it has been known for many years that it is beneficial to have straighter fibers because they need little beating to become active in the fiber network compared to curved fibers (Lobben 1975). In other words, straighter fibers result in better strength properties.

Table 4. *Length weighted fiber length, fines content, fiber width, fiber curl, kink and vessel content of eucalyptus pulp (Paper V).*

Sample Eucalyptus III	Fiber length (mm)	Fines content (%)	Fiber width (µm)	Curl value (%)	Kink content (1/m)	Vessel content (1/m)
Reference unbeaten	0.83	1.29	16.0	23.1	3121	34.6
Reference beaten	0.84	*1.44*	15.9	*21.7*	2751	*28.2*
CMC-treated unbeaten	0.83	1.13	15.9	21.9	2496	23.9
CMC-treated beaten	0.86	1.20	15.8	19.3	1920	*22.7*

Hardwood pulps and especially tropical hardwood pulps contain large vessel elements (Chapter 3.1.3), which can result in vessel picking problems in papermaking (Gopichand et al. 1990). Surprisingly, the vessel and kink content decreased for the CMC-treated pulp compared to the untreated pulp *(Table 4)* (Paper V). Can this mean that the vessel picking problems related to eucalyptus pulp may be remarkably reduced after the fibers have been CMC-treated? Or can it just be an error in the FiberLab measurement? This discussion is continued in Chapter 5.3.2.

The sorption degree results and WRV values clearly show that hardwood pulps and softwood pulps behave in different ways *(Figures 10-12).* Therefore, the question was raised whether the differences in responses of the pulp were caused by the fines content or some other morphological property. Can CMC be sorbed onto both fibers and fines? To cast light on these questions, CMC-modified hardwood pulp was fractionated with a hydrocyclone and DDJ in order to separate fines from fibers.
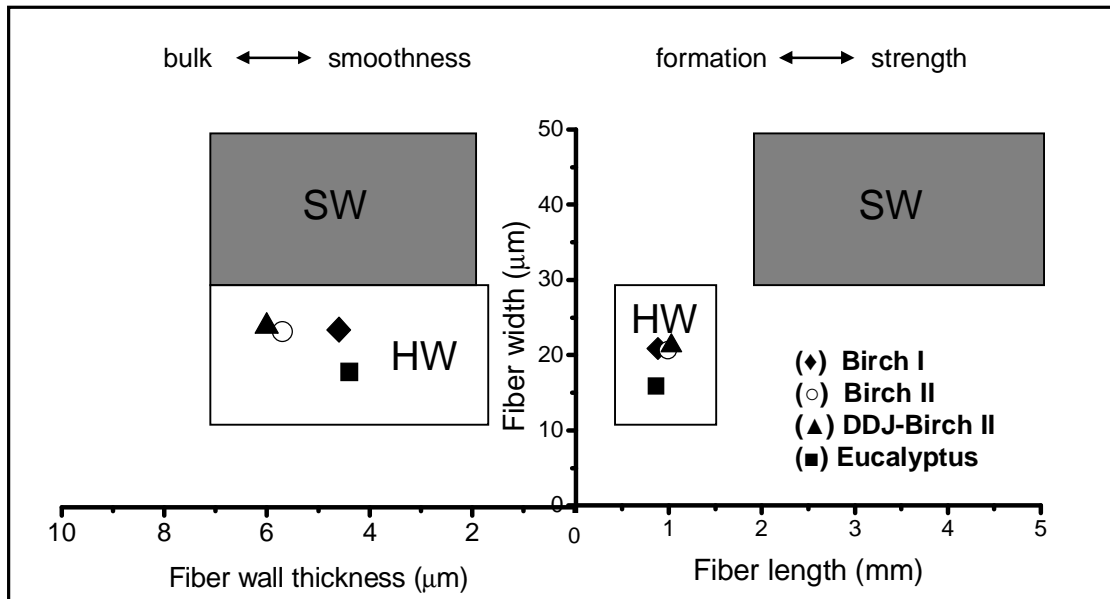
Figure 15. *Mapping of the properties of birch and eucalyptus pulp compared to softwoods (SW) and hardwood (HW) pulp dimensions in general (Lindström L-A 2002). Abbreviations: (♦) Birch I pulp (Paper III), (○) Birch II pulp (Paper IV), (▲) DDJ-Birch II pulp (Paper IV), (■) Eucalyptus pulp (Paper V).*

An unbeaten hardwood pulp (birch I) was hydrocyclone fractionated with a yield of 23% to 30% for the reject fiber fraction and 70% to 77% for the accept fiber fractions (Paper III). The differences in average fiber length were surprisingly small after hydrocyclone fractionation when analyzed with the KajaaniFiberLab *(Table 5).* In addition, fiber width, fiber length, cell wall thickness (CWT), curl and coarseness values were higher for the reject fiber fractions. Similar results for fiber coarseness, curl value and cell wall thickness of the reject fraction have been reported (Paavilainen 1992, Panula-Ontto 2003). It seems highly probable that the hydrocyclone separates the thick walled and coarser latewood fibers in the reject fraction from the thinwalled earlywood in the accept fraction. This has been shown earlier (Jones et al. 1966, Kure K-A et al. 1999, Paavilainen 1992).

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In *Table 5* it can be seen that the reject fiber fraction contains less CMC compared to the accept fiber fraction analyzed by methanolysis (GC). When the hardwood pulp reject and accept fractions were further fractionated with DDJ, the CMC-treated accept fractions contained more fines, xylan and CMC, but also straighter fibers (Paper III). These results are in accordance with the results presented by Panula-Ontto (2003) who showed that fines and straighter fibers are concentrated in the accept fiber fraction after hydrocyclone fractionation. The results presented in *Table 5* also indicate that fines have an important role in CMC sorption and that CMC also can be sorbed onto fines. But since fines contain more hemicellulose and therefore are more charged than fibers (Retulainen et al. 2002), CMC is mainly sorbed onto fibers.

Table 5. *Fiber dimensions and deformations of hydrocyclone fractionated birch I pulp analyzed with the KajaaniFiberLab. Hydrocyclone fractionation yield and fines content after DDJ fractionation and CMC content were analyzed with methanolysis-GC for the accept and reject pulp fractions (Paper III).*

Sample Birch I	Reference Reject	Reference Accept	CMC-treated Reject	CMC-treated Accept
Fiber length (mm)	*1.09*	0.91	1.11	0.89
Fines content (%)	0.80	1.40	0.74	1.31
CWT (µm)	5.1	4.7	4.9	4.6
Fiber width (µm)	*23.9*	20.6	23.4	20.4
Curl value (%)	*19.5*	14.8	20.4	14.8
Coarseness (mg/m)	*0.098*	0.084	0.096	0.081
Fractionation yield (%)	22.9	*77.1*	30.4	69.6
Fines content DDJ	2	0.5	0.7	*3.6*
CMC content (%)	-	-	0.38	*0.48*

5.3 Sheet properties of CMC-modified pulps

5.3.1 Softwood pulps

Strength properties of CMC-modified softwood pulps

An increase in swelling (or WRV) brings about an improvement in the plasticity and flexibility of the fibers and in consequence, an increase in their ability to bond extensively during sheet formation. Therefore, it is obvious that the dramatic increase in WRV values seen for softwood pulp *(Figure 12a)* would lead to high tensile and internal strengths, also when the comparison is made at a constant sheet density *(Figures 16a, 16c)* (Paper I). During beating the tensile and internal strengths of the CMC-treated pulp develop faster than those of the untreated (reference) pulps. A slight increase in tensile stiffness index was also observed after CMC modification *(Figure 16b).* In addition, it has been suggested by Mitikka et al. (1999) that microfibrillation of the external fiber surface is one of the most important factors in the formation of interfiber bonds. Laine and coworkers (2002) have also reported similar internal and tensile strength properties due to CMC treatments. Because the DS of the CMC and method of sorption were different in the two investigations a direct comparison is cumbersome.
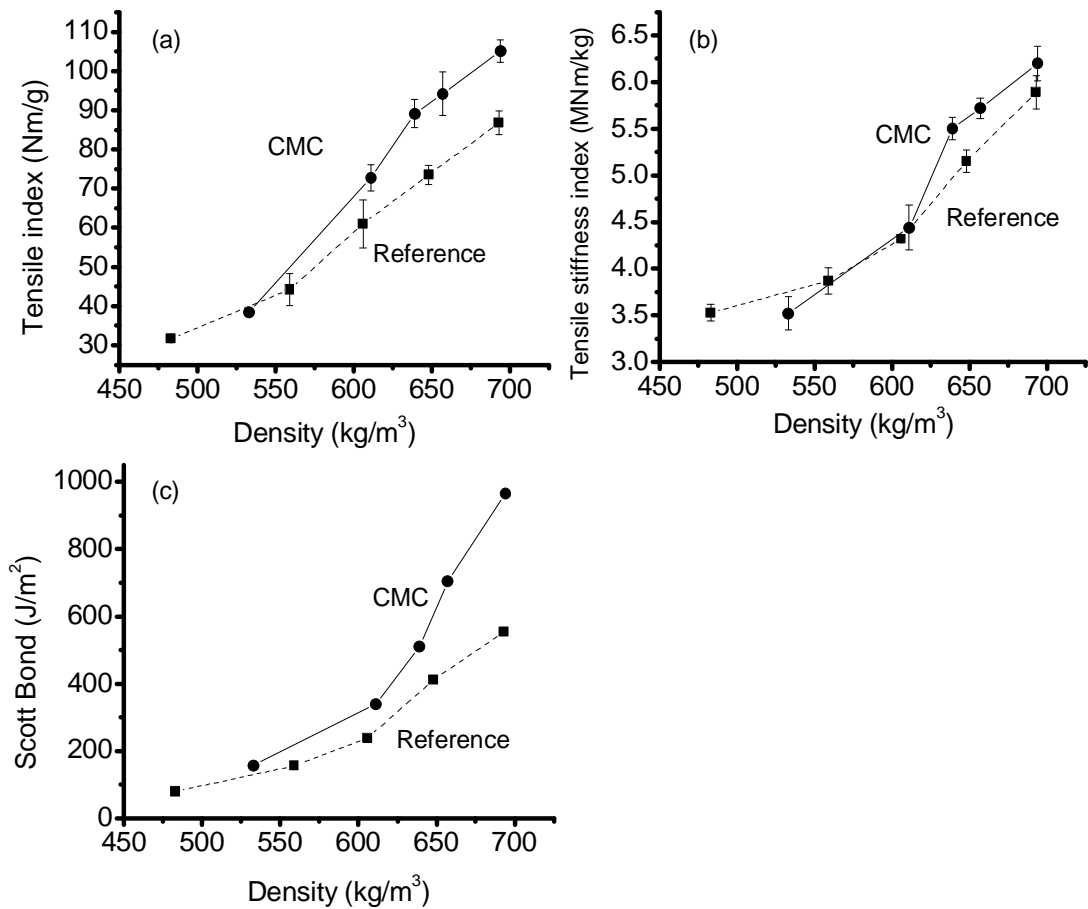
Figure 16. *Effect of modifying softwood with CMC (1% CMC addition, DS 0.2) on (a) tensile index, (b) tensile stiffness index and (c) Scott Bond values of the paper sheets relative to their density (Paper I). The solid (CMC) and dashed lines (reference) denote changes caused by beating (PFI 0, 1000, 2000, 4000 and 7000 rev.).*

A trend in papermaking is towards increased recycling of drainage waters; hence there is growing interest in understanding the effects of the higher electrolyte concentrations on paper properties. To shed more light on this aspect, the effect of an electrolyte on sheet formation was investigated by preparing laboratory sheets in a dilute electrolyte solution (Paper I). When the sheets were prepared in sodium chloride the density of the CMC-modified (DS 0.2) sheets were exceptionally low, whereas the bonding properties (tensile and internal strength) decreased slightly but still remained at a high level. In conclusion, the internal

strength values increased by 70%, tensile stiffness by 10% and tensile index values by 30% after CMC modification of beaten (4000 rev.) softwood pulp.

Strength properties of CMC- and surfactant-modified softwood pulps

Only a few attempts have been made to study the effect of surfactants on paper properties. The main effect of adding surfactants to mechanical and chemical pulps (Bruun et al. 1975, Christensen 1969) and sulfite pulp (Touchette et al. 1960) has been a decrease in strength properties. The results of the present study show a remarkable increase in internal (Scott Bond) and tensile strength when softwood pulp has first been treated with CMC and then with a surfactant (*Figure 17)* (Paper II). Optimum conditions were reached with C_{12}TAB (dodecyltrimethylammonium bromide, $C_{15}H_{34}BrN$) as evidenced by the Scott Bond values*.* Half of the maximum increase in the internal strength values was achieved after adding only 0.02% surfactant on fibers *(Figure 17a).* When the surfactants C_{14}TAB and C_{16}TAB were added the Scott Bond values increased in the same way as for C_{12}TAB in the beginning but started to drop dramatically after adding 0.1% surfactant on fibers. The surfactant addition on reference pulps without CMC did not increase the internal strength values at all, which is in accordance with the earlier results (Bruun et al. 1975, Christensen 1969).

One important fact to remember is that CMC is first permanently attached on the surface of the fibers and then the surfactants are added. Therefore, it is very unlikely that a free CMC-surfactant phase would exist in the fiber-CMC-surfactant system. Both cellulose and CMC polymer chains are quite stiff and therefore it is improbable that any micellar aggregates are formed in the fiber-CMC-surfactant system. One speculation could be that the surfactants can associate with CMC on the anionic fiber surface by ionic and hydrophobic interactions. But further research is needed to clarify the interaction between the fiber-CMC-surfactant system.
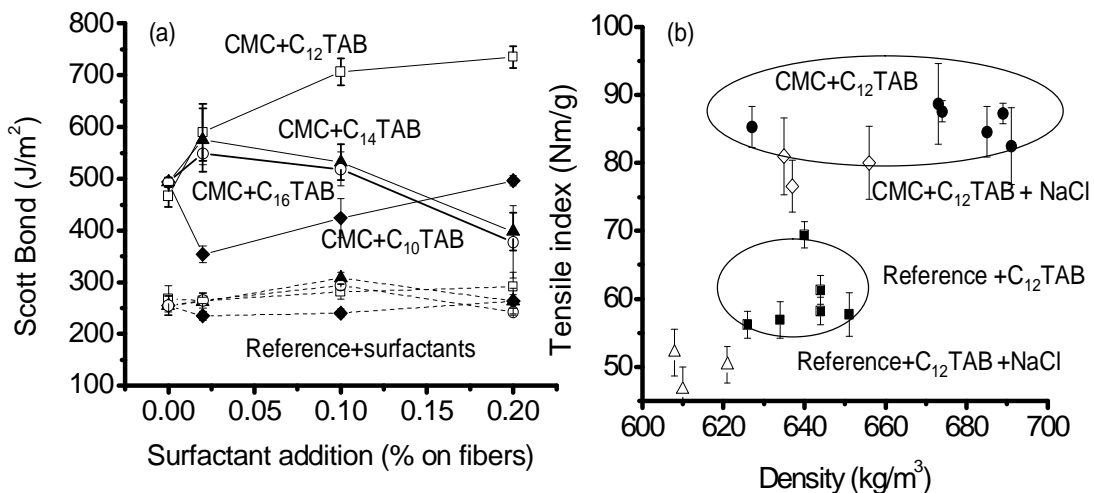
Figure 17. (a) Effect of modifying softwood fibers with CMC (DS 0.32) and surfactants (♦ $C_{10}TAB$, □ $C_{12}TAB$, ▲ $C_{14}TAB$, ○ $C_{16}TAB$) on sheet density and internal strength (b) effect of modifying softwood fibers with CMC (DS 0.32), electrolyte (0.05 M NaCl) and surfactant $C_{12}TAB$ on sheet density and tensile strength (● CMC-$C_{12}TAB$, ◊ CMC-$C_{12}TAB$-NaCl, ■ Reference-$C_{12}TAB$, ∆ Reference-$C_{12}TAB$-NaCl) (Paper II).

According to the study by Barck et al. (1994) the association of the surfactant with the CMC polymer chain increases when the chain length of the surfactant increases. This could explain why the Scott Bond values of $C_{10}TAB$ are so low (Paper II). However, further research is needed to explain why $C_{12}TAB$ gives so high Scott Bond values *(Figure 17)*. One speculation is that the cellulose-CMC-surfactant may behave in a similar way as a polyelectrolyte multilayer with repeated adsorption of cationic and anionic polymers (Wågberg et al. 2002). Because the formed layer is thick and more flexible, a significant improvement in strength properties is obtained. Accordingly, polyelectrolyte multilayers of cationic starch and CMC have been shown to enhance the strength properties of chemical pulp (Pettersson et al. 2006a, Pettersson et al. 2006b).

When the handsheets were prepared in slurries of $C_{12}TAB$-CMC-treated pulp fibers in the presence of an electrolyte, the tensile strength properties dropped by

approximately 10% *(Figure 17b)* (Paper II). In other words, almost all the positive effects of adding the surfactants gained in water were eliminated when an electrolyte was added before sheet making. Seemingly, the screening of the electrostatic attraction by the electrolyte between CMC and cationic surfactant influences the complex formation unfavorably from the point of view of strength properties.

ESEM sheet properties

To shed more light on the sheet properties presented above, the structure of the sheets was examined by environmental scanning electron microscopy (ESEM) (Paper I, II). ESEM images of the sheets made from CMC-treated pulp suggested extensive formation of microcompressions and some rupture of bonded areas during drying *(Figure 18b)*. No ruptures and little microcompressions were visible in ESEM images of sheets that were made from a CMC-treated pulp in 0.05 M sodium chloride (*Figure 18d).* The microfibrils on the fiber surface formed large bonded areas in crossings and narrow bridges between fibers. The surface of the fibers seemed to be smoother and cleaner when the CMC pulps were treated with an electrolyte before sheet preparation (Paper I). These findings indicated that decreased shrinkage of the partially destabilized cellulose microfibril (CMF) gel on the fiber surfaces was a major reason for the decrease in deformations in the electrolyte solution. The low amount of deformations also led to improved out-of-plane and in-plane tear indices (data not shown).
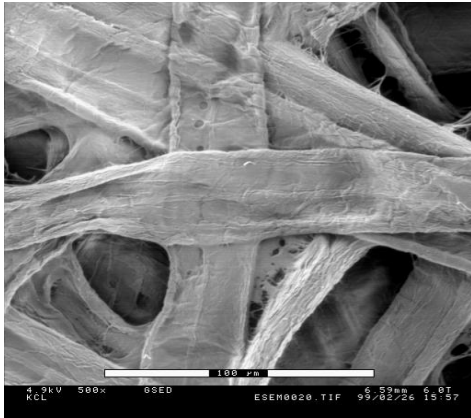
(a) Untreated pulp, sheeted in water

(b) CMC-treated pulp, sheeted in water

(c) Untreated pulp, sheeted in 0.05 M NaCl

(d) CMC-treated pulp, sheeted in 0.05 M NaCl
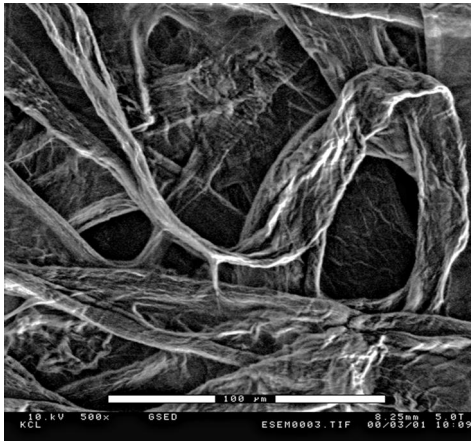
(e) Untreated pulp and 0.1 % surfactant, sheeted in water
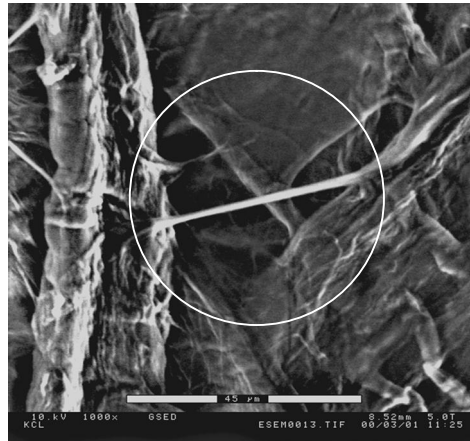
(f) CMC-treated pulp and 0.1% surfactant, sheeted in water

Figure 18. ESEM images of untreated and CMC-treated beaten (PFI 2000 rev.) softwood pulps sheeted *(a-b)* in water (Paper I), *(c-d)* in 0.05 M NaCl (Paper I) and *(e-f)* in water when surfactant (0.1% C_{12}TAB) was added (Paper II).

Furthermore, when the surfactant (C_{12}TAB) was added in the sheet-preparation stage (Paper II), the ESEM images of the sheets suggested strong "gum/ropelike" fibril bridges between the fibers *(Figure 18f)*. These strong bridges may at least partly explain the improved strength properties of the handsheets prepared *(Figure 17).* In contrast, the reference sheets were very clean and bridges were hard to find on the surface of the fibers (*Figure 18e*).

5.3.2 Hardwood pulps

Effect of fines

Generally, fines contribute to sheet consolidation, wet web strength and interfiber bonding. The hardwood pulp (birch II) was DDJ-fractionated in order to get more information about the role of the fines for the strength properties of CMC-modified sheets (Paper IV). According to Retulainen et al. (1993), the main consequences of fines are increased density and improved activation of fiber segments and fiber wall material. The results of the present study illustrated in *Figures 19 and 20* correlated well with the proposed increased densities and improved activation reported by Retulainen et al. (1993). However, strength increased dramatically when the nonfractionated pulps were beaten, whereas no strength gains were observed for the fractionated pulps due to beating. This dramatic increase in internal strength cannot be merely explained by the slight increase in WRV after the CMC treatment (*Figures 12b, 13a).* A marked increase (100%) in internal strength was observed especially when the nonfractionated pulps were CMC-treated, plate-dried and beaten (Paper IV). One explanation could be that the nonfractionated beaten pulp contains more fines, thus leading to higher internal strength values. Similar results have been published by Retulainen et al. (1996) who showed that interfiber bonds can be strengthened by adding dry strength chemicals and fines. Generally, it can be said that fines

have a positive effect on density, tensile and internal strength, tensile stiffness and light scattering and a negative effect on tear strength (Retulainen et al. 1993). This is clearly seen in *Figures 19-20* as a decrease in density, internal strength and tensile strength when the pulps were DDJ-fractionated (Paper IV). The same decreasing trends were also seen for the CMC-modified fractionated pulps. Similar trends for fractionated and nonfractionated sheets were observed when they were drum-dried *(Figure 19a).* Paavilainen (1990) has proposed that the total surface area and bonding ability are the most important characteristics of the chemical pulp fines. Generally, fines affect the drainage rate negatively and fiber-to-fiber bonding positively. However, the increased swelling and flexibility of fibers caused by beating has the same kind of effect on the fiber network as fines addition (Retulainen et al. 1993).

Figure 19. *Effect of fractionation, CMC treatment and drying conditions on **(a)** drum-dried **(b)** plate-dried hardwood sheets (birch II) on Scott Bond versus density. The solid lines (CMC) and dashed lines (REF) denote changes caused by beating (0 and 30 kWh/t) (Paper IV). Individual points denote hydrocyclone fractionated birch I pulp, as indicated by the key in (a) (Paper III).*
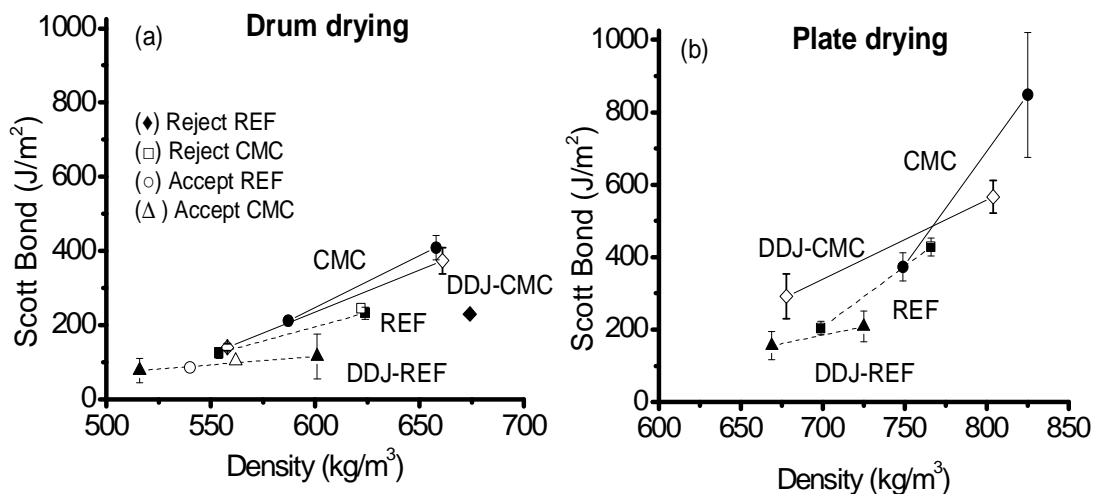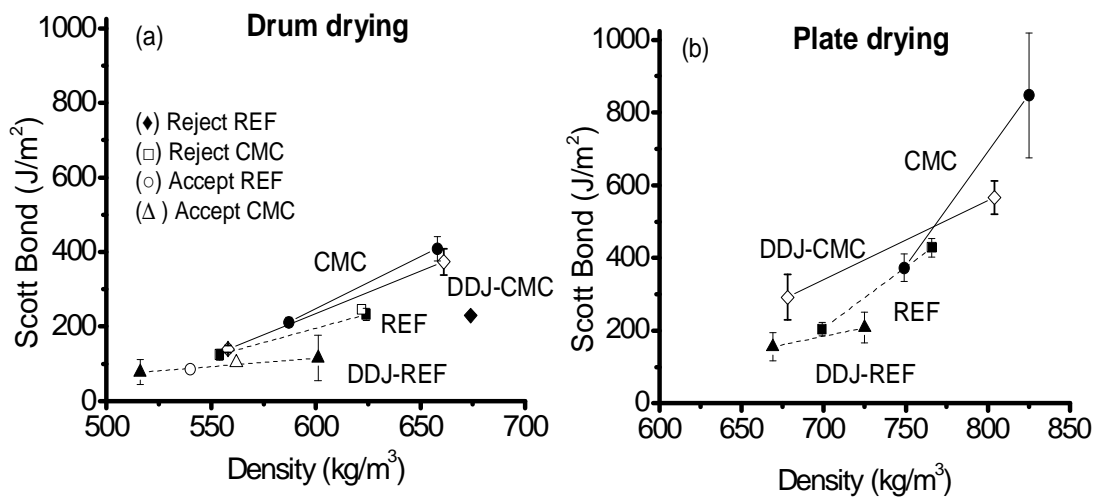
Figure 20. *Effect of fractionation, CMC treatment and drying conditions on (a) drum-dried (b) plate-dried hardwood sheets (birch II) on tensile index versus density (Paper IV). The solid lines (CMC) and dashed lines (REF) denote changes caused by beating (0 and 30 kWh/t).*

In general, the strength properties increase more when both fines and fibers are present (nonfractionated pulp), especially when the sheets were dried under restraint (*Figures 19-20).* One exception to this was the accept fraction that gave lower densities and internal strength properties than the reject fraction, although the accept fraction contained more fines, straighter fibers and more CMC *(Table 5)* (Paper III). This can be due to the fact that the reject fraction contains longer fibers, but also because of the small difference in fiber length distribution between the rejects and accepts after hydrocyclone fractionation *(Figure 8b, Table 5).* Earlier studies have shown that the accept fraction usually has higher density and fines content (Panula-Ontto 2003) and therefore also higher tensile and bonding strength (Jones et al. 1966, Li et al. 1999, Paavilainen 1992).

In addition, similar tends in tensile strength properties were seen for both plate- and drum-dried sheets *(Figure 20)* (Paper IV). In other words, it seems more important to have the fines present in the z-directional strength than in tensile

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strength, but also to have both fines and fibers present when the pulp is CMC-modified. It is clearly seen in *Figures 19-20* that the fines increase the tensile and internal strength properties of the CMC-modified sheets only slightly, except for the plate-dried and CMC-treated sheets.

Only a slight increase in internal strength properties was seen when pulps sheets were prepared in circulating water (Paper IV). Maybe CMC can bind the fines into the fiber network so that they do not end up in the circulating water and therefore the strength properties are independent of whether circulating water is used or not.

Effect of drying technique

The effect of drying on handsheets was examined with two different methods: 1) drum drying (freely dried) and 2) plate drying (restraint dried). *Figures 21-22* show that the density values of the plate-dried sheets were significantly higher than those for the drum-dried sheets, due to the more compact structure of the sheets when dried on a plate (Paper IV, V). However, the densities were in general lower for eucalyptus pulp than for birch pulp, probably due to the higher stiffness caused by lower hemicellulose content (Patt et al. 2006) and narrow, thick-walled fibers of eucalyptus pulp fibers compared to birch. The chemical compositions of birch and eucalyptus are different, with birch containing in general more hemicellulose and less cellulose and lignin than eucalyptus (Morud 1972, Patt et al. 2006). The higher density of birch can partly be explained by the higher hemicellulose content, which has been shown to improve fiber bonding and swelling (shrinkage). In addition, fibers with higher shrinkage, caused by the hemicellulose content, will be subject to greater stress during restraint drying of the sheets, which leads to an improvement in tensile strength properties (Wahlström et al. 2000b).

Figure 21. *Effect of CMC treatment and drying conditions on (a) drum-dried (b) plate-dried hardwood sheets (birch II, eucalyptus) on tensile index versus density (Paper IV, V). The solid lines (CMC) and dashed lines (REF) denote changes caused by beating (0 and 30 kWh/t).*
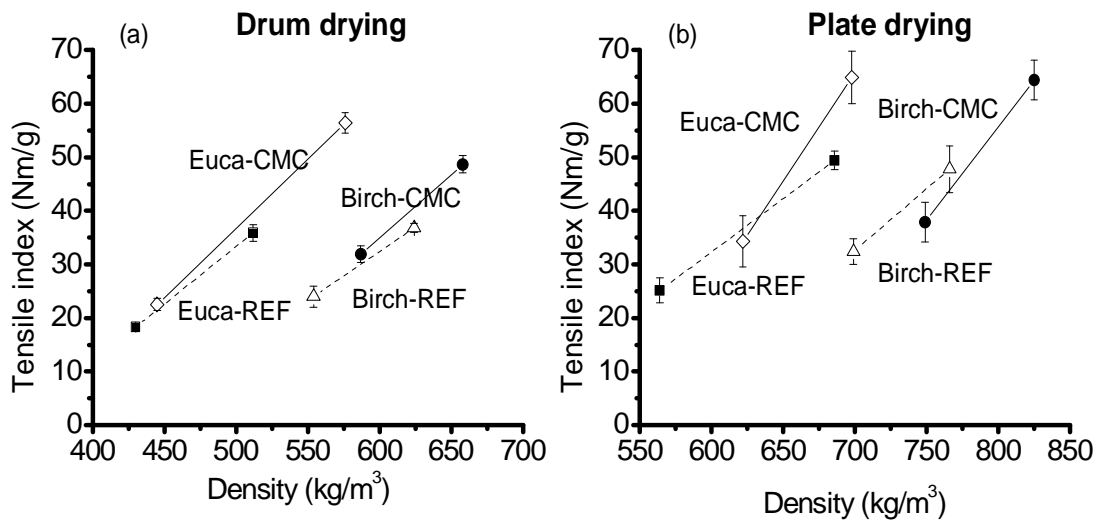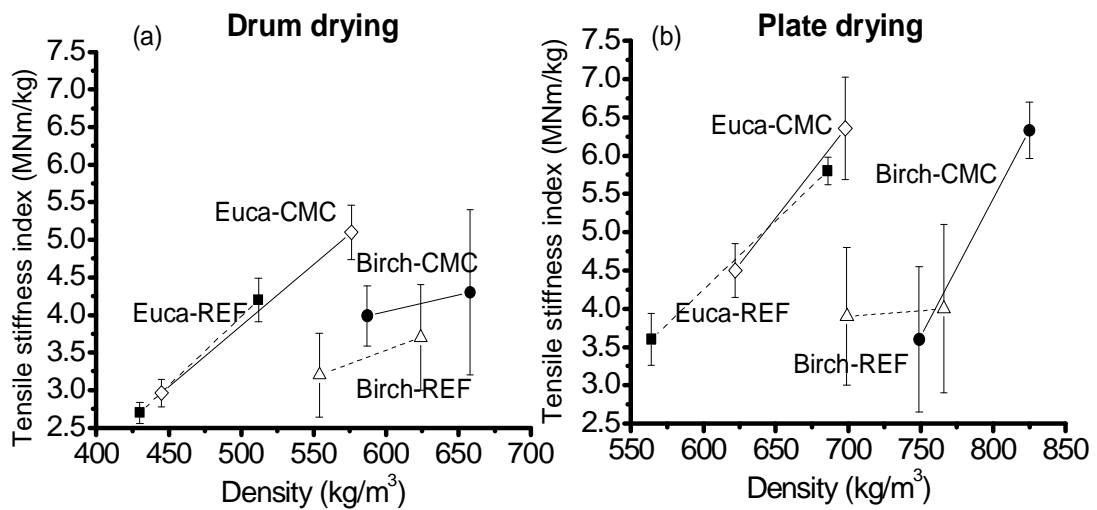

Figure 22. *Effect of CMC treatment and drying conditions on (a) drum-dried (b) plate-dried hardwood sheets (birch II, eucalyptus) on tensile stiffness index versus density (Paper IV, V). The solid lines (CMC) and dashed lines (REF) denote changes caused by beating (0 and 30 kWh/t).*

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Moreover, the tensile stiffness and tensile strength values were higher for the CMC-modified plate-dried sheets, especially when the pulps were beaten *(Figure 21-22)* (Paper IV, V). Similar results have been reported by Lindström (2002) who showed that eucalyptus has higher tensile strength than birch at a constant density. Because eucalyptus has a greater number of fibers per gram of pulp and a smaller tendency to collapse due to the higher cellulose content of the fibers, the tensile strength properties of eucalyptus pulp are better than those of birch pulp compared at a constant sheet density. It has been reported earlier that eucalyptus has a lower fibril angle than birch (Claudio-da-Silva et al. 1982), which could also explain the superior strength properties of eucalyptus.

Significant increases in tensile stiffness (60%), tensile index (30%) and Scott Bond values (100%) were recorded when the birch pulp was CMC-treated, beaten and dried under restraint (Paper IV). *Figure 21-22* shows that also the strength properties of eucalyptus pulp increase after CMC treatment but not to the same extent as for birch pulp. Furthermore, only a small increase in tensile stiffness was seen for the drum-dried birch sheets *(Figure 22).* One major difference between eucalyptus and birch pulps is that eucalyptus also gives high strength properties for the reference pulp, so the increase in tensile stiffness of eucalyptus pulp after CMC modification is not so dramatic as that of birch pulp. *Figure 22* clearly shows that also drum-dried CMC-treated eucalyptus pulp gives surprisingly high tensile stiffness (Paper V). In general, the tensile properties of eucalyptus are lower for unbeaten pulp, whereas when beaten the tensile properties increase to the same level as for birch pulp. When eucalyptus and birch pulp are compared, plate-dried eucalyptus pulp gives tensile strength properties similar to those of drum-dried birch (Paper IV, V).

The good tensile properties of the CMC-treated hardwood pulps are partly due to the drying technique. The influence of the drying technique on tensile properties, apparent in *Figures 21-22,* has been studied by Wahlström (2000a). When the sheets are dried under restraint, with neither shrinkage nor stretch allowed during

the drying process, the tensile properties are higher than when freely dried (Chance 1992, Lobben 1975, Wahlström 2000a). The same increasing trend in tensile stiffness when drying under restraint was also clearly seen in the results illustrated in *Figure 22* (Paper IV, V). Similar results as shown in *Figure 22* have also been reported by Zhang et al. (2004) who showed that sheets dried on a plate had higher density, tensile and internal strength properties than cylinder-dried sheets. The difference in sheet structure of freely and restraint dried paper are illustrated in *Figure 23*. Generally, the final impact of drying on paper strength is in fact a combination of many things; drying stresses, the degree of shrinkage, the solids content at which shrinkage takes place, the type of raw materials used and their fiber properties, the extent of beating, the fiber orientation of the wet paper and the drying strategy (Vainio et al. 2006).
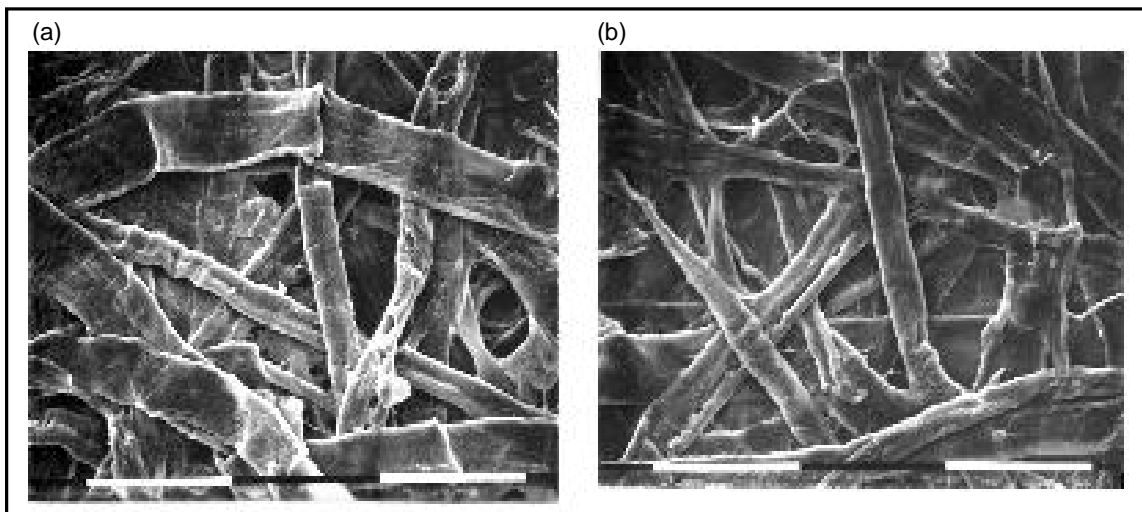

Figure 23. (a) Freely dried paper (note deformed fibers due to free shrinkage) and *(b)* paper with restrained drying shrinkage (Kiiskinen et al. 2000).

Effect of fiber deformations

Many factors affect the tensile and internal strength of paper, such as the interfiber bonding degree, fiber strength and moisture content (Wahlström 2000a)

and so on. But also fiber morphology plays an important role in determining the final strength of paper, because mechanical treatments such as refining and handling of chemical pulp fibers introduce curl, kinks and microcompressions to the fibers, which affect the tensile strength of the final sheet. Several authors have studied the effects of fiber deformation (fiber kink, curl) on pulp sheet properties (Joutsimo et al. 2005, Mohlin et al. 1996, Omholt 1999, Page et al. 1979, Seth 2006). Straight fibers have been found to have higher tensile stiffness than deformed fibers due to their higher fiber segment activation (Joutsimo et al. 2005). Beating reduces the degree of fiber deformation and thus increases the stiffness of fibers. Accordingly, *Table 4* shows that beaten eucalyptus pulp has lower curl values than unbeaten pulps, thus leading to higher tensile strength and tensile stiffness properties *(Figures 21-22)* (Paper V). Fiber deformations have been found to have a much larger effect on the sheet's tensile strength than on its elastic modulus (Seth 2006).

Furthermore, when a sheet is dried under restraint and prevented from shrinking, the shrinkage stresses at the fiber-fiber bonds remove some of the slackness left by crimps and kinks in the unbonded segment, and thus straighten them. The stress distribution in the network is improved and the fibers are able to resist more load (Seth 2006).

As discussed above, fibre deformation (curl) is a very important fibre property. An increase in strength is commonly attributed either to increased bonding through increased flexibility or fibrillation, or to increased shrinkage stress. According to Page (1985) an even more important factor is that more than half of the improvement upon beating comes from straightening out of the fibres that have been curled and kinked during pulping and bleaching. This should be kept in mind when laboratory results are interpreted and papermaking processes are planned.

Vessel picking tendency of eucalyptus pulp sheets

The short and narrow fibers of eucalyptus kraft pulps give a unique combination of formation, strength and opacity in papermaking (Morud 1972). One problem with eucalyptus pulps is, however, that they contain large vessel elements, which cause vessel picking problems in printing (Gopichand et al. 1990). Vessel picking is a phenomenon where the hardwood vessel elements in the paper surface tend to be picked off by the ink-tackiness of the printing press, creating white spots in the printing surface. The vessel picking can be reduced by selecting suitable chips, by hydrocyclone separation (Ohsawa et al. 1984), by reducing the size of the vessels by refining (Byrd et al. 1969, Colley 1975), or by increasing the vessel to fiber bonding (Ohsawa 1988).

An increased vessel and ray content also correlates with lower strength properties, studies differ to their relative impact (Amidon 1981). The results of the present study show that pulps with an increased vessel content result in handsheets with lower strength properties *(Figures 21-22, Table 4).* Furthermore, as shown in *Table 4*, the vessel content was decreased when the eucalyptus pulp was beaten, as could be expected, but also when the pulp had been CMC-treated (Paper V). This unique feature of CMC modification to reduce the vessel content was further investigated with a new method for examining the vessel picking tendency developed by KCL (Blomstedt et al. 2007, Panula-Ontto et al. 2007).

Table 6. *Vessel picking results for eucalyptus plate-dried sheets analyzed with an image analyzer (Blomstedt et al. 2007).*

Number of picks/cm^2	Reference Unbeaten	Reference Beaten	CMC-treated Unbeaten	CMC-treated Beaten
Ink	19.31	3.12	8.77	2.32
Back trap	2.91	1.65	1.74	1.31
TOTAL	***22.22***	4.77	***10.51***	3.63
Picked area, µm^2				
Ink	0.53	0.09	0.22	0.04
Back trap	0.07	0.04	0.04	0.02
TOTAL	**0.60**	0.12	**0.26**	0.07

Table 6 clearly shows that the vessel picking tendency is reduced after CMC modification, especially for beaten eucalyptus pulp (Blomstedt et al. 2007). These results correlate with the inexplicable decreasing vessel content of CMC-modified eucalyptus pulp presented in *Table 4.* It seems possible that the CMC modification of eucalyptus pulp can change the shape of the vessel element or break the vessel elements so that the vessel content decrease dramatically after CMC modification *(Table 7).* Maybe the vessel elements can bind into the fiber network more strongly after CMC treatment, resulting in lower picking tendency. Byrd (1969) has shown that surface treatment of offset papers containing oak vessels, with corn and potato starches and low-viscosity carboxymethyl cellulose, greatly reduces vessel picking. Moreover, when the eucalyptus pulps were beaten, the vessel picking of the untreated (reference) and CMC-treated samples was almost at the same level (Table 6), because refining effectively reduces the size of the vessel elements, as reported by Byrd et al. (1969) and Colley (1975). It seems highly likely that CMC treatment of eucalyptus pulp reduces the vessel picking tendency. This means that printing quality could be significantly improved for pulps containing vessel elements after they have been CMC-modified (Blomstedt et al. 2007).

Table 7. *Fiber and vessel content (pieces) of eucalyptus pulp analyzed by light microscope (Blomstedt et al. 2007).*

Samples	Reference Unbeaten	Reference Beaten	CMC-treated Unbeaten	CMC-treated Beaten
Fibers	5746	6038	5503	5189
Vessels	*21*	*18*	*12*	*20*
Broken vessels	*2*	7	*6*	8
Vessel pieces	4	7	5	7

5.3.3 Comparison between CMC-modified softwood and hardwood pulps

The amount of CMC sorbed on pulps was found to depend on several factors, including DP and DS of CMC, charge of CMC, pH and ionic strength of the sorption medium and degree of beating of the pulp and so on. In a previous study, CMC molecules of low DP were found to be preferably sorbed from a solution of depolymerized Nymcel ZSB-16 that had a wide molecular weight distribution (Mitikka-Eklund et al. 1999). The amount of sorbed CMC on the pulp increased strongly for beaten fibers and for CMC with a lower degree of substitution (Paper I). Unbeaten softwood pulps (Paper I) sorbed 10-25% more CMC than hardwood pulps (Paper IV, V), whereas beating of pulp caused 30-40% more CMC to be sorbed onto softwood pulps than on hardwood pulps at 1% CMC addition (Figures 10-11). The different sorption degrees could partly be explained by the different beating equipments used. Wang and coworkers have shown that PFI-beating of softwood pulp results in more internal fibrillation and straighter fibers than Voith-Sulzer beaten pulp when beaten to a similar level (Wang et al. 2007). This could explain why more CMC is sorbed onto softwood than hardwood fibers.

Sorption of CMC on unbeaten and especially beaten pulps led to an increase in their water retention values compared to the untreated (reference) pulps (*Figures 12-13*) (Paper I, IV, V). Especially sorption of CMC on beaten softwood pulps led to a dramatic increase in their water retention values (WRV), which could be partly explained by the large diffuse extensions of microfibrils on the fiber surface

seen in the CLSM images after CMC modification *(Figure 14)*. However, the WRV values of hardwood pulp (Paper IV, V) did not increase as much as those of softwood pulp (Paper I), probably because the level of sorption is higher in softwoods than in hardwoods. ECF-bleached hardwood pulps have been found to have a higher total amount of charged groups than a similar softwood pulp (Laine et al. 1997b). Since the repulsion is therefore smaller for softwood pulps, more CMC is sorbed onto the fibers. Another explanation is that beaten softwood pulps (pine) have longer and thicker fibrils in the fiber surface compared to hardwood pulps (birch, eucalyptus) (Claudio-da-Silva et al. 1982). This could explain why softwood pulps result in so much higher WRV values and better strength properties than hardwood pulps especially for CMC-modified pulps. It has been shown that more fibrillated fibers sorb CMC more readily onto the fibers (Jokinen et al. 2006). In other words, fibrillation of the external surface of fibers is an important factor for the CMC modification of the fiber surface *(Figure 14)*. However, the swelling of hardwood fibers, with their thinner cell walls and higher hemicellulose content (higher charge) should be more extensive than the swelling of softwood fibers (Laine et al. 1997a). Furthermore, more swollen fibers have been shown to be straighter (Mohlin U-B 2005). So is the improved strength properties of softwood due to improved bonding or to straighter fibers?

The strength properties (Scott Bond, tensile index and tensile stiffness index) of the untreated and CMC-treated softwood and hardwood pulps are illustrated in *Figure* 24 (Paper I, II, IV). It can be seen that all strength properties were dramatically improved when they where CMC-treated and especially when the pulps were beaten. Softwood pulp (Paper I) had in most cases better strength properties than hardwood pulp (Paper IV) when dried in a drum dryer. This can be partly explained by the fact that softwood fibers are longer than hardwood fibers and that more CMC is sorbed onto the softwood fibers than hardwood fibers. Another possible reason is that PFI mills have been shown to result in more internal fibrillation and straighter fibers than Voith-Sulzer beaten softwood pulp when beaten to a similar level (Wang et al. 2007). This could also partly

explain why PFI-beaten softwood pulp displays better tensile and internal strength properties than Voith-Sulzer beaten hardwood pulp. From *Figure 24* it can be seen that when softwood pulp was treated with CMC and a surfactant, there was a further increase in the tensile and internal strength properties of the sheets (Paper II).
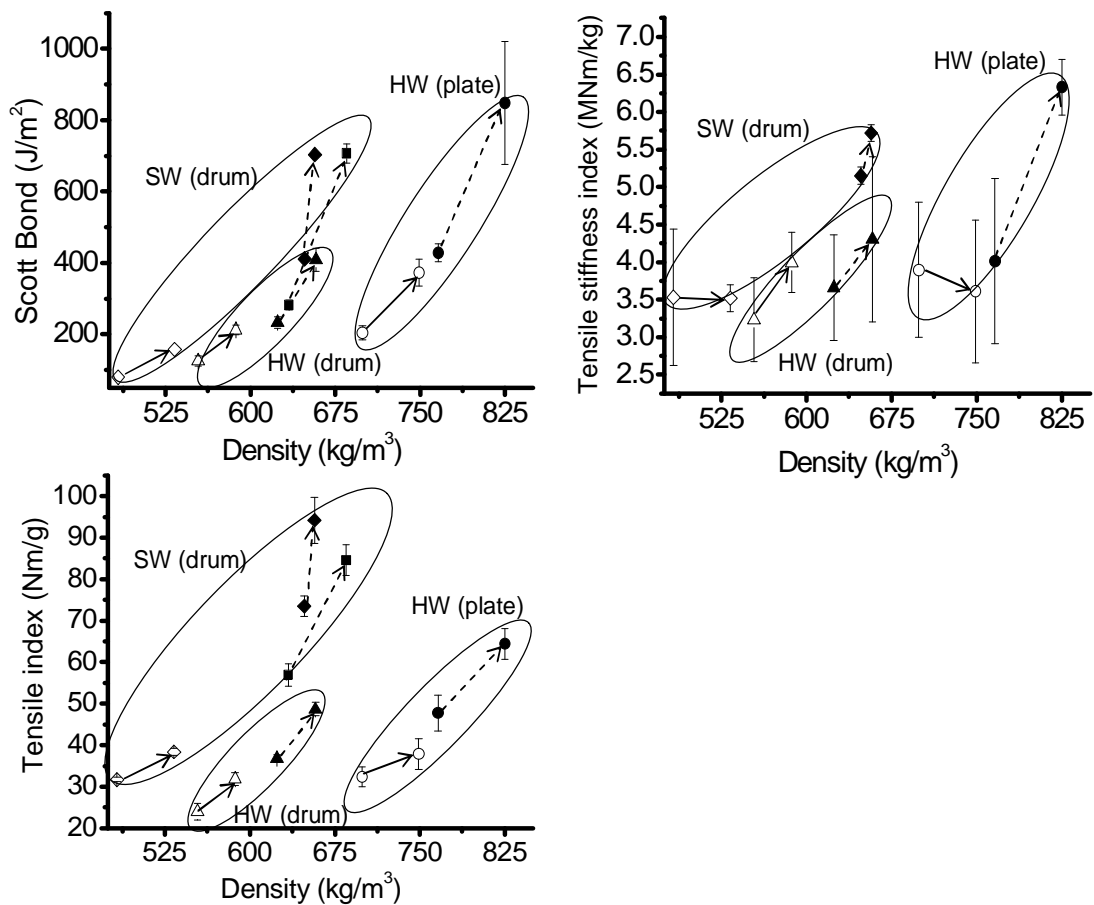
Figure 24. *Effect of CMC treatment (1% CMC addition, pH 12) of unbeaten (solid lines) and beaten (dashed lines) spruce (SW, PFI 4000 rev., SR 19) and birch II (HW, Voith Sulzer 30kWh/t, SR 23) pulps on sheet density and* *(a)* *Scott Bond,* *(b)* *tensile stiffness index and* *(c)* *tensile index (Paper I, II, IV). The first point illustrated the untreated (REF) point and the second the CMC-treated (CMC) point. The sheets were dried on a plate or in a drum. The CMC- and surfactant (0.1% C_{12}TAB)-treated pulp was PFI-refined for 2000 rev. (◊ SW unbeaten drum-dried, ♦ SW beaten drum-dried, ■ SW+surfactant beaten drum-dried, Δ HW unbeaten drum-dried, ▲ HW beaten drum-dried, ○ HW unbeaten plate-dried, ● HW beaten plate-dried).*

Furthermore, when pulps were dried under restraint the beaten CMC-modified hardwood pulps resulted in higher Scott Bond, tensile stiffness and density values but lower tensile index values compared to drum-dried softwood pulp *(Figure 24).* A substantial increase (60%) in the tensile stiffness index, Scott Bond (50%) and tensile index (35%) were observed when the hardwood pulp was CMC-treated, beaten and dried under restraint (Paper IV). The good tensile properties originated from the different drying technique coupled with the strength improvements of CMC modification, as discussed earlier in Chapter 5.3.2.

An increasing trend in papermaking is to reduce grammage or basis weight while trying to keeping the strength properties at the same level. The results of the present study strongly suggest that basis weight can be reduced by modifying both softwood and hardwood fibers with CMC. In other words, less fibers are needed to gain the same strength properties, which means that for example more sustainable packaging materials could be manufactured. Previous similar studies, have shown that the basis weight can be reduced by treating the fibers with CMC (DS 0.5) and cationic starch (Retulainen et al. 1996).

The main conclusions are that the biggest improvement in strength properties was achieved when the hardwood pulps were CMC-treated, beaten, and dried under restraint (Paper IV, V). Softwood pulp gave high strength properties also for drum-dried CMC-modified sheets (Paper I), especially when the pulp was both CMC- and surfactant-modified (Paper II). In addition, the best strength properties of CMC-modified pulps were achieved after beating, which is in accordance with the findings of Stratton (1989). Ekevåg and coworkers (2004) have studied the sorption of CMC onto kraft pulps during cooking and the effects of subsequent bleaching. They showed that CMC treatment during the kraft cook leads to an improvement in tensile strength, although a large part of the added CMC was degraded during the cook. In other words, only a part of the effect of CMC remained after bleaching. It was shown that the degraded CMC was attached to the interior of the cell wall and as a consequence a significant

reduction in the positive effect of CMC was observed due to the loss of CMC molecules from the fiber surface. These results strongly indicate that CMC modification is not so suitable in the cooking or bleaching stage. Against this background, CMC modification should preferably be done after the beating or refining stage to get the best possible improvement of fiber quality properties.

6 CONCLUSIONS AND SUGGESTIONS

The strength and topology of the sorption of CMC on cellulosic fibers was mainly controlled by DS and DP of the CMC. A significant improvement in internal and tensile strength properties was seen for CMC-modified softwood and hardwood pulps, especially when the pulps were beaten. The tensile stiffness values increased the most when the hardwood pulp sheets were dried under restraint on a plate, which is closer to the drying in real papermaking. These kinds of papers can be useful when high stiffness is required, for example in packing materials. The CMC modification method presented in this study strongly indicates that CMC could be added as an integral step in the papermaking process, for instance, after refining or beating. Another promising result was that CMC modification significantly reduces vessel picking for eucalyptus pulps.

More fundamental research is needed to fully understand the mechanism behind the cellulose-CMC and cellulose-CMC-surfactant system. This could be done by studying the CMC sorption with for example a quartz crystal microbalance on cellulose model surfaces, which would considerably enhance our understanding of this phenomenon. Furthermore, to be able to apply this CMC modification method on industrial scale, industrial production of CMC with low DS is required.

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