Lappeenranta
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THE EFFECTS OF SOME FURNISH AND PAPER STRUCTURE RELATED FACTORS ON WET WEB TENSILE AND RELAXATION CHARACTERISTICS

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ABSTRACT

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The objective of this thesis was to identify the effects of different factors on the tension and tension relaxation of wet paper web after high-speed straining. The study was motivated by the plausible connection between wet web mechanical properties and wet web runnability on paper machines shown by previous studies.

The mechanical properties of wet paper were examined using a fast tensile test rig with a strain rate of 1000%/s. Most of the tests were carried out with laboratory handsheets, but samples from a pilot paper machine were also used. The tension relaxation of paper was evaluated as the tension remaining after 0.475 s of relaxation (residual tension).

The tensile and relaxation properties of wet webs were found to be strongly dependent on the quality and amount of fines. With low fines content, the tensile strength and residual tension of wet paper was mainly determined by the mechanical interactions between fibres at their contact points. As the fines strengthen the mechanical interaction in the network, the fibre properties also become important. Fibre deformations caused by the mechanical treatment of pulp were shown to reduce the mechanical properties of both dry and wet paper. However, the effect was significantly higher for wet paper.

An increase of filler content from 10% to 25% greatly reduced the tensile strength of dry paper, but did not significantly impair wet web tensile strength or residual tension. Increased filler content in wet web was shown to increase the dryness of the wet web after the press section, which partly compensates for the reduction of fibrous material in the web. It is also presumable that fillers increase entanglement friction between fibres, which is beneficial for wet web strength.

Different contaminants present in white water during sheet formation resulted in lowered surface tension and increased dryness after wet pressing. The addition of different contaminants reduced the tensile strength of the dry paper. The reduction of dry paper tensile strength could not be explained by the reduced surface tension, but rather on the tendency of different contaminants to interfere with the inter-fibre bonding. Additionally, wet web strength was not affected by the changes in the surface tension of white water or possible changes in the hydrophilicity of fibres caused by the addition of different contaminants.

The spraying of different polymers on wet paper before wet pressing had a significant effect on both dry and wet web tensile strength, whereas wet web elastic modulus and residual tension were basically not affected. We suggest that the increase of dry and wet paper strength could be affected by the molecular level interactions between these chemicals and fibres. The most significant increases in dry and wet paper strength were achieved with a dual application of anionic and cationic polymers. Furthermore, selectively adding papermaking chemicals to different fibre fractions (as opposed to adding chemicals to the whole pulp) improved the wet web mechanical properties and the drainage of the pulp suspension.

Keywords: Paper strength, wet web, tension, relaxation, runnability

UDC 676.017.73 : 676.017.42 : 676.026.2

PREFACE

The studies presented in this doctoral thesis were carried out at VTT (Technical Research Centre of Finland) in Jyväskylä. Metso Paper Oy supported this research and made this thesis possible.

I would like to express my warmest thanks to Professors Isko Kajanto and Hannu Manner for their support and advice during this work. I would also like to thank Dr. Elias Retulainen for his encouragement, patience and extremely valuable advice during this thesis. I am also grateful to my pre-examiners Dr. Rolf Wathén and Dr. Heikki Kettunen for their invaluable suggestions to enhance the structure and content of this thesis.

My sincerest thanks go to Ph. Lic. Matti Kurki and M.Sc. Juan Cecchini for leading me into the depths of paper machine runnability. Further, I thank M.Sc. Janne Kataja-aho, M.Sc. Jarmo Kouko, M.Sc. Vesa Kunnari, M.Sc. Pekka Martikainen and M.Sc. Antti Oksanen for participating actively in the studies of this thesis. I also thank my superiors Dr. Janne Poranen, M.Sc. Terhi Saari and Ph. Lic. Harri Kiiskinen for their support and understanding during this thesis.

I am also grateful for all the help and support I received from my colleagues, and especially the laboratory staff at VTT who conducted much of the practical work during this thesis.

Thanks go to my parents, Marja Järnstedt and Ahti Salminen, for all the help and support they have always given me. Further, I would like to thank my sister Susanna Erikkilä and her family for their encouragement.

I would also like to express my gratitude to my friends for giving me a sense of balance that allowed me to define a reasonable scope for this thesis.

Foremost, my warmest and deepest thanks go to my wife, Hanna, my son Valtteri and my daughter Fanni, for their support, love and never-ending patience.

Pirkkala, August 2010

Kristian Salminen

- to Hanna, Valtteri and Fanni-

CONTENTS

LIST OF SYMBOLS AND ABBREVIATIONS

Symbols used in the thesis

Breaks	percentage of downtime caused by breaks, %
Broke	percentage of broke, %
C	fibre coarseness, mg/m
DT_S	scheduled downtime, %
DT_U	unscheduled downtime, %
F	the force to pull a platinum ring of a precisely known dimension, mN
S	tensile stiffness, N/m
E	efficiency of one sub-process, -
E_{tot}	total efficiency, -
EF	production efficiency, %
L	contour length of fibre, mm
l	projection length of fibre, mm
m	grammage of the web, kg/m^2
m_A	added mass (mass of the boundary layer), kg/m^2
P	perimeter of the average fibre cross-section, m
$\Delta p(t)$	pressure loss caused by the filtrating pulp layer, Pa
$\Delta \overline{p}$	pressure difference over the web, Pa
R	radius of curvature of the moving web, m
r	radius of the curvature of water meniscus, m
$R_{\%}$	relaxation percentage, %
RBA	the relative bonded area, -
$T_{release}$	release tension, N/m
T	tension, N/m
TS	tensile strength, N/m
T_{max}	maximum tension/initial tension (immediately after straining), N/m
T_{res}	residual tension at certain strain after certain relaxation time, N/m
v	velocity of the web, m/s
v_1	velocity of the web at the first supporting point, m/min
v_2	velocity of the web at the second supporting point, m/min

W_{adh}	adhesion energy, J/m^2
β	release angle, radian
ε_T	strain of the web, -
μ	coefficient of friction, -
γ	surface tension, mN/m
$R_{f,tot}$	flow resistance of pulp, kg/m^{2}s
$q_T(t)$	flow rate (total flux) of the fluid phase given by the surface position detector at a given time, m^3/s.
$q_T(t)$	flow rate (total flux) of the fluid phase given by the surface position detector at a given time, m^3/s.

Abbreviations

A-PAM	anionic polyacrylamide
BK	bleached kraft pulp
BS	digester operations
CD	cross direction
CMC	carboxymethylated cellulose
C-PAM	cationic polyacrylamine
CSF	Canadian standard freeness
D1	second chlorine dioxide bleaching stage
D2	third chlorine dioxide bleaching stage
D/C	chlorine dioxide bleaching stage containing chlorine
DCS	dissolved and colloidal substances
DDA	dynamic drainage apparatus
DDJ	dynamic drainage jar
DIP	de-inked pulp
DP	degree of polymerisation
DS	degree of substitution
E/O	alkaline extraction with oxygen stage
G-PAM	glyoxylated polyacrylamine
LFF	long fibre fraction (R16+R25 fractions separated with Bauer McNett apparatus)

LWC	lightweight coated (paper)
MD	machine direction
N	number of samples
News	newsprint (paper)
O2	oxygen delignification
PAE	polyamide epichlorohydrin
P300/R400	pulp passing through a 300 mesh screen and remaining on a 100 mesh screen
PC	personal computer
PGW	pressure groundwood
PP	pulps prepared at pilot scale
PUD	pulsed ultrasound-Doppler anemometer
PVA	polyvinyl alcohol
R100	pulp remaining on 100 mesh screen
R25	pulp remaining on 25 mesh screen
R16	pulp remaining on 16 mesh screen
RH	relative humidity
SC	supercalendered (paper)
SW	softwood
T.E.A.	tensile energy adsorption
TMP	thermomechanical pulp
WRV	water retention value
y/R	dimensionless position in y-direction
x/R	dimensionless position in x-direction

1. INTRODUCTION

The main target of the paper manufacturer is to make a product with the desired material properties. To do this economically, the good runnability of paper machine is required. Paper machine runnability is often evaluated by the number of web breaks in proportion to production speed. To attain good runnability, the paper must run well (with a low number of web breaks) in each sub-process along the entire paper machine line. Figure 1 shows a simplified statistical approach on how the efficiency of each sub-process (E) affects the total efficiency of the paper machine (E_{tot}). In this case 'efficiency' refers to the likelihood that each sub-process will run without web breaks. In a situation of high overall efficiency, the efficiency of each sub-process is relatively high ($E_{tot}=0.97^6=0.83$). If all sub-processes have deteriorated efficiency evenly, the total efficiency decreases significantly ($E_{tot}=0.95^6=0.74$). In the case of major problems in only one sub-process, the total efficiency of the paper machine is reduced considerably ($E_{tot}=0.95^5\times0.85=0.73$). In practice, it is common for one of the sub-processes to cause most of the web breaks, leading to a poor total efficiency. To enhance the total efficiency, it is important to identify the bottlenecks in the line and to optimise the process and furnish to minimise production losses caused by these bottlenecks [1, 2].

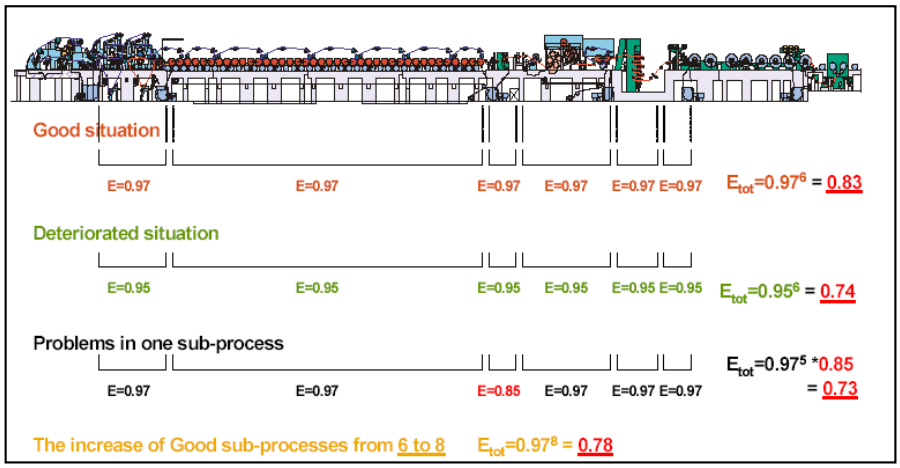

Figure 1. Schematic example of the effects of sub-process efficiency to total efficiency of on-line papermaking concept [2].

Since mill scale trials to optimise furnish are very expensive, it is necessary to predict how changes in furnish affect paper machine runnability. This can be done by modelling or by measuring the paper properties (on laboratory scale) that are believed to correlate with paper machine runnability [3].

Traditionally, the ability of furnish to run on a paper machine has been evaluated by determining the mechanical properties of dry paper, such as tensile strength and tear energy. The combination of tear energy and tensile strength has also been widely used (typically, tear energy at a constant tensile strength level) as a criteria to predict the runnability of furnish on a paper machine [1, 4]. However, no published studies have shown a clear connection between tear energy and paper machine runnability. Since the 1990s, fracture toughness has been proposed as an indicator to predict the ability of dry paper to tolerate defects [1, 5]. Since many of the runnability problems occur in the wet state, measuring of wet web strength has been widely used to predict the effects of furnish composition on wet web runnability [6-14]. The combination of the tensile strength and strain at break of wet web has also been used as an indicator for the runnability of furnishes [15, 16].

However, according to the author's knowledge, none of the methods mentioned above have been conclusively shown to correlate with paper machine runnability. There are some indications that the mechanical properties (tension and tension relaxation) of wet web at a high strain rate could be used to predict the runnability of furnish in press-to-dryer transfer and at the beginning of the dryer section on the paper machine [17-22]. However, there is little information on what factors determine these mechanical properties.

This thesis presents how different factors relevant in papermaking affect wet paper tensile strength and relaxation characteristics at a high strain rate.

2. OBJECTIVE AND STRUCTURE OF THE THESIS AND THE AUTHOR'S CONTRIBUTION

The objective of this thesis is to identify the main factors in papermaking that affect wet web tensile and relaxation characteristics. This information can be important when optimising the runnability of wet web on a paper machine. Good runnability of the beginning part of the paper machine (when the paper is still wet) is required to attain high production efficiency of the entire papermaking line [2].

Relevant scientific literature is reviewed in chapters 3-6. Chapter 3 presents an overview of the role of runnability in papermaking and a discussion of the challenges to improving efficiency. Chapter 4 deals with the structure and properties of fibres and fines and their effect on different paper properties. Chapter 5 addresses the effect of fibre orientation and wet pressing on the mechanical properties of fibre network. The effects of different chemicals and the way in which they contribute to water removal and the mechanical properties of both dry and wet paper are investigated based on literature in Chapter 6.

Chapter 7 describes the different materials and methods used in this study. Chapters 8-13 present the experimental results of this thesis. Chapter 8 presents and discusses the role of fines and fibres on the mechanical properties of dry and wet paper. Chapter 9 deals with the effect of fibre orientation and filler content on wet and dry web mechanical properties. In Chapter 10, the effect of the fibre shape on dry and wet paper properties is reported and discussed. In addition, the effect of white water composition (Chapter 11) and the addition of different polymers (Chapters 12 and 13) are presented and discussed. Chapter 14 summarises the findings and conclusions of this thesis and presents some suggestions for further research.

The author's contribution to this thesis can be summarised as follows:

Structure and contents of thesis: Planning of the contents and structure of this thesis under the tutelage of supervisors. Writing of the first draft and corrections of the thesis during the review process. Drafting literature surveys, conclusions and discussions to the thesis (with the guidance of both supervisors and reviewers). The following summary details the author's contribution to the experimental work of this thesis.

Chapters 8 and 11: Planning of the experiments in part, a major part of measurements and analyses of the results (concerning mechanical properties of dry and wet paper), guidance of other laboratory work.

Chapter 9: Re-analysing of results and new findings from existing data.

Chapter 10: Planning of the experiments in part, guidance of laboratory work, part of measurements and analyses of the results (concerning the mechanical properties of dry and wet paper).

Chapter 12: Planning of the experiments, guidance of laboratory work and analyses of the results.

Chapter 13: Planning of experiments in part, measurements and analyses of the results (concerning the mechanical properties of dry and wet paper), guidance of other laboratory work.

Some of the data used in this thesis have been reported earlier in the following publications:

1. Retulainen, E. & Salminen, K., ***Effects of furnish-related factors on tension and relaxation of wet webs***, Transactions of the 14th Fundamental Research Symposium, September 2009, Oxford, UK

2. Salminen, K., Cecchini J., Retulainen, E. & Haavisto, S., ***Effects of selective addition of papermaking chemicals to fines and long fibres on strength and runnability of wet paper***, PaperCon Conference, May 2008, Dallas, Texas, USA

3. Kouko, J., Salminen, K. & Kurki, M., ***Laboratory scale measurement procedure of paper machine wet web runnability: Part 2***, Paperi ja Puu, 89(2007)7-8

4. Kunnari, V., Salminen, K. & Oksanen, A., ***Effects of fibre deformations on strength and runnability of wet paper***, Paperi ja Puu, 89(2007)1

5. Salminen, K. & Retulainen, E., ***Effects of fines and fiber fractions on dynamic strength and relaxation characteristics of wet web***, Progress in Paper Physics Seminar, October 2006, Oxford, USA

6. Salminen, K., Kouko, J. & Kurki, M., ***Prediction of wet web runnability with a relaxation test***, The 5th Biennial Johan Gullichsen Colloquium, November 2005, Helsinki, Finland

3. PAPER WEB ON PAPER MACHINES

The main function of paper machine is to produce an even network from pulp suspension by gradually removing water from it. When the pulp suspension enters the headbox and thus the paper machine, its dryness level is typically between 0.1-1%. The first water removal is driven by gravity when the paper enters the wire section from the headbox. As paper travels further in the wire section, water removal is assisted by different vacuum units. After the wire section, the dryness of the paper is typically 20%. The dryness of paper increases to 40-50% during wet pressing. The remaining water in paper web is removed in the dryer section, which increases the dryness to 90-98% [23-25].

Modern paper machines are about 100 meters long and they have an average production speed up to 1800 m/min. This means that paper undergoes rapid changes in both its structure and its physical and chemical properties during processing. Additionally, paper experiences high in-plane and out-of-plane loads during manufacturing. Paper's ability to tolerate these external loads during manufacturing significantly affects the runnability of the papermaking process [3].

3.1 Challenges to efficiency

Figure 2 shows the average annual production speed and efficiency of the top five machines for four major paper grades from the years 1997 to 2008. In this figure paper machine production efficiency is determined by Formula (1), which shows that production efficiency is affected by scheduled and unscheduled downtimes in the paper machine, web breaks and the amount of broke [26].

$$EF = \left[\left(100 - \left(DT_S + DT_U + Breaks\right)\right) \cdot \left(100 - Broke\right)\right] / 100 \quad (1)$$

where

	EF	production efficiency, %
	DT_S	scheduled downtime, %
	DT_U	unscheduled downtime, %
	$Breaks$	percentage of downtime caused by web breaks, %
	$Broke$	percentage of broke, %.

During the last decade, the efficiency and average production speed of the top five paper machines of all major paper grades have significantly increased as shown in Figure 2. Newsprint machines have high efficiency and average production speed. Paper machines producing wood-free uncoated grades also have high efficiency but their average production speed is significantly lower compared to newsprint machines. Paper machines producing SC and LWC grades have a higher average production speed than wood-free machines, but their efficiency is lower. The low efficiency of SC and LWC paper machines can be partly explained by the fact that they typically have on-line coaters and supercalenders, which increase the amount of sub-processes and downtime associated with the clean-up and recovery from web breaks. Another explanation for the low efficiency of SC and LWC grades is that the quality requirements of these paper grades have increased, thus leading to a drop in the percentage of sellable paper (increased amount of broke) [26].

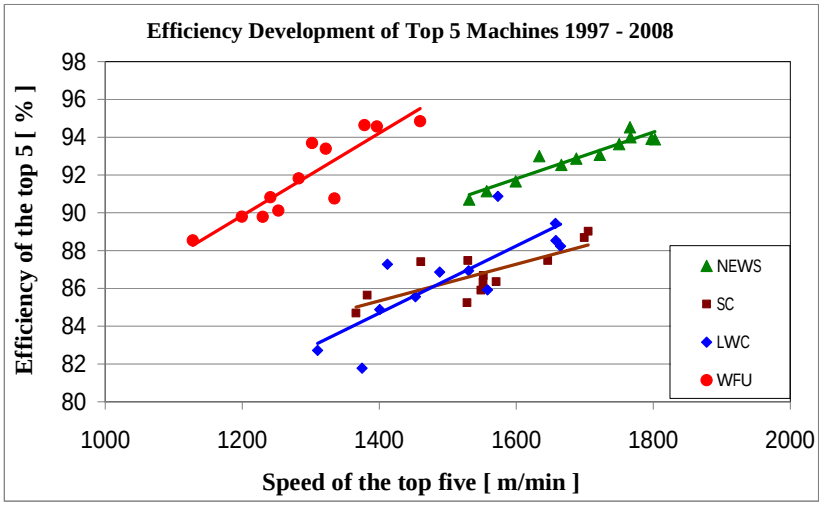

Figure 2. *The efficiency and average production speed of the top 5 machines in the world from the years 1997 to 2008 for different paper grades* [26].

As shown in Figure 2, the fastest paper machines have an average running speed of nearly 1800 m/min [26]. The practical maximum width of paper machines today is about 11 metres, because raising the width would require significant investments (increased radius of cylinders) to eliminate vibrations of the cylinders at high speeds. To increase the amount of produced paper on a paper machine, web breaks, broke and downtime in general must be minimised and the production speed maximised [3].

3.2 Occurrence of web breaks on paper machine

The increase of paper machine production speed is often limited by an increase of web breaks and many paper machines are thus forced to run below their design speed. To increase paper machine production speed, the locations and reasons for the web breaks caused by production speed increase must be identified before they can be reduced. Hokkanen [27] studied the location of web breaks on a Finnish magazine paper machine (a follow-up study, lasting six months), whose first open draw was located at the press section between the third and fourth press nips (Figure 3). His study showed that many of the web breaks occurred in the first open draw (centre roll) and immediately after it. This means that the majority of the recorded web breaks happened when the paper was wet (dryness 40-60%).

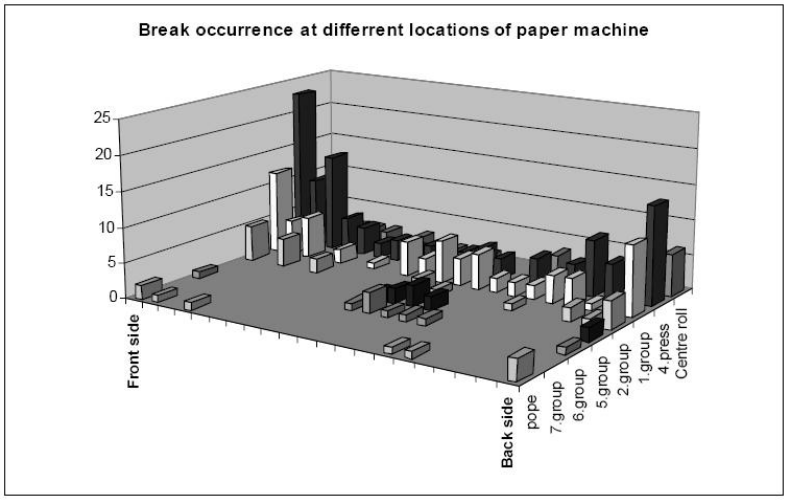

Figure 3. *The location of web breaks in machine- and cross direction* [27]. *The data was collected during a follow-up study lasting six months for a Finnish magazine paper machine.*

Figure 3 shows also that some web breaks also occurred during reeling at pope. It should also be noticed that relatively high amount of web breaks started at the edges of the paper. This study lacks information on web breaks occurring during the finishing of paper, since these were not reported.

3.3 Causes of web breaks

Many published studies that deal with the topic of web breaks (especially in pressroom) are based on the fact that web breaks can be explained by the high tension or low strength of the paper web. The web breaks can occur if some part of the web is too weak or tension at some part of the web is too high. There are statistical variations in both the strength and tension of the web and they can be described with strength and tension distributions. Web breaks are possible in the strength/tension range where the two distributions overlap (see Figure 4) [28-32].

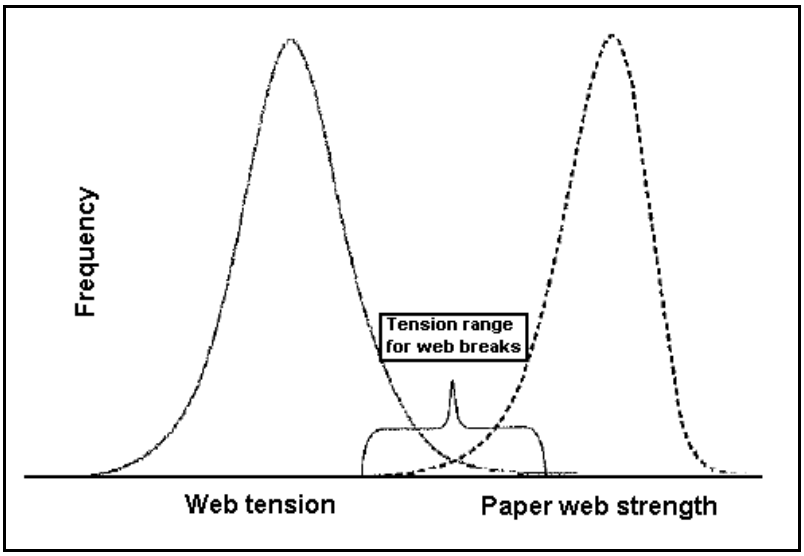

Figure 4. Tension range where web breaks can occur [30].

This approach shows that only increasing the average strength of the web does not necessary result in a lower web break rate. Better alternatives are to increase the minimum value of the web strength and decrease the maximum value of the web tension. Some studies have suggested that lowest values of tensile strength are caused by defects and that the amount, size, shape and position (whether it is at the edge or the centre of the web) of these defects affect the probability of web breaks in pressrooms [28, 33]. The defects may be classified in two different categories; the first category is the macroscopic visible defects, such as holes, cuts, bursts and wrinkles. The other category is the natural disorder in paper, such as formation, local fibre orientation and variation of wood species [33].

According to Ferahi and Uesaka [34], web breaks caused by macro defects no longer constitute a major proportion of web breaks in modern pressrooms. In fact, according to their study, macro defects were responsible for only 2% of all web breaks (1/50 web breaks), despite the good correlation shown in literature between the defects and the amount of web breaks when the tests were carried out using pilot scale tests. According to Deng et al. [35], nominal tension levels applied in pressrooms are significantly lower than those typically used in such pilot tests. Therefore, in order to have macro defect driven web breaks in the pressroom, paper should contain defects and the web tension should be at a level where these defects cause a local fracture of paper. Based on Deng et al. [35], the probability of both events occurring at the same time is relatively small.

On the other hand, the natural disorder in paper i.e. unevenness in the paper structure caused by the uneven material distribution of fibres, fines and fillers as well as non-uniformity in basis weight (formation), orientation, etc. increase variations in the strength properties of paper [28-32] and the magnitude of this kind of disorder is reported to have a connection with web breaks in pressrooms [35, 36].

Roisum summarised the effects of different factors causing high tension and low strength and thus charted the reasons for web breaks as a diagnostic tree (Figure 5) [37]. The diagnostic tree can be utilised as a simplified tool that helps to isolate problem areas more quickly than the traditional try-and–error approach. It shows the main parameters affecting web breaks, but does not reveal the reasons behind them.

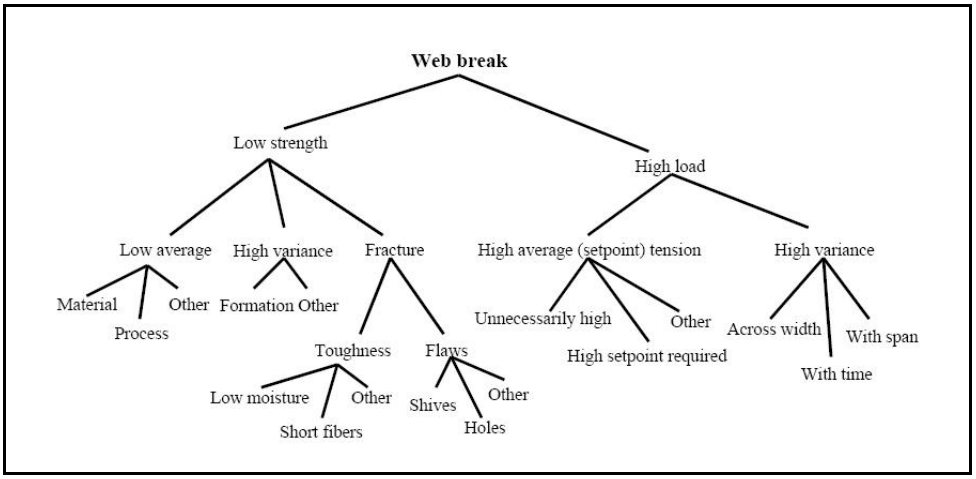

Figure 5. *Diagnostic tree* [37]. *A simplified tool that helps to isolate problem areas more quickly than the traditional try-and–error approach.*

The runnability of paper web has been typically evaluated and optimised by the mechanical properties of dry paper [1, 4]. However, since many of the web breaks on paper machines occur in the wet state, it is clear that wet web handling at the press section and at the beginning of the dryer section - as well as the mechanical properties of wet paper – are important factors that affect the runnability of a paper machine [2, 38]. Upgrading a paper machine to improve web handling is often expensive and therefore it is tempting to consider the possibility of optimising pulps in terms of the wet web mechanical properties.

Mardon et al. [6] evaluated wet web runnability on paper machine with initial wet web strength. They found a connection between wet web strength and paper machine runnability for newsprint pulps, but the correlation was poor for paper grades containing chemical pulps. In addition to wet web strength, stretch has been considered as an important factor affecting wet web behaviour on paper machines [7].

Seth et al. [15, 16] combined wet web strength and stretch in estimating the runnability of different pulps on paper machine. They created a method that utilises so-called failure envelope curves (Figure 6). In this method, the dryness of formed handsheets is varied by changing the wet pressing pressure. The runnability of the wet web is characterised by constructing the failure envelope curve. This is done by joining the values of tensile strength and stretch obtained over a range of moisture contents.

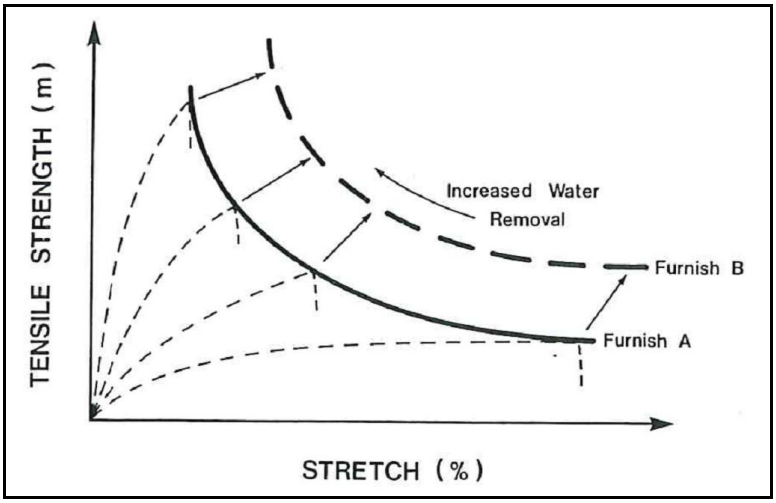

Figure 6. *The failure envelopes for two furnishes. Vectors connect points obtained at similar sheet-making conditions* [16]. *Furnish B is clearly ranked better by this method than furnish A, since it has both higher tensile strength and stretch.*

As water is removed, the strength of different pulps can be compared at constant dryness or at similar wet pressing conditions. In Figure 6, furnish B is clearly ranked better by this method than furnish A, since it has both higher tensile strength and stretch. Seth et al. [16] found a positive correlation with the position of different pulps in the failure envelope curve and the average production speed of four similar Canadian newsprint machines (see Figure 7).

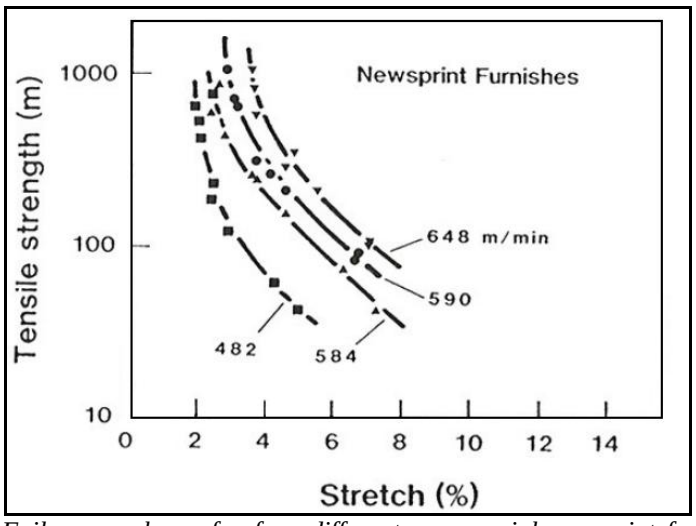

Figure 7. *Failure envelopes for four different commercial newsprint furnishes and the average machine speeds at which they were being run* [16].

The furnish runnability is thus found to be improved when the failure envelope curve moves up and right. Seth et al. [16] stated that the limitation of this method is that it does not apply if strength or strain is the more important factor. There are cases where an increase in tensile strength is associated with a decrease of stretch, and vice-versa. However, the results of the study made by these authors indicate that there is a connection between paper machine runnability and the mechanical properties of wet paper.

3.4 Web tension after the press section

In many paper machines today, the first open draw occurs between the press and dryer sections. In the open draw, wet web is transferred from one surface to another without the support of any fabrics. During the open draw, the stability of the running web depends mainly on the web tension. After press section, the dryness of the wet web varies typically between 40-50% and this means that the tensile stiffness of the web is only 10-15% of the stiffness of dry paper [17, 20]. Accordingly, a considerable speed difference (typically 2-5%) is required to create enough tension to transfer the web and to guarantee a stable run of the paper web in the open draw [17].

The tension needed to transfer the web over the open draw is reported to be mainly dependent on aerodynamic pressure force generated by local pressure differences (over the web), the adhesion energy between paper and cylinder, the release angle (the angle between the web and tangent of the roll surface set to the release point) and on the speed and grammage (including the mass of boundary layer that moves with the web) of the web as presented in Formula (2) [3].

$$T_{release} = \Delta\bar{p}R + (m + m_A)v^2 + \frac{W_{adh}}{(1 - \cos\beta)} \qquad (2)$$

where

$T_{release}$	release tension, N/m
$\Delta\bar{p}$	pressure difference over the web, N/m^2
R	radius of curvature of the moving web, m
m	grammage of the web, kg/m^2
m_a	added mass (mass of the boundary layer), kg/m^2
v	speed of the web, m/s
W_{adh}	adhesion energy, J/m^2
β	release angle, radian.

If the production speed of paper machine is increased and the release angle and radius of the curvature of the paper web remain constant, the tension required in the open draw has been estimated to increase as presented in Figure 8 [39].

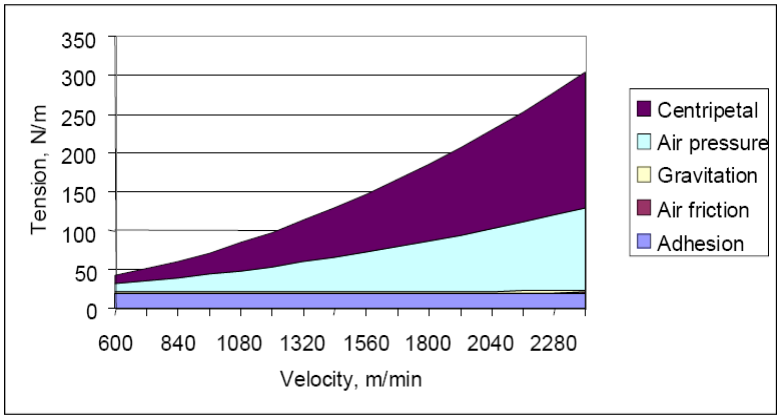

Figure 8. *Predicted web tension components on the open transfer of the press section* [39]. *The release angle and radius of the curvature of the paper web are constant with at all velocity levels (W_{adh}=2.5 J/m^2, m=0.11 kg/m). The quantity of air friction is low and it does not show in the figure.*

The studies done by Edvardsson and Uesaka [40, 41] concur with the result shown in Figure 8. These authors examined the runnability problems in open draws (by modelling) and assessed their limitations in increasing the maximum production speed of paper machines. They showed that at a given draw level and with specific mechanical properties of wet paper, the open draw remains steady until the paper machine reaches a certain production speed. Once this production speed is reached, the stability of the system is lost and the web strain significantly increases, leading to instability and thus to web breaks. Similar instability is also triggered by a fluctuation in the wet web properties. Based on their studies, tensile stiffness and dryness of wet web are the main factors affecting open draw stability as well as the detachment point where the web is released from the roll.

The tension of paper web in open draw is created by straining. With continuous moving webs, the strain is created by the velocity difference between the supporting points of the web as presented in Formula (3) (cf. e.g. text book [3]).

$$\varepsilon_T \approx \frac{v_2 - v_1}{v_1} \tag{3}$$

where ε_T strain of the web, -

v_1 velocity of the web in first supporting point, m/min

v_2 velocity of the web in second supporting point, m/min.

Based on this the tension created by straining for elastic materials can be calculated using Formula (4) [3].

$$T = \varepsilon_T \cdot S \tag{4}$$

where T tension, N/m

S tensile stiffness, N/m.

Figure 9 illustrates the tension behaviour of the web in open draw (the open draw exists between points A and B). The velocity difference between the press section and dryer section causes strain which is illustrated in the upper left-hand corner of the figure. The straining behaviour presented in Figure 9 is only valid for totally elastic material [42]. The tension of the web increases immediately when the paper enters the open draw and it remains constant throughout the rest of the open draw [43]. According to Kurki et al. [42], due to the viscoelastic nature of wet paper, the increase of strain is typically non-linear and dependent on the viscoelasticity of the web as shown in Figure 10.

After the open draw, the velocity of the web remains constant for a considerable time. During this time, the tension created in the open draw does not remain constant, but lowers rapidly, i.e. tension relaxation occurs. Typically 50-60% of the tension created in straining is lost during the 0.5 s relaxation time [17, 20, 22]. In this thesis, the remaining tension (after a specific time) is referred to as residual tension.

An increase of straining generates higher tension in the open draw and after relaxation (residual tension) as shown in Figure 9. However, increased straining is accompanied by negative effects on the mechanical properties and quality of the final product. For example, strain at break, porosity and the z-directional (thickness directional) delamination energy of the final dry paper are greatly dependent on the straining that paper undergoes during manufacturing in the paper machine line. Because of this, straining of paper on paper machines is often minimised [44, 45].

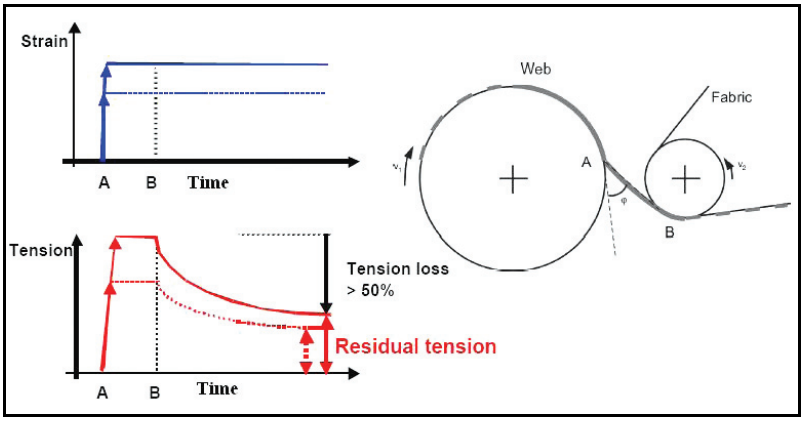

Figure 9. *Schematic presentation of web tension drop in the wet paper web during press-to-dryer section transfer (two draw levels). Figure is modified from* [3, 17].

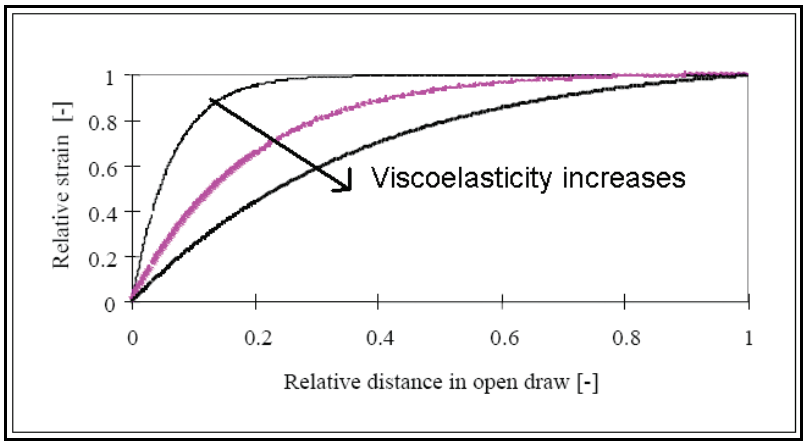

Figure 10. *Relative strains in an open draw with different material kinematic viscosities. Kinematic viscosity in the model used for making these curves describes the viscoelasticity of the web. Figure is slightly modified from* [42].

Lowered tension due to relaxation may lead to slackening of the wet paper. This causes wrinkling, bagging, fluttering and weaving of the web which can lead to web breaks. In modern single felted dryer sections, the problematic areas of paper with low tension level are mainly found in converging and diverging gaps between the dryer cylinders and the fabric [3].

When the web tension is too low at the beginning of dryer section, the web easily attaches to the cylinder surface instead of following the drying fabric (Figure 11, point A). This means that the web travels without any support of the dryer fabric. At point B, there is a pressure difference caused by the air layer transported by the roll and fabric. This difference in pressure tends to detach the web from the fabric. At point C centripetal forces act on the sheet causing instability [3, 38].

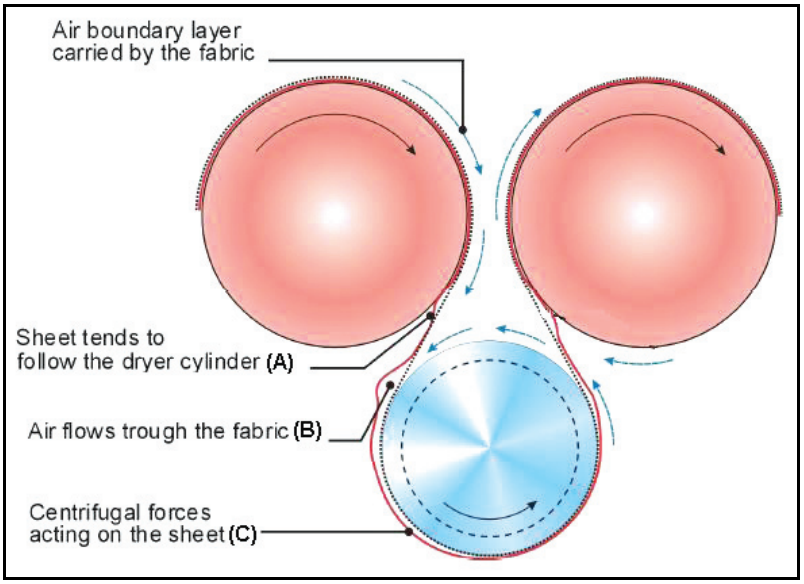

Figure 11. Problems caused by air flows in single felted dryers. Figure is slightly modified from [38].

To maintain stability of the running web, different solutions to stabilise the running web have been developed. The most important function of these sheet stabilisers is to reduce the pressure on the fabric side of the sheet in the region of the diverging gap (see Figure 11, point A). There is a corresponding reduction of the pressure difference driving air through the fabric and the pressure difference over the paper web creates a force that draws the web against the fabric. The first sheet stabilisers reduced the air pressure level on the fabric side in a limited zone or in the whole pocket [46]. As the production speed of paper machines increased, the requirement level of pressure difference was raised. This led to the use of separate zones in stabilisers, which generate varying levels of pressure. One of these concepts is presented in Figure 12. A high pressure difference generated by the sheet stabiliser is required to eliminate the effects of the pressure difference in the diverging gap and adhesion forces (Figure 12, high vacuum zone) while a significantly lower pressure difference is required to neutralise the effect of increased pressure in the converging gap caused by the air layer transported by roll and fabric surface (Figure 12, low vacuum zone) [3].

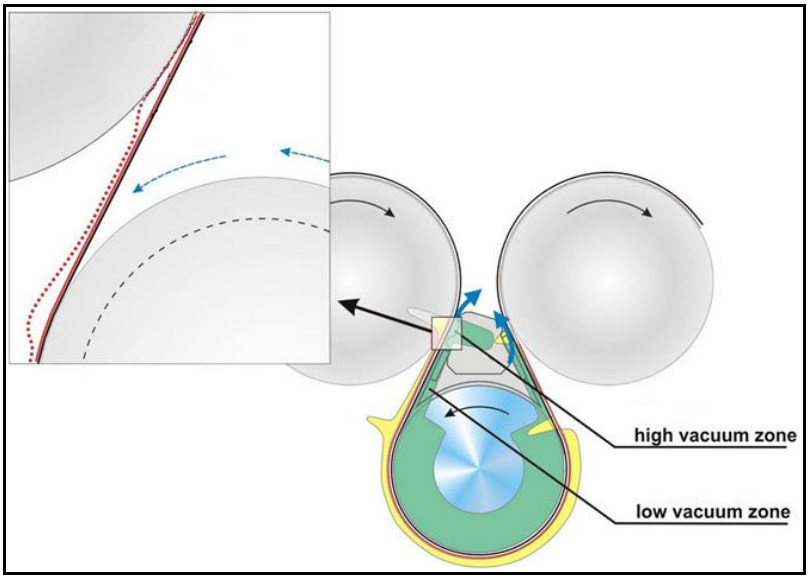

Figure 12. Sheet stabiliser with a high-vacuum zone in the opening dryer nip; web stabilised from dashed line position against the fabric [3].

According to Leimu [46], doubling the production speed of a paper machine triples the pressure difference in the diverging gap (Figure 11, point A). The increase of pressure difference caused by increased paper machine production speed leads to a situation in which the wet web is following the cylinder instead of the fabric for a longer distance, as shown in Figure 13. The detachment point affects the length of free draw from the cylinder surface to the fabric and it thus influences the stability of the running web.

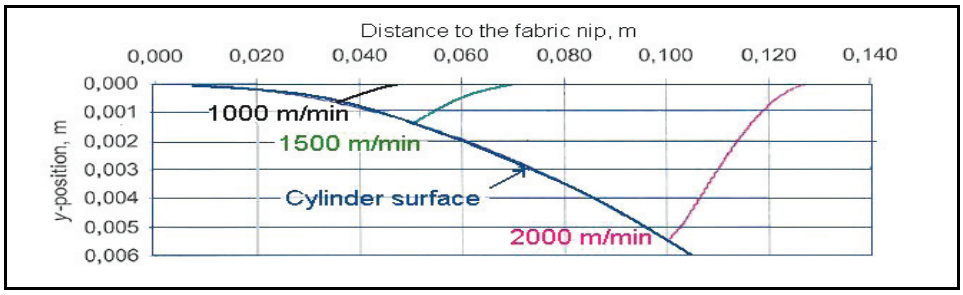

Figure 13. Computed web detachment with a production speeds of 1000 m/s, 1500 m/s and 2000 m/s, T=125 N/m, W_{adh}=0.25 J/m^2. The figure is slightly modified from [46]. *T=web tension, W_{adh} =adhesion energy.*

In addition to a pressure difference over the web, adhesion and web tension also play an essential role in the detachment of the web. The tension of the web at this part of the paper machine is dependent on the amount of tension caused by straining in the press-to-dryer transfer and the reduction of the tension (tension relaxation). The effect of web tension on the detachment point of the web is presented in Figure 14 [46].

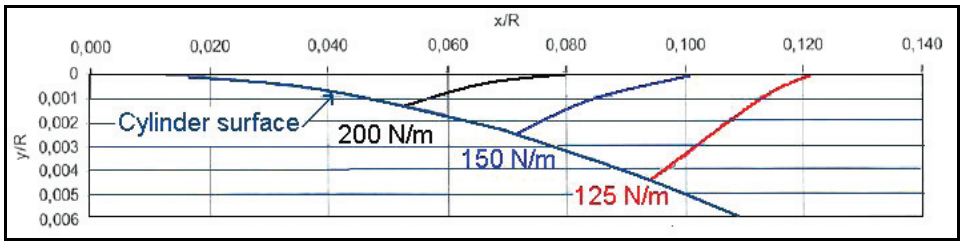

Figure 14. Computed web behaviour with a constant adhesion separation work of 0.25 J/m2 while the web tension has values of 125 N/m, 150 N/m and 200 N/m. The figure is slightly modified from [46].

The studies of Leimu [46] showed that a reduction of web tension from 150 N/m to 125 N/m at the beginning of the dryer section requires a 50% increase in the pressure difference generated by the sheet stabilisers to ensure a similar release from cylinder surface. Since sheet stabilisers have relatively high operating costs (because of their high energy consumption) in addition to investment costs [46], it is tempting to increase the web tension at the beginning of dryer section by optimising the mechanical properties of the wet web to minimise the need for sheet stabilisers.

During the open draw in press-to-dryer transfer the stability of the running web is also greatly affected by the release angle. When the release angle is high, a small variation in tension can cause significant changes in the release angle, which leads to instability in the release line. All types of unevenness in the paper (in the machine and cross direction) also lead to increased instability of the web. For example, changes in the cross machine dryness profile after the press section cause an unstable release from the centre roll due to a variation in the adhesion and the tensile stiffness of the wet web. Unstable fibre orientation profile of the web can lead to wrinkling and unevenness in the final product [47].

As shown earlier in Figure 8 and Formula (2), adhesion affects the tension required in open draws. Adhesion forces between the paper web and centre roll are mainly surface tension forces. Adhesion between paper and the cylinder surface has been reported to be dependent on release angle, pulp type, properties of cylinder surface (mainly roughness and surface energy) and the properties of the medium (the surface tension and the content of different dissolved and colloidal substances in the water) [48-52].

The effect of the dryness of the wet web on adhesion is contradictory. Increased dryness results in thinner water film between paper web and the cylinder surface, which increases adhesion forces. On the other hand, increased dryness creates discontinuity of the water film, which reduces adhesion forces. If adhesion of fibres on the cylinder surface is higher than the cohesion within the rest of the sheet, individual fibres and fines located on the paper surface might be separated from the web surface (see Figure 15). This event is often referred to as picking. The removal of material from paper affects the integrity of the paper surface. In addition, the removal of material might lead other materials to partially detach from the web, which can increase picking in the following sub-processes [48-52].

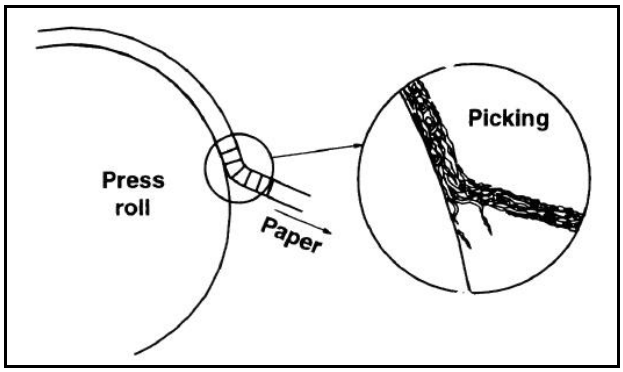

Figure 15. Peeling wet sheet from the press roll [52]. *Fibre picking occurs during the peeling when the adhesion between the roll surface and fibres is higher than the cohesion between fibres in the fibre network.*

In modern paper machines, open draws have been often replaced with closed draws (supported draws), where the paper web is transferred from one sub-process to another through the use of fabrics. The main idea in closed draws is to reduce the effect of the centripetal forces affecting the web. Like in open draws, adhesion forces between the wet paper and the supporting surface must also be overcome in closed draws i.e. tension is required in the transfer. In addition to the successful release of the web, the web must have higher adhesion to the surface to which it is transferred than to the surface from which it is transferred. To ensure tension is high enough, straining is also required in closed draws. Although this type of transfer is referred to as a closed draw, the web receives no support during its transfer from one fabric to another. Closed draws reduce the tension required in the open draw, but due to the lower tension resulting from reduced straining, the web handling problems can increase at the beginning of the dryer section [3, 53].

3.5 Prediction of wet paper behaviour in web transfer at laboratory scale

As shown in Chapter 3.4 (the studies of Leimu [46]), web tension at the beginning of the dryer section has an effect on the stability of the running web. The tension of the web at the beginning of the dryer section is dependent on the tension created by straining (in open draw) and on the relaxation of that tension. Both tension development during straining and tension relaxation are greatly affected by the viscoelastic properties of the web. Viscoelasticity means that mechanical properties of paper are dependent on the strain rate [54].

Traditionally, tensile strength measurements have been carried out using strain rates of only a few millimetres per minute (see for example [16]), while the strain rates at the open draws on paper machines are very high. The study of Andersson and Sjöberg [55] showed the effect of strain rate (between 0.011-13.2 mm/min) on apparent tensile strength and tensile stiffness of dry paper (see Figure 16A). The study by Hardacker [56] showed that strain rate affects not only the apparent mechanical properties of fibre networks but also those of individual fibres (Figure 16B).

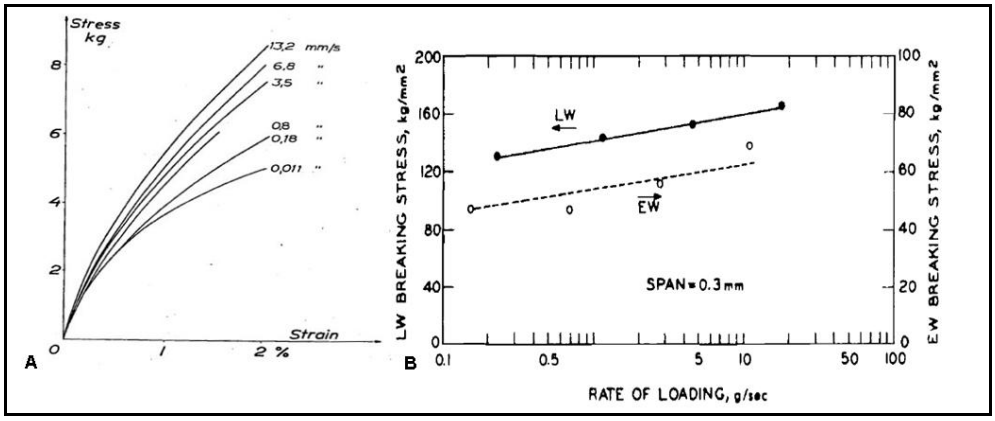

Figure 16. Figure A: Stress-strain diagrams for MG kraft pulp with different strain rates [55]. *Figure B: Breaking stress of the Douglas-fir fibres as a function of rate of tensile loading* [56].

Retulainen and Salminen [22] showed that the increase of the strain rate from 1%/s to 1000%/s (0.001 to 1 m/s, with a 100 mm long paper strip) increased the initial tension of wet handsheets (made from bleached kraft pulp) at a given strain level (highest tension before relaxation) by 45% and reduced residual tension by 15% (Figure 17A). Both the increase of initial tension and the reduction of residual tension seemed to be proportional to the logarithm of the strain rate. At 1%/s strain rate, about 18% of the tension created by straining is lost in 0.475 seconds, while at a strain rate of 1000%/s, an even 55% loss of tension occurs (Figure 17B). This is in line with the studies of Green [57], who assessed the effect of strain rate on relaxation of dry paper. He found that the initial tension and the tension relaxation during short time scales increased with a rising strain rate. However, he also showed that residual tension of dry paper after a longer relaxation time is not dependent on the strain rate.

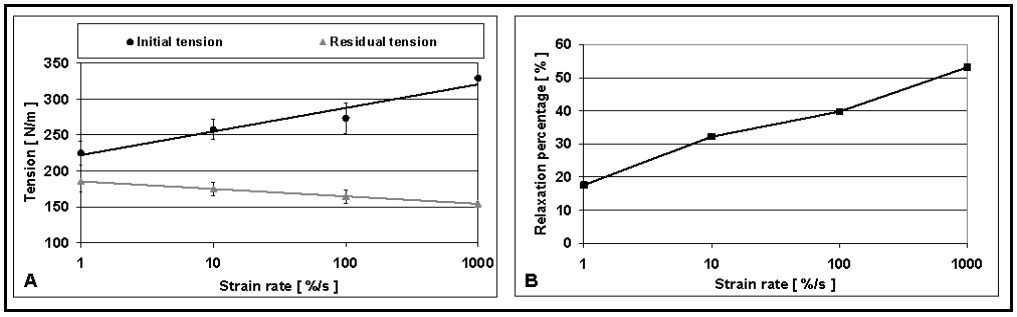

Figure 17. Figure A: The dependence of maximum tension (initial tension) and residual tension on the strain rate (bleached softwood chemical pulp) at 2% strain [22]. *Figure B: The dependence of relaxation percentage on the strain rate (bleached softwood chemical pulp) at 2% strain. Figure B is modified from* [22]. *Dryness of the samples was 65%.*

Due to the viscoelastic nature of paper, in order to simulate tension and tension relaxation in the press-to-dryer transfer on a paper machine, it is beneficial to do the measurements at laboratory scale in conditions that reproduce those of an actual paper machine (i.e. with a high strain rate and similar moisture content) as accurately as possible. It is not likely that an increase in strain rate would result in different order of tensile strength with different pulps, but the values obtained by using a high strain rate are at more relevant level.

As mentioned earlier, the tension of the web at the beginning of the dryer section is greatly affected by the initial tension created during web transfer. In addition to the amount of straining, the initial tension is also affected by the tensile stiffness of the web. Kekko et al. [58] showed that for handsheets, the initial tension and residual tension (tension after 0.475 s) had a linear relation at a given strain level (1%) and strain rate that covered a wide range of dryness (see Figure 18). They also reported a similar relationship for dry paper with a longer relaxation time (9.5 seconds).

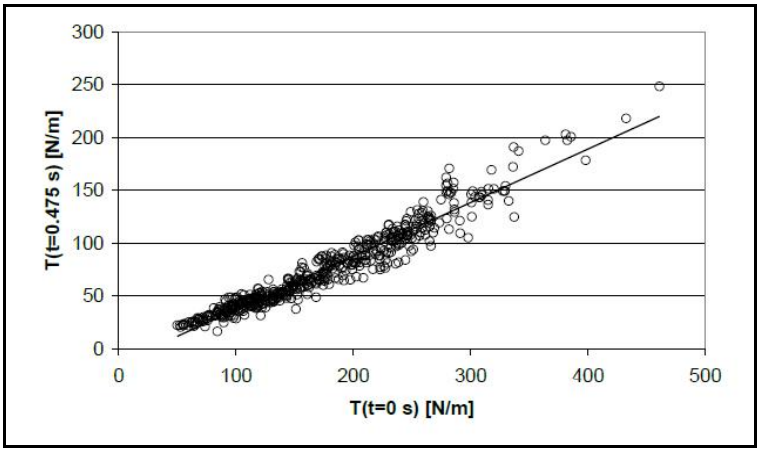

Figure 18. Correlation of initial, T(t=0 s), and residual (T(t=0.475 s), tension at a strain at ε=1% for never dried handsheets of 60 g/m2 basis weight (varying ratio of mechanical and chemical pulp, N=537). The span length of samples was 100 mm. Dryness varied in the interval 25…77%, the filler content in the interval 0…20% and strain rate was 1000%/s [58].

However, in both cases, some variations occurred in residual tension between different samples at a specific initial tension level. Figure 18 shows that different samples with an initial tension of approximately 290 N/m had residual tension values that ranged between 100 and 175 N/m. This is in line with the findings by Jantunen [47], who showed that the relaxation percentage during short time scales (0.3 and 0.6 seconds) is greatly affected by dryness of the sheet, pulp type and the refining level of the pulp at a given strain level.

In addition to the pulp properties, the relaxation percentage of dry and wet paper is greatly dependent on the amount of straining. The relaxation percentage of dry paper increases with rising strain (Figure 19A). This result is in line with the study by Andersson and Sjöberg [55]. In contrast to dry paper, the relaxation percentage of wet paper reduces with increasing strain (Figure 19B). One explanation for this result could be that when wet paper is slightly strained, fibres straighten, and thus the corresponding tension relaxation percentage is higher with lower strain levels.

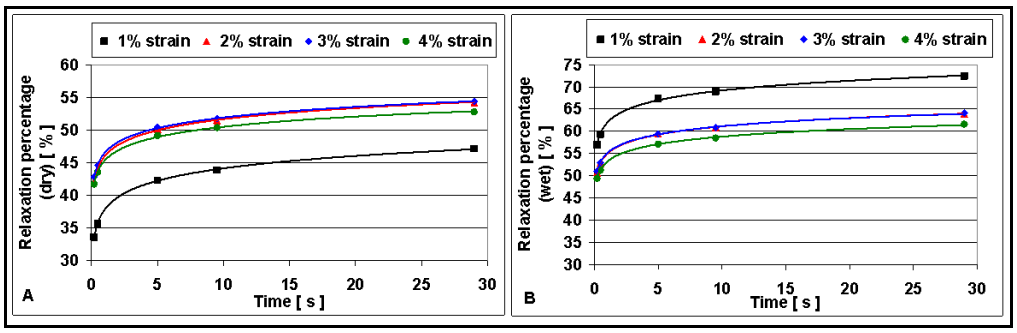

Figure 19. Figure A: The dependence of residual percentage of dry handsheets made from pine kraft pulp on relaxation time and the amount of straining. B: The dependence of relaxation percentage of wet (dryness 62%) handsheets made from pine kraft pulp on relaxation time and the amount of straining.

These results show that in order to predict wet web tension behaviour at the beginning of the dryer section, in addition to tensile strength and tensile stiffness, the tension relaxation (during a short time scale) of the wet web should also be known.

To simulate wet web strength and tension relaxation in press-to-dryer transfer and at the beginning of dryer section a rig called Impact was utilised in this thesis. This device uses a velocity of 1.0 m/s, which is approximately 3000 times higher than that used in standard tensile testing methods [17, 18, 20]. In relaxation tests, the paper is strained to a certain level and the development of tension is measured for 0.475 seconds. The test rig and testing procedure is presented in more detail in Chapter 7.1.

4. FURNISH AND MECHANICAL PROPERTIES OF WET WEB

Furnishes used in papermaking contain fibres (liberated from wood chemically, mechanically or through a combination of the two), fines, a high amount of water, several different chemicals and fillers. The quality and amount of each constituent has significant effect on mechanical properties of dry and wet paper [23].

4.1 Fibre structure

The cell wall of wood fibres consists of a middle lamella (ML), a primary wall (P), and a secondary wall which can be divided based on its structure into three layers (S1, S2 and S3) and lumen. The middle lamella binds the fibres to one other and is not part of the actual cell wall. The primary wall consists of cellulose, hemicelluloses, pectin, protein and lignin. The layers of the secondary wall differ from one other in their structure and chemical composition. The clearest structural difference is found in the distinct orientation of the microfibrils. The S2 layer of the cell is the biggest part of the cell wall (80-95%), and therefore, it is generally believed to have the greatest effect on the mechanical properties of fibres. In the S2 layer, the microfibrils have relatively low (10-30º) degree angle compared to the axial direction of fibre, which makes the fibre strong [59, 60].

4.2 Fibre morphology

Fibre morphology typically includes length, width and cell wall thickness. Fibre morphology of both chemical and mechanical pulps is known to have significant effects on the optical and mechanical properties of paper. The morphological properties of fibres vary significantly between different wood species, but also within a stem. As a raw material, wood is non-uniform and thus variations in the pulp fibre properties are significant. The variation is especially high with softwood species because at the beginning of the growth season, they form wide, thin-walled springwood fibres and subsequently go on to form narrow, thick-walled summerwood fibres [61- 64].

The data published by Paavilainen [65] showed a good correlation between cell wall thickness and the coarseness of fibres (i.e. the weight of fibres per meter) for different wood species. Increased coarseness of different sulphate fibres results in lower dry paper tensile index, higher porosity and tear energy, while increased length weighted fibre length increases the tensile strength and tear energy of dry handsheets.

The studies of Retulainen [66] agree with these findings. Higher coarseness leads to a lower amount of fibres per mass and fibres with lower coarseness have a higher tendency to collapse, which increases the relative bonded area of fibres. Paavilainen [65] stated that the amount of fibres in the network and the ability of fibres to collapse alone cannot explain the differences in the tensile strength between fibres with different coarseness and that good bonding ability is actually a more important factor than the amount of load bearing fibres. She suggested that fibre collapse responds clearly to surface smoothness and light scattering, but less to the strength of the fibre network. Based on her studies, she also concluded that with a similar chemical composition, fibre flexibility seems to be the main factor to explain the differences in the strength of papers made from fibres with different coarseness.

Seth [67] showed that the wet web tensile strength of unbleached softwood kraft pulp rises linearly with increasing fibre length (see Figure 20A). Different length distribution but a similar coarseness of fibres was obtained by guillotining oriented sheets of the same original pulp. Seth [67] also showed that increased coarseness decreases the wet web strength (divided by fibre length) linearly (Figure 20B). The results of the effect of fibre length on wet web strength were interpolated to dryness 30% and the effect of coarseness to dryness levels 25% and 30%.

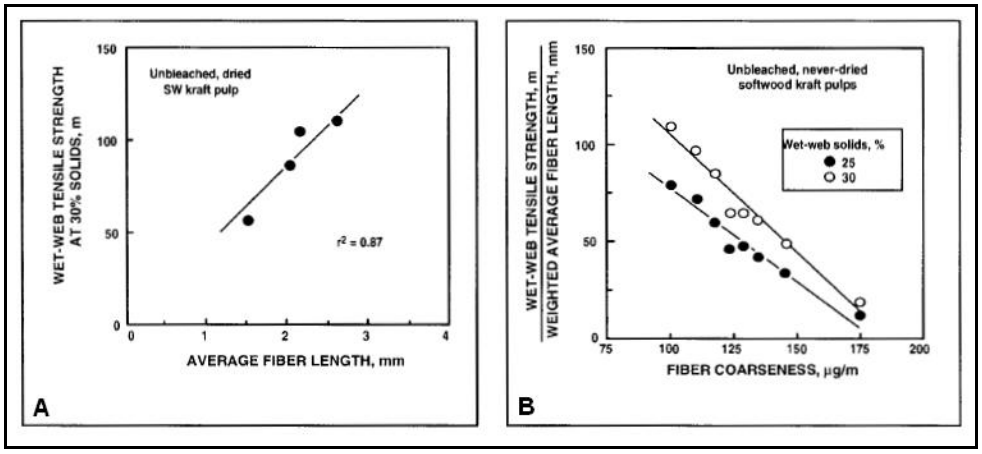

Figure 20. Figure A: Wet web tensile strength at 30% solids as a function of fibre length of the pulp. The fibre length in this figure is length-weighted average, and was obtained by image analysis. Figure B: Wet web tensile strength divided by average fibre length for two web solids as a function of fibre coarseness [67].

In addition to fibre morphology, also different deformations and defects of fibres are known to have significant effects on mechanical and paper technical properties of paper [68-73].

4.3 Fibre defects and deformations

Several studies have shown that pulp produced at mill scale experiences a significant reduction in strength compared pulp produced at laboratory or pilot scale [68-73]. MacLeod [68] studied the strength delivery of a pulp mill. The strength delivery was calculated from tear indexes, each at a fixed, mid-range breaking length. He defined the unbleached pilot plant pulps (PP) as having 100% tear-tensile performance (tear energy at a given tensile strength level), and thus they were used as references for all strength comparisons with the mill-made pulps. He showed that only 72% of dry paper strength is retained at mill scale compared to pulps prepared at the pilot plant (PP) (see Figure 21). The biggest loss in pulp strength occurs in digester operations (BS), but some strength was also lost in oxygen delignification (O2) and bleaching (D/C, E/0, D1 and D2).

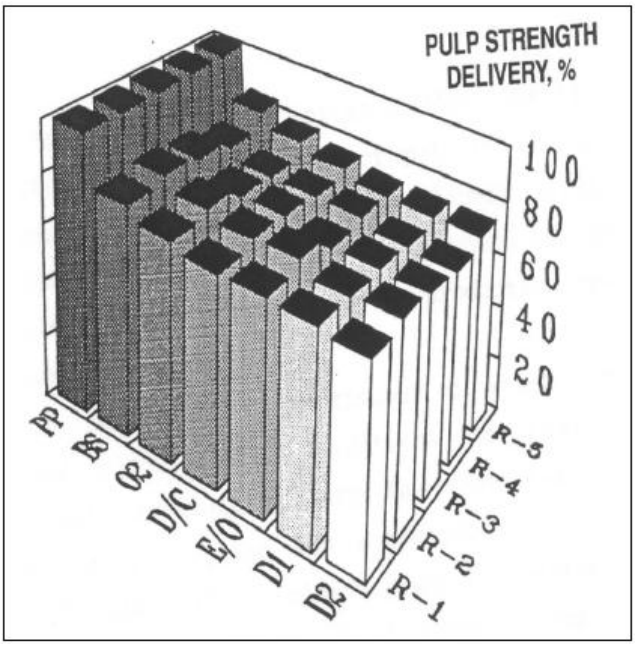

Figure 21. In tear-tensile pulp strength delivery, pulp mill's brown stock average 82%, the post-O2 pulp 77%, and the fully-bleached pulp 72% [68]. *PP=pulps prepared at pilot scale, BS=digester operations, O2=oxygen delignification, D/C, E/0, D/1, D/2=bleaching sequences and R-(1-5)=sampling rounds. Tear-tensile pulp strength delivery means tear energy of pulps at a given tensile strength level.*

MacLeod [68] stated that a similar use of chemicals in pulp manufacturing at pilot plant and at mill means that the loss in strength must be owed to reasons other than chemicals. The unevenness of delignification in pulp mills was suggested as one reason, but he believed that it alone cannot explain such a great reduction in strength. He concluded that the differences in strength must be owed to physical changes in fibres. The use of the basket hanging technique by MacLeod et al. [72, 73] showed that mill-cooked, never-blown pulp can have almost the same strength as laboratory-made pulp (or pulp made at pilot plant). Pulp blowing in mill generates changes in fibres such as increased dislocations, kinks, curls and microcompressions which is the main reason behind the reduction in pulp strength.

Bränvall and Lindström [70] suggested that the higher strength of laboratory-made pulps could be partly explained by the higher surface charge of fibres compared to mill-cooked pulps, which makes the fibrils more flexible or makes them “ruffle”, since negative charges on fibrils make them repel one other. Danielsson and Lindström [74] showed that also alkaline hydrolysis during digester operations reduces the chain length of hemicelluloses, which leads to a reduction of paper strength. Since pulping liquors in industrial systems circulate for a longer time than they do in laboratory preparations, more hydrolysis of hemicelluloses occurs, which could also explain a part of the reduction in strength. Danielson and Lindstöm [74] stated that the reduced chain length enables part of the hemicelluloses to enter the fibre wall and thus less hemicelluloses remain on the fibre surface. However, it is likely that the highest loss in strength is owed to physical changes in fibres i.e. different deformations.

Various types of deformations can be found in the cell wall of wood fibres. Deformations can be caused by growing stresses or by tree movement in high wind. Wood processing, such as chipping, defiberisation or medium consistency unit operations also cause a deformation of fibres [70, 75-77].

Figure 22 introduces different fibre deformations and shows their effect on the corresponding stress-strain curves [78]. In Figure 22A (state I), the fibre is in its natural state and the stress-strain curve is steep and linear. Figure 22B (state II) shows how microcompression and dislocations in the fibre cause a clear yield point where the shape of the curve changes due to the straightening of the fibre. A fibre with a curl of moderate amplitude reduces the elastic modulus fibres appreciably as shown in Figure 22C (state III). The elastic modulus of the fibres is further decreased with an increased amount of curls and crimps in the fibres. The fibres take almost no load until sufficient strain has been reached (Figure 22D) (state IV) [78].

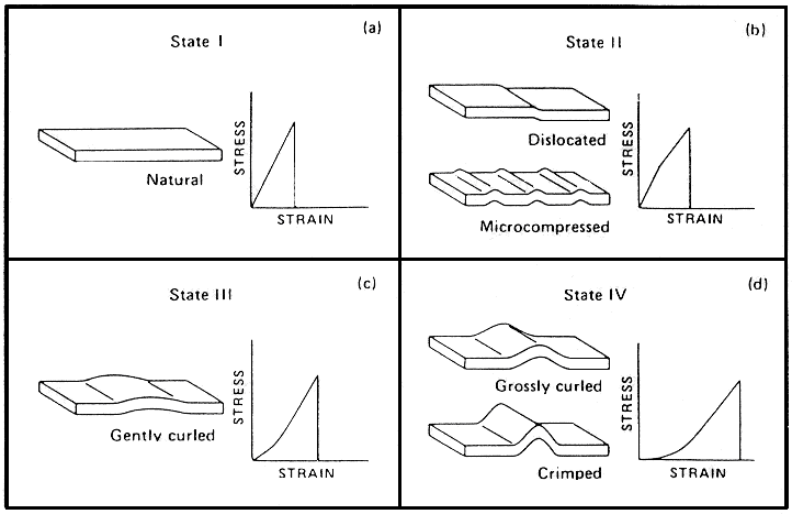

Figure 22. Various states of fibres and the corresponding stress-strain-curves [78].

Fibre curliness is often determined by the shape factor of fibres. The shape factor is defined as a ratio between the projection length (end to end distance) and the contour fibre length. This ratio is multiplied by 100% when presenting the results. This is shown also in Formula (5) and Figure 23 [77].

$$\text{Shape factor} = (\text{projection length of fibres} / \text{contour length of fibre}) \cdot 100\% \quad (5)$$

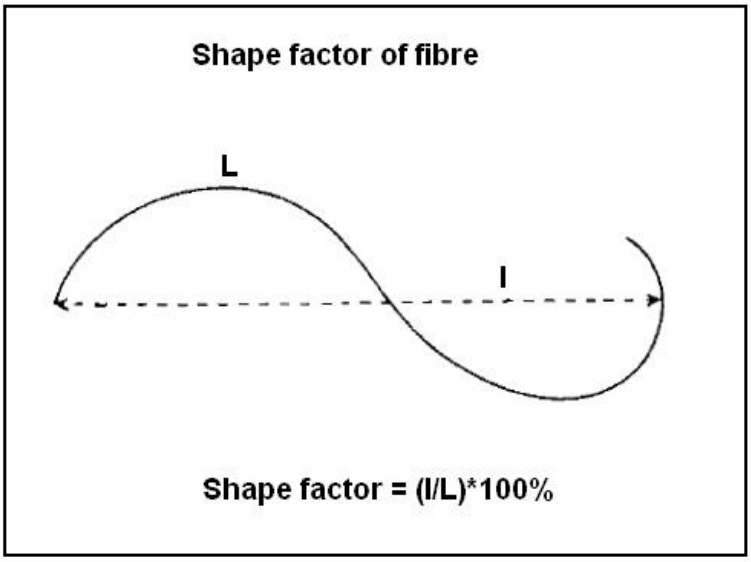

Figure 23. Determination of the shape factor of fibres which is based on the end to end distance and the contour fibre length [77].

If fibres are straight i.e. no curls or other deformations exist, all segments in the network transmit the load from one bond to another during straining. If the network contains curly fibres, the load across a segment with curls is not transmitted until the curl is straightened. This means that these segments do not fully participate in load shearing, which leads to lowered tensile strength (Figure 24B) and tensile stiffness index (Figure 25B) of dry paper, but higher stretch to break (Figure 25A). Figure 24A shows that tear index increases when the fibres in the network are deformed. The deformed fibres transfer therefore stresses to larger area and to more bonds, which in breaking consume more energy and is seen as higher tear index [79-83].

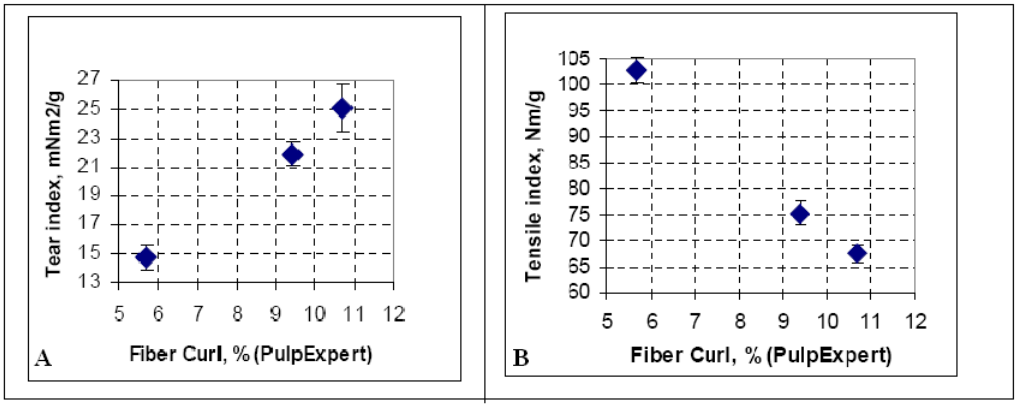

Figure 24. Figure A: The development of tear index as a function of fibre curl for unbleached pulps. Figure B: Tensile index of the pulp sheets as a function of fibre curl for unbleached pulps. Error bars show a 95% confidence interval of the mean of the measurement [80].

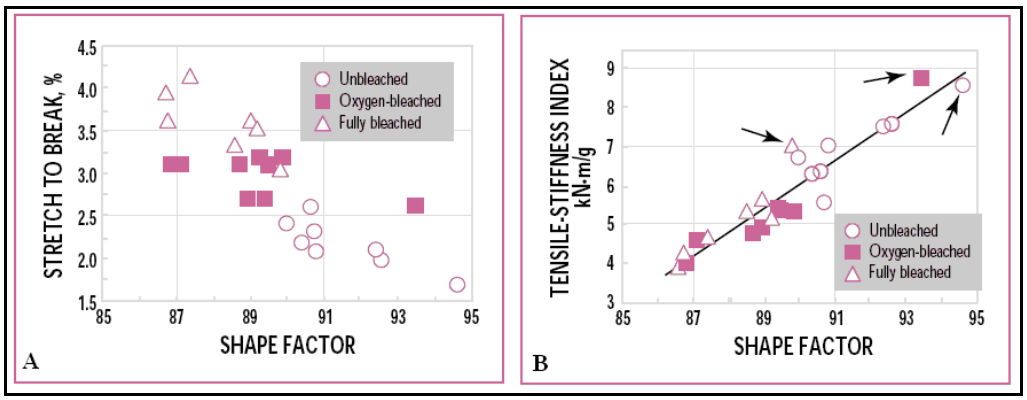

Figure 25. Figure A: Stretch to break for the unbeaten commercial pulps decreased with increasing shape factor, i.e., with decreasing fibre curl. Figure B: Tensile-stiffness index decreased with decreasing shape factor, i.e., with increasing degree of fibre deformation (curl). Points marked with an arrow represent unbeaten laboratory pulps; all other pulps were unbeaten and commercially produced [79].

Study made by Mohlin et al. [79] showed that increased curliness of fibres reduces their zero-span strength (which is commonly used as a fibre strength index). They argued that curly fibres do not carry load in zero-span measurements and strength of fibres could only be predicted from straight fibres. However, Wathén [84] showed that curliness of fibres itself has no effect on dry or wet zero-span strength and that all fibres carry load during zero-span tests weather they are curly or straight.

Increased curliness of fibres has been shown to increase the bulk and porosity of handsheets. Increased curliness of fibres reduces the drainage resistance of most pulps (which has been seen as an increase in the CSF value). A greater amount of curly fibres has been shown to increases the light scattering coefficient of paper (due to reduced bonding), resulting in slightly higher brightness and opacity. In addition, increased curliness is known to increase the hygroexpansion of the fibre network [85-87].

Gurnagul and Seth [10] reported that a small increase in fibre curliness slightly reduces tensile strength but significantly increases strain at the break of wet paper. This leads to pulp improvement when it is estimated based on the failure envelope curve [10, 16, 83].

Chemical pulp fibres are known to straighten in low consistency refining. Although the mechanism is not yet fully understood, both swelling and mechanical straining during refining are believed to be the main mechanisms. Refining has been shown to reduce the number of kinks and curls, and to increase the strength of individual fibres (zero span test) [85, 88, 89]. Figure 26 shows that the shape factor of fibres increases up to a certain refining energy level. This shows that part of the deformation of the fibres is reversible in refining [85].

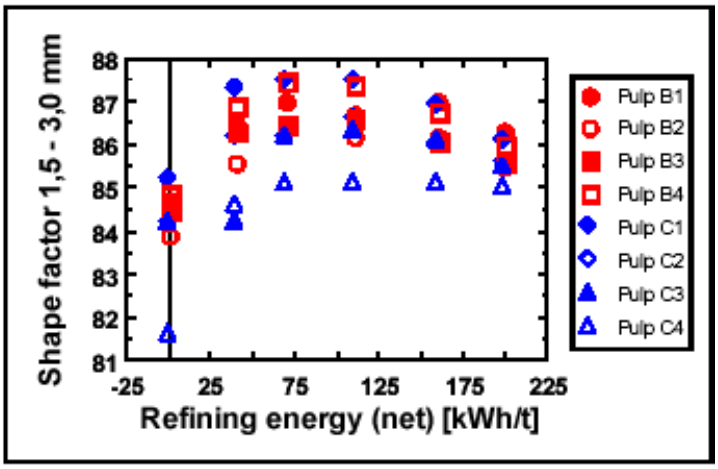

Figure 26. Shape factor for the fibre length interval 1.5-3.0 mm as a function of energy consumption in industrial refining [85].

It has been noted that the drying of pulps under axial tension can enhance the stress-strain behaviour of single fibres (Jentzen effect) [90]. The tension during drying straightens the fibres, pulling out dislocations and other defects while also decreasing the fibril angle. This phenomenon is also expected to create changes at the molecular level of cellulose and hemicellulose. Refining increases the swelling of fibres which leads to a higher Jentzen effect during drying [90, 91]. Seth [81] suggested that the increase of tensile strength of the fibre network during refining is greatly dependent on straightened fibres, which improves the load-carrying ability by increasing the activation of the network. He came to this conclusion by comparing the tensile strength of dry handsheets made from curly and straight fibres at a given light scattering coefficient (which, based on his statement, correlates well with relative bonded area in the network), which was varied by either refining or wet pressing. With curly fibres, the handsheets made from refined pulp yielded a higher tensile strength than wet pressed sheets at a constant light scattering coefficient level. For straight fibres, similar tensile strengths were obtained at a given light scattering coefficient regardless of whether the bonded area was increased by refining or by wet pressing.

4.4 Fines and small-sized materials in papermaking

In addition to fibres, small particles play a significant role in papermaking. Such small particles include fillers, pigments, fine particles of fibrous material and colloidal substances [92]. A rough classification of the small-sized materials in papermaking is presented in Table I.

Table I. Classification of small-size material [92].

Fines type	Origin	Morphology	Content, %	Size, µm
Mechanical fibre fines	TMP, PGW	Fibrils, flakes, ray-cells, etc.	10-40	Fibril length: <200 Width: 0.2-10 Lamellas: <20 Flour stuff: 20-300
Primary fibre fines	Unbeaten chemical pulp	Ray-cells, lignin flakes from middle lamella	2-10	Softwood ray cells: Length: 10-160 Width: 2-50
Secondary fibre fines	Beaten chemical pulp	Fibrils peeled of the cell wall		
Tertiary fines	DIP, broke from mill	Fibre fines, fillers, coating pigments, latexes, additives, stickies, etc.	Variable	Variable
DCS	Wood	Very fine dispersion, which may form larger agglomerates	From spruce: 1-2	0.1-2
Fillers	Filler addition, paper additives	Clay, calcium, talc, etc.	0-40	0.2-10

Fines are typically considered the part of pulp that passes through the 200 mesh screen. This definition is also applied in many standards. Some studies have considered the fraction that passes through 100 or 150 mesh screen as fines. However, relatively long particles pass through the screen due to their low thickness. Many optical fibre analysers consider fines as particles with a length of less than 0.2 mm. It is obvious that fines, however they are defined, consist of quite heterogeneous material [92-94].

The fines content of mechanical pulps typically varies between 30-50%. It consists of flakes and lamellas, band- and thread-like fibrils, pores and ray-cells. The proportions of these fine materials are greatly dependent on the processing conditions of refining [95].

The fines content of chemical pulps for printing papers is typically much lower than of mechanical pulps. Chemical pulp fines are typically divided into primary and secondary fines. Primary fines consist of a coarser fraction rich in ray cells and finer fraction of fibrils and lamellas. Secondary fines, which are determined as the fines created in refining, are mainly broken fragments, fibrils of fibres and the thin lamellas of fibre surfaces [92].

In general, fines are flexible, highly swollen particles with a high specific surface area, and thus they have a major effect on wet end chemistry, water removal and the mechanical as well as optical properties of the paper web [96, 97]. Chemical pulp fines mainly affect sheet properties by increasing the density and the bonded area in the sheet, but they are known to have only a minor effect on specific bond strength [97]. Sheets made from chemical pulp fines (mainly fibrillar fines) have a high density, typically between 1100-1200 kg/m^3, while sheets made of mechanical pulp (TMP) fines yield a density of 450-500 kg/m^3 [98].

One way to classify fines is according to their physical properties i.e. either they are flake-like or fibrillar. This division is quite rough. For chemical pulps, almost all fines are more or less fibrillar. For mechanical pulps, the amount of fibrillar fines, i.e. fibrillar content, is one of the key parameters affecting the mechanical properties of paper. Fibrillar content increases as the refining energy rises. This is because flake-like fines are mainly formed from the lignin-rich middle lamella and primary wall, whereas fibrils are formed mainly when refining the secondary wall [95]. Fibrillar fines are known to provide high tensile strength for dry paper but they have only a minor effect on light scattering, while flake-like fines yield high light scattering values but produce a significantly smaller increase in dry paper strength compared to fibrillar fines (Figure 27).

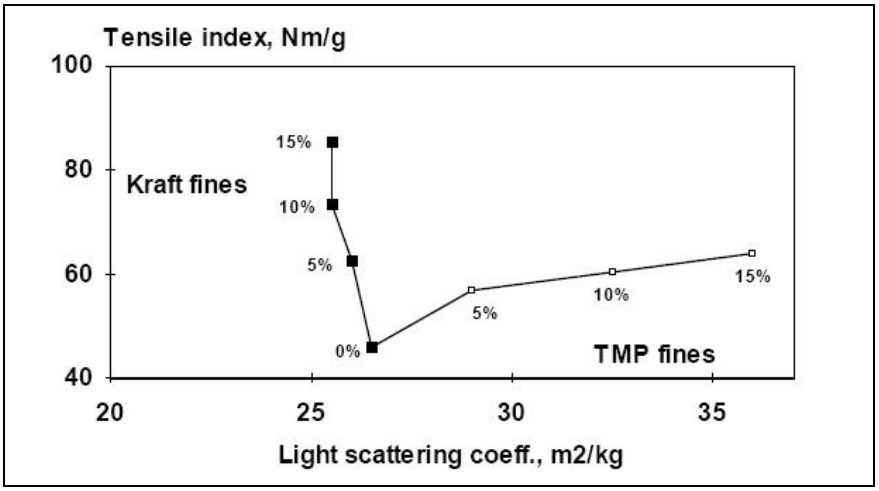

Figure 27. The effect of TMP and kraft fines addition on the tensile index-light scattering coefficient combination [97].

Luukko [95] studied the effect of adding fibril-rich and flake-rich TMP fines and fines from kraft pulp to TMP long fibres on wet web strength (Figure 28). Adding fibril-rich TMP fines yielded higher wet web tensile strength than flake-like fines. The high surface area of fibril-rich fines was estimated to be the main reason for the difference between the samples. Higher tensile strength values for wet web were achieved by adding kraft fines as opposed to fibrillar TMP fines. This was explained by the higher surface area and hydrophilicity of kraft fines, which is believed to increase the surface tension forces in the network.

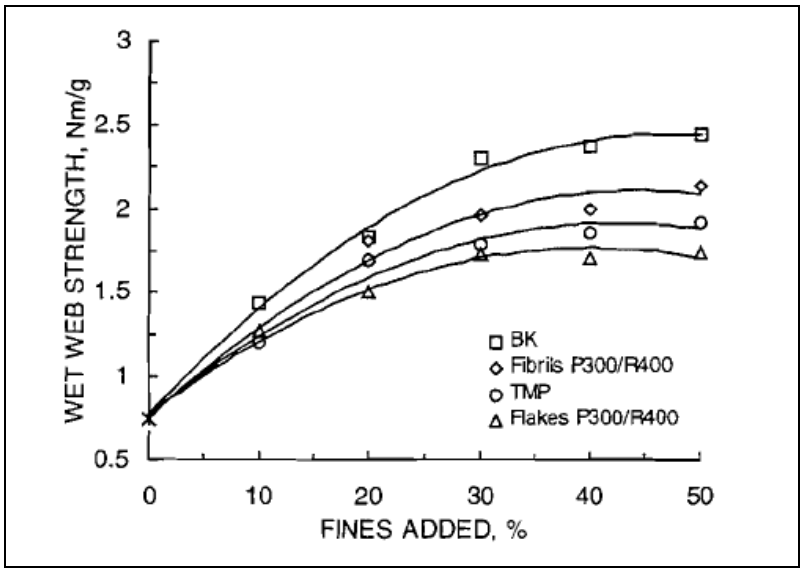

Figure 28. Effect of amount of different fines on initial wet web strength. Fines blended with R100 fibres of an accepted TMP pulp (CSF 50 ml) [95].

Corson [99] showed that adding fines (0…40%) to a long fibre fraction increases the wet web tensile strength at a constant wet pressing pressure more than adding fines to middle or short fibre fractions. He also noticed that adding TMP fines to a particular long fibre had only a minor effect on tensile strength when compared at constant wet pressing pressure, but increased strength significantly at a given dryness level. When adding chemical pulp fines the strength increased also at constant wet pressing conditions. He also showed that fines addition to TMP long fibres affected the dryness after constant wet pressing with low wet pressing pressures (with pressures that provided dryness between 10…30%). When the wet pressing pressure, and thus dryness after wet pressing was increased, the effect of fines on dryness after wet pressing was reduced.

Wet webs (dryness below 30%) are assumed to be mainly held together by friction between the fibres and the surface tension forces. Both the friction and surface tension forces increase when fines are present in the inter-fibre spaces in the network. Fines are known to reduce water removal after the press section because they carry a significantly higher amount of water per unit of dry mass than fibres [93]. However, this means that pulps with high fines content reach a point where all free water between fibres is removed at lower dryness level.

Fines of chemical pulps have a chemical content similar to that of fibres. For mechanical pulps, the situation is generally different. Sundberg et al. [100] separated different fractions of mechanical pulps (fibrils, microfines, flakes and ray cells) and compared their chemical composition. They showed that all types of fines contain more lignin and less cellulose than fibres. Of the compared fines, fibrils contained the greatest amount of cellulose and the least amount of lignin. The ray cells and flakes contained a great quantity of lignin, a low quantity of cellulose and a significant quantity of arabinogalactan, xylans and pectins.

Rundlöf [101] compared the mechanical and optical properties of mechanical pulp fines taken immediately after the refiner (fresh fines) and of fines taken from a pulp diluted with white water (white water fines). According to his findings, the tensile index of dry paper increases significantly with fresh fines addition, while addition of white water fines leads to a significant reduction in paper strength. Rundlöf [101] also noted that the light adsorption coefficient increases with both types of fines, but more for white water fines. The chemical characterisation of fines revealed only minor differences in the lignin and carbohydrate contents of the fines and in the size and morphology. The only major difference was found in the extractive amount of the fines, which was significantly higher for the white water fines. Rundlöf [101] also showed that washing the white water fines with acetone (which dissolves the extractives from fibre surface) can significantly enhance their bonding ability.

Karnis [102] showed that there is no significant difference in the pulp and the handsheet properties of latent and delatent fines from mechanical pulp. With a certain fines content, delatent fines provide higher retention and lower freeness than those containing latent fines.

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4.5 Fillers

The presence of fillers enhances the optical properties of paper, such as brightness and opacity. Other quality properties of paper such as smoothness and ink receptivity are also improved when fillers are added. The economical benefits in using fillers are remarkable, since they are less expensive than pulps. The problem with small filler particles is that they have very poor mechanical retention and therefore, chemical additives are required to enhance retention. The addition of these chemicals causes flocculation of the fibres and reduces the evenness of the network (formation). The retention of fillers is known to be dependent on aspects such as size, shape and charge of the fillers. The surface area of fibrous material, the grammage and formation of the sheet, the molecular weight and the charge density of the retention chemicals also have a significant effect on the retention of the fillers [103-106].

The increase of filler content is generally known to deteriorate the tensile strength of dry paper due to lowered grammage and density of the fibre network, RBA (relative bonded area) and the strength of bonds [106]. Aggregates of fillers, fines and fibres cover the fibre-fibre crossings in the web structure, preventing the development of hydrogen bonds between fibres. Due to intensive flocculation, poor formation leads to uneven stress distribution during straining and therefore decreases the tensile strength of dry paper [107].

In addition to the properties of furnish, the structure of the network has significant effect on mechanical properties of both dry and wet paper. The following chapter presents a brief review of the effects of two important factors on mechanical properties and structure of paper: fibre orientation and wet pressing.

5. NETWORK STRUCTURE AND MECHANICAL PROPERTIES OF WET WEB

Paper is a heterogeneous and porous network constructed from fibrous material, fillers and different chemicals. In the papermaking process, fibres tend to form flocks which lead to differences in the local basis weight of paper. Even so, in paper network, there is a high probability of finding similar basis weight values at short distances [108]. The basis weight distribution is therefore not totally random. The structure of the paper web affects the uni- and multiaxial mechanical properties of paper web, which affects how paper can resist the forces affecting the web during papermaking processes and end use [3].

5.1 Fibre orientation

In machine-made papers, more fibres are aligned in the machine direction than perpendicular to it. Fibre orientation refers to this anisotropy in the structure of paper [108]. The target fibre orientation level for each paper grade and for each paper machine is determined by the requirements of the final product and the demands of the process. Fine paper grades, which are the main research target in this thesis, are typically produced using low fibre orientation (which is controlled with the jet/wire ratio). This is because fibres mainly shrink in the cross direction and too high orientation could therefore cause adverse effects, such as reduced CD dimensional stability, and increase the wrinkling during printing. Local variations in fibre orientation also have a strong effect on the cockling of paper. An increased orientation also leads to higher tensile strength and tensile stiffness of the final product in the machine direction and tear energy in the cross direction. However, at the same time, tensile strength and stiffness in the cross direction decrease along with dimension stability. On the other hand, increased fibre orientation results in higher MD tensile stiffness of wet paper, which facilitates the press-to-dryer transfer and therefore improves the stability of the running web in the open draw [109].

In addition to fibre orientation, dryness of the wet web after wet pressing has a significant effect on wet web behaviour in press-to-dryer transfer and at the beginning of the dryer section [110].

5.2 Effect of wet pressing

Wet pressing consolidates the wet web by removing water from it. The dryness of the web when entering the press section is typically about 20%. At this dryness level, water is already expelled from fibre walls. In modern press sections, the last press nip typically operates in the dryness range of 40-50% [110]. Water removed from the paper web during wet pressing contains particles originating from the web. However, the amount of removed particles (mainly fines and fillers) is quite small and therefore this rarely affects the z-direction materials distribution in paper to such an extent that it would have a significant effect on paper properties [111, 112]. Due to wet pressing, some pores in the fibre wall are closed, causing fibre hornification. Hornification in wet pressing has also been called “wet hornification” [113]. Wet pressing increases the average density of paper and it can have a significant effect on the z-direction density distribution [114]. The change in density induced by wet pressing is greatly affected by the properties of the used furnish. Pulps with low bonding ability or high stiffness result in low density [110]. The increase in the sheet density in wet pressing affects many of the mechanical properties of dry paper. Web consolidation improves fibre bonding which results in increased tensile strength, burst strength, and z-directional delamination energy. On the other hand, the opacity, stiffness, and compressibility of the paper reduce when the intensity of wet pressing increases.

The wet pressing is dependent on at least the following parameters [110]:

- Nip pressure and pressure distribution,
- nip residence time,
- temperature,
- properties of the web.

The mechanical properties of the wet web, such as tensile stiffness and tensile strength, are known to increase rapidly with increasing dryness [115]. Figure 29 shows that increased dryness after the press section increases the paper machine production speed still giving an acceptable runnability (amount of web breaks) with a wood-free paper grade.

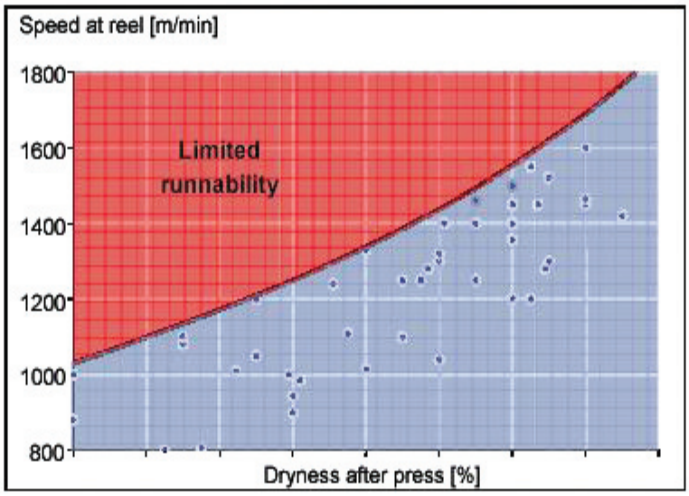

Figure 29. *Speed vs. dryness after press* [115]. *The production speed of paper machine giving an acceptable runnability with a wood-free paper grade increases with increasing dryness (the actual dryness values are not presented).*

However, in some cases (especially for wood-free grades), it is not the efficiency of dewatering in wet pressing that limits the increase of production speed, but the strong market requirements for high bulk. Figure 30 shows how the increased dryness of wet web caused by more intensive wet pressing reduces the bulk of the end product. Because of this, a higher production speed of wood-free paper grades cannot practically be achieved by increasing dryness through more intensive wet pressing [115].

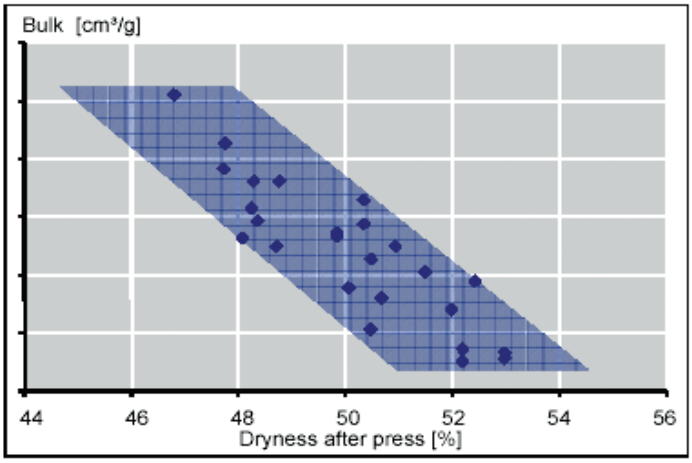

Figure 30. *Bulk after press vs. dryness after press* [115]. *Bulk of paper (actual values are not presented) reduces with more intensive wet pressing.*

According to Paulapuro [110], very little can be done to optimise the wet pressing variables or press configuration in a way that higher wet web stiffness and strength could be achieved at a given dryness. There is more potential for optimising pulp composition, networks structure or use of chemicals to improve the mechanical properties of wet web.

However, it is not common that paper mills use chemicals that are especially designed to improve the mechanical properties of wet web. Therefore, it is important to identify the main factors that affect the mechanical properties of wet web and to understand how the papermaking chemicals used today influence wet web properties. In addition, it would be valuable to discover what kind of chemicals and adding strategies could be used to improve wet web mechanical properties.

6. PAPERMAKING CHEMICALS AND MECHANICAL PROPERTIES OF WET WEB

6.1 Surface tension and dissolved and colloidal substances

The surface tension of pure water is 72 mN/m [116]. The water used in papermaking never reaches such a high surface tension because it contains a large amount of dissolved and colloidal substances. These materials are derived from wood constituents like lignin, hemicelluloses and extractives. Many additives used in papermaking, such as bleaching agents, defoamers, dispersants and wet end additives, also have a significant effect on water properties in the paper machine. Today's trend of closing the white water circuits of paper machines leads to a situation in which the amount of all these substances increases [117-119]. Laleg et al. [120] showed that the addition of cationic starch can lead to an increase in surface tension. Cationic starch is believed to deactivate some of the surface active additives used in papermaking. However, presence of too much cationic starch causes a reduction in surface tension. The effect of some contaminants on surface tension of white water is presented in Figure 31.

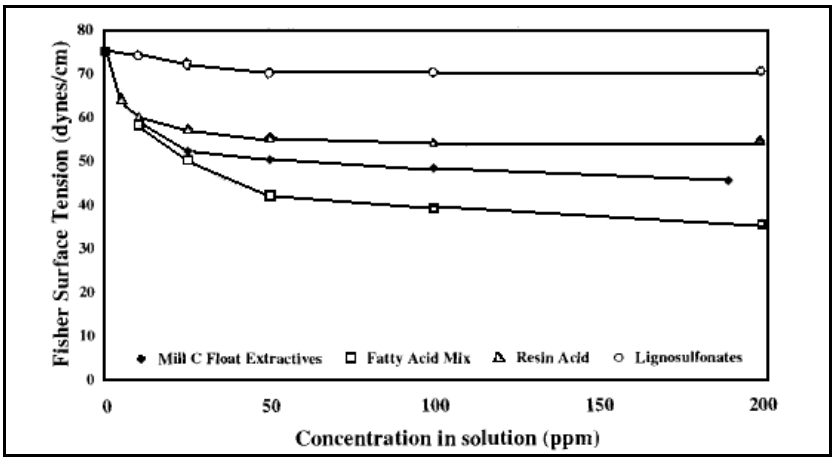

Figure 31. Effect of various contaminants on surface tension [117]**.**

The contamination of white water with different contaminants decreases surface tension as well as the strength of dry paper as shown in Figure 32. According to Tay [117], many chemicals in white water make the fibrous material more hydrophobic and therefore hinder the formation of inter-fibre bonds, which can partly explain the reduction of dry paper strength.

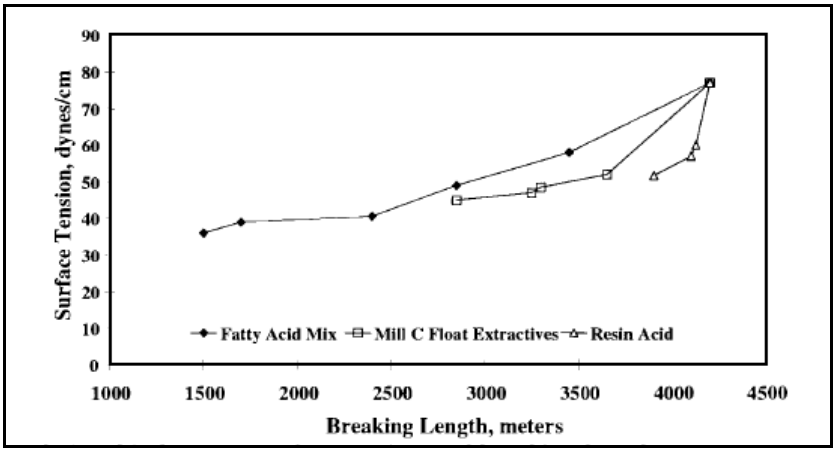

Figure 32. Relationship between surface tension and breaking length [117]. *Breaking length was determined from handsheets made from CTMP pulp.*

Lyne and Gallay [11, 12] accomplished a study in 1954, in which they examined the effects of dryness (Figure 33A) on the breaking length of wood (line 1) and glass (line 2) fibre networks. At a dryness level of around 25%, the breaking length of the network made from glass fibres reaches a maximum and then starts to decrease, whereas the breaking length of the network made from wood fibres continues to increase as dryness increases. Based on this result, they suggested that the strength of wet web (up to a dryness level of 25%) originates from surface tension forces and friction between fibres. Above this level of dryness, inter-fibre bonding starts to play an essential role. The authors further addressed this in another study that showed how decreased surface tension reduces the tensile strength of the network made from glass fibres (Figure 33B). The biggest difference in the breaking length of samples having different surface tension levels is reached at the point at which the strength of networks is the highest (at dryness 25%), but it greatly affects the strength of the network at higher dryness levels as well.

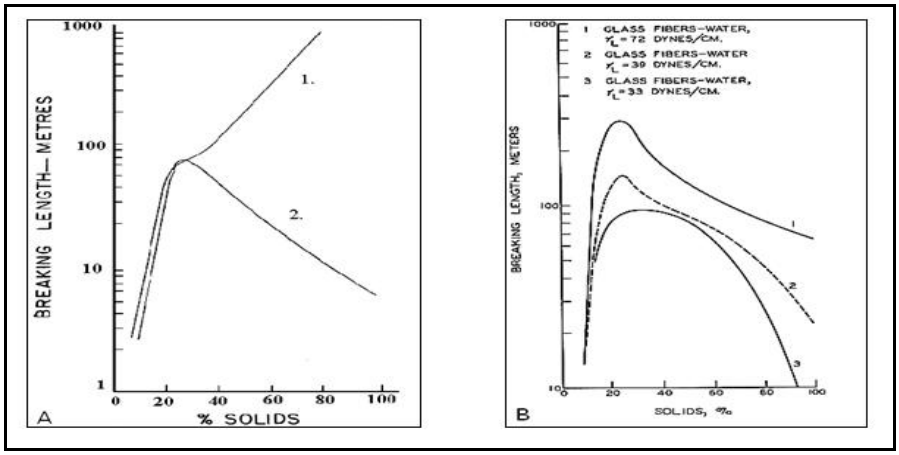

Figure 33. Figure A: Effect of dryness on the breaking length of wood (1) and glass (2) fibres. Figure is slightly modified from [12]. *Figure B: Effect of reduced surface tension on strength development of glass fibre* webs [12].

Nordman and Eravuo [121] also examined how wet web strength was affected when different surfactants were added to white water. They showed that at a given surface tension level, wet web strength is greatly dependent on the chemical used.

Gierz [122] suggested that water is made up of small short-lived clusters which may be classified as either solid-like or fluid-like. The solid-like component consists of rigid, hydrogen-bonded ring structures while the fluid-like component consists of non-rigid, less hydrogen-bonded chain structures. According to Goring [123], the amount of fluid-like water increases close to fibre surfaces, since surfaces rich in hydroxyl groups act as structure breakers and fluid-like water molecules bind to the surface of cellulose via hydrogen bonds (Figure 34). Gierz [122] called this water bound water. He stated that the amount of bound water is dependent on the properties of fibre surfaces and the amount of fines. The higher the fibrillar content of fibres and the amount of fines, the higher is the amount of bound water. When two fibres with high amount of bound water get close to each other, a high adhesion between these fibres is formed.

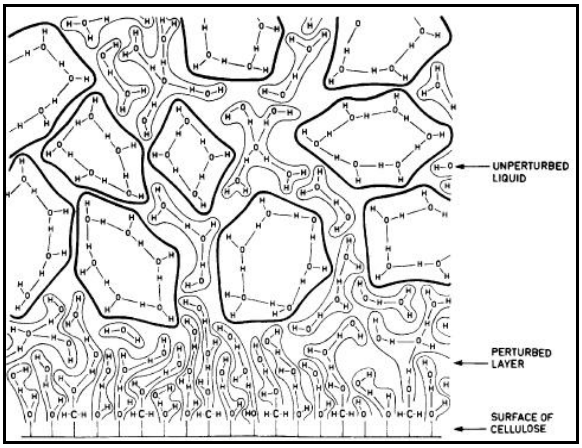

Figure 34. Conceptual drawing of the perturbed layer produced in water adjacent to a cellulose surface immersed in water [123].

Based on the belief that wet webs are mainly held together by surface tension forces (capillary forces) and friction between fibres [124], Page [125] suggested the following Formula (6) to quantify wet web strength.

$$TS = \frac{\mu \cdot \gamma \cdot P \cdot L \cdot RBA}{12C \cdot r} \tag{6}$$

where

	TS	tensile strength, N/m
	μ	coefficient of friction, -
	γ	surface tension, mN/m
	P	perimeter of the average fibre cross-section, m
	L	fibre length, m
	RBA	relative bonded area, -
	C	coarseness, g/m
	r	radius of the curvature of water meniscus, m.

Tejado and Van de Ven [126] stated that this kind of approach to wet web strength underestimates the strength of wet paper by at least one order of magnitude and that wet web strength increases and capillary forces decrease with increasing dryness. Based on their study, the authors concluded that entanglement friction between fibres governs wet web strength when dryness of the web is higher than 30%.

The formula (Formula (6)) published by Page [125], however, presents the widely held view of some of the main factors affecting wet web mechanical properties. Unfortunately, many of the parameters in the equation are difficult to measure and they change when the moisture content varies. In addition, the equation does not directly take into account, for example, fibre shape, dryness or fibrillar content of the material.

6.2 Dry and wet strength additives

Starch is the most commonly used additive in papermaking. Its main purpose is to enhance the strength properties of dry paper [127]. Starch is a water-soluble chemical composed of amylopectin (which has a branched molecular structure) and amylose (which has a linear molecular structure). The mechanism by which starches increase strength of paper is not fully understood, but it is believed to increase the bonded area and the strength of bonds between fibres [128, 129].

Several wet strength additives are currently used in papermaking to increase the permanent wet strength of dried papers. These additives serve to increase or strengthen existing bonds; to protect existing bonds; to form bonds that are insensitive to water and to produce a network of material that physically entangles with fibres. The chemical reactivity of these additives can be of two kinds: either the polymers can react with one another (homo-cross-linking) or they can react with cellulose or with the materials at the cellulose interfaces (co-cross-linking). Homo-cross-linking wet strength additives are adsorbed on the cellulose and form a cross-linked network when the paper is dried. When the paper containing wet strength additives comes into contact with water, rehydration and swelling of the cellulose are restricted by the chemical network and thus a portion of the original dry strength is encased and preserved [130]. In a co-cross-linking mechanism, the fibres are cross-linked by the wet strength chemicals. The bonds then persist after any naturally occurring bonding has been destroyed by water. In this case, covalent cross-linking would lead to a stronger, more permanent form of wet strength, whereas ionic bonding would provide a more temporary form [131].

6.3 Wet web strength additives

Traditional wet strength additives do not enhance wet web strength, i.e. the strength of never dried wet webs. This is because wet strength additives typically require heating and curing time [131]. A typical way to improve wet web strength by chemicals is to increase the water removal of pulp, for example, through the use of different retention aids. Increased dryness of the wet web increases tensile stiffness and tensile strength. However, a higher amount of flocculation and increased dryness after the forming section does not necessary guarantee higher dryness and thus wet web strength after the press section.

One way to improve wet web mechanical properties would be to use chemical additives that increase interactions between fibres in the wet state. To enhance the mechanical properties of the wet web through chemical additives, the chemical additives should increase interactions between fibres without any curing time or high curing temperature. In addition, they should work well with other additives at the wet end of the paper machine. Some examples of chemicals that could potentially be used to increase wet web strength are presented next.

*G-PAM: G*lyoxal was early found to have good cross-linking properties under moist conditions. Glyoxylated polyacrylamide resins (G-PAM) have been widely used in tissue production to provide temporary wet strength. In recent years, G-PAM has been presented as efficient wet web strength additives for other paper grades as well. The benefit over traditional wet strength agents is that it works before drying and has smaller effects on the wet strength properties of dried paper (i.e. it does not deteriorate repulping). Glyoxylated polyacrylamide resins (G-PAM) are produced by allowing C-PAM to react with glyoxal as shown in Figure 35 [131, 132].

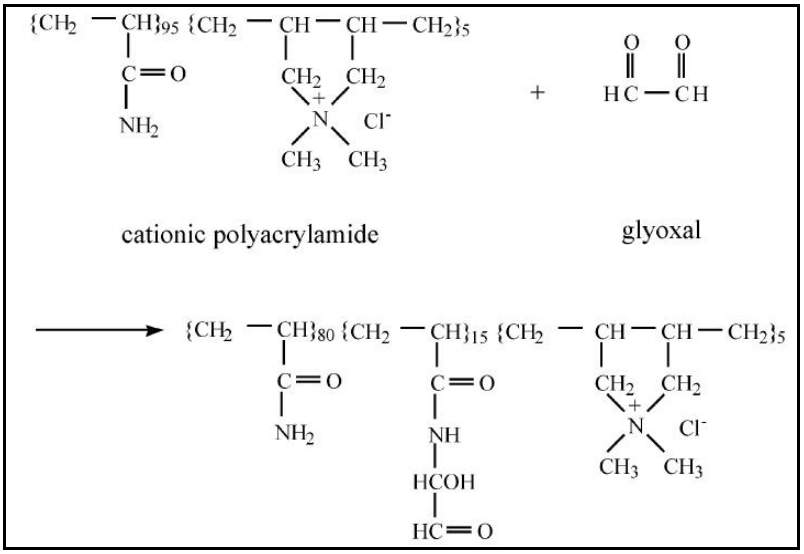

Figure 35. Glyoxylated cationic polyacrylamide [131].

G-PAM is active because of three active groups: unreacted amines (which create hydrogen bonds and increase dry strength), amides reacted with glyoxal (which enhance wet web strength) and quaternary ammonium cations (which interact with negatively charged fibres). The reactivity of G-PAM can be varied by using different amounts of glyoxal in the manufacturing process [131].

Aldehyde starch: Some earlier studies have shown that starch containing aldehyde groups can also increase wet web strength [129, 133]. These modified starches can form covalent bonds and have electrostatic interactions with cellulose. Increased strength is a combination of these effects. Aldehyde isomerises to its diols, which enables covalent bonding with cellulose through acetal or hemiacetal bonding (Figure 36). Conventional cationic starches have not been found to increase the tensile strength of wet webs, because they do not have the cross-linking effect that aldehyde groups offer in modified starches [129].

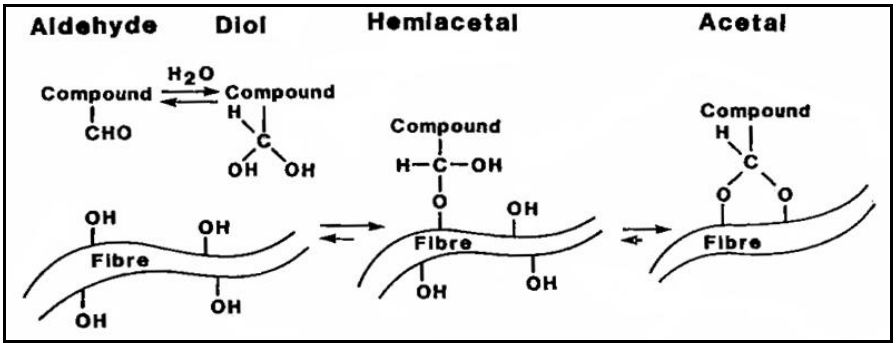

Figure 36. Conversion of aldehyde groups to diols and the formation of hemiacetal and acetal bonds between the aldehyde and hydroxyl groups [131].

Aldehyde starch can be modified to yield a cationic or anionic product. Cationic aldehyde starch is found to be particularly effective in this regard because of its affinity to cellulosic pulp. Laleg et al. [129] showed that adding cationic starch to pulp reduces the wet web tensile strength of handsheets made from a mixture of kraft pulps (80% hardwood and 20% softwood) (Figure 37). The negative effect of starch on wet web strength was more pronounced when greater amounts of starch were added. This concurs with the findings of Myllytie [134], who reported that cationic starch reduces wet web strength of handsheets having dryness level below 65%. Laleg et al. [129] showed that unlike cationic starch, aldehyde cationic starch increased the breaking length of wet web at a constant dryness level and the strengthening effect was greater when more cationic aldehyde starch was added.

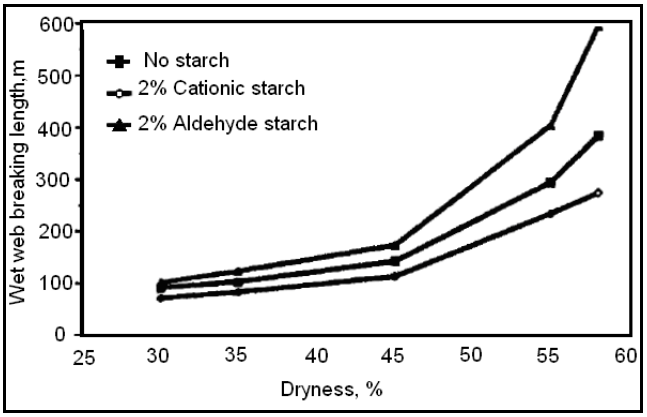

Figure 37. Improvement in sheet strength on addition of CS and CAS [129]. *CS=cationic starch and CAS=cationic aldehyde starch. The tests were carried out with handsheets made from a mixture of kraft pulps (80% hardwood and 20% softwood).*

Cationic aldehyde starch has also been reported to increase flocculation and augment the strength of rewetted paper, but no significant effect on bulk and tear energy has been found. Aldehyde starch was also reported to work well on papers with high filler content and in the presence of other chemicals [129].

The increase of wet web strength with aldehyde starch is known to be higher with furnishes that have low amount of fines. The type of fines is also known to affect its efficiency: The higher the surface area of fines, the lower the effect. Bleaching of pulp has also been shown to reduce its effect. Cationic demand and the amount of dissolved and colloidal substances have been reported to have minor or no deactivating effect on the efficiency of aldehyde starches [129, 133, 135].

CMC (carboxylmethyl cellulose): CMC is an anionic polymer produced by introducing carboxylmethyl groups to the cellulose chain. The degree of substitution and the chain length of the cellulose backbone affect its properties. When the degree of substitution exceeds 0.3, CMC becomes water soluble [136, 137]. The molecular structure of CMC is presented in Figure 38.

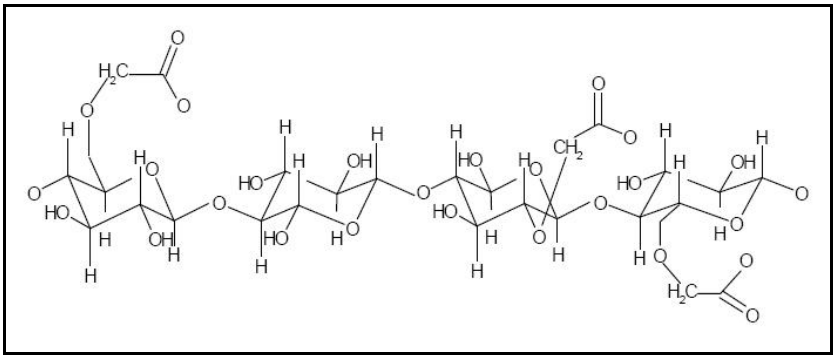

Figure 38. Structure of carboxymethyl cellulose [136].

The effect of CMC on dry and wet web tensile strength has been widely studied [136, 138-141]. According to Myllytie et al. [140], CMC disperses cellulose fibrils and thus promotes the fibre surface fibrillation while increasing the hydration on fibre surfaces. Fibril dispersion and hydration increase the mobility of molecules and molecular level mixing in the bonding domain and thus improve bonding.

Chitosan: Chitosan is a high molecular mass linear carbohydrate, prepared by hydrolising the N-acetyl groups from the natural polymer chitin [142, 143]. Chitin is the second most abundant biopolymer after cellulose; it exists as a structural polymer in the shells of crustaceans (and in fungi), and thus providing a renewable source of chitosan. Generally, chitosan itself is not a well defined polymer, but rather a class of polymers. The molecular structure of chitosan is presented in Figure 39.

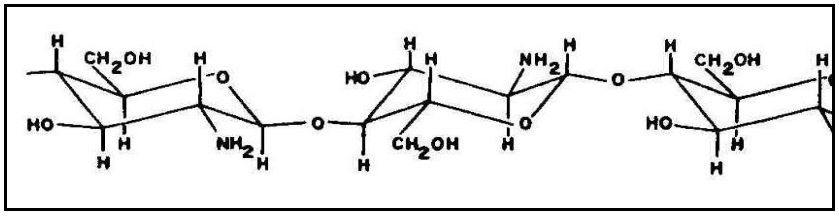

Figure 39. Molecular structure of chitosan [142].

Chitosan has been found to enhance the strength of dry, wet and rewetted papers [141-144]. Chitosan carries primary amine functional groups and therefore its charge and solubility are pH dependent [142]. Because of this, its efficiency as a strength additive is also greatly affected by the pH-value of the furnish; this is because the retention of chitosan is greatly dependent on pH as seen in Figure 40 [143]. To use chitosan in papermaking also at lower pH levels and to have acceptable retention, chitosan must be added in other ways than to furnish. Allan [143] suggested that one such possibility may be spraying of chitosan to already formed web.

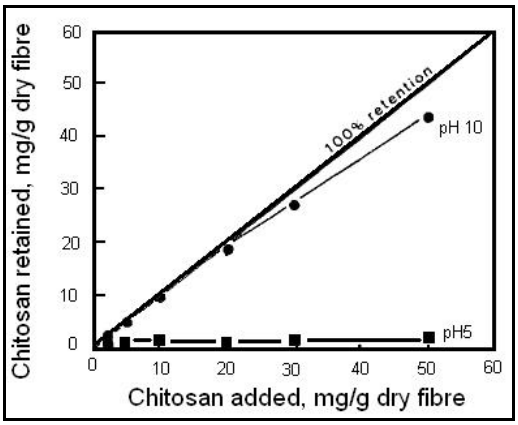

Figure 40. Isotherms of chitosan adsorption onto bleached hardwood kraft pulp at pH 5 and pH 5 [142].

TEMPO oxidation: Saito and Isogai [145] oxidated cellulose fibres using so-called TEMPO oxidation. TEMPO oxidation refers to the catalytic oxidation of carbohydrates. Oxidation creates carboxylate and aldehyde groups. The aldehyde groups form acetal and hemiacetal bonds which increase wet web strength (in a way similar to aldehyde starch). The amount of aldehyde groups can be controlled by adding NaClO during oxidation. The addition of aluminium sulphate in handsheet making has been shown to further increase the wet and dry paper strength of TEMPO-oxidised pulps.

6.4 Selective addition of papermaking chemicals

The trend in papermaking has been towards lower basis weights, decreased amounts of softwood kraft pulp and an increased use of fillers and recycled fibres. The main driver for this kind of development is savings on costs and raw materials. All these changes tend to result in lower strengths of both the wet and dry web. To maintain the necessary strength in papers, a greater quantity of strength additives is often required [128].

As mentioned in Chapter 6.2, starch is the most common strength additive used to increase strength of dry paper in papermaking. Synthetic polymers are used to improve drainage and especially the retention of fine particles and fillers. These particles alone are too small to be mechanically retained on the wire. Therefore these particles should make aggregates with each other or bind to fibres with the help of chemicals. Important characteristics during dewatering at the wet end are flock size, flock strength and the flocculation ability. These can be controlled mainly by molecular weight, conformation and the charge density of the polymers used in the wet end of a paper machine. In the ideal case, a high retention of fine particles, good formation and good drainage are simultaneously obtained [128, 146, 147].

The increased use of different chemicals leads to higher costs. Therefore it is essential to use papermaking chemicals efficiently. Earlier studies [128, 148] have shown that the selective addition of chemicals to different fibre fractions can improve paper strength. Stratton [128] showed that adding both PAE and CMC (in a ratio of 0.4:1.0) on a long fibre fraction of unbleached kraft pulp before mixing with fines results in higher dry, moist (dry paper in high RH) and wet strength than the addition of those chemicals to the whole pulp or to both fractions separately before mixing. In the same study the effect of adding chemicals before refining to pulp to adsorb them only to long fibres was unsuccessful [128]. This result might be explained by the fact that some part of the outer wall (where polymers are expected to be adsorbed) is removed during refining. A study done by Retulainen et al. [148] with bleached kraft pulp showed that a selective addition of both starch and CMC to the long fibre fraction (as opposed to adding the chemicals to the whole pulp) can increase the z-directional delamination energy (Scott bond strength) (Figure 41). No difference was found when the additives were added to the whole pulp or to the fines fraction. Based on this finding, the authors suggested that even with chemical pulp (which typically contains a relatively small amount of fines) most of the additives are adsorbed on fines [148].

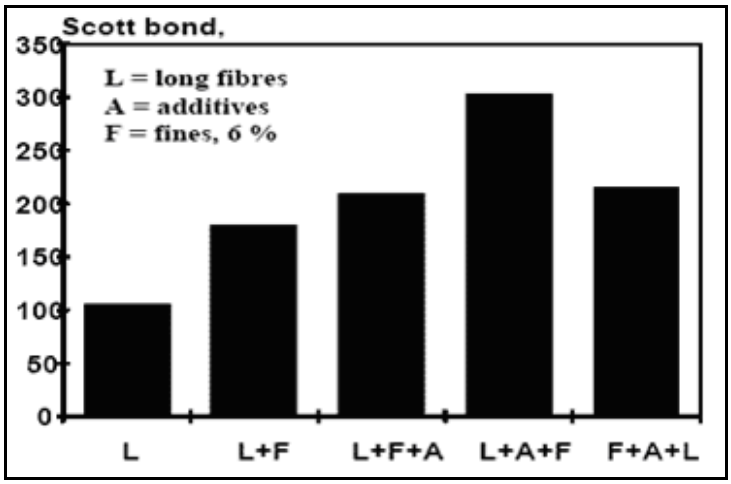

Figure 41. *Effect of blending order on Scott bond strength of handsheets from long fibre fraction. L=long fibres; A=additives; F=fines* [148]. *Handsheets were made from bleached kraft pulp.*

Hubbe and Cole [149, 150] showed that by selectively adding C-PAM to chemical pulp fines instead of mixing it in the whole pulp enhances the drainage of the pulp. However, adding C-PAM to the long fibre fraction alone is less effective than adding it to the whole pulp. The test was carried out with pulps containing primary and secondary fines. The effect was similar for both mixtures, but the difference was higher with pulp containing secondary fines as can be seen in Figure 42. The addition of C-PAM to fines increases the flocculation of fines, which reduces the surface area of fibrous material, leading in turn to improved drainage.

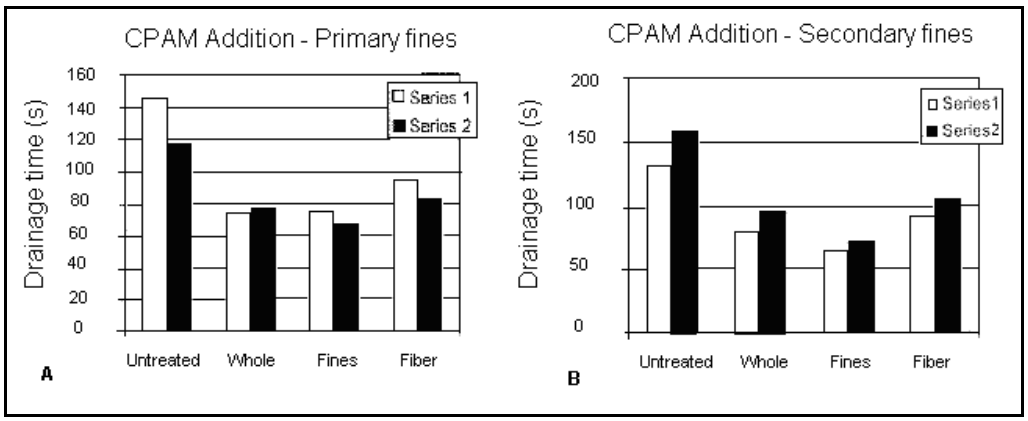

Figure 42. *Figure A: Drainage of systems involving primary fines, depending on the mode of addition of cationic flocculant. Figure B: Drainage of systems involving secondary fines, depending on the mode of addition of cationic flocculant* [149].

Law et al. [151, 152] demonstrates that the retention and drainage of thermomechanical pulps can be enhanced by cationisation of a part of a long fibre fraction. However, the cationisation destroys some of the carboxylic groups in the fibres, reducing the inter-fibre bonding between fibres and thus decreasing the strength of the paper. They compensated the loss of strength with TEMPO oxidation of the long fibres (which converts the primary alcohol groups into carboxylic acid).

EXPERIMENTAL PART

7. MATERIALS AND METHODS

In this chapter, the measurements and materials used in the experiments of this thesis are described for each chapter of the experimental part. Standardised measurements refer to the standards that were used in this thesis while the special measurements are presented in more detail.

CHAPTER 8: FINES, FIBRES AND MECHANICAL PROPERTIES OF DRY AND WET WEB

Raw materials: Commercial never-dried bleached softwood kraft pulp (CSF 500 ml) and commercial never-dried TMP pulp (latency removed, CSF 45 ml), both from Finnish mills.

Refining: Both pulps were refined in a Finnish paper mill. As the softwood kraft pulp contained only a limited amount of fines after mill refining, the pulp was further refined to SR 75 in a Valley beater to facilitate fines fractionation.

Production of long fibres and fines: Fines were separated from the pulps manually using a 200 mesh screen and a shower. After this, fines were sedimented in big tanks to increase their consistency. The long fibre fractions (R16+R25) were separated with a Bauer McNett apparatus.

Handsheet making: Wet and dry handsheets having grammage of 60 g/m^2 were formed (with white water circulation) adapting SCAN-CM 64:00 (for details, see Chapter 7.1).

Samples:

- TMP long fibres
- TMP long fibres + 10% TMP fines
- TMP long fibres + 20% TMP fines
- TMP long fibres + 10% kraft fines
- TMP long fibres + 20% kraft fines
- kraft long fibres
- kraft long fibres + 10% kraft fines
- kraft long fibres + 20% kraft fines

Measurements: Fibre morphological properties were determined with a commercial fibre analyser called FibreMaster, which is developed by STFI (Skogsindustrins Tekniska Forskningsinstitut). CSF was measured according to SCAN-C 21:65, grammage of the sheets according to SCAN-P 6:75, thickness of handsheets according to SCAN-P 7:75 and WRV (water retention value) according to SCAN-C 62:00. Drainage time was measured manually during sheet forming with a digital timer. Dry and wet paper in-plane mechanical properties were determined by the Impact device (described in Chapter 7.1). Shrinkage potential of wet pressed handsheets was determined by the method described in Chapter 7.5.

CHAPTER 9: FIBRE ORIENTATION, FILLER CONTENT AND MECHANICAL PROPERTIES OF DRY AND WET WEB

Raw materials: A mixture of commercial never-dried bleached hardwood (70%) and softwood (30%) kraft pulps from a Finnish mill. Filler ($CaCO_3$) content was 10% (in filler trials, the filler content was varied).

Refining: Pulps were refined in a Finnish paper mill.

Making of paper samples: Wet and dry (wet samples were dried in laboratory) paper samples having grammage of 70 g/m^2 were produced with a pilot paper machine having production speed 900 m/min. The pilot paper machine had a gap former and a press section with three press nips. The third nip in the press section was a shoe press nip.

Measurements: Dry and wet paper mechanical in-plane properties were determined by the Impact device (described in Chapter 7.1). The only difference compared to handsheet samples was that the lengths of the samples were 180 mm. On-line web tension was measured in press-to-dryer transfer.

CHAPTER 10: FIBRE DEFORMATIONS AND MECHANICAL PROPERTIES OF DRY AND WET WEB

Raw materials: Commercial never-dried bleached softwood kraft pulp (CSF 460 ml) from a Finnish mill.

Refining: The pulp was refined in a Finnish paper mill.

Treatments: The dryness of pulp was increased from 4% (consistency after mill refining) to 25% in a specially designed thickening device (excluding hot disintegrated sample). Hot disintegration was made to the original pulp according to SCAN-C 18:65. The thickened pulps were then mechanically treated for 15 and 45 minutes at room temperature in a Kenwood kitchen mixer with a blade that is shown in Figure 43. The mixing speed was 60 rpm. The mechanical treatment was applied under a lid to minimise the changes in dryness of the pulp during the treatment.

Figure 43. The commercial Kenwood kitchen mixer that was used for the mechanical treatment of the softwood kraft pulp.

Making of handsheets: Wet and dry handsheets having grammage of 60 g/m^2 were formed (without white water circulation) adapting SCAN-CM 26:99 (for details, see Chapter 7.1). Some of the handsheets were dried according to the standard, others were allowed to shrink freely during drying and still others were dried between two jaws in a Lloyd LR10k tensile test rig, while they were dried with hot air (105^{o}C). Before the samples were dried between the jaws, they were strained by 3%.

Samples:

- Thickened pulp
- Hot disintegrated pulp
- Pulp mechanically treated for 15 minutes
- Pulp mechanically treated for 45 minutes

Measurements: Fibre morphological properties were determined with a commercial fibre analyser called FibreMaster, which is developed by STFI (Skogsindustrins Tekniska Forskningsinstitut). Figures of fibres were scanned with a commercial scanner (UMAX powerLook 3000) of layers of fibres that were removed from handsheets by tape stripping. Grammage of the sheets were measured according to SCAN-P 6:75, thickness of handsheets according to SCAN-P 7:75, CSF according to SCAN-C 21:65 and WRV according to SCAN-C 62:00. Light scattering coefficient was determined according to SCAN-P 8:93. Drainage time was measured during sheet forming with a digital timer manually. Dry and wet paper in-plane relaxation characteristics were determined using the Impact device (described in Chapter 7.1), tensile properties were determined using a commercial Lloyd LR10k test rig (using strain rate 22 mm/min) according to SCAN-P 38:80 and z-directional delamination energy was measured with a Huygen device according to T 560 om-07. Shrinkage potential of wet pressed handsheets was determined by the method described in Chapter 7.5.

CHAPTER 11: WHITE WATER COMPOSITION AND MECHANICAL PROPERTIES OF DRY AND WET WEB

Raw materials: Commercial dried bleached softwood kraft pulp from a Finnish mill.

Refining: The pulp was beaten to CSF 500 ml with a Valley beater.

Handsheet making: Wet and dry handsheets having grammage of 60 g/m^2 were formed (with white water circulation) adapting SCAN-CM 64:00. The procedure was similar to what is presented in Chapter 7.1, except the used chemicals were added to both the recirculation water and the water used for diluting the pulp suspension before sheet making.
Samples:

- Deionised water
- TMP filtrate obtained after peroxide bleaching (from UPM Kymmene Jämsänkoski mills), pulp diluted in deionised water at a 1:6 ratio
- 100 ppm non-ionic surfactant Liptol S-100, (Brenntag Nordic Oy), fatty polyether type surfactant that is used typically in de-inking.
- 100 ppm oleic acid ($C_{18}H_{34}O_2$) Sigma-Aldrich 75093 (Fluka)
- 100 ppm defoamer De-Airex 7061, (Hercules), a mixture of different surfactants.

Measurements: Grammage of the sheets were measured according to SCAN-P 6:75 and thickness of handsheets according to SCAN-P 7:75. Thickness of wet handsheets was measured adapting SCAN-P 7:75, since the measurements were made between plastic sheets to avoid compression of the wet sheets. Light scattering coefficient was determined according to SCAN-P 8:93. Drainage time was measured during sheet forming with a digital timer manually and the surface tension of white water was determined by the method presented in Chapter 7.3. The in-plane mechanical properties of dry and wet paper were determined using the Impact device (described in Chapter 7.1). Shrinkage potential of wet pressed handsheets was determined by the method described in Chapter 7.5. The extractives in TMP filtrate was determined according to a method developed by Åbo Akademi. Charge of white water was determined using a commercial device from Mütek (PCD-Titrator two) and pH of white water was determined using a commercial (Schott pH-meter handylab 1) device.

CHAPTER 12: POLYMERS AND MECHANICAL PROPERTIES OF DRY AND WET WEB

Raw materials: Commercial never-dried bleached softwood kraft pulp from a Finnish mill.

Refining: Pulp was refined to CSF 370 ml with a pilot scale conical refiner.

Handsheet making: Wet and dry handsheets having grammage of 60 g/m^2 (of the base paper without any chemicals) were formed (without white water circulation) adapting SCAN-CM 26:99. The procedure was similar to what is presented in Chapter 7.1, except the spraying of chemicals was carried out (at 0.5% consistency) before wet pressings. The spraying procedure is presented in Chapter 7.2.

In one trial point, the pulp was divided in two fractions (50%/50%) and chemicals were added to both pulp fractions (chemicals were added at least 30 minutes before combining the pulps). Before forming of sheets the pulps were mixed in a DDJ mixer for 20 s.

Samples:

- Reference with no chemicals
- CMC (DS 0.7, DP 140) added by spraying, 1 g/m^2
- CMC (DS 0.7, DP 140) added by spraying, 2 g/m^2
- Chitosan (made from crab shells, with a relative molecular weight of 400 000 g/mol, and 19% acetylation) added by spraying, 1 g/m^2
- CMC (DS 0.7, DP 140) + chitosan (made from crab shells, with a relative molecular mass of 400 000 g/mol, 19% acetylation) both added by spraying, 1 g/m^2 + 1 g/m^2
- PVA (degree of hydrolysis 99%, DP 1800) added by spraying, 1 g/m^2
- CMC (DS 0.7, DP 140) + C-PAM (molecular weight 10-12 Mg/mol, charge density 2 meq/g) both added by spraying, 1 g/m^2 + 0.5 g/m^2
- C-PAM (molecular weight 10-12 Mg/mol, charge density 2 meq/g) + A-PAM (molecular weight 8-9 Mg/mol, charge density -1 meq/g) both added by spraying, 0.5 g/m^2 + 0.5 g/m^2
- C-PAM (molecular weight 10-12 Mg/mol, charge density 2 meq/g) + A-PAM (molecular weight 8-9 Mg/mol, charge density -1 meq/g) both added to pulp, 5 kg/t + 5 kg/t

Measurements: Grammage of the sheets were measured according to SCAN-P 6:75, thickness of handsheets according to SCAN-P 7:75 and air permeance according to SCAN-P 26:78. In-plane mechanical properties of dry and wet paper were measured using the Impact device (described in Chapter 7.1).

CHAPTER 13: SELECTIVE ADDITION OF PAPERMAKING CHEMICALS AND MECHANICAL PROPERTIES OF WET WEB

Raw materials: Commercial never-dried bleached hardwood kraft pulp from a Finnish mill.

Production of long fibres and fines: The pulp was fractionated with a pressure screen in two different fractions (short fibre and long fibre fractions). To ensure suitable fractionation performance, a pilot screen was utilised (OptiScreen model FS50). The basket type used was a Nimax type, ϕ0.20 mm, with appropriate operational parameters which were optimised accordingly. The approbated reject ratio (in mass and volume) was utilised to create substantial differences in the average fibre length between the fibre fractions.

Handsheet making: Wet handsheets having grammage of 60 g/m^2 were formed (with white water circulation) adapting SCAN-CM 64:00 (for details, see Chapter 7.1), except C-PAM was added into the short fibre fraction and cationic starch (cooked for 30 min at T=97^{o}C) into the long fibre fraction before forming of the sheets. Each fraction and the respective additive were first mixed in a DDJ mixer for 30 s. Subsequently the fractions were combined and mixed for 10 s. The amount of added C-PAM was 200 g/t and 4 kg/t for cationic starch calculated based on the whole furnish used (long fibres + short fibres).

Samples:

- Reference with no chemicals
- Wet end cationic starch (4 kg/t, D.S. 0.035) and C-PAM (200 g/t, molecular weight 6-7 Mg/mol, charge density 1 meq/g) added to whole pulp
- Wet end cationic starch (4 kg/t, D.S. 0.035) added to long fibre fraction and C-PAM (200 g/t, molecular weight 6-7 Mg/mol, charge density 1 meq/g) added to short fibre fraction

Measurements: The drainage properties (flow resistance and drainage time) of pulp were measured with a tailor-made drainage tester presented in Chapter 7.4. The in-plane mechanical properties of wet paper were measured with the Impact test rig (described in Chapter 7.1).

7.1 Tensile strength and relaxation measurements with an Impact test rig

Dry handsheets of 60 g/m^2 were formed according to SCAN-C 27:76. Wet handsheets were formed adapting SCAN-CM 26:99 (without white water circulation) or SCAN-CM 64:00 (with white water circulation). The wet pressings were done at two different pressure levels (50 kPa and 350 kPa) to reach two different dryness levels for the wet handsheets. Wet samples were cut to a width of 20 mm and dry samples to 15 mm, both with a sample length of 100 mm. Wet samples were stored in an air-proof condition (in a plastic bag) at a temperature of 7°C in order to maintain the level of dryness.

Mechanical properties of dry and wet paper samples were determined with the Impact device. The Impact device (Figure 44) uses a velocity of 1.0 m/s, which is approximately 3000 times higher than that used in standard tensile testing methods [17, 18, 20]. Before measurements, the samples were attached between two jaws. The lower jaw moved to the desired position creating strain. The upper jaw was equipped with a load sensor. The amount of strain was controlled simply by determining the gap between the lower jaw and target surface. The amount of strain was measured with a laser sensor.

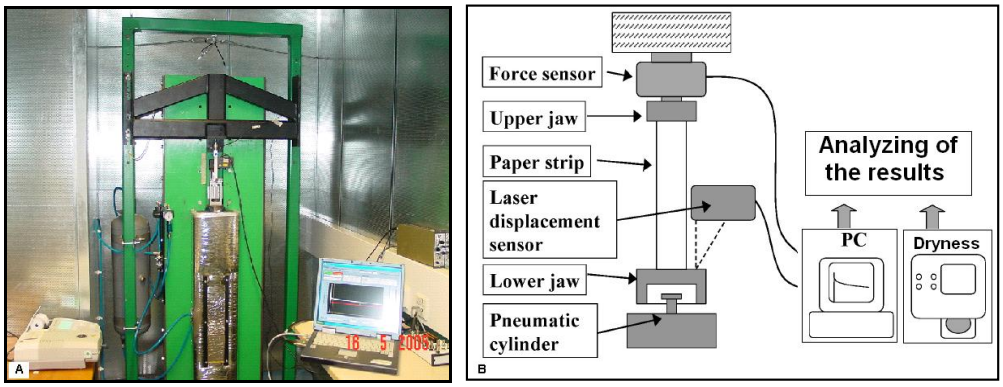

Figure 44. *Figure A: Impact test rig* [20]. *Figure B: Principle of test procedure with Impact* [17].

In Impact tests, 10-14 samples were measured at each dryness level. The validity of each result was tested using Dixon-Massey criteria (SCAN-G 2:63). For each dryness level (and measured quantity) dryness of 4-6 samples was determined using a Metler Toledo HR73 infra red dryer.

Relaxation test

The relaxation properties (maximum tension (or initial tension), residual tension and relaxation percentage) of wet samples were mostly determined at 1% and 2% strains. The relaxation time used for wet samples was 0.475 s. The tension measured after this relaxation time is referred to as residual tension. The highest tension after straining is called maximum tension, which also refers to the initial tension. Figure 45 shows an example of a curve from a relaxation test of wet paper.

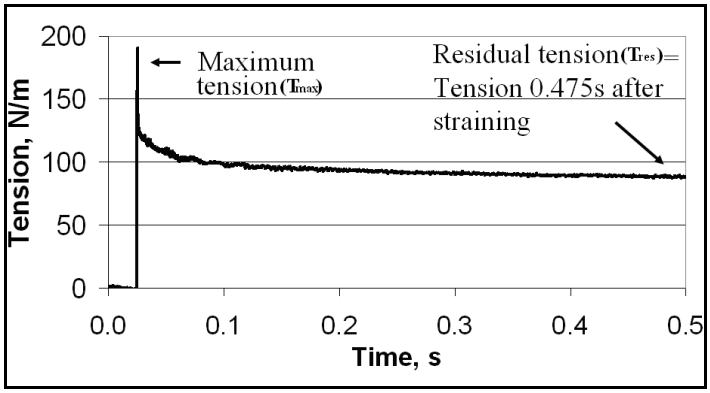

Figure 45. Tension-time-figure of relaxation [17]. *The tension-time-figure is made with TMP handsheet for a 350 kPa wet pressed sample with Impact test rig using strain rate of 1 m/s. The sample was strained to 1% strain.*

The amount of the relaxation was described as a tension relaxation percentage, and calculated using Formula (7) [152].

$$R_{\%} = \frac{T_{\max} - T_{res}}{T_{\max}} \cdot 100\,\%, \tag{7}$$

where $R_{\%}$ relaxation percentage, %

T_{max} maximum tension (initial tension), N/m

T_{res} residual tension, N/m.

The greater the relaxation percentage, the more tension is lost during relaxation. The relaxation percentage is a useful parameter when evaluating the relaxation tendency of the paper web.

Tensile strength test

Tensile strength, strain at break and elastic modulus (maximum slope at the beginning of stress-strain curve) were the main parameters established from the test when straining samples to the breakpoint (see Figure 46).

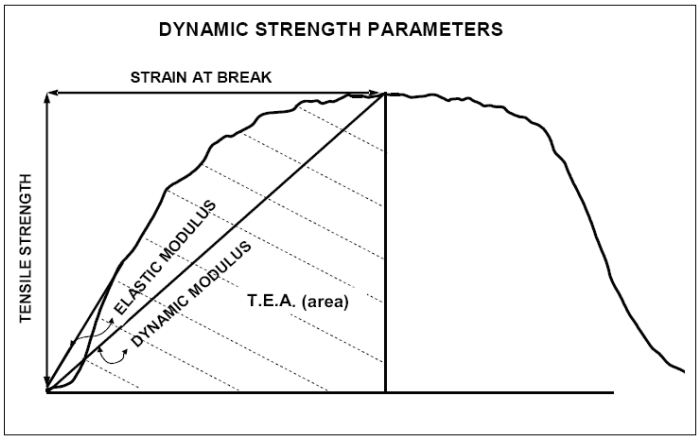

Figure 46. Tension-strain-figure of dynamic tensile strength test [17]. *The tension-strain-figure is made with TMP handsheet for a 350 kPa wet pressed sample with Impact test rig using strain rate of 1 m/s.*

Presentation of the results

The results of wet samples in this thesis are mainly presented as a function of dryness. The mechanical properties (tensile strength, elastic modulus, residual tension and maximum tension) of wet web are known to be highly dependent on the dryness (30-90%) [9, 17]. Thus, wet web properties in this thesis are presented with an exponential or power fit to describe the effect of the dryness. Figure 47 shows that the exponential fit well describes the effect of dryness on wet web tensile strength (Figure 47A) and residual tension (Figure 47B) for wet handsheets when dryness is varied by changing the pressure in wet pressing.

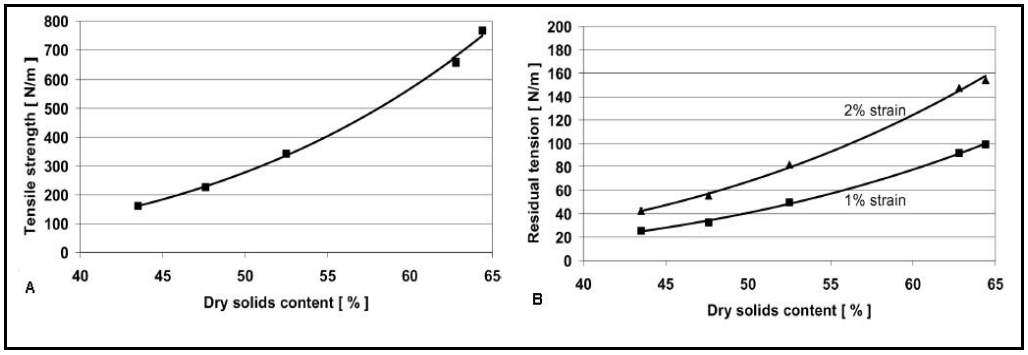

Figure 47. *Figure A: The dependence of tensile strength on dry solids content. Figure B: The dependence of residual tension (1% and 2% strains) on dry solids content* [22]. *The tests were carried out with wet handsheets made from bleached kraft pulp.*

The mechanical properties of dry papers presented in this thesis are indexed with sheet grammage. It would have also been beneficial to determine the exact basis weights of the wet handsheets, but this was not done and therefore the results of wet paper samples are not indexed with grammage, unless otherwise specified.

7.2 Spraying of chemicals

In the spraying of chemicals, formed handsheets were attached to the wire with a vacuum which also enhanced the penetration of chemicals into the paper during spraying. All chemicals were diluted to 0.5% consistency before spraying. CMC was mixed (at room temperature) for 60 minutes, PVA was mixed (at 80^{o}C) for 2 hours, chitosan (dissolved in 1% acetic acid and then diluted to 0.5% consistency) was mixed for 1 hour (at room temperature), A-PAM and C-PAM were mixed (at room temperature) over night. The unit, which consisted of a vacuum box, a screen plate and wire was on a rail, and it was moved with an electric motor. The amount of sprayed chemical was adjusted (by spraying water to dry handsheet) by changing the speed of this unit, while the spray remained constant and was immobilised. In the case of a dual application of chemicals, similar spraying was carried out in two steps. The principle of the spray device is presented in Figure 48.

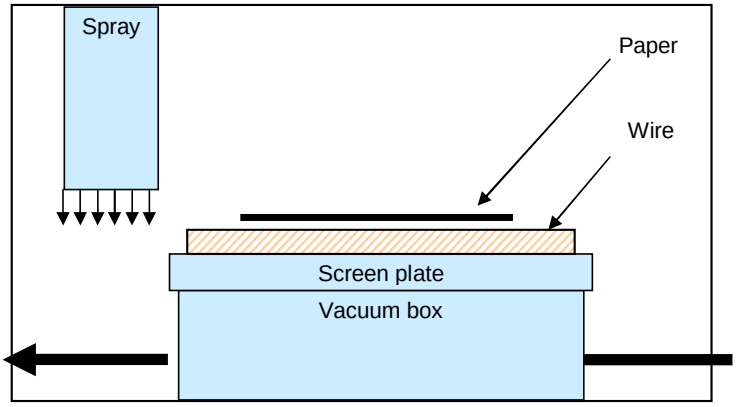

Figure 48. Principle of the spray device.

After spraying, the handsheets were wet pressed and samples for testing were prepared as presented in Chapter 7.1

7.3 Surface tension measurements

The surface tension measurements were done using the commercial KRÜSS K9 device. The method utilises the principle of the du Noüy ring method, measuring the necessary force, F (Figure 49B) to pull a platinum ring of a precisely known dimension free from the surface film of the water sample (Figure 49A) [154].

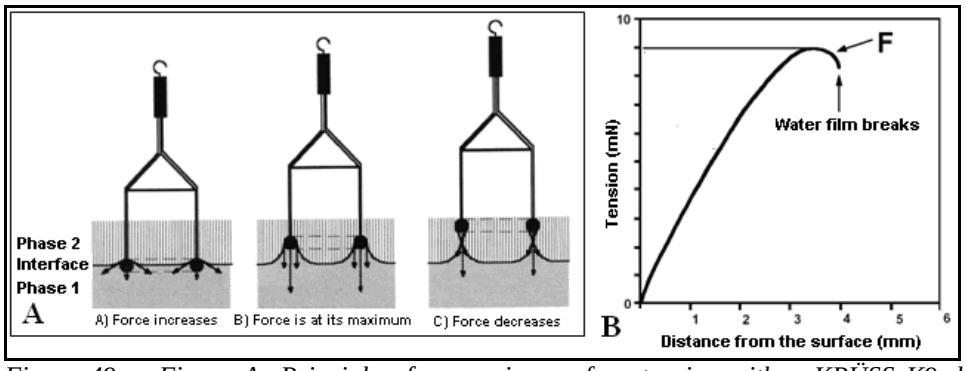

Figure 49. Figure A: Principle of measuring surface tension with a KRÜSS K9 device. Figure B: The tension-distance curve from which the surface tension is determined. Figure modified from [154].

Surface tension was measured from white water after 15 handsheets were formed. The possible solid particles were not removed from the white water before measurements.

7.4 Drainage measurements

A gravity-driven filtration device was utilised as a tool to predict the dewatering properties of the pulps (Figure 50). The amount of pulp used in one test run was 10 grams (abs.), yielding 0.15% as the initial consistency. The additives that were used were mixed in a separate mixing bowl for a sufficient contact time (10 minutes for cationic starch and 10 s for C-PAM). After mixing, the sample was poured into the filtration device [155].

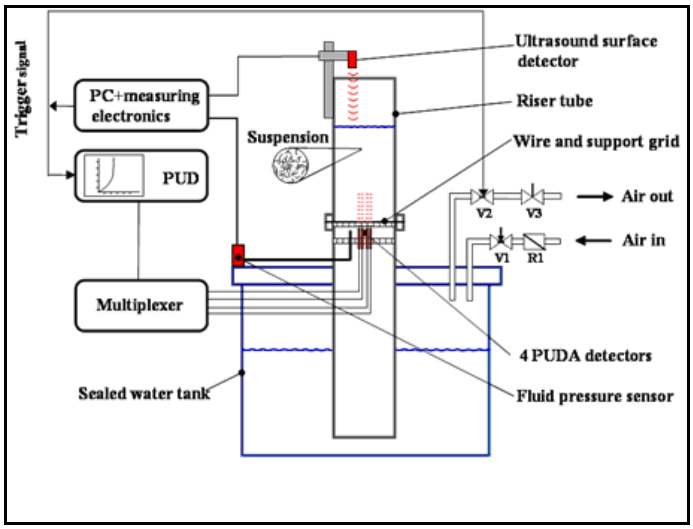

Figure 50. Schematic illustration of the filtration device [155].

Flow resistance caused by the filtrating suspension was estimated using Formula (8). Flow resistance caused by the wire was subtracted from the total resistance by determining the flow resistance for water [155].

$$R_{f,tot} = \frac{\Delta p(t)}{q_T(t)} \tag{8}$$

where $R_{f,tot}$ flow resistance of pulp, kg/m^{2}s

$\Delta p(t)$ pressure loss caused by the filtrating the pulp layer, Pa

$q_T(t)$ flow rate (total flux) of the fluid phase given by the surface position detector, m^3/s.

7.5 Shrinkage potential measurements

The measurements of shrinkage potential were done on 350 kPa wet pressed handsheets. In this procedure, four holes were stamped onto wet paper samples using a specially designed plate with four spikes (one in each corner). After this, the samples were dried and allowed to shrink freely on a table (at relative humidity 50% and temperature 23^{o}C) for at least 12 hours. While the samples shrunk, the placement of holes in the sheets also changed. The shrinkage potential was determined as the relative difference of a rectangular perimeter that was fitted to the holes before and after the free shrinkage of paper.

8. FINES, FIBRES AND MECHANICAL PROPERTIES OF DRY AND WET WEB

In this chapter, the main findings of the effects of fines and fibres on wet web mechanical properties are presented. Shrinkage and drainage affect web runnability and the quality of the final product and are thus also analysed here. To clarify the findings of this study, only the samples with long fibres and long fibres with 20% of fines are used to present the results of the wet handsheets. All the results are found in Appendix I.

8.1 Drainage and shrinkage

Drainage time during sheet forming is similar for TMP and kraft long fibre fractions as shown in Figure 51. The addition of TMP fines to TMP long fibres have no effect on drainage time, whereas the addition of kraft fines (20%) to TMP long fibres increases drainage time from 3.9 s to 5.7 s. A combination of kraft long fibres and kraft fines results in the longest drainage time (12.2 s). It seems that drainage time during sheet moulding is mainly dependent on the surface area of the fibrous material. Kraft fines and fibres have a higher surface area than TMP fines and fibres, respectively [92].

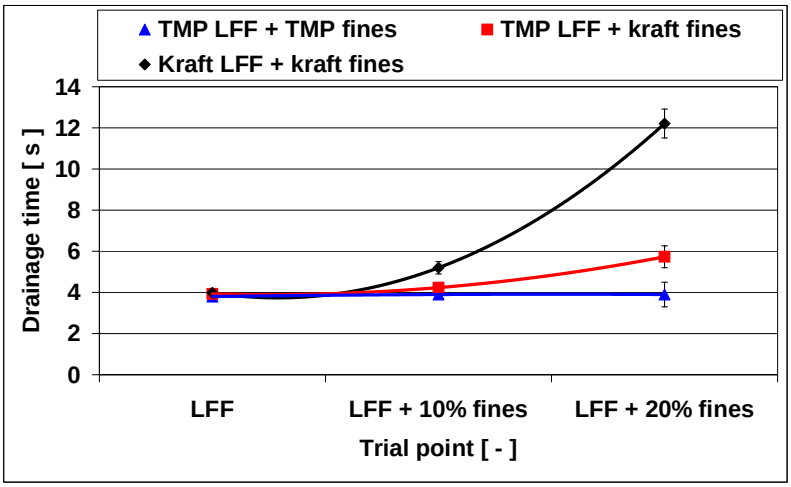

Figure 51. The effect of adding kraft and TMP fines to TMP and kraft long fibres on drainage time during forming of handsheets (polynomial fit). Error bars show a 95% confidence interval of the mean of the measurement (LFF=long fibre fraction).

The density and shrinkage potential of handsheets are strongly affected by the type of fibres and fines, as can be seen in Figure 52. The density of handsheets made from kraft and TMP long fibres are 570 kg/m^3 and 290 kg/m^3, respectively. Adding kraft fines to the TMP long fibre fraction increases both density and shrinkage significantly more than adding TMP fines. This is in line with the results reported by Gierz [122], who indicated the high capacity of kraft fines to increase the cohesion forces in wet paper and thus augment the density of the sheet. With TMP fibres, the increase of shrinkage with increasing density shows a similar slope with the addition of both kraft and TMP fines. The slope is significantly steeper for pulp containing kraft long fibres than for TMP long fibres.

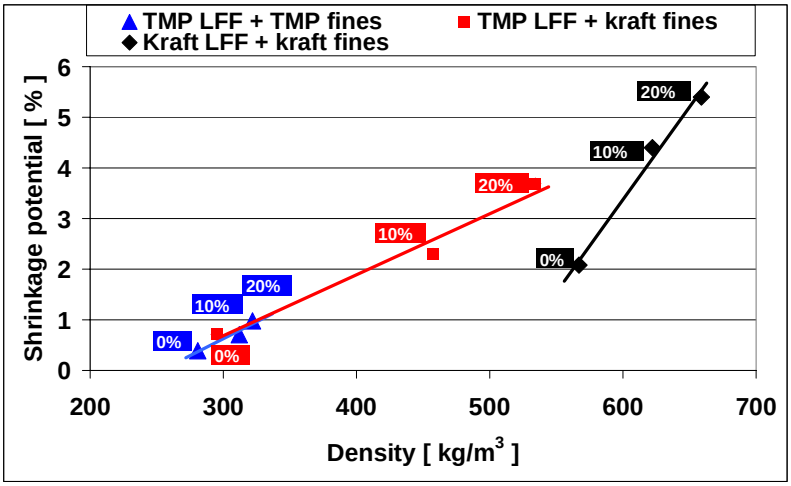

Figure 52. The effect of adding kraft and TMP fines to TMP and kraft long fibres on the shrinkage potential of handsheets during drying as a function of the density of dry handsheets (linear fit). The percentages given in the figure describe the amount of fines in the handsheets (LFF=long fibre fraction).

Adding 20% of kraft fines to kraft long fibres or to TMP long fibres result in a similar increase in shrinkage potential. This result contradicts earlier studies [45, 124], in which axial stiffness of bonded fibre segments presents a considerable resistance to paper shrinkage (since TMP fibres are stiffer than kraft fibres, the network containing TMP long fibres could be expected to shrink less). The contradiction might be explained by the dominating effect of kraft fines during shrinkage (high shrinking force). Further studies would be needed to confirm this finding.

8.2 Mechanical properties of dry paper

The tensile index of the dry handsheets made of kraft long fibres is significantly higher than with TMP long fibres as seen in Figure 53A. The average fibre lengths of these fibres are similar (TMP=2.1 mm and kraft=2.0 mm), which excludes the effect of fibre length on the results. TMP fibres have higher coarseness (TMP 0.25 mg/m and kraft 0.18 mg/m) than kraft fibres, which makes TMP fibres stiffer than kraft fibres. In addition, higher coarseness (and similar fibre length), means that handsheets made of TMP long fibres contain less fibres in a mass unit and thus a lower number of inter-fibre bonds and load bearing fibres than handsheets made of kraft long fibres.

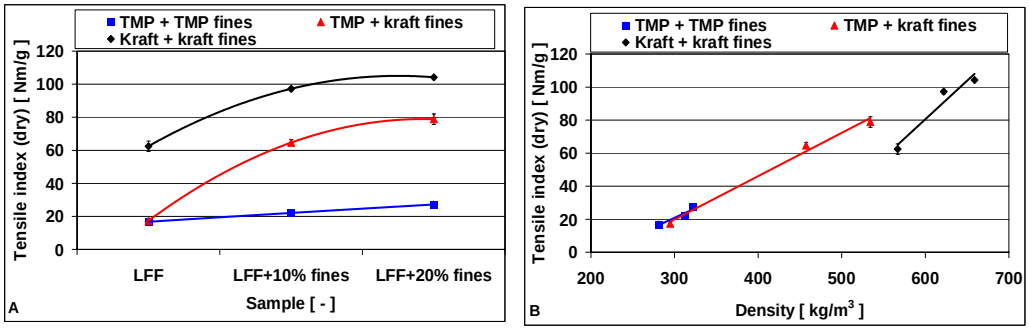

Figure 53. *Figure A: The effect of adding kraft and TMP fines to TMP and kraft long fibres on the tensile index of dry handsheets (polynomial fit) measured by the Impact test rig at a strain rate of 1 m/s. Figure B: The effect of adding kraft and TMP fines to TMP and kraft long fibres on the tensile index of dry handsheets as a function of the density of dry handsheets (linear fit). Error bars show a 95% confidence interval of the mean of the measurement (LFF=long fibre fraction).*

Paavilainen [65] compared springwood and summerwood softwood fibres at constant refining. Based on her studies, the bonding ability of fibres is more important factor effecting dry paper tensile strength than the number of load bearing fibres. This agrees with the results presented in Figure 53B, which shows that density has linear relationship with tensile strength of dry handsheets. Inter-fibre bonding occurs mainly between hydroxyl groups of cellulose and hemicellulose, while the bonding ability of lignin is relatively low. According to Rennel [156], this is why the specific bond strength of mechanical pulps is approximately 1/3-1/2 lower than for chemical pulps. The flexibility of chemical pulp fibres is 3-10 times higher than mechanical pulp fibres and a part of chemical pulp fibres collapse during wet pressing. Increased flexibility and the collapse of fibres increase the area of fibre-fibre bonds [65].

The addition of both, TMP and kraft fines to long fibres improve tensile strength of dry paper. Addition of fines increases the size and amount of inter-fibre bonds. Because of this, the number of segments between bonds increases and their length decreases. Addition of fines has been reported to increase the activation of fibre network during drying. The lateral shrinkage of fibres is transmitted at bond areas to axial shrinkage of neighbouring fibres. If the shrinkage of the network is restrained, the shrinkage of bonded areas causes the free fibre segment to dry under stress and the slackness of the fibre segments is removed. When fibre network dried under restrain are strained, more segments are in readiness to carry load. The main cause for activation, the shrinkage stress, is significantly increased when fines are added [66, 158].

Adding kraft fines has a higher effect on the tensile strength of dry paper than adding TMP fines to long fibres of both pulp types. According to Retulainen et al. [98], this is mainly due to the higher surface area and the hydrophilicity of kraft fines, which lead to a higher bond strength and bonded area. Kraft fines are also known to increase drying stress more than TMP fibres, which increases the activation of the fibre network during drying [66].

8.3 Mechanical properties of wet web

Adding kraft fines to TMP long fibres increases the wet web tensile strength more than adding TMP fines at a given dryness (Figure 54). This result is in line with the findings of Luukko [95], who stated that the explanation for this is that kraft fines are more fibrillar (and thus they have higher surface area) and hydrophilic than TMP fines which improves their bonding ability and is believed to increase the surface tension forces due to the higher volume of bound water at constant dryness [122].

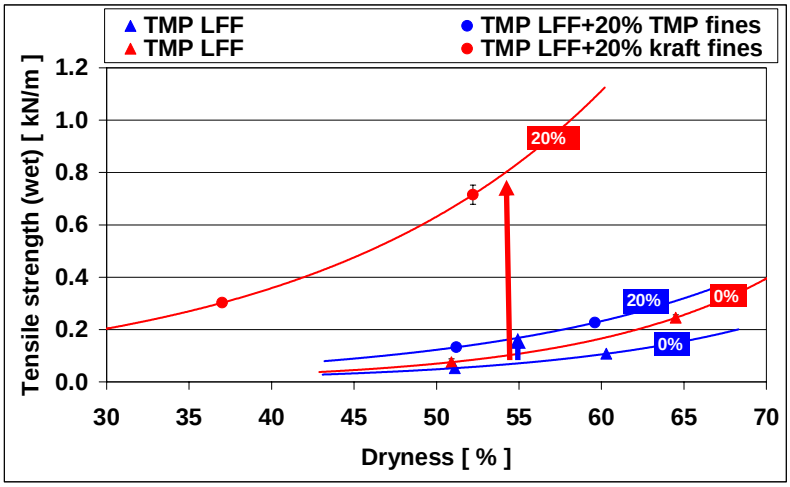

Figure 54. *The effect of adding kraft and TMP fines to TMP long fibres on tensile strength of wet handsheets as a function of dryness (exponential fit is used to describe the effect of dryness) measured by the Impact test rig at strain rate 1 m/s. Error bars show a 95% confidence interval of the mean of the measurement. The percentages given in the figure describe the amount of fines in the handsheets (LFF=long fibre fraction).*

Fibrillar fines and the fibrils of fibres are believed to cause interlocking between fibres which improves wet web strength [124]. The addition of TMP fines have only a minor effect on dryness after wet pressing, while the addition of kraft fines decreases dryness considerably. There is a minor difference in the wet web strength curves for the two TMP long fibre fractions. This is because fractionations of TMP pulps and the preparation of the handsheets were carried out at two different stages. This shows that when fractionation is involved, perfect repeatability of the test procedure cannot be ensured.

Wet handsheets made from kraft long fibres give significantly higher wet web tensile strength than the ones made from TMP long fibres as shown in Figure 55. Due to lower coarseness there are more (approximately 1.5-time more) fibres and thus higher surface area of fibrous material in sheets made from kraft long fibres compared to TMP. Increased surface area has been reported to lead to higher surface tension forces in the wet web (at least at dryness below 30%). More flexible kraft fibres gives better response to Campbell's forces [157], which is believed to improve formation of fibre-fibre contacts [65]. Adding kraft fines increases wet web tensile strength for both TMP and kraft long fibres at a given dryness, but at the same time dryness after wet pressing decreases. However, even when comparing the results after constant wet pressing the increase in wet web strength is significant. Adding 20% kraft fines to kraft long fibres give higher wet web tensile strength than adding to TMP long fibres at a given dryness, but the relative difference reduces significantly compared to handsheets made from pure long fibre fractions.

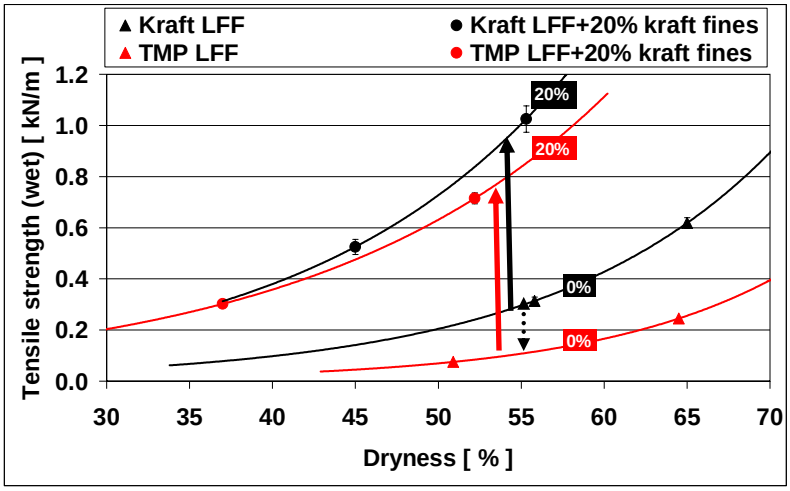

Figure 55. *The effect of adding kraft fines to TMP and kraft long fibres on tensile strength of wet handsheets as a function of dryness (exponential fit is used to describe the effect of dryness) measured by the Impact test rig at strain rate 1 m/s. Error bars show a 95% confidence interval of the mean of the measurement. The percentages given in the figure describe the amount of fines in the handsheets (LFF=long fibre fraction).*

Adding both, kraft and TMP fines to TMP long fibres increases the residual tension of wet handsheets at a given dryness as shown in Figure 56. Adding 20% TMP fines to TMP long fibres increases the residual tension by 150%, while the increase with same amount of kraft fines is 570% at a given dryness of 55%. Adding 20% TMP fines to the TMP long fibre fraction has a relatively greater effect on residual tension than on wet web tensile strength at a given dryness level, since the increase of tensile strength at a given dryness level of 55% is approximately 100% as presented earlier in Figure 54.

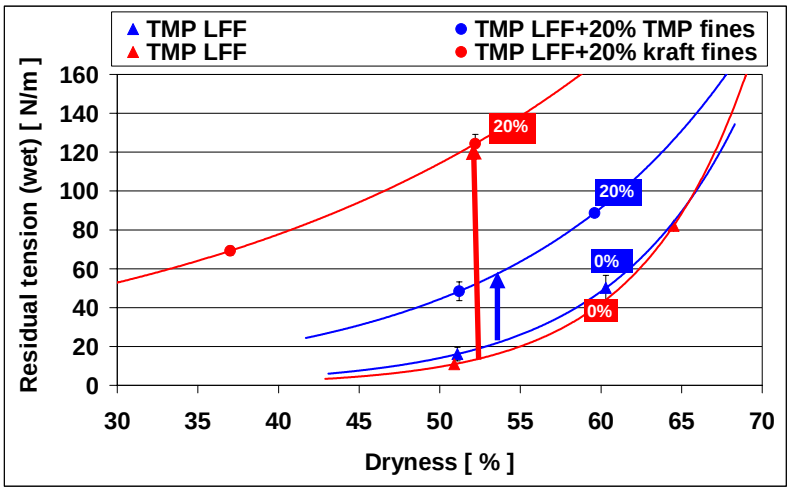

Figure 56. *The effect of adding TMP and kraft fines to TMP long fibres on wet web residual tension at 1% strain as a function of dryness (exponential fit is used to describe the effect of dryness) measured by the Impact test rig at strain rate 1 m/s. Error bars show a 95% confidence interval of the mean of the measurement. The percentages given in the figure describe the amount of fines in the handsheets (LFF=long fibre fraction).*

Figure 57 shows that the residual tension of wet handsheets is dependent on the amount and quality of fines. At a given dryness of 55%, adding 20% kraft fines to TMP long fibres yields a residual tension 80% higher than when 20% kraft fines are added to kraft long fibres. This result differs from wet web tensile strength, where the combination of kraft long fibres and 20% of kraft fines yielded the highest values. This result is surprising because TMP pulp has higher coarseness and therefore contains a significantly lower number of load bearing fibres per mass unit than kraft pulp. This result shows that with increasing interactions, the properties of fibres become more important. In case of residual tension, when interactions between fibres are high (due to high amount of kraft fines), TMP fibres seem to be beneficial. Based on this finding, a combination of stiff fibres and highly fibrillar fines are expected to give high residual tension values. It can be speculated that the addition of heavily refined kraft pulp (with a high amount of fines) to wood containing paper grades may significantly increase the residual tension of wet web, while the addition of less refined kraft pulp would lead to a reduction of the residual tension. This result is interesting, since kraft pulps used in paper grades containing mechanical pulps are often refined quite gently to give dry paper high tear energy.

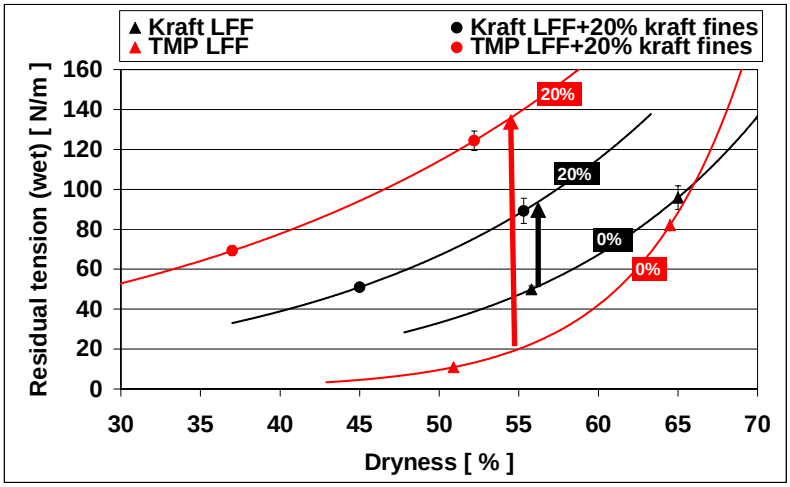

Figure 57. *The effect of adding of kraft fines to long TMP and kraft long fibres on residual tension of wet handsheets at 1% strain as a function of dryness (exponential fit is used to describe the effect of dryness) measured by the Impact test rig at strain rate 1 m/s. Error bars show a 95% confidence interval of the mean of the measurement. The percentages given in the figure describe the amount of fines in the sheets (LFF=long fibre fraction).*

Figure 58 shows that in 0.475 s, samples made from TMP and kraft long fibres lose approximately 80% and 60% (respectively) of the tension created by straining (at a given dryness of 55%). The relaxation percentage of the network made from kraft long fibres is not as strongly dryness- or fines-dependent as a network made from TMP long fibres (increased dryness decreases the relaxation percentage for all samples). The relaxation percentage is similar when 20% of kraft fines are added regardless of the long fibre fraction.

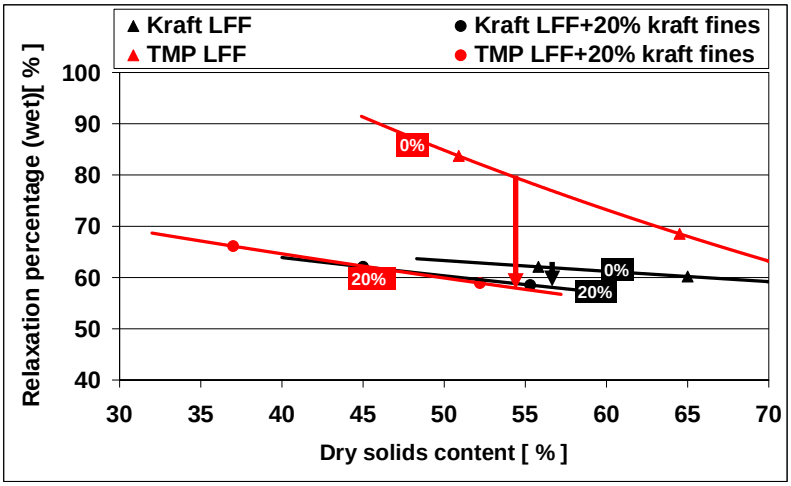

Figure 58. The effect of adding kraft fines to kraft and TMP long fibres on relaxation percentage of wet handsheets at 1% strain as a function of dryness (polynomial fit is used to describe the effect of dryness) measured by the Impact test rig at strain rate 1 m/s. The percentages given in the figure describe the amount of fines in the sheets (LFF=long fibre fraction).

The results presented here show that the properties of both fines and fibres play an essential role in wet and dry web mechanical properties. When 20% of fines are added, the quality of fines seems to be more important than the fibre properties for wet web tensile strength, while for residual tension, fibre properties are also essential. In the next chapter, the effects of fibre orientation and filler content on dry and wet paper tensile and relaxation characteristics are examined.

9. FIBRE ORIENTATION, FILLER CONTENT AND MECHANICAL PROPERTIES OF DRY AND WET WEB

In this chapter, the effects of fibre orientation and filler content on the mechanical properties of wet and dry paper produced with a pilot paper machine are examined. The main findings of this study are presented in this chapter. All the results are found in Appendix II.

9.1 Fibre orientation

The MD/CD ratio of tensile strength is similar for dry and wet samples as a function of the jet/wire ratio as shown in Figure 59. At all jet/wire ratios, the residual tension of wet paper yields a higher MD/CD ratio than the tensile strength of dry and wet paper. The minimum values of mechanical properties are not reached at jet/wire ratio 1, because the jet hits the wire at an angle of approximately 5^{o} (unfortunately, the exact value was not recorded). In addition, it should be noted that the minimum MD/CD ratio is about 1.5 instead of 1. This means that orientation of fibres occurs at all jet/wire ratios because flows inside the head box serve to orient the fibres [108].

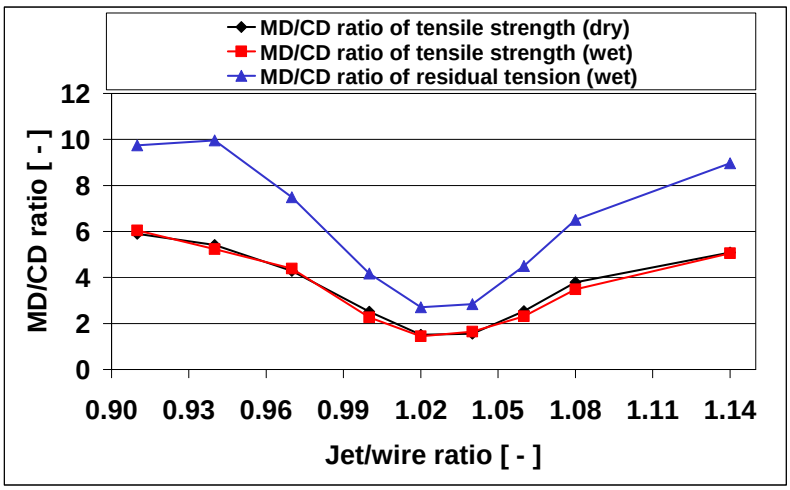

Figure 59. The MD/CD ratio of tensile strength and residual tension at 1% strain (all measured by the Impact test rig at a strain rate of 1 m/s) of wet (and dry for tensile strength) fine paper produced by a pilot paper machine with a production speed of 900 m/min (grammage 70 g/m^2, hardwood 70% and softwood 30%, filler content 10%) as a function of the jet/wire ratio. Error bars show a 95% confidence interval of the mean of the measurement.

Figure 60 shows the effects of the jet/wire ratio on the tensile strength and tension of wet web in the press-to-dryer transfer. At an MD/CD ratio of 2.5 (or at a jet/wire ratio of 1.06), which is typical for fine paper grades [109], the tension in the open draw is 120 N/m and the tensile strength of wet paper is 380 N/m. This means that the tension in the press-to-dryer transfer is only 30% of the tensile strength of the wet paper. On the other hand, the production speed of the pilot paper machine was only 900 m/min, while the fastest fine paper machines have an average production speed of about 1400 m/min [26] (see Chapter 3.2, Figure 2). Pakarinen and Kurki [39] predicted that the increase of production speed from 900 m/min to 1400 m/min would increase the tension required in the open draw by approximately 100% (see Chapter 3.4, Figure 8). This means that at a production speed of 1400 m/min, the tension of the web in the open draw would be 240 N/m, i.e., 60% of the tensile strength of the wet web. This finding shows that with the very fastest fine paper machines, the strength of the wet paper may also become a critical factor. However, with slow or average speed fine paper machines (in the case of machine with a stable release from centre roll), wet web strength may not be such a critical factor affecting wet web runnability at the press-to-dryer transfer. The critical factor would then be the stability of the web, which is affected by the paper's ability to maintain tension after straining.

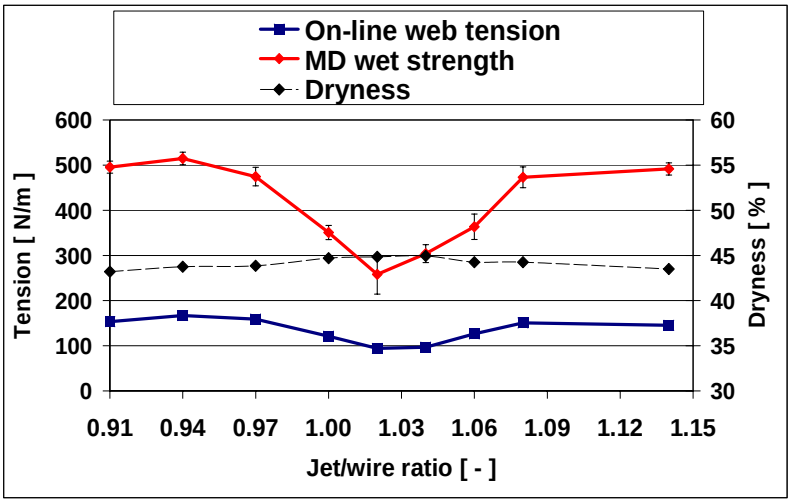

Figure 60. The effect of jet/wire ratio on dryness, MD tensile strength and on-line tension of the wet web in press-to-dryer transfer (tensile strength measured by an Impact test rig at a strain rate of 1 m/s) for fine paper samples produced by a pilot paper machine with a production speed of 900 m/min (grammage 70 g/m^2, hardwood 70% and softwood 30%, filler content 10%). Error bars show a 95% confidence interval of the mean of the measurement.

Figure 60 also shows that the dryness of samples increases slightly close to the unity point. This may have minor effect on the wet paper results. However, the difference in the dryness of the samples close to the unity point is below 1%-unit, which is quite similar to the accuracy of dryness measurements used in this study. For this reason, the effect of fibre orientation on wet web mechanical properties is presented and discussed here without adjusting the results to a certain dryness level.

Higher fibre orientation obtained by moving the jet/wire ratio from the unity point increases residual tension of wet samples as shown in Figure 61. The change in the residual tension is highest close to the unity point (jet/wire ratio=1) and the effect of the jet/wire ratio on the residual tension is higher on the drag side than on the rush side. An increase of residual tension saturates or even starts to reduce (especially on the drag side) when the jet/wire ratio is high. An increase in the speed difference leads to higher shear forces between the suspension and the wire. The reduction in residual tension occurs probably because a high shear rate ruptures the already settled mat. In paper formation studies, a similar effect has been reported [108].

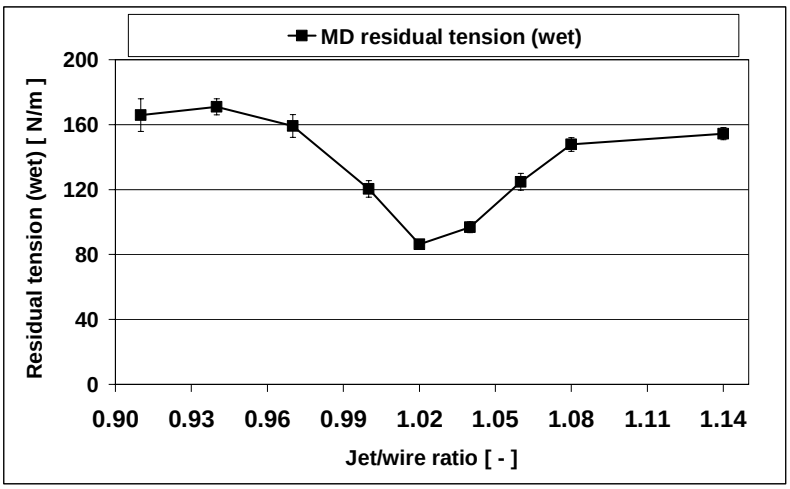

Figure 61. The effect of jet/wire ratio on MD residual tension (measured by the Impact test rig at a strain rate of 1 m/s) for wet fine paper samples produced by a pilot paper machine with a production speed of 900 m/min (grammage 70 g/m^2, hardwood 70% and softwood 30%, filler content 10%) at 1% strain. Error bars show a 95% confidence interval of the mean of the measurement.

An increase in the fibre orientation leads to a reduction in the relaxation percentage in the machine direction and to an increase in the cross direction, as shown in Figure 62. Increased orientation augments the number of fibres parallel to the load, which means that at a given strain level, the amount of tension exerted on a single fibre does not necessarily change significantly despite a high increase in tension.

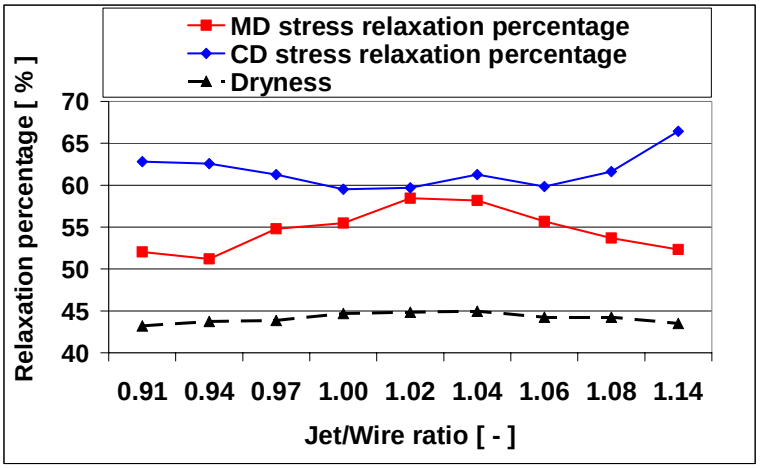

Figure 62. The effect of jet/wire ratio on relaxation percentage at 1% strain of wet fine paper samples produced by a pilot paper machine with a production speed of 900 m/min (grammage 70 g/m^2, hardwood 70% softwood 30%, filler content 10%) measured by an Impact test rig at a strain rate of 1 m/s.

Increased fibre orientation results in increased MD tensile stiffness, tensile strength and reduces the relaxation percentage of wet paper. Higher fibre orientation facilitates a higher tension in the press-to-dryer transfer and less tension relaxation at the beginning of the dryer section.

However, the target fibre orientation level for each paper grade and for each paper machine is determined by the requirements of the final product and the demands of the process. In practise, the operating window on a specific paper machine is quite narrow and thus the possibility to increase wet web strength or residual tension by changing the jet/wire ratio is limited [109]. Because of this, in order to improve wet web runnability on a specific paper machine, optimising pulps in terms of the wet web mechanical properties is often required.

9.2 Filler content

The tensile strength of dry paper decreases significantly with increasing filler content (increasing filler content from 10% to 25% reduced tensile strength by 40%) as seen in Figure 63. The decrease in tensile strength cannot only be explained by the replacement of fibrous material by fillers, since it is strongly reduced even when indexed strength values correspond to the amount of fibrous material. This result agrees with the earlier findings that filler particles reduce bonding of fibrous material (see for example [106]).

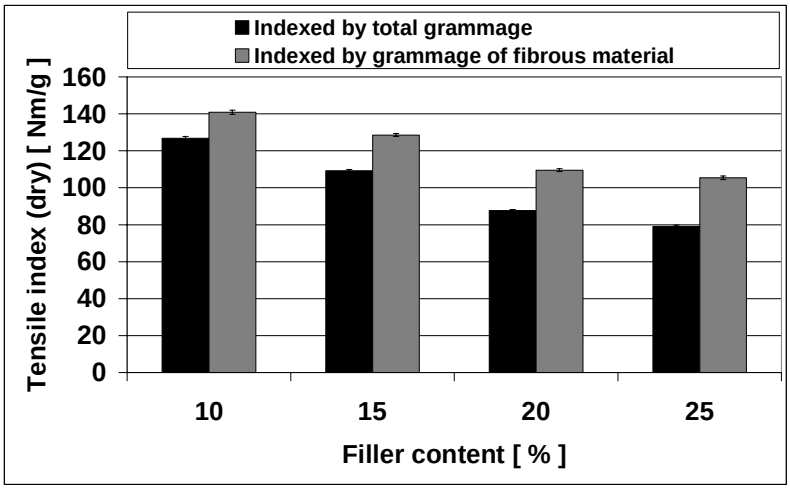

Figure 63. The effect of filler ($CaCO_3$) content on the tensile index (measured by the Impact test rig at a strain rate of 1 m/s and indexed with estimated grammage of 70 g/m^2) of dry fine paper samples produced by a pilot paper machine with a production speed of 900 m/min (hardwood 70% and softwood 30%).

In contrary to dry samples, tensile index (Figure 64) and residual tension (Figure 65) of wet web are not considerably reduced when filler content is increased from 10% to 25%. When results are indexed by the grammage of fibrous material, tensile strength is at similar level and residual tension increases when filler content is increased from 10% to 25%. Increased filler content increases the dryness of the web but reduces the amount of fibrous material. Increase in dryness of paper when filler content increases might partly explain why the mechanical properties of wet web do not reduce. On the other hand, fillers as minerals and fibrous material bind different amounts of water to their structure at wet state and therefore, the increase in dryness caused by higher filler content does not necessary result in higher fibre/water ratio (i.e. less free water between the fibres).

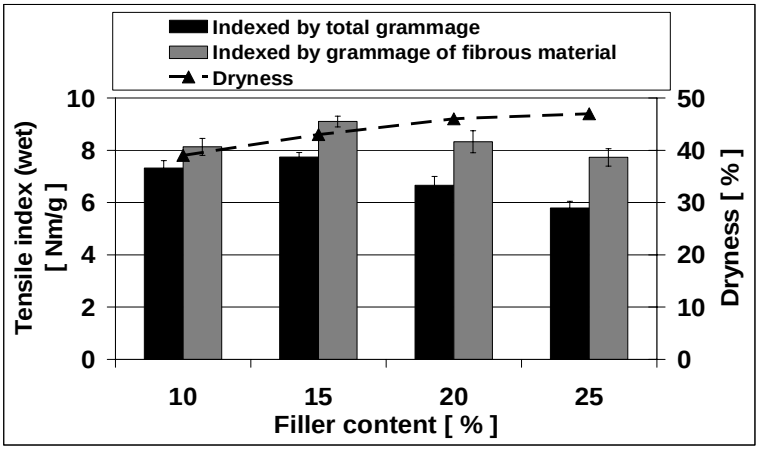

Figure 64. The effect of filler ($CaCO_3$) content on the tensile index (measured by the Impact test rig at a strain rate of 1 m/s and indexed with estimated grammage of 70 g/m^2) of wet fine paper samples produced by a pilot paper machine with a production speed of 900 m/min (hardwood 70% and softwood 30%).

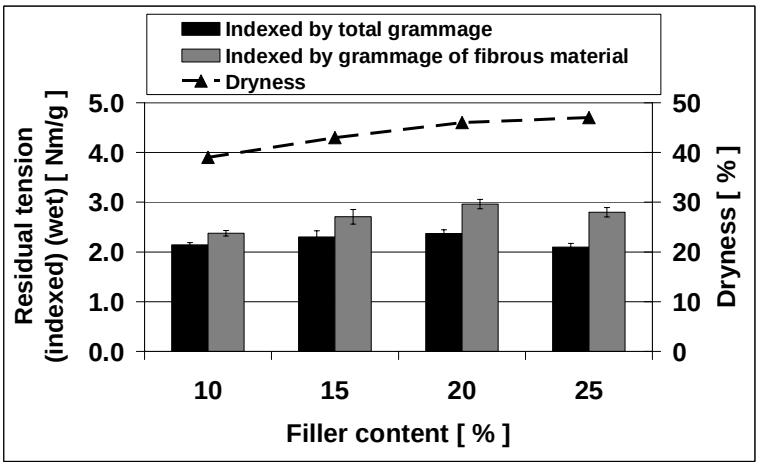

Figure 65. The effect of filler ($CaCO_3$) content on the residual tension at 1% strain (measured by the Impact test rig at a strain rate of 1 m/s and indexed with estimated grammage of 70 g/m^2) of wet fine paper samples produced by a pilot paper machine with a production speed of 900 m/min (hardwood 70% and softwood 30%).

These results partly agree with the findings of de Oliveira et al. [159, 160], who showed that increase of fillers can improve wet web strength at a given dryness if filler agglomerates have an optimal size and size distribution (the size of filler agglomerated were not determined in this study). They showed that relatively small filler agglomerates can increase fibre entanglement friction and thus lead to higher wet web strength.

10. FIBRE DEFORMATIONS AND MECHANICAL PROPERTIES OF DRY AND WET WEB

In this chapter, the effect of mechanical treatment of softwood chemical pulp on fibre deformation is examined. Fibre deformations generated by mixing pulp at a high consistency is estimated based on changes in the fibre shape factor. Further, the connection between fibre shape and mechanical properties of wet and dry paper are studied. The main findings are presented in this chapter. All the results are found in Appendix III.

10.1 Water removal and shrinkage

As shown in Table II, mechanical treatment of pulp at high consistency (25%) reduces the shape factor of fibres but causes no significant changes in fibre length, fines content or in the amount of kinks. Freeness increases and drainage time during sheet forming decreases as the duration of the mechanical treatment of the fibres increases. The difference in freeness values between hot disintegrated pulp and pulp mechanically treated for 45 minutes is 185 ml. When water is filtered through a forming fibre mat, curlier fibres may form a more porous mat that accelerates water removal [83]. The increase of fibre network porosity with increased fibre curliness can partly explain the increase of dryness after constant wet pressing (50 kPa) and the reduced density of dry handsheets. Table II also shows that WRV decreases slightly with increasing duration of the mechanical treatment. It is likely that mechanical treatment at relatively high dryness dried the surface of fibres, leading to mild hornification and thus reduction in WRV.

Table II. Properties of the pulps used in this study.

Sample description	CSF, ml	Aver. fibre length, mm	Fines content, %	Kinks, 1/mm	WRV, -	Light scatter. coeff. m^2/kg	Drainage time, s	Dryness after 50 kPa wet press, %	Dryness after 350 kPa wet press, %	Shape factor, %	Density of dry paper, kg/m^3
Hot disintegrated	460	2.3	6.6	0.59	1.87	19.5	4.9	40	55	84.0	703
Thickened pulp	513	2.3	7.4	0.57	1.97	19.2	4.8	41	55	83.7	689
15 min mechanically treated	642	2.3	7.0	0.59	1.73	20.2	4.3	43	54	80.4	684
45 min mechanically treated	645	2.3	7.0	0.59	1.69	20.4	4.3	46	55	78.5	662

Figure 66 shows scanned images from layer-stripped handsheets made from the hot disintegrated pulp (Figure 66A) and the pulp mixed for 45 minutes (Figure 66B). These figures present fibres on the handsheet surface. The handsheets made from the pulp mixed for 45 minutes has fibres clearly curlier than handsheets made from hot disintegrated pulp. This shows that the difference between the shape of fibres also remains in the dry handsheets.

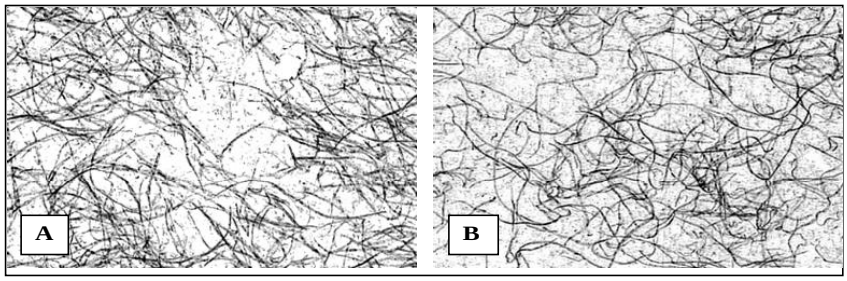

Figure 66. A scanned image of a layer stripped from the handsheets (made from bleached softwood kraft pulp) of hot disintegrated pulp (Figure A) and pulp mixed for 45 minutes (Figure B).

The shrinkage potential of wet pressed handsheets decreases as the shape factor of fibres increases (Figure 67). This is probably because mechanical treatment reduces the stiffness of fibres [78], which could be expected to reduce the fibres' capacity to resist shrinkage forces [124]. According to Pulkkinen et al. [161], a higher variation in fibre shrinkage leads to greater shrinkage of sheets during drying. It is possible that mechanical treatment increases the distribution in the shrinkage of fibres, however this was not studied in this thesis.

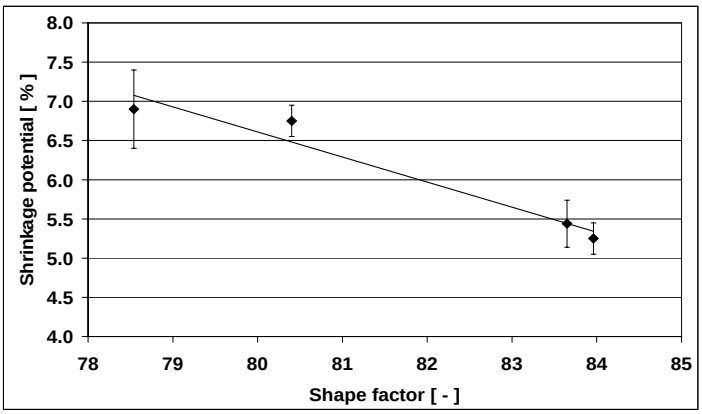

Figure 67. The relation between shape factor and shrinkage potential of handsheets made from softwood kraft pulp. Error bars show a 95% confidence interval of the mean of the measurement.

10.2 Mechanical properties of dry paper

The tensile index and elastic modulus of dry samples increase linearly as the shape factor increases with all used drying strategies (Figure 68), a finding which concurs with previous studies [79-82]. Increased curliness of fibres in the network leads to more uneven activation of the network, which means that fewer segments participate in load shearing simultaneously (at the early stage of straining), which can be seen as a lowered elastic modulus. As straining is increased, the slack segments also start to carry load, but at that point some of the fibre-fibre bonds start to break and therefore the maximum load that paper can tolerate without breaking e.g. the tensile strength of paper is reduced [79-82]. The drop in density and the minor increase in the light scattering coefficient (see Table II) indicate a reduction in the overall bonded area in the handsheet, which could also reduce tensile strength (reduced bonded area may be partly explained by the minor hornification of fibres during mixing). The tensile strength of samples dried under restrain is 20-30% higher and the elastic modulus values are 200-300% higher than for freely dried samples.

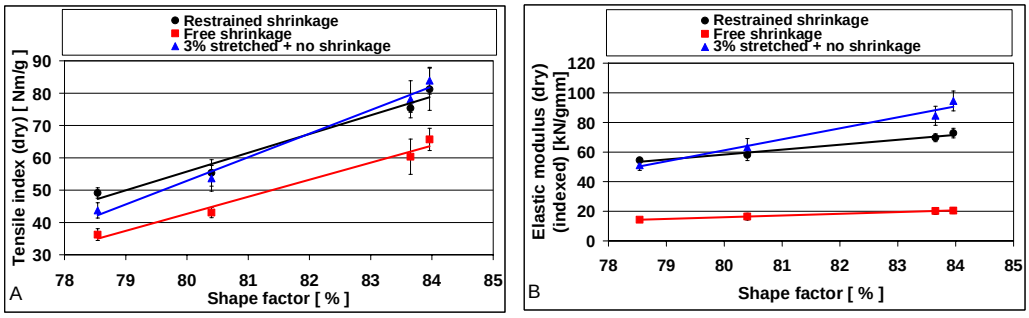

Figure 68. The effect of the shape factor of fibres on the tensile index (Figure A) and elastic modulus (Figure B) (measured by the Lloyd tensile test rig at a strain rate 22 mm/min) of handsheets made from bleached softwood kraft pulp, which were dried with different strategies (linear fit). Error bars show a 95% confidence interval of the mean of the measurement.

Wahlström [45] has reported of similar findings. He also noticed that the shrinkage or straining during drying has a greater effect on the elastic modulus than on the strength of dry paper. Restrained drying causes activation (straightening of fibre segments) of the fibre network during drying which explains the increase of the tensile strength and tensile stiffness compared to freely dried samples. In this case, however, 3% of straining during drying shows no effect on tensile strength and only a minor effect on the elastic modulus compared to restrained shrinkage of the fibre network.

Strain at break of fibre network increases when curliness of fibres increases (see Figure 69). This is because of the slack fibre segments which have to be straightened before they are able to carry load. The difference between strain at break values of freely dried and restraint shrinkage samples is 5-7%-units. The difference is similar to the amount of shrinkage of freely dried samples (compare to shrinkage potential values in Figure 67). Similar results have been earlier reported by Wahlström [45].

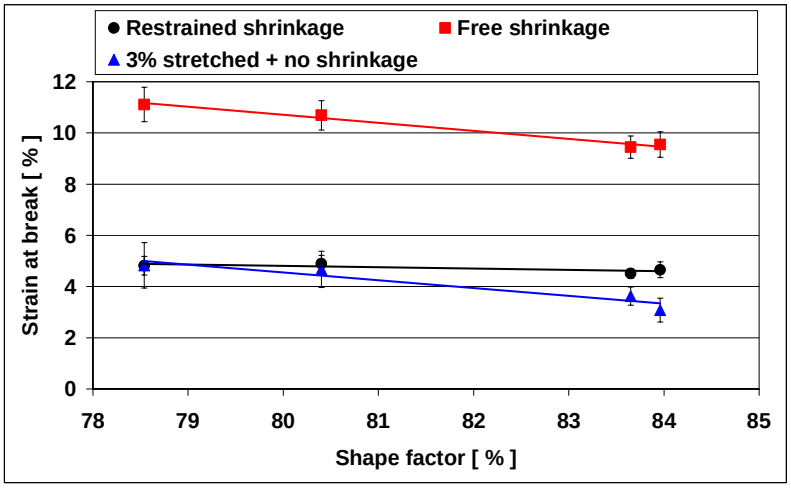

Figure 69. *The relation between the shape factor of fibres and strain at break (measured by Lloyd tensile test rig at a strain rate 22 mm/min) of dry handsheets (linear fit). Error bars show a 95% confidence interval of the mean of the measurement.*

A 5%-unit increase in the shape factor of fibres reduces z-directional delamination energy by approximately 20%, with both restrained drying samples and samples that were strained 3% during drying as shown in Figure 70. Since samples having higher shape factor have higher density and lower light scattering values (which indicates that the bonded area of samples with higher shape factor is higher), it is likely that the reduction of z-directional delamination energy with increasing shape factor is related to the way in which fibres are entangled with each other in the z-direction with different trial points.

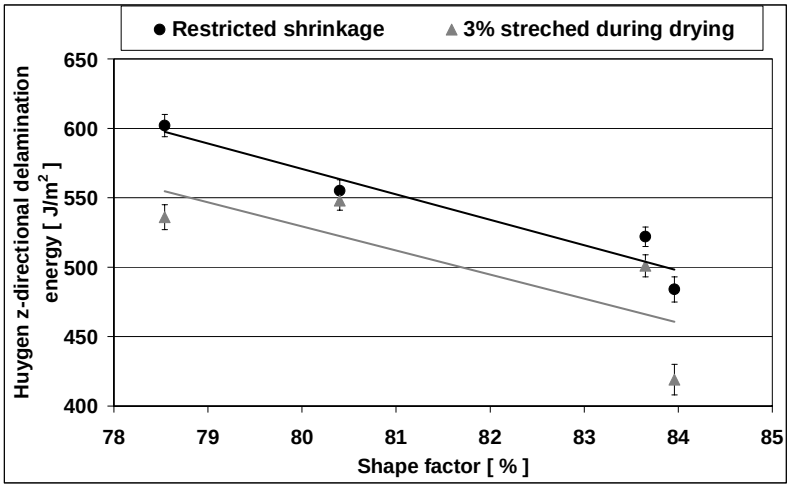

Figure 70. The correlation between the shape factor of fibres and z-directional delamination energy (measured by Hyugen device) of dry handsheets. Error bars show a 95% confidence interval of the mean of the measurement

Straining (3%) of the web during drying seems to reduce the z-directional delamination energy at a given shape factor compared to restrained drying samples (8% on average), even though the difference is not so clear between all trial points. Undulating fibres in the network that undergo wet straining tend to straighten, which causes the fibres to be pushed apart in the z-direction. This breaks the existing fibre-fibre bonds and reduces the bonded area in the sheet, which explains the reduction of the z-directional delamination energy [162].

10.3 Wet web properties

Reduced shape factor of fibres increases dryness of wet webs after similar wet pressing of 50 kPa, but has no effect at 350 kPa wet pressing level (Figures 71A and 72A). Increase in shape factor of fibres increases tensile strength and residual tension of all samples weather they are compared at a given dryness or at constant wet pressing conditions. At a given dryness, both tensile strength and residual tension increases almost linearly when the shape factor of fibres increases (Figures 71B and 72B). The reason for wet paper tensile strength loss with increased curliness of fibres has been reported to be similar to dry paper i.e. increased curliness leads to lowered amount of fibre segments carrying load during straining [10,15].

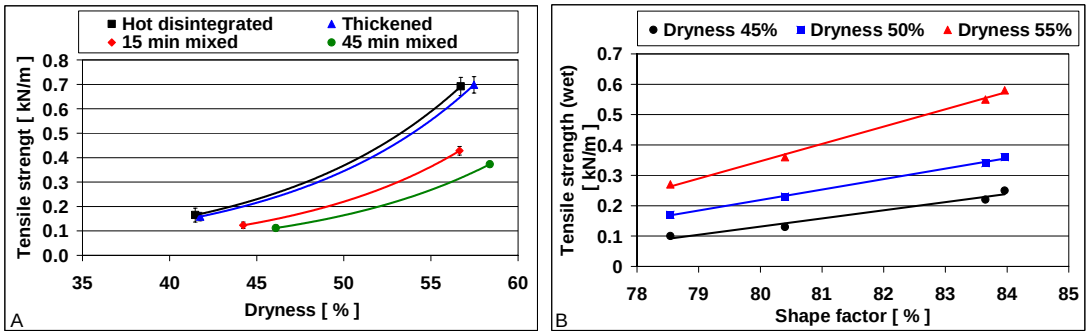

Figure 71. Tensile strength (measured by Lloyd tensile test rig at a strain rate 22 mm/min) of wet handsheet (Figure A) as a function of dryness (an exponential fit is used to describe the effect of dryness) and at a given dryness (Figure B) as a function of shape factor (linear fit). Error bars show a 95% confidence interval of the mean of the measurement.

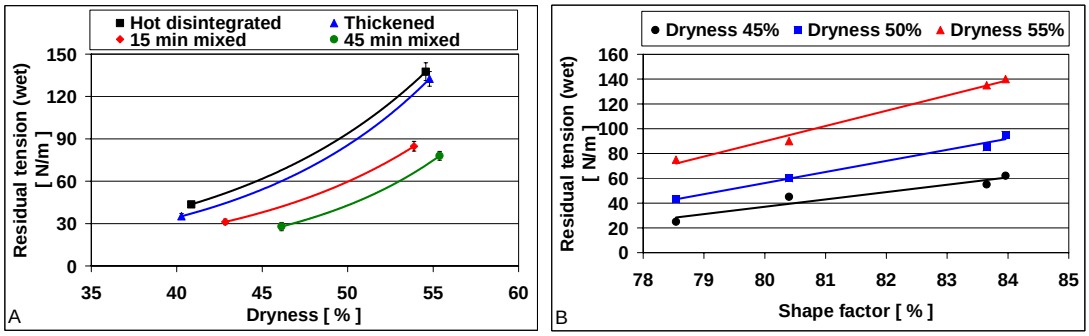

Figure 72. Residual tension (measured by the Impact test rig at a strain rate 1 m/s) of wet handsheet (Figure A) as a function of dryness (an exponential fit is used to describe the effect of dryness) and at a given dryness (Figure B) as a function of shape factor (linear fit). Error bars show a 95% confidence interval of the mean of the measurement.

Figure 73 shows that a 5%-unit increase in the shape factor of fibres results in approximately a 120% rise in the wet web tensile strength and in the residual tension (at a given dryness of 50%), while the dry paper tensile index increases by only 70%. The reason for this could be that the fibre segments are longer and the fibre segment length distribution is wider for wet paper than for dry paper due to the fact that wet paper has fewer bonds (more uneven distribution in the length and slackness of the fibre segments). In addition, dying the network under stress (restraint drying) reduces the slackness of the fibre segments (activation of the fibre network increases) [91].

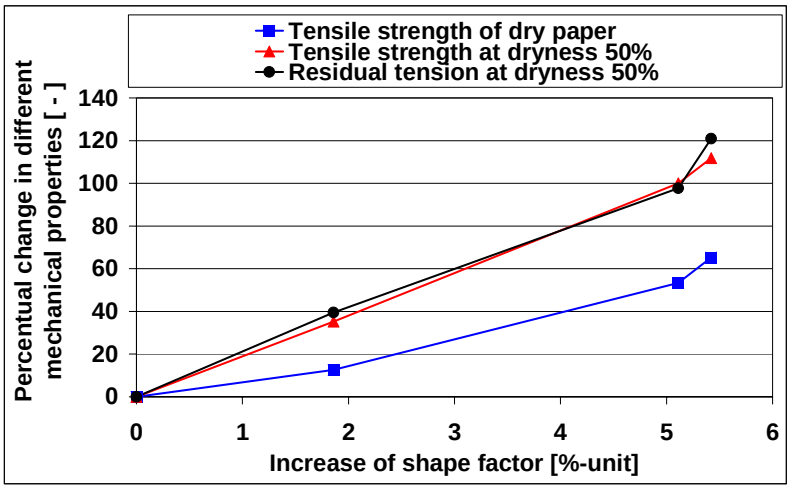

Figure 73. Percentual change of dry and wet (dryness 50%) web tensile strength and wet (dryness 50%) web residual tension as a function of change in fibre shape factor.

This result (Figure 73) indicates that increased fibre curliness may be significantly more detrimental for wet web runnability than one could predict based on the reduction of dry paper tensile strength. Perez and Kallmes [82] stated that most papers reach only about 60% of their strength potential (of dry paper) because they have curled fibres. Based on the findings made in this thesis the strength potential of wet webs gained with curly fibres may be even lower. In order to improve paper strength, Seth [81] suggested that paper mills could consider straightening fibres before supplying them to paper makers. He indicated that straightening would be easier to never-dried fibres, but execution of this would require new equipments.

11. WHITE WATER COMPOSITION AND MECHANICAL PROPERTIES OF DRY AND WET WEB

This chapter examines the effects of several typical chemical substances used in papermaking on the surface tension of white water and mechanical properties of dry and wet paper. The main findings of this study are presented in this chapter. All the results are found in Appendix IV.

11.1 Surface tension, drainage and dryness

The surface tension of deionised water in this study was originally 72 mN/m. Mixing the water with chemical pulp during handsheet making reduces the surface tension to 54 mN/m (surface tension of the white water). The reduction is due to the substances which dissolve from the pulp [117-119]. Mixing of TMP filtrate (obtained after peroxide bleaching), non-ionic surfactant or oleic acid to white water further lowers the surface tension by 10 units or more (Table III).

The drainage time of the handsheets varies between 4.5-6.7 s. The drainage is slowest when a TMP filtrate is used, due to some of the solid material present in the filtrate. The presence of some solid material in the TMP filtrate is also observed as an increased light scattering coefficient. In addition, there is no significant correlation between the drainage time and the surface tension of white water. This result contradicts the findings of a study done by Isaksson [163], who showed that as a result of the reduction of the surface tension through the addition of a non-ionic surfactant to pulp suspension, the dewatering time with a DDÅA (modified DDA) device is considerably lowered. However, it should be noted that Isaksson used only one type of chemical, while in this study several different chemicals were used. In addition, a study by Touchette and Jennes [164] showed that the addition of anionic and non-ionic surfactants to pulp suspension reduces CSF. Based on these studies, drainage appears to be more dependent on the chemical added than on the surface tension of white water. Table III presents the surface tension of white water, the dryness and density of wet and dry handsheets, the drainage time during sheet formation, the shrinkage potential of wet pressed handsheets, the pH of white water and the light scattering coefficient of handsheets.

Table III. Added chemicals, surface tension of white water, dryness and density of wet and dry handsheets, drainage time during sheet forming, pH of white water, shrinkage potential of wet pressed handsheets and light scattering coefficient of dry handsheets.

Trial point	Added chemical [ppm]	Surface tension [mN/m]	Dryness [%]			Density [kg/m^3]			Drainage time [s]	pH [-]	Shrinkage potential [%]	Light scatt. coefficient [m^2/kg]
			50 kPa	350 kPa	Dry	50 kPa	350 kPa	Dry				
Deionized water	-	54	48.4	61.7	92.5	382	501	632	4.5	6.9	3.1	26.0
TMP filtrate	-	44	52.6	62.5	92.6	379	492	596	6.7	7.2	3.0	33.3
Surfactant	100	42	57.8	65	92.5	412	553	613	5.1	6.7	3.0	25.2
Oleic acid	100	41	52.8	63	91.1	384	482	622	5.0	6.5	3.1	25.8
Defoamer	100	49	48.7	60.6	91.1	374	512	631	4.5	6.8	3.4	26.0

Figure 74 shows the correlation between surface tension and average dryness (50 kPa and 350 kPa samples) of wet pressed handsheets. Samples with the lowest surface tension values also have the highest average dryness after wet pressing. However, the correlation between the average dryness of wet pressed sheets and surface tension is relatively poor (R^2=0.61). In order to have a statistically significant correlation with five trial points, the R^2 value should be higher than 0.77 [165]. This indicates that changes in dryness cannot be explained by lowered surface tension alone. This observation supports the findings made by Norman and Eravuo [121], who claimed that the type of used chemical affects the relation between lowered surface tension and a change in dryness after wet pressing.

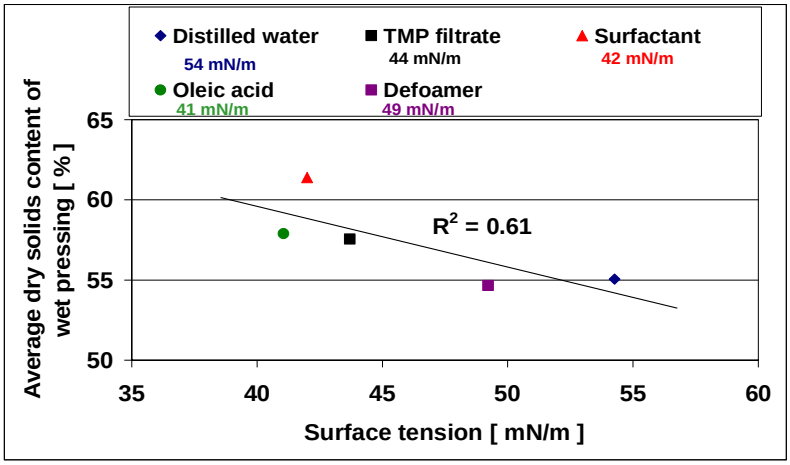

Figure 74. The correlation between surface tension of white water and the average dry solids content (average of 50 kPa and 350 kPa wet pressed samples) of wet pressed handsheets (linear fit).

Different contaminants are known to affect the hydrophilicity/hydrophobicity of fibre surfaces in different ways [117]. This might explain for example why the presence of surfactant gives higher dryness after constant wet pressing than oleic acid, even though they have very similar surface tension levels. It should be noted that TMP filtrate also increased dryness after wet pressing (compared to the reference point) despite the presence of fine solid material. Wearing et al. [118] reported of similar findings (with 50 kPa and 1000 kPa wet pressing pressure levels) when forming sheets using white water from two TMP mills.

The average dryness values of wet pressed handsheets vary significantly in presence of different chemicals in the white water. Based on laboratory scale wet pressing, it is impossible to predict how high the effect of lowered surface tension would be on dryness after the press section on paper machine. From an energy perspective, the result is still interesting, since a 1%-unit increase in dryness after the press section changes the moisture ratio of paper by approximately 4%, which has a significant effect on the energy consumption in the dryer section.

11.2 Mechanical properties of dry paper

The tensile strength of dry paper is highest for samples made with deionised water as shown in Figure 75A. When handsheets are formed with white water containing filtrate from the TMP mill or with white water containing non-ionic surfactant, the tensile strength decreases by 12% and 17%, respectively, compared to handsheets made from deionised water. In principle, surfactants lower the surface tension and are thus are expected to reduce the surface tension forces (Campbell's forces [157], which draw surfaces together as paper is dried) between fibres. However, it has been suggested that the addition of surfactants interferes with the inter-fibre bonding by blocking the bond sites, which could also explain the reduction in dry paper tensile strength (see for example [166-168]). The latter mechanism gets support from the fact that cationic surfactants are known to be more harmful to strength of dry paper than anionic or non-ionic surfactants, which have less tendency to adsorb onto anionic cellulose fibres [166].

When handsheets are formed with white water containing filtrate from TMP mill, the reduction of dry paper tensile strength is in line with several earlier studies [101, 166, 168]. This reduction is believed to be related on the presence of extractives, which inhibit the bonding ability of fibrous material (the amount and quality of extractives in the TMP filtrate are listed in Appendix IV). The addition of oleic acid to white water had a significant effect on the surface tension, but only a minor effect on the tensile index of dry paper. This result partly contradicts the findings of studies such as those by Tay [117], Wearing et al. [118] and Brandal and Lindheim [168] who found that the addition of oleic acid is very detrimental to dry paper strength. Tay [117] stated that the reason that an addition of oleic acid reduces dry paper tensile strength can be explained by their long straight hydrocarbon chain with polar group at the end, which makes them a good boundary lubricant, thus preventing bonding between fibres.

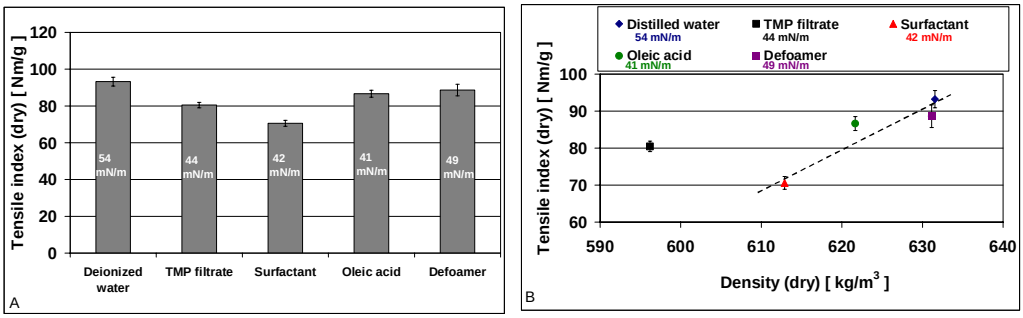

Figure 75. The tensile index (measured by an Impact test rig at a strain rate of 1 m/s) of dry handsheets as such (Figure A) and as a function of density of dry sheets made using white water that contained different chemicals. The surface tension values of white water are marked on the bars (Figure A) and on the legend (Figure B). Error bars show a 95% confidence interval of the mean of the measurement.

Figure 75B shows a connection between density and tensile index of dry paper (excluding when handsheets are formed with water from the TMP mill). This indicates that the reduction of dry paper tensile index (when adding different additives) is more related to the reduction of bonded area in the sheet than on the reduction of the strength of the inter-fibre bonds (since sheet density and bonded area in the sheet have been shown to have a clear connection (see for example [66])).

11.3 Mechanical properties of wet web

Figure 76A shows the effect of white water composition on the tensile strength of wet web. The addition of all substances (100 ppm) increase dryness and thus wet web strength after similar wet pressing of 50 kPa. At a given dryness level, the surfactant series has the lowest wet web tensile strength, while other trial points are at a similar level. This result indicates that tensile strength of wet web at a given dryness level (at least between dryness 45-65%) is not affected by the surface tension of white water. This finding is in line with the studies published by Lindqvist et al. [169], Wearing et al [118] and de Oliveira et al. [170]. Lindqvist et al. [169] added several levels of one non-ionic surfactant to reduce the surface tension of the white water used in sheet forming. In their study, the wet strength on a given dryness was unaffected when surfactant was added, until the addition level exceeded critical micelle concentration i.e. to the point where surfactants start to create micelles. After this point the wet strength paper at a given dryness level was significantly reduced. The results by Wearing et al. [118] also showed that forming sheets with white water obtained from a TMP mill (surface tension of the white water was 52 mN/m) has no or only minor effect on wet web strength at a given dryness level compared to handsheets made from deionised water.

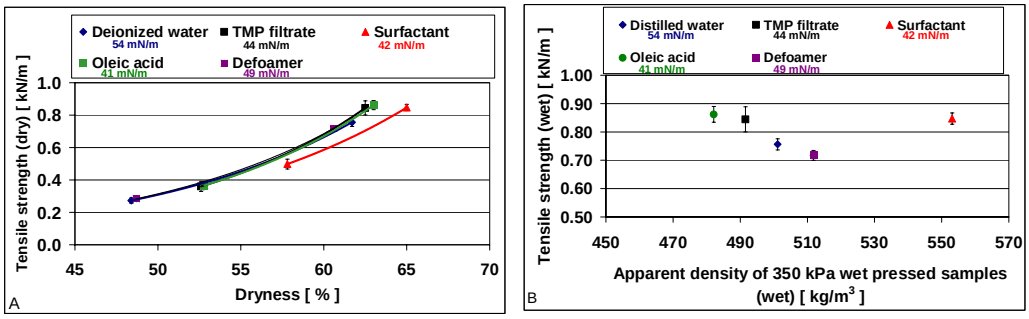

Figure 76. The tensile index (measured by an Impact test rig at a strain rate of 1 m/s) of wet hand sheets as such (Figure A) and as a function of apparent density of wet sheets made using white water that contained different chemicals. The surface tension values of white water are marked on the bars (Figure A) and on the legend (Figure B). Error bars show a 95% confidence interval of the mean of the measurement.

De Oliveira et al. [170] also noted that the addition of surfactants reduces wet web strength. In contrast to earlier studies [11, 12], the findings of these authors suggested that the reduction of wet web strength resulted by adding surfactants cannot be explained directly by lowered capillary forces when the dryness is higher than 30%. They concluded that the addition of surfactants (lowered surface tension) results in a situation in which fibres are further from one another at a dryness of 30% and thus entanglement friction is lower when the dryness increases. The findings of this study partly contradict this theory, since wet web strength is only reduced with addition of surfactants, despite reduced surface tension with all additives (compared to handsheets made from deionised water). However, the adsorption of surfactants to fibre surface is believed to smooth the fibre surface [171] and this could possibly reduce the friction between fibres.

In addition to reducing surface tension, different contaminants are known to affect the hydrophilicity/hydrophobicity of fibre surfaces [117], as mentioned earlier. Since no effect on the wet web strength was observed with added chemicals other than surfactants, the findings of this study conflict with the theory that the wettability (hydrophilicity) of fibres has a significant effect on wet web strength. This is in line with the studies published by Tajedo and van de Ven [126, 172] who also noticed that the strength of the wet web was not reduced when fibres were hydrophobised using different chemicals. Based on their results, Tajedo and van de Ven [126, 171] concluded that the friction between fibres plays a major role in wet web strength. This conclusion is also supported by the fact that the apparent density and tensile strength of wet webs (after 350 kPa wet pressing) has no positive correlation (higher capillary forces are assumed to draw fibres together and thus increase density) as shown in Figure 76B.

The addition of (100 ppm) of different chemicals has only minor effect on residual tension (Figure 77) at a given dryness level. This result supports the conclusions that surface tension of water has no or only moderate effect on the mechanical properties of wet web above dryness 30%.

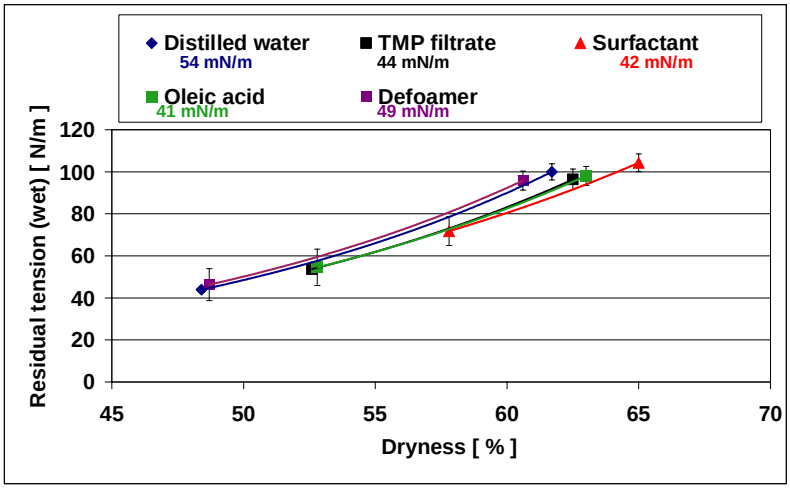

Figure 77. The effect of adding different chemicals to white water used during sheet forming on residual tension (measured by the Impact test rig at strain rate 1 m/s) of wet handsheets at 1% strain as a function of dryness (exponential fir is used to describe the effect of dryness). The surface tension values of white water are marked on the legend. Error bars show a 95% confidence interval of the mean of the measurement.

Surprisingly, in contrary to dry paper strength, wet web tensile strength and residual tension are both increased when results are compared after similar wet pressing (especially at 50 kPa wet pressing pressure) due to improved dryness. This indicates that the presence of different contaminants in white water may not be as harmful to wet web runnability as one can expect based on the earlier studies concerning the effect of different contaminants on the mechanical properties of dry paper (see for example [117]).

12. POLYMERS AND MECHANICAL PROPERTIES OF DRY AND WET WEB

This chapter examines the effects of adding different polymers (by spraying on wet web before wet pressing) on the in-plane mechanical properties of dry and wet paper. The main findings of this study are presented in this chapter. All the results are found in Appendix V.

12.1 Mechanical and some paper technical properties of dry paper

Figure 78 shows that spraying CMC on wet handsheets before wet pressing increases the tensile index of dry handsheets by 25% at both addition levels (1 g/m^2 and 2 g/m^2). This result is in line with several studies published on the wet end addition of CMC (see for example [136, 138, 139, 173]). Addition of CMC has been expected to break the weak bonding between agglomerated fibrils and induce electrostatic stabilisation. As a result of this, CMC disperses fibrils on the fibre surface which leads to increased interactions between fibres [136, 140, 174]. In addition, it has been also reported that the addition of CMC increases the specific bond strength but not the relative bonded area. This argument is based on the fact that the addition of CMC increases strength, but has no effect on light scattering or density [173]. Duker and Lindström [138] showed that the addition of CMC reduces the amount of kinks and increases the shape factor of fibres (i.e. reduces curliness). CMC has also been shown to improve the formation of the paper. The increase of strength properties through improved formation, reduced amount of kinks or increased shape factor of fibres can be disregarded in this study, since CMC is added to an already formed wet handsheet and thus barely affects these factors.

The addition of polyvinyl alcohol also increases dry paper strength, which is in line with the research presented earlier in the literature [175, 176]. Polyvinyl alcohol is a hydrophilic polymer carrying hydroxyl group on its each repeating unit, which permits the development of hydrogen bonds with hydroxyl and carboxylic groups of cellulose fibres, thus enhancing the tensile strength of dry paper [177]. The addition of chitosan improves dry paper tensile index by 13%. The structural similarity of chitosan to cellulose and the electrostatic interactions, as well as the possibility of covalent bonds forming between chitosan and cellulose have been proposed as explanations for the increase in dry paper strength [142].

The highest tensile index is achieved by a dual application of CMC and chitosan. The dual application of A-PAM and C-PAM also increases tensile index significantly, but the dual application of CMC and C-PAM has no effect on the dry paper tensile index. This result partly concurs with previous findings on polyelectrolyte multilayers (opposite charged polymers added sequentially to pulp, see for example [178-183]). Polyelectrolyte multilayers have been found to increase the molecular contact area in the fibre-fibre joints [178]. These multilayers were also found to create a larger number of fibre-fibre contacts in the sheet [183]. The use of polyelectrolyte multilayers has been shown to increase dry paper strength with only a minor reduction in density, light scattering or the formation of the sheet [182]. The increase of strength has been demonstrated to be greatly dependent on the adsorption of these polymers, which is affected by several parameters, such as electrolyte concentration, the type of electrolyte and the charge density [179]. The adsorption of the polymers was not determined in this study.

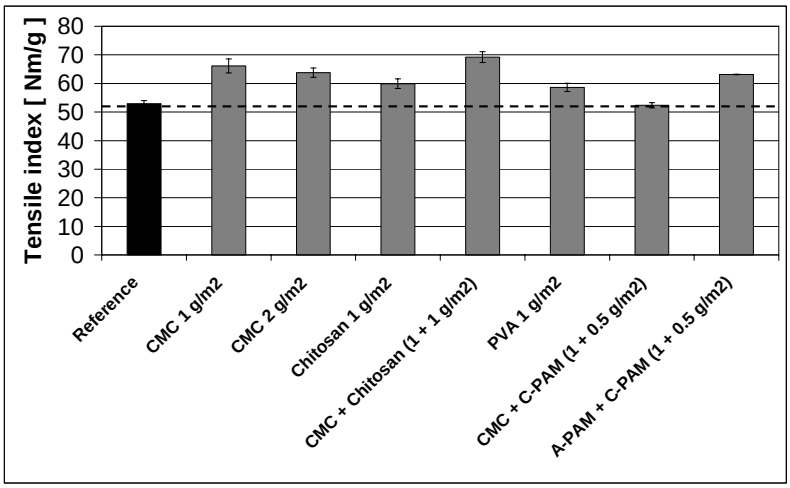

Figure 78. The effect of adding different polymers by spraying to formed handsheets on tensile index (measured by the Impact test rig at strain rate 1 m/s) of dry handsheets made from softwood kraft pulp. Error bars show a 95% confidence interval of the mean of the measurement.

The spraying of different polymers has no effect on the density of dry paper (Figure 79A) despite a high increase of the tensile index. This indicates that addition of different polymers increases the strength of fibre-fibre bonds but do not increase the number of these bonds (see for example [66, 173]). Surprisingly, the spraying of chemicals increases the air permeance of dried paper by 35% on average (from 1500 to 2000 ml/min) even though the spraying was done before wet pressing, when dryness of the handsheets was approximately 10% (Figure 79B).

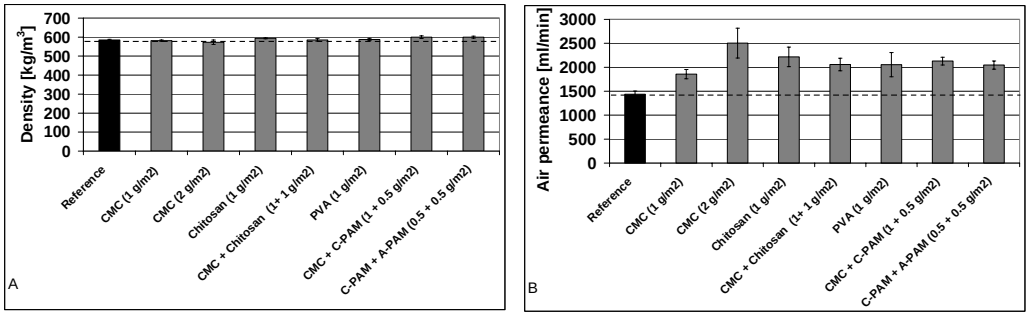

Figure 79. The effect of adding different polymers by spraying to formed handsheets on density (Figure A) and air permeance (Figure B) of dry handsheets made from softwood kraft pulp. Error bars show a 95% confidence interval of the mean of the measurement.

Increased tensile strength with constant density is beneficial form many paper grades, especially for wood-free paper grades and boards, where the bulk of paper is very important for the final product functionality [115].

12.2 Mechanical properties of wet web

The effect of the studied polymers on wet web tensile strength is presented in Figure 80. CMC increases wet web strength similarly for both addition levels (1 g/m^2 and 2 g/m^2). The dispersion of fibrils when CMC is added to pulp [136, 174] is believed to increase molecular level interactions between fibres due to the increased surface area (due to hydration of fibrils on the fibre surface) [140]. It is worth noting that CMC have no effect on wet web strength at lower dryness levels (at a given dryness), but a clear increase in wet web strength is obtained at dryness levels above 55%. This result with CMC is in line with the findings of Myllytie [134]. He showed that the tensile strength development with increasing dryness varies significantly for different polymers. The increase of wet strength with increasing dryness is quite similar with CMC and chitosan. Myllytie [134] showed that use of chitosan also disperses fibrils, but the effect is smaller than with CMC. Laleg and Pikulik [142] suggested that chitosan increases wet web tensile strength through covalent bonding between cellulose and chitosan. As the chitosan is dissolved in mild acetic acid, the amine group protonates and thus has a cationic charge [142]. Therefore, it is possible that electrostatic interactions between cationic amine group of chitosan and anionic fibre surface are also involved, which may also affect on wet web strength [140].

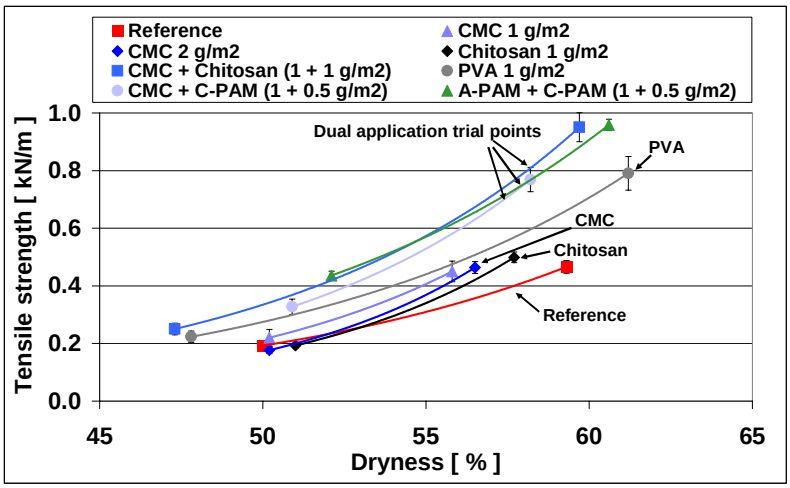

Figure 80. *The effect of adding different polymers by spraying to formed handsheets on tensile strength of wet handsheets (made from kraft pine) as a function of dryness (exponential fir is used to describe the effect of dryness) measured by the Impact test rig at strain rate 1 m/s. Error bars show a 95% confidence interval of the mean of the measurement.*

Addition of polyvinyl alcohol increases wet web strength (also at dryness levels below 55%). It is likely that polyvinyl alcohol as high molecular weight polymer having high affinity to fibres may increase molecular level interaction between fibres at wet state. The dual application of CMC and chitosan increases wet web tensile strength significantly more than the addition of CMC or chitosan alone. This result concurs with the findings of Myllytie [140] for wet end addition. Based on the earlier studies published in the literature [129, 140]. It could be suggested that wet web strength results from a combination of covalent bonding (due to chitosan) and increased fibril dispersion, which could lead to greater molecular level interaction between fibres. However, since similar increase in wet web strength is obtained also with a combination of CMC and C-PAM and the combination of A-PAM and C-PAM than with CMC and Chitosan, it seems more likely that increased molecular level interaction between fibres (weather they are or electrostatic of chemical nature) explains the strength increase of wet web rather than formation of covalent bonds.

The addition of different polymers has only a marginal effect on elastic modulus (Figure 81A) and residual tension (Figure 81B) of wet webs. The increase of residual tension and elastic modulus is below 10% with all chemicals compared to the reference point with no chemicals. This result indicates that elastic modulus and residual tension of wet webs are more affected by the ability of fibre segments to carry load at small strain levels, rather than strength of interactions between fibres.

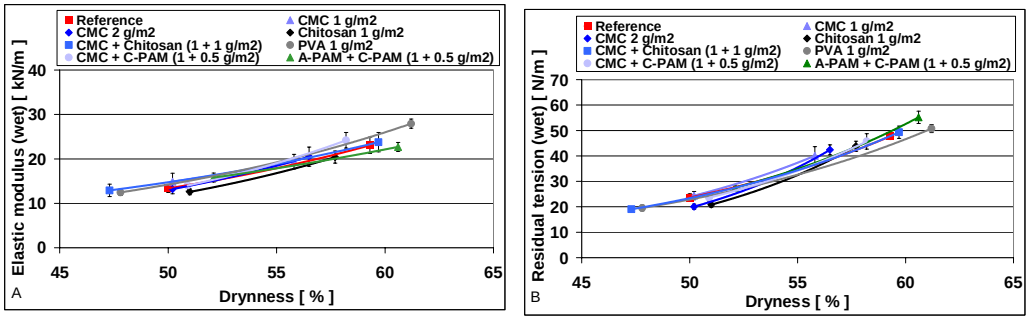

Figure 81. The effect of adding different chemicals by spraying to formed handsheets on residual tension at 2% strain (Figure A) and elastic modulus (Figure B) of wet handsheets (made from softwood kraft pulp) as a function of dryness (exponential fit is used to describe the effect of dryness) measured by the Impact test rig at strain rate 1 m/s. Error bars show a 95% confidence interval of the mean of the measurement.

The addition of CMC yields lower dryness after a constant wet pressing pressure of 350 kPa than addition of other chemicals. This disagrees with the theory proposed by Mesic [184], who stated that increase of retained surface water (which was noticed by the high increase of WRV) when adding CMC should not affect dryness after wet pressing since surface water is easily removed during wet pressing.

Figures 82A and 82B show the effect of opposite-charged polymers (A-PAM and C-PAM) on dry and wet web tensile strength. The addition of A-PAM to half of the pulp and C-PAM to the other half before mixing the pulps has almost no effect on dry and wet web strength, whereas the sequential addition of polymers through spraying results in a marked improvement of dry and wet web strength. This result can be partly explained by the drastic reduction in the formation of dry handsheets (the actual values of formation were not determined), when these polymers were added selectively to pulp, whereas there was no visible effect on formations when polymers were sprayed on an already formed fibre network. The increase of dry paper strength produced by layering anionic and cationic polymers (polyelectrolyte multilayer) is in line with several earlier studies [178-183], as mentioned earlier.

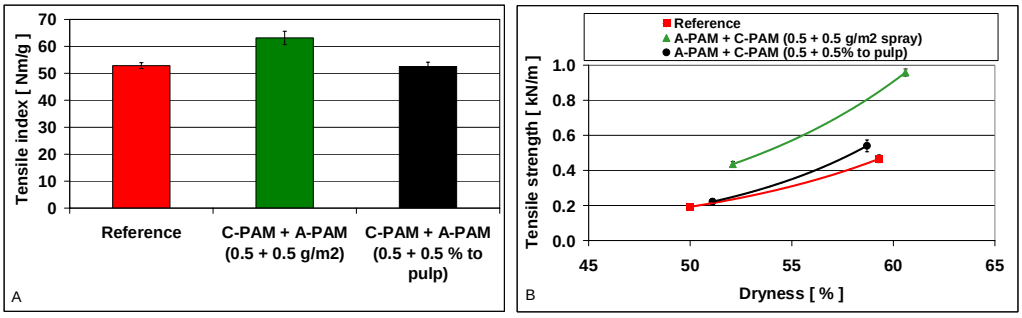

Figure 82. The effect using different adding strategies of A-PAM and C-PAM on tensile index (Figure A) of dry handsheets and tensile strength (Figure B) of wet handsheets (made from softwood kraft pulp) as a function of dryness (exponential fit is used to describe the effect of dryness) measured by the Impact test rig at strain rate 1 m/s. Error bars show a 95% confidence interval of the mean of the measurement.

A significant increase in dry paper strength together with a simultaneous improvement of drainage and retention has been reported when anionic and cationic polymers are pre-mixed before adding the mixture to the pulp. These mixtures are typically referred as polyelectrolyte complexes (see for example [178, 185-188]). Ankerfors et al. [178] showed that polyelectrolyte complexes have lower adsorption to fibres than polyelectrolyte multilayers. However, at a given adsorption level, the addition of polyelectrolyte complexes improves dry paper tensile strength more than the polyelectrolyte multilayers. Because of this also spraying of polyelectrolyte complexes on wet paper would be interesting.

A drawback of many chemicals (including some of the chemicals presented in this chapter) is that they are relatively expensive and the benefit of using them, despite the possible increase in paper machine production speed, can lead to diseconomy. Therefore it is important to optimise the use of chemicals and find new ways to use them in a more efficient way. The following chapter examines the effect of selective addition of chemicals to pulp.

13. SELECTIVE ADDITION OF PAPERMAKING CHEMICALS AND MECHANICAL PROPERTIES OF WET WEB

This chapter examines how the selectively adding of commercial cationic starch to the long fibre fraction and C-PAM to the short fibre fraction affects pulp drainage and the mechanical properties of the wet web. The main findings of this study are presented in this chapter. All the results are found in Appendix VI.

13.1 Drainage properties

The addition of cationic starch and C-PAM either to the whole pulp or selectively to different fractions decreases flow resistance (Figure 83A), which results in reduced drainage time (Figure 83B). However, the selective addition of cationic starch to long fibres and C-PAM to the short fibre fraction appears to be more effective than adding those chemicals to the whole pulp (drainage resistance and drainage time is further decreased by 20-25%).

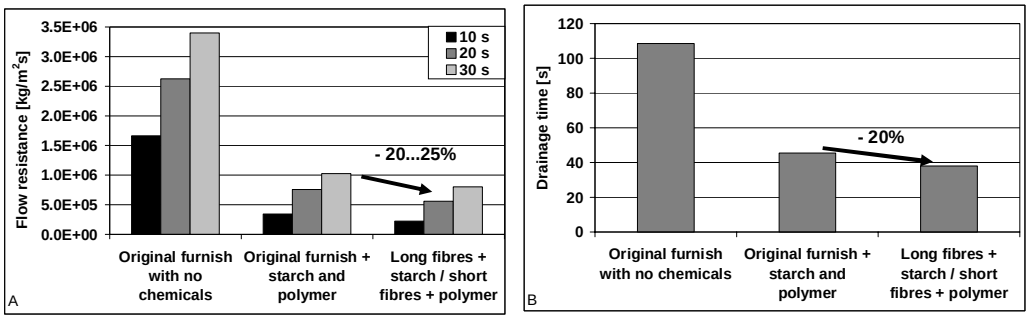

Figure 83. The effect of different addition strategies of cationic starch and C-PAM on flow resistance after 10 s, 20 s and 30 s (Figure A) and drainage time (Figure B) of birch kraft pulp measured by a one-dimensional gravity-driven filtration device.

These results concur with the results published by Hubbe and Cole [149, 150]. Drainage is improved by the selective addition of chemicals because when C-PAM is added to the short fibre fraction, the flocculation of fine material increases, causing a reduction in the surface area of fibrous material. It is also possible that selective addition of chemicals improved attachment of fines to fibres which can prevent the fines from migrating to choke points (unattached fines tend to stuck in locations where they obstruct flow) [150].

13.2 Mechanical properties of wet web

The addition of cationic starch and C-PAM to the whole pulp has no effect on the tensile strength of wet samples compared to the sample with no chemical addition as seen in Figure 84. Figure 84B shows that addition of cationic starch and C-PAM either to the whole pulp or selectively to different pulp fractions increase strain at break of the wet handsheets. Laleg et al. [129] and Myllytie [134] reported of significant reduction of wet web strength when cationic starch was added to pulp. This kind of reduction is not seen in this study. The selective addition of cationic starch to long fibre fraction and C-PAM to short fibre fraction significantly increases tensile strength at a given dryness level (at 50% dryness, the strength of the wet web is increased by 25%). One possible explanation for the increase of wet web strength is that the addition of C-PAM to only short fibre fractions would prevent the flocculation of long fibres, which would lead to better formation than when chemicals are added to whole pulp. Unfortunately, the formation values of the sheets were not determined. It also possible that fines retention would have increased due to the selective addition of chemicals. Furthermore, it is also possible, that the selective addition of chemicals generates pulp with both cationic and anionic surfaces. This could increase electrostatic/chemical interactions which are believed to affect the strength of wet web [189].

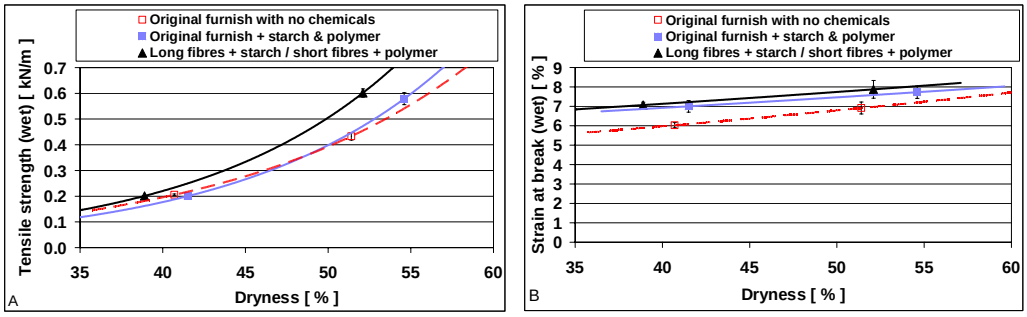

Figure 84. The effect of using different adding strategies of cationic starch and C-PAM to birch kraft pulp on tensile strength (Figure A) and strain at break (Figure B) (measured by the Impact test rig at strain rate 1 m/s) of wet handsheets as a function of dryness (exponential fit is used to describe the effect of dryness). Error bars show a 95% confidence interval of the mean of the measurement.

Residual tension at a given dryness decreases significantly (by 15%) when cationic starch and C-PAM are added to the whole pulp compared to the sample with no chemical addition (Figure 85). Similar results were reported earlier by Retulainen and Salminen [22]. A selective addition of those chemicals shows no reduction in residual tension compared to the pulp without chemicals.

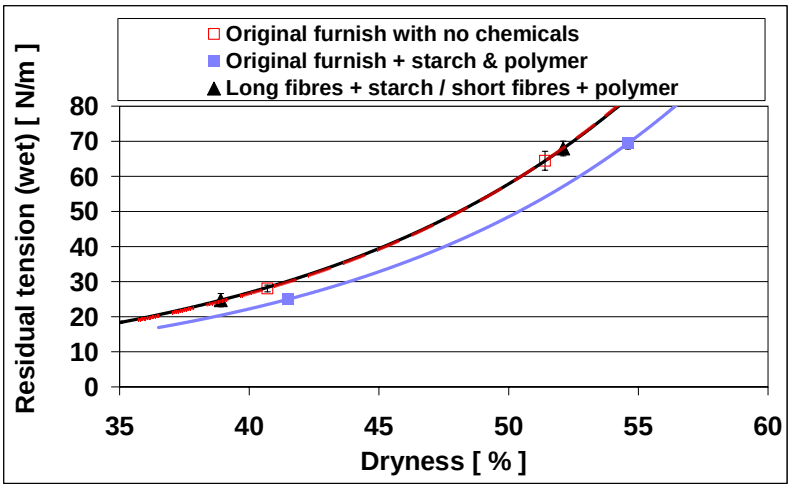

Figure 85. The effect of using different adding strategies of cationic starch and C-PAM to birch kraft pulp on residual tension (measured by Impact test rig at strain rate 1 m/s) of wet handsheets as a function of dryness (exponential fit is used to describe the effect of dryness). Error bars show a 95% confidence interval of the mean of the measurement.

The reason why the addition of cationic starch and C-PAM to the whole pulp reduces residual tension but has no effect on wet web tensile strength is dubious. However, the selective addition of those chemicals resulted in both, higher tensile strength and residual tension of wet web compared to adding of the chemicals to the whole pulp.

14 CONCLUSIONS

The objective of this thesis was to identify the effects of different factors on the tensile strength and the relaxation characteristics of wet web at high-speed straining. The study was based on the premise that wet web mechanical properties at a high strain rate can be used to predict the tension behaviour of wet web at the beginning of the drying section on a paper machine. The quality and quantity of fines, the shape and orientation of fibres in the network, the filler content, the different chemicals present in the white water, and the type and adding strategy of papermaking chemicals were shown to have a significant effect on the mechanical properties of both dry and wet paper.

It was found that the tensile and relaxation properties of wet webs are strongly dependent on the quality and amount of fines. With low fines content, the tensile strength and residual tension of wet paper were mainly determined by the mechanical interactions between fibres at their contact points. As the fines strengthen the mechanical interaction in the network, the fibre properties also become important. TMP fibres were shown to offer higher potential for improving the residual tension of the wet web, whereas the wet web strength was higher with kraft fibres. Based on this, it can be concluded that the addition of heavily refined kraft pulp (with a high amount of fines) to wood containing paper grades could increase the residual tension of wet web significantly, while the addition of less refined kraft pulp would lead to a reduction of the residual tension. Kraft pulp is typically refined quite gently to give paper high tear energy.

If the network contains curly fibres, the load over a curled segment is not transmitted until the curl is straightened. Fibre curliness is known to significantly deteriorate the tensile strength and tensile stiffness of dry paper. The effect of fibre curliness was shown to be substantially higher for wet web strength and residual tension than for dry paper strength. One suggested explanation is that the fibre segments are longer and the fibre segment length distribution is wider for wet paper than for dry paper due to the fact that wet paper has fewer bonds. Additionally, shrinkage during drying reduces the slackness of fibre segments in the network.

The results of this thesis indicate that increasing fibre straightness has significant potential to augment the residual tension and tensile strength of wet webs made of chemical pulps. The straightening of fibres could be carried out, for example, through optimised refining or by straining fibres during drying in the pulp mill.

The increase of filler content from 10% to 25% significantly reduced the tensile strength of dry fine paper, but had only a moderate effect on wet web tensile strength and residual tension. When the results were indexed by the grammage of fibrous material, the tensile strength was at a quite similar level and the residual tension of the wet web was increased when filler content was increased from 10% to 25%. Increased filler content in the wet web reduced the amount of fibrous material in the web, but augmented dryness after wet pressing. In addition, the presence of fillers was concluded to increase the friction between wet fibres, leading to enhanced mechanical properties of the wet web. Based on these findings, it can be assumed that an increase of filler content with fine paper grades is not necessarily limited by the impaired wet web mechanical properties. However, the increase of filler content may be hindered for example by increased dusting or a reduced bending stiffness of dry paper.

The addition of different contaminants (a TMP filtrate containing extractives, surfactant, oleic acid and defoamer) to white water during sheet formation resulted in lowered surface tension and increased dryness after wet pressing. The addition of different contaminants reduced the tensile strength of dry paper. However, this reduction could not explain the decreased surface tension, but instead pointed to the tendency of different contaminants to interfere with the inter-fibre bonding. Surprisingly, and in contrary to earlier theories, no connection was found between wet web tensile strength and the surface tension of white water. Based on the results presented here, it was concluded that the friction between fibres has a very important effect on wet web strength.

The spraying of CMC, PVA and chitosan on wet paper before wet pressing improved wet web strength. CMC and chitosan started to improve wet web strength above a dryness level of approximately 55%, while PVA improved wet web strength also at lower dryness levels. Earlier studies have shown that polyelectrolyte multilayers of anionic and cationic polymers increase the molecular contact area in the fibre-fibre joints and thus increase the strength of dry paper. The results of this study showed that the layering of polymers (two layers) can improve the strength of the wet web significantly more (relatively) than dry paper. This shows that the layering of polymers also increased the interactions between fibres in the wet state. It is also plausible that the spraying of anionic polymer to the outermost layer could reduce the adhesion between the wet web and the anionic centre roll on a paper machine. In practice, the generation of polymer multilayers or even a bi-layer on the paper machine by spraying is challenging and therefore the amount sprayed polymers should be minimised. In addition, it is possible that the spraying of polymers on a high-speed web may be challenging due to the air flow that travels with the web. This air flow may cause chemicals to spread, thus affecting the evenness of the spray and leading to serious contamination issues.

The selective addition of cationic starch to long fibres and C-PAM to short fibres instead of adding the chemicals to the whole pulp was shown to be a conceivable way to improve both the pulp drainage and the mechanical properties of the wet web at a given dryness. In our findings, the improvement in drainage caused by adding cationic polymer to a short fibre fraction was due to the increased flocculation of fines and thus, to a reduced surface area of fibrous material. One possible explanation for the improvement of wet web mechanical properties is that the addition of C-PAM to short fibre fractions alone prevents the flocculation of long fibres, leading to better formation than when chemicals are added to the whole pulp. It is also possible that the retention of fines increased due to the selective addition of chemicals or that the selective addition of chemicals generated pulp with both cationic and anionic surfaces, thus leading to a greater quantity of molecular level interactions.

It is likely that the selective addition of chemicals enables a reduction in the cost of chemicals, in addition to improved drainage and intensified wet web mechanical properties. The challenge is to optimise the fractionation of the pulp before adding chemicals and to make the fractionation consistent enough to avoid problems related to the thickening of the fines/short fibres.

Based on the results presented in this thesis, the residual tension of the wet web is greatly affected by both the initial tension and by tension relaxation. Residual tension increases with an enhanced activation of the fibre network. The addition of chemicals increases the strength of fibre-fibre joints, which augments wet web strength but has no effect on fibre network activation and thus does not influence wet web elastic modulus or residual tension. The friction between wet fibres seems to have a greater effect on wet web strength than generally believed, while surface tension forces do not affect the web so much above a dryness level of 30%.

It would be useful to compare the mechanical properties of wet webs for a specific paper grade and similar paper machines with different productions speeds to verify the connection between mechanical properties of wet paper and the maximum production speed of the paper machine. More information on the effects of different fillers and their aggregates on dry and wet paper properties would be useful. It would also be enlightening to clarify how the spraying of chemicals affects their adsorption compared to pulp addition. Additionally, more detailed information is needed on how molecular weight, charge density and the ratio of the anionic and cationic charge of different polyelectrolytes in dual applications affect wet web properties. Finally, it would be interesting to clarify how the spraying of different polyelectrolyte complexes (mixtures of anionic and cationic polymers) affects the mechanical properties of dry and wet paper.

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APPENDICES

Appendix I	Results from Chapter 8 in table form
Appendix II	Results from Chapter 9 in table form
Appendix III	Results from Chapter 10 in table form
Appendix IV	Results from Chapter 11 in table form
Appendix V	Results from Chapter 12 in table form
Appendix VI	Results from Chapter 13 in table form

Appendix I: Results from Chapter 8 in table form

Dynamic tensile strength measurement with Impact test rig						
TMP LFF & TMP fines						
	Strain rate	1.0	m/s			
	Sample length	100	mm			
	Sample width	20	mm			
	Grammage of samples	60	g/m^2			
	Wet pressing	50	kPa			
Dryness [%]			35.0	51.1	51.6	51.2
Trial point			**Unfractioned**	**LFF**	**LFF+10% fines**	**LFF+20% fines**
Test rig			Impact	Impact	Impact	Impact
Average values	Tensile strength	[kN/m]	0.184	0.052	0.101	0.132
	Strain at break	[%]	4.85	1.09	1.86	2.49
	Dynamic modulus	[kN/m]	3.83	5.33	5.57	5.44
	Elastic modulus	[kN/m]	22.86	20.33	17.80	16.97
	T.E.A.	[mJ]	13.91	0.91	2.90	5.01
Deviations	Tensile strength	[kN/m]	0.004	0.002	0.002	0.003
(95% confidence)	Strain at break	[%]	0.245	0.152	0.155	0.199
	Dynamic modulus	[kN/m]	0.23	0.79	0.36	0.42
	Elastic modulus	[kN/m]	7.86	6.33	3.17	4.08
	T.E.A.	[mJ]	0.77	0.11	0.31	0.43
	Strips	[-]	9	9	11	11

Dynamic tensile strength measurement with Impact test rig						
TMP LFF & TMP fines						
	Strain rate	1.0	m/s			
	Sample length	100	mm			
	Sample width	20	mm			
	Grammage of sample	60	g/m^2			
	Wet pressing	350	kPa			
Dryness [%]			49.4	60.3	60.7	59.6
Trial point			**Unfractioned**	**LFF**	**LFF+10% fines**	**LFF+20% fines**
Test rig			Impact	Impact	Impact	Impact
Average values	Tensile strength	[kN/m]	0.322	0.107	0.225	0.226
	Strain at break	[%]	3.79	0.79	1.94	2.22
	Dynamic modulus	[kN/m]	8.59	13.78	11.74	10.36
	Elastic modulus	[kN/m]	34.55	40.21	21.93	23.13
	T.E.A.	[mJ]	18.21	1.32	5.97	7.19
Deviations	Tensile strength	[kN/m]	0.007	0.003	0.008	0.008
(95% confidence)	Strain at break	[%]	0.316	0.063	0.230	0.239
	Dynamic modulus	[kN/m]	0.81	0.85	0.92	1.51
	Elastic modulus	[kN/m]	19.63	8.29	7.66	7.99
	T.E.A.	[mJ]	1.52	0.16	1.12	0.66
	Strips	[-]	11	9	10	11

Dynamic tensile strength measurement with Impact test rig
TMP LFF & TMP fines

	Strain rate	1.0	m/s			
	Sample length	100	mm			
	Sample width	20	mm			
	Grammage of samples	60	g/m^2			
	Dry samples					
Dryness [%]			90.7	90.4	91.1	91.1
Trial point			**Unfractioned**	**LFF**	**LFF+10% fines**	**LFF+20% fines**
Test rig			Impact	Impact	Impact	Impact
Average values	Tensile strength	[kN/m]	3.130	1.048	1.371	1.638
	Strain at break	[%]	2.09	0.98	1.25	1.34
	Dynamic modulus	[kN/m]	156.59	112.49	118.13	126.32
	Elastic modulus	[kN/m]	234.41	131.12	143.08	167.74
	T.E.A.	[mJ]	63.57	9.42	15.71	20.70
Deviations	Tensile strength	[kN/m]	0.088	0.063	0.055	0.087
(95% confidence)	Strain at break	[%]	0.152	0.076	0.155	0.087
	Dynamic modulus	[kN/m]	9.96	8.22	12.04	6.58
	Elastic modulus	[kN/m]	30.67	12.37	23.75	20.25
	T.E.A.	[mJ]	4.91	1.30	1.59	1.78
	Strips	[-]	10	11	11	10

Relaxation measurement with Impact test rig (1% strain)
TMP LFF & TMP fines

	Strain	1	%			
	Relaxation time	0.475	s			
	Strain rate	1.0	m/s			
	Sample length	100	mm			
	Sample width	20	mm			
	Grammage of samples	60	g/m^2			
	Wet pressing	50	kPa			
Dryness [%]			35.0	51.1	51.6	51.2
Trial point			**Unfractioned**	**LFF**	**LFF+10% fines**	**LFF+20% fines**
Test rig			Impact	Impact	Impact	Impact
Average values	Initial tension	[N/m]	126.20	60.62	94.50	121.39
	Residual tension	[N/m]	53.76	16.10	33.57	48.39
Deviations	Initial tension	[N/m]	3.32	3.43	7.21	8.93
(95% confidence)	Residual tension	[N/m]	3.79	3.41	4.11	4.86
	Strips	[-]	10	10	10	10

Relaxation measurement with Impact test rig (1% strain)
TMP LFF & TMP fines

	Strain	1	%			
	Relaxation time	0.475	s			
	Strain rate	1.0	m/s			
	Sample length	100	mm			
	Sample width	20	mm			
	Grammage of sample	60	g/m^2			
	Wet pressing	350	kPa			
Dryness [%]			49.4	60.3	60.7	59.6
Trial point			**Unfractioned**	**LFF**	**LFF+10% fines**	**LFF+20% fines**
Test rig			Impact	Impact	Impact	Impact
Average values	Initial tension	[N/m]	206.31	137.22	190.04	192.77
	Residual tension	[N/m]	95.42	50.10	86.25	88.71
Deviations	Initial tension	[N/m]	7.04	6.53	5.61	3.34
(95% confidence)	Residual tension	[N/m]	4.27	3.40	3.58	1.86
	Strips	[-]	10	10	10	10

Some paper technical properties
TMP LFF & TMP fines

Trial point			**Unfractioned**	**LFF**	**LFF+10% fines**	**LFF+10% fines**
Test rig						
Average values	Density	[kg/m^3]	470	281	312	322
	Grammage	[g/m^2]	60.7	62.6	62.1	60.2
	Shrinkage	[%]	2.45	0.39	0.70	0.98
Deviations	Density	[kg/m^3]	3	4	5	7
(95% confidence)	Grammage	[g/m^2]	0.5	1.5	1.4	1.1
	Shrinkage	[%]	0.06	0.36	0.12	0.08

Dynamic tensile strength measurement with Impact test rig
TMP LFF & chemical pulp fines

	Strain rate	1.0	m/s			
	Sample length	100	mm			
	Sample width	20	mm			
	Grammage of samples	60	g/m^2			
	Wet pressing	50	kPa			
Dryness [%]			35.6	50.9	42.2	37.0
Trial point			**Unfractioned**	**LFF**	**LFF+10% fines**	**LFF+20% fines**
Test rig			Impact	Impact	Impact	Impact
Average values	Tensile strength	[kN/m]	0.199	0.075	0.225	0.302
	Strain at break	[%]	5.32	1.55	3.16	4.03
	Dynamic modulus	[kN/m]	3.83	4.92	7.13	7.56
	Elastic modulus	[kN/m]	14.24	7.98	13.20	23.94
	T.E.A.	[mJ]	16.53	1.52	9.66	18.02
Deviations	Tensile strength	[kN/m]	0.005	0.013	0.011	0.004
(95% confidence)	Strain at break	[%]	0.53	0.11	0.04	0.25
	Dynamic modulus	[kN/m]	0.36	0.80	0.34	0.45
	Elastic modulus	[kN/m]	2.03	0.98	0.56	1.83
	T.E.A.	[mJ]	2.19	0.25	0.43	1.47
	Strips	[-]	11	11	11	11

Dynamic tensile strength measurement with Impact test rig
TMP LFF & chemical pulp fines

	Strain rate	1.0	m/s			
	Sample length	100	mm			
	Sample width	20	mm			
	Grammage of samples	60	g/m^2			
	Wet pressing	350	kPa			
Dryness [%]			56.6	64.5	54.3	52.2
Trial point			**Unfractioned**	**LFF**	**LFF+10% fines**	**LFF+20% fines**
Test rig			Impact	Impact	Impact	Impact
Average values	Tensile strength	[kN/m]	0.404	0.245	0.507	0.715
	Strain at break	[%]	4.74	1.72	3.28	4.95
	Dynamic modulus	[kN/m]	8.59	14.28	15.36	14.47
	Elastic modulus	[kN/m]	20.26	19.28	32.01	36.60
	T.E.A.	[mJ]	27.23	5.02	22.30	47.44
Deviations	Tensile strength	[kN/m]	0.027	0.011	0.068	0.022
(95% confidence)	Strain at break	[%]	0.26	0.06	0.21	0.11
	Dynamic modulus	[kN/m]	0.72	0.82	1.56	0.62
	Elastic modulus	[kN/m]	1.30	1.46	2.76	1.82
	T.E.A.	[mJ]	2.35	0.34	3.85	1.49
	Strips	[-]	11	11	11	11

Dynamic tensile strength measurement with Impact test rig
TMP LFF & chemical pulp fines

	Strain rate	1.0	m/s			
	Sample length	100	mm			
	Sample width	20	mm			
	Grammage of samples	60	g/m^2			
	Dry samples					
Dryness [%]			89.4	91.1	90.3	90.1
Trial point			**Unfractioned**	**LFF**	**LFF+10% fines**	**LFF+20% fines**
Test rig			Impact	Impact	Impact	Impact
Average values	Tensile strength	[kN/m]	3.302	1.050	4.007	4.781
	Strain at break	[%]	2.17	1.13	2.39	2.68
	Dynamic modulus	[kN/m]	153.03	93.57	168.41	180.31
	Elastic modulus	[kN/m]	233.06	104.60	245.29	264.98
	T.E.A.	[mJ]	66.95	9.55	89.35	120.42
Deviations	Tensile strength	[kN/m]	0.11	0.05	0.12	0.19
(95% confidence)	Strain at break	[%]	0.13	0.06	0.13	0.22
	Dynamic modulus	[kN/m]	6.91	4.71	6.11	9.95
	Elastic modulus	[kN/m]	20.40	8.79	13.72	19.66
	T.E.A.	[mJ]	6.53	0.82	7.51	14.54
	Strips	[-]	11	10	10	10

Relaxation measurement with Impact test rig (1% strain)						
TMP LFF & chemical pulp fines						
	Strain	**1**	%			
	Relaxation time	**0.475**	s			
	Strain rate	**1.0**	m/s			
	Sample length	**100**	mm			
	Sample width	**20**	mm			
	Grammage of samples	**60**	g/m^2			
	Wet pressing	**50**	kPa			
Dryness [%]			35.6	50.9	42.2	37.0
Trial point			**Unfractioned**	**LFF**	**LFF+10% fines**	**LFF+20% fines**
Test rig			Impact	Impact	Impact	Impact
Average values	Initial tension	[N/m]	157.26	66.95	122.44	204.30
	Residual tension	[N/m]	50.17	10.91	24.47	69.23
Deviations	Initial tension	[N/m]	7.50	4.32	29.56	5.34
(95% confidence)	Residual tension	[N/m]	3.93	1.61	19.21	2.35
	Strips	[-]	10	10	11	10

Relaxation measurement with Impact test rig (1% strain)						
TMP LFF & chemical pulp fines						
	Strain	**1**	%			
	Relaxation time	**0.475**	s			
	Strain rate	**1.0**	m/s			
	Sample length	**100**	mm			
	Sample width	**20**	mm			
	Grammage of samples	**60**	g/m^2			
	Wet pressing	**350**	kPa			
Dryness [%]			56.6	64.5	54.3	52.2
Trial point			**Unfractioned**	**LFF**	**LFF+10% fines**	**LFF+20% fines**
Test rig			Impact	Impact	Impact	Impact
Average values	Initial tension	[N/m]	272.30	260.79	278.65	302.62
	Residual tension	[N/m]	107.61	82.07	106.76	124.33
Deviations	Initial tension	[N/m]	9.17	14.38	29.07	9.91
(95% confidence)	Residual tension	[N/m]	5.39	2.98	12.25	4.88
	Strips	[-]	10	10	10	8

Some paper technical properties						
TMP LFF & chemical pulp fines						
Trial point			**Unfractioned**	**LFF**	**LFF+10% fines**	**LFF+20% fines**
Test rig						
Average values	Density	[kg/m^3]	463	295	457	534
	Grammage	[g/m^2]	60.5	60.6	62.0	60.6
	Shrinkage	[%]	2.59	0.71	2.30	3.69
Deviations	Density	[kg/m^3]	3	6	6	6
(95% confidence)	Grammage	[g/m^2]	0.4	1.2	0.9	1.4
	Shrinkage	[%]	0.07	0.07	0.06	0.08

Dynamic tensile strength measurement with Impact test rig
Chemical pulp LFF & chemical pulp fines

	Strain rate	1.0	m/s			
	Sample length	100	mm			
	Sample width	20	mm			
	Grammage of samples	60	g/m^2			
	Wet pressing	50	kPa			
Dryness [%]			48.1	55.8	50.8	45.0
Trial point			**Unfractioned**	**LFF**	**LFF+10% fines**	**LFF+20% fines**
Test rig			Impact	Impact	Impact	Impact
Average values	Tensile strength	[kN/m]	0.307	0.314	0.550	0.525
	Strain at break	[%]	4.03	3.14	5.24	5.54
	Dynamic modulus	[kN/m]	8.51	10.13	10.61	9.60
	Elastic modulus	[kN/m]	29.60	48.62	45.98	34.24
	T.E.A.	[mJ]	16.40	12.31	34.91	35.42
Deviations	Tensile strength	[kN/m]	0.011	0.015	0.019	0.030
(95% confidence)	Strain at break	[%]	0.27	0.12	0.19	0.20
	Dynamic modulus	[kN/m]	0.43	0.37	0.55	0.42
	Elastic modulus	[kN/m]	3.73	11.84	5.12	5.05
	T.E.A.	[mJ]	1.93	1.09	2.38	3.11
	Strips	[-]	10	10	10	10

Dynamic tensile strength measurement with Impact test rig
Chemical pulp LFF & chemical pulp fines

	Strain rate	1.0	m/s			
	Sample length	100	mm			
	Sample width	20	mm			
	Grammage of samples	60	g/m^2			
	Wet pressing	350	kPa			
Dryness [%]			58.1	65.0	66.2	55.3
Trial point			**Unfractioned**	**LFF**	**LFF+10% fines**	**LFF+20% fines**
Test rig			Impact	Impact	Impact	Impact
Average values	Tensile strength	[kN/m]	0.713	0.618	1.609	1.025
	Strain at break	[%]	4.92	3.96	5.69	5.78
	Dynamic modulus	[kN/m]	14.68	16.19	28.55	17.92
	Elastic modulus	[kN/m]	69.00	73.06	102.67	55.06
	T.E.A.	[mJ]	41.92	31.81	101.87	66.08
Deviations	Tensile strength	[kN/m]	0.018	0.021	0.069	0.051
(95% confidence)	Strain at break	[%]	0.12	0.22	0.13	0.13
	Dynamic modulus	[kN/m]	0.28	0.80	1.68	0.89
	Elastic modulus	[kN/m]	11.62	13.17	12.91	9.32
	T.E.A.	[mJ]	1.95	1.46	8.84	8.60
	Strips	[-]	10	10	10	10

Dynamic tensile strength measurement with Impact test rig
Chemical pulp LFF & chemical pulp fines

	Strain rate	1.0	m/s			
	Sample length	100	mm			
	Sample width	20	mm			
	Grammage of samples	60	g/m^2			
	Dry samples					
Dryness [%]			92.2	92.6	91.9	92.1
Trial point			**Unfractioned**	**LFF**	**LFF+10% fines**	**LFF+20% fines**
Test rig			Impact	Impact	Impact	Impact
Average values	Tensile strength	[kN/m]	4.504	3.857	6.061	6.290
	Strain at break	[%]	2.65	2.39	3.43	3.50
	Dynamic modulus	[kN/m]	171.24	163.66	176.94	180.57
	Elastic modulus	[kN/m]	373.27	347.11	430.42	443.34
	T.E.A.	[mJ]	119.05	91.56	207.24	219.12
Deviations	Tensile strength	[kN/m]	0.162	0.195	0.132	0.069
(95% confidence)	Strain at break	[%]	0.19	0.25	0.11	0.12
	Dynamic modulus	[kN/m]	7.10	9.93	5.70	6.82
	Elastic modulus	[kN/m]	33.77	31.08	57.82	64.46
	T.E.A.	[mJ]	13.66	14.58	8.82	7.32
	Strips	[-]	10	10	10	10

Relaxation measurement with Impact test rig (1% strain)
Chemical pulp LFF & chemical pulp fines

	Strain	1	%			
	Relaxation time	0.475	s			
	Strain rate	1.0	m/s			
	Sample length	100	mm			
	Sample width	20	mm			
	Grammage of samples	60	g/m^2			
	Wet pressing	50	kPa			
Dryness [%]			48.1	55.8	50.8	45.0
Trial point			**Unfractioned**	**LFF**	**LFF+10% fines**	**LFF+20% fines**
Test rig			Impact	Impact	Impact	Impact
Average values	Initial tension	[N/m]	117.40	131.77	159.24	134.50
	Residual tension	[N/m]	51.13	49.96	61.39	50.99
Deviations	Initial tension	[N/m]	4.59	7.19	8.87	9.78
(95% confidence)	Residual tension	[N/m]	4.02	2.57	4.78	3.39
	Strips	[-]	10	10	10	10

Relaxation measurement with Impact test rig (1% strain)
Chemical pulp LFF & chemical pulp fines

	Strain	1	%			
	Relaxation time	0.475	s			
	Strain rate	1.0	m/s			
	Sample length	100	mm			
	Sample width	20	mm			
	Grammage of samples	60	g/m^2			
	Wet pressing	350	kPa			
Dryness [%]			58.1	65.0	66.2	55.3
Trial point			**Unfractioned**	**LFF**	**LFF+10% fines**	**LFF+20% fines**
Test rig			Impact	Impact	Impact	Impact
Average values	Initial tension	[N/m]	207.63	240.73	347.04	215.06
	Residual tension	[N/m]	84.83	95.82	138.91	89.20
Deviations	Initial tension	[N/m]	9.14	14.40	34.10	22.16
(95% confidence)	Residual tension	[N/m]	7.01	9.55	14.91	10.12
	Strips	[-]	10	10	9	10

Some paper technical properties
Chemical pulp LFF & chemical pulp fines

Trial point			**Unfractioned**	**LFF**	**LFF+10% fines**	**LFF+20% fines**
Test rig						
Average values	Density	[kg/m^3]	587	567	622	659
	Grammage	[g/m^2]	60.2	61.8	62.3	60.4
	Shrinkage	[%]	4.05	2.08	4.40	5.40
Deviations	Density	[kg/m^3]	10	6	5	6
(95% confidence)	Grammage	[g/m^2]	0.7	2.5	1.1	0.7
	Shrinkage	[%]	0.06	0.09	0.11	0.08

Appendix II: Results from Chapter 9 in table form

Dynamic tensile strength measurement with Impact test rig											
Pilot PM samples with different jet/wire-ratios											
Fine paper MD											
	Strain rate	1.0	m/s								
	Sample length	180	mm								
	Sample width	20	mm								
	Grammage of samples	70	g/m^2								
Dryness [%]			43.2	43.8	43.9	44.7	44.9	45.0	44.3	44.3	43.5
Trial point	**Jet/wire ratio**	**[-]**	**0.91**	**0.94**	**0.97**	**1**	**1.02**	**1.04**	**1.06**	**1.08**	**1.14**
Test rig			Impact	Impact	Impact	Impact	Impact	Impact	Impact	Impact	Impact
Average values	Tensile strength	[kN/m]	0.50	0.51	0.47	0.35	0.26	0.30	0.36	0.47	0.49
	Strain at break	[%]	2.31	2.55	2.18	2.27	2.36	2.25	2.31	2.40	2.52
	Dynamic modulus	[kN/m]	48.90	35.95	36.82	30.16	29.50	27.99	27.60	38.59	35.74
	Elastic modulus	[kN/m]	21.82	20.31	21.81	15.47	10.96	13.54	15.73	19.91	19.57
	On-line web tension	[N/m]	153	167	159	121	94	97	126	151	145
	Dry paper tensile strength	[kN/m]	6.25	6.41	5.84	4.53	3.32	3.41	4.37	5.87	6.33
Deviations	Tensile strength	[N/m]	13.32	13.94	20.47	15.59	43.81	19.85	28.06	23.14	13.53
(95% confidence)	Strain at break	[%]	0.31	0.23	0.09	0.11	0.24	0.17	0.16	0.26	0.20
	Dynamic modulus	[kN/m]	17.93	6.12	3.22	3.35	8.39	2.55	2.70	6.84	1.82
	Elastic modulus	[kN/m]	2.88	1.75	0.89	0.76	1.71	1.04	0.64	1.95	1.54
	Dry paper tensile strength	[N/m]	256	205	245	199	106	72	179	241	259
	Strips	[-]	10	10	10	10	10	10	10	10	10

Dynamic tensile strength measurement with Impact test rig											
Pilot PM samples with different jet/wire-ratios											
Fine paper CD											
	Strain rate	1.0	m/s								
	Sample length	180	mm								
	Sample width	20	mm								
	Grammage of samples	70	g/m^2								
Dryness [%]			43.2	43.8	43.9	44.7	44.9	45.0	44.3	44.3	43.5
Trial point	**Jet/wire ratio**	**[-]**	**0.91**	**0.94**	**0.97**	**1**	**1.02**	**1.04**	**1.06**	**1.08**	**1.14**
Test rig			Impact	Impact	Impact	Impact	Impact	Impact	Impact	Impact	Impact
Average values	Tensile strength	[kN/m]	0.08	0.10	0.11	0.15	0.18	0.18	0.16	0.14	0.10
	Strain at break	[%]	5.70	5.73	5.12	4.66	4.67	4.94	5.53	5.80	6.08
	Dynamic modulus	[kN/m]	1.44	1.72	2.14	3.35	3.84	3.74	2.85	2.35	1.60
	Elastic modulus	[kN/m]	5.55	7.78	7.49	11.01	11.88	12.33	8.50	7.14	7.24
	Dry paper tensile strength	[kN/m]	1.06	1.18	1.36	1.80	2.19	2.19	1.72	1.55	1.24
Deviations	Tensile strength	[N/m]	13.32	13.94	20.47	15.59	43.81	19.85	28.06	23.14	13.53
(95% confidence)	Strain at break	[%]	0.31	0.23	0.09	0.11	0.24	0.17	0.16	0.26	0.20
	Dynamic modulus	[kN/m]	17.93	6.12	3.22	3.35	8.39	2.55	2.70	6.84	1.82
	Elastic modulus	[kN/m]	2.88	1.75	0.89	0.76	1.71	1.04	0.64	1.95	1.54
	Dry paper tensile strength	[N/m]	23.31	34.33	29.93	50.45	48.20	92.12	37.92	58.95	27.36
	Strips	[-]	10	10	10	10	10	10	10	10	10

Relaxation measurement with Impact test rig (1% strain)											
Pilot PM samples with different jet/wire-ratios											
Fine paper MD											
	Strain	1	%								
	Relaxation time	0.475	s								
	Strain rate	1.0	m/s								
	Sample length	180	mm								
	Sample width	20	mm								
	Grammage of samples	70	g/m^2								
Dryness [%]			43.2	43.8	43.9	44.7	44.9	45.0	44.3	44.3	43.5
Trial point	**Jet/wire ratio**	**[-]**	**0.91**	**0.94**	**0.97**	**1**	**1.02**	**1.04**	**1.06**	**1.08**	**1.14**
Test rig			Impact	Impact	Impact	Impact	Impact	Impact	Impact	Impact	Impact
Average values	Initial tension	[N/m]	345.75	350.42	351.99	270.45	207.46	231.40	281.65	319.09	323.93
	Residual tension	[N/m]	165.85	171.00	159.13	120.39	86.22	96.80	124.79	147.78	154.43
Deviations	Initial tension	[N/m]	39.24	29.33	17.26	20.41	17.60	23.87	16.62	21.37	18.39
(95% confidence)	Residual tension	[N/m]	16.24	8.01	11.38	8.22	3.08	5.35	8.43	9.58	6.08
	Strips	[-]	10	10	10	10	10	10	10	10	10

Relaxation measurement with Impact test rig (1% strain)

Pilot PM samples with different jet/wire-ratios

Fine paper CD

	Strain	1	%								
	Relaxation time	0.475	s								
	Strain rate	1.0	m/s								
	Sample length	180	mm								
	Sample width	20	mm								
	Grammage of samples	70	g/m^2								
Dryness [%]			43.2	43.8	43.9	44.7	44.9	45.0	44.3	44.3	43.5
Trial point	**Jet/wire ratio**	**[-]**	**0.91**	**0.94**	**0.97**	**1**	**1.02**	**1.04**	**1.06**	**1.08**	**1.14**
Test rig			Impact	Impact	Impact	Impact	Impact	Impact	Impact	Impact	Impact
Average values	Initial tension	[N/m]	45.76	45.90	54.87	71.28	78.90	87.85	69.12	59.15	51.32
	Residual tension	[N/m]	17.01	17.18	21.26	28.87	31.79	34.02	27.76	22.70	17.22
Deviations	Initial tension	[N/m]	3.81	3.36	3.85	4.29	4.21	6.32	2.54	4.97	4.70
(95% confidence)	Residual tension	[N/m]	1.01	1.07	0.89	1.97	1.79	2.38	1.43	1.14	2.30
	Strips	[-]	10	10	10	10	10	10	10	10	10

Dynamic tensile strength measurement with Impact test rig

Pilot PM samples with different filler contents

Fine paper MD

	Strain rate	1.0	m/s			
	Sample length	180	mm			
	Sample width	20	mm			
	Grammage of samples	70	g/m^2			
Dryness [%]			38.6	43.0	45.7	46.8
Trial point	**Filler content**	**[%]**	**10%**	**15%**	**20%**	**25%**
Test rig			Impact	Impact	Impact	Impact
Average values	Tensile strength	[kN/m]	0.51	0.54	0.47	0.41
	Strain at break	[%]	2.91	2.28	2.16	2.28
	Dynamic modulus	[kN/m]	32.09	35.45	30.42	30.20
	Elastic modulus	[kN/m]	17.97	23.93	21.68	17.87
	On-line web tension	[N/m]	161.55	164.25	191.25	137.25
	Dry paper tensile strength	[kN/m]	8.87	7.65	6.13	5.53
Deviations	Tensile strength	[N/m]	20.35	12.16	23.70	17.43
(95% confidence)	Strain at break	[%]	0.45	0.18	0.20	0.17
	Dynamic modulus	[kN/m]	10.29	8.93	8.81	2.93
	Elastic modulus	[kN/m]	2.64	1.87	1.34	1.26
	Dry paper tensile strength	[N/m]	72.30	45.30	44.70	50.45
	Strips	[-]	10	10	11	10

Relaxation measurement with Impact test rig (1% strain)

Pilot PM samples with different filler contents

Fine paper MD

	Strain	1	%			
	Relaxation time	0.475	s			
	Strain rate	1.0	m/s			
	Sample length	180	mm			
	Sample width	20	mm			
	Grammage of samples	70	g/m^2			
Dryness [%]			38.6	43.0	45.7	46.8
Trial point	**Filler content**	**[%]**	**10%**	**15%**	**20%**	**25%**
Test rig			Impact	Impact	Impact	Impact
Average values	Initial tension	[N/m]	322.06	348.69	350.38	313.13
	Residual tension	[N/m]	149.79	161.06	165.86	146.99
Deviations	Initial tension	[N/m]	20.77	33.26	27.58	18.33
(95% confidence)	Residual tension	[N/m]	5.58	13.93	8.46	8.02
	Strips	[-]	10	10	10	10

Appendix III: Results from Chapter 10 in table form

Drying method	Restrained shrinkage/wet samples				
Trial point	Unit	Ref. thickened	15 min mech. treated	45 min mech. treated	Hot disintegrated
Shape Factor	%	83.65	80.4	78.54	83.96
Kinks	1/mm	0.37	0.65	0.82	0.36
CSF	ml	513	642	645	460
WRV	-	1.97	1.73	1.69	1.87
Drainage Time	s	4.81	4.34	4.22	4.92
Tensile Index	Nm/g	75.3	55.3	49.1	81.2
Strain at break	%	4.5	4.9	4.8	4.7
Elastic modulus	N/mm^2	4181	3482	3271	4367
Z-directional delamination energy, Huygen	J/m^2	522	555	602	484
Residual Tension, 50 kPa, 2%	N/m	43.6	31.2	27.9	35.2
Residual Tension, 350 kPa, 2%	N/m	137.6	84.8	78.0	132.5
Tensile Strength, N/m 50 kPa	N/m	159	123	112	165
Tensile Strength, N/m 50 kPa	N/m	698	428	373	691
Strain at break, 50 kPa	%	3.9	5.4	5.6	4.1
Strain at break, 350 kPa	%	6.6	8.7	8.9	6.0
Dryness 50 kPa	%	41.8	44.2	46.1	41.5
Dryness 350 kPa	%	57.5	56.6	58.4	56.7
Grammage	g/m^2	61.9	64.0	59.2	61.6
Density	kg/m^3	689	684	662	703
Light Scattering coefficient, m^2/kg	m^2/kg	19.2	20.4	20.2	19.5
Deviations					
(95% confidence)		Ref. thickened	15 min mech. treated	45 min mech. treated	Hot disintegrated
Average Shape Factor	%	0.17	0.34	0.28	0.11
Kinks	1/mm	0.01	0.01	0.02	0.00
Drainage Time	s	0.07	0.09	0.06	0.05
Tensile Index	Nm/g	75.3	55.3	49.1	81.2
Strain at break	%	0.2	0.3	0.4	0.3
Elastic modulus	N/mm^2	162	229	81	196
Z-directional delamination energy, Huygen	J/m^2	7	8	8	9
Residual Tension, 50 kPa, 2%	N/m	2.4	3.2	3.2	4.3
Residual Tension, 350 kPa, 2%	N/m	10.2	8.0	5.5	4.8
Tensile Strength, N/m 50 kPa	N/m	17.2	13.0	12.1	28.4
Tensile Strength, N/m 50 kPa	N/m	33.4	17.6	12.1	36.9
Strain at break, 50 kPa	%	0.3	0.5	0.7	0.4
Strain at break, 350 kPa	%	0.3	0.3	0.6	0.2
Dryness 50 kPa	%	0.6	0.2	0.4	1.3
Dryness 350 kPa	%	0.7	1.0	0.2	1.2
Grammage	g/m^2	0.5	1.2	0.7	0.7
Density	kg/m^3	9.7	6.8	7.5	7.3
Light Scattering coefficient, m^2/kg	m^2/kg	19.2	20.4	20.2	19.5

Drying method		Free shrinkage			
Trial point	Unit	Ref. thickened	15 min mech. treated	45 min mech. treated	Hot disintegrated
Shrinkage	%	5.4	6.8	6.9	5.3
Tensile Index	Nm/g	60.3	43.1	36.2	65.7
Strain at break	%	9.4	10.7	11.1	9.5
Elastic modulus	N/mm^2	1215	984	860	1231
Deviations		Free shrinkage			
(95% confidence)		Ref. thickened	15 min mech. treated	45 min mech. treated	Hot disintegrated
Shrinkage	%	0.3	0.2	0.5	0.2
Tensile Index	Nm/g	5.7	1.6	1.8	4.3
Strain at break	%	0.4	0.6	0.7	0.5
Elastic modulus	N/mm^2	140	136	79	125

Drying method		3% straining			
Trial point	Unit	Ref. thickened	15 min mech. treated	45 min mech. treated	Hot disintegrated
Tensile Index	Nm/g	78.1	53.7	43.7	83.9
strain at break	%	3.63	4.68	4.83	3.08
Elastic modulus	N/mm^2	5070	3788	3068	5668
Z-directional delamination energy, Huygen	J/m^2	501	548	536	419
Deviations		3% straining			
(95% confidence)		Ref. thickened	15 min mech. treated	45 min mech. treated	Hot disintegrated
Tensile Index	Nm/g	5.7	4.0	2.4	4.1
Strain at break	%	0.4	0.7	0.9	0.5
Elastic modulus	N/mm^2	387	361	208	403
Z-directional delamination energy, Huygen	J/m^2	8	7	9	11

Appendix IV: Results from Chapter 11 in table form

Dynamic tensile strength measurement with Impact test rig

Strain rate	1.0	m/s	
Sample length	100	mm	
Sample width	20	mm	
Grammage of samples	60	g/m²	
Wet pressing	50	kPa	

Dryness [%]			48.4	52.6	57.8	52.8	48.7
Trial point			**Distilled water**	**TMP filtrate**	**Surfactant**	**Oleaic acid**	**Defoamer**
Test rig			Impact	Impact	Impact	Impact	Impact
Average values	Tensile strength	[kN/m]	0.27	0.36	0.50	0.37	0.28
	Strain at break	[%]	4.70	4.61	4.93	4.78	4.43
	Dynamic modulus	[kN/m]	5.81	7.80	10.18	7.71	6.43
	Elastic modulus	[kN/m]	14.61	16.24	21.17	15.89	13.87
	T.E.A.	[mJ]	16.42	20.68	29.37	21.53	16.08
Deviations	Tensile strength	[N/m]	22.22	50.82	48.72	40.60	7.40
(95% confidence)	Strain at break	[%]	0.22	0.40	0.37	0.42	0.32
	Dynamic modulus	[kN/m]	0.39	0.74	1.55	1.03	0.51
	Elastic modulus	[kN/m]	2.49	2.65	2.86	2.88	2.03
	T.E.A.	[mJ]	1.92	4.85	2.81	3.16	1.21
	Strips	[-]	7	10	10	10	11

Dynamic tensile strength measurement with Impact test rig

Strain rate	1.0	m/s	
Sample length	100	mm	
Sample width	20	mm	
Grammage of samples	60	g/m²	
Wet pressing	350	kPa	

Dryness [%]			61.7	62.5	65.0	63.0	60.6
Trial point			**Distilled water**	**TMP filtrate**	**Surfactant**	**Oleaic acid**	**Defoamer**
Test rig			Impact	Impact	Impact	Impact	Impact
Average values	Tensile strength	[kN/m]	0.76	0.84	0.85	0.86	0.72
	Strain at break	[%]	5.21	5.14	5.07	5.17	5.04
	Dynamic modulus	[kN/m]	14.52	16.43	16.76	16.72	14.27
	Elastic modulus	[kN/m]	30.96	31.07	33.61	35.54	28.85
	T.E.A.	[mJ]	45.22	49.84	48.31	50.95	41.81
Deviations	Tensile strength	[N/m]	37.54	70.97	31.73	45.01	27.87
(95% confidence)	Strain at break	[%]	0.12	0.17	0.32	0.23	0.35
	Dynamic modulus	[kN/m]	0.80	1.27	0.96	1.28	0.77
	Elastic modulus	[kN/m]	3.10	3.15	4.06	4.95	4.57
	T.E.A.	[mJ]	2.40	5.86	4.53	2.76	4.36
	Strips	[-]	8	10	10	10	10

Dynamic tensile strength measurement with Impact test rig

	Strain rate	**1.0**	m/s	
	Sample length	**100**	mm	
	Sample width	**20**	mm	
	Grammage of samples	**60**	g/m^2	
	Dry samples			

Dryness [%]			Dry	Dry	Dry	Dry	Dry
Trial point			**Distilled water**	**TMP filtrate**	**Surfactant**	**Oleaic acid**	**Defoamer**
Test rig			Impact	Impact	Impact	Impact	Impact
Average values	Tensile strength	[kN/m]	5.39	4.69	4.49	5.13	5.23
	Strain at break	[%]	3.72	3.94	3.10	3.61	3.47
	Dynamic modulus	[kN/m]	144.84	119.56	145.65	143.05	151.40
	Elastic modulus	[kN/m]	406.25	346.72	403.59	417.24	391.64
	T.E.A.	[mJ]	208.67	192.49	149.55	193.35	187.59
Deviations	Tensile strength	[N/m]	224.56	136.69	168.38	181.25	266.84
(95% confidence)	Strain at break	[%]	0.16	0.28	0.25	0.32	0.25
	Dynamic modulus	[kN/m]	5.24	8.96	9.05	12.95	12.88
	Elastic modulus	[kN/m]	34.95	15.81	23.16	49.10	31.15
	T.E.A.	[mJ]	16.70	14.40	17.17	19.77	17.20
	Strips	[-]	10	10	10	10	8

Relaxation measurement with Impact test rig (1% strain)

Strain	**1**	%	
Relaxation time	**0.475**	s	
Strain rate	**1.0**	m/s	
Sample length	**100**	mm	
Sample width	**20**	mm	
Grammage of samples	**60**	g/m^2	
Wet pressing	**50**	kPa	

Dryness [%]			48.4	52.6	57.8	52.8	48.7
Trial point			**Distilled water**	**TMP filtrate**	**Surfactant**	**Oleaic acid**	**Defoamer**
Test rig			Impact	Impact	Impact	Impact	Impact
Average values	Initial tension	[N/m]	114.57	130.90	171.94	136.15	122.43
	Residual tension	[N/m]	43.92	53.74	71.79	54.51	46.33
Deviations	Initial tension	[N/m]	4.44	7.04	23.90	10.55	8.16
(95% confidence)	Residual tension	[N/m]	1.96	2.67	11.13	13.99	12.30
	Strips	[-]	10	9	10	10	10

Relaxation measurement with Impact test rig (1% strain)

Strain	**1**	%	
Relaxation time	**0.475**	s	
Strain rate	**1.0**	m/s	
Sample length	**100**	mm	
Sample width	**20**	mm	
Grammage of samples	**60**	g/m^2	
Wet pressing	**350**	kPa	

Dryness [%]			61.7	62.5	65.0	63.0	60.6
Trial point			**Distilled water**	**TMP filtrate**	**Surfactant**	**Oleaic acid**	**Defoamer**
Test rig			Impact	Impact	Impact	Impact	Impact
Average values	Initial tension	[N/m]	242.21	236.03	257.50	237.60	222.66
	Residual tension	[N/m]	99.96	96.33	104.30	98.09	95.82
Deviations	Initial tension	[N/m]	12.35	18.76	16.05	18.24	16.86
(95% confidence)	Residual tension	[N/m]	6.20	8.14	6.79	7.29	7.37
	Strips	[-]	10	10	10	10	10

Relaxation measurement with Impact test rig (2% strain)

	Strain	2	%				
	Relaxation time	0.475	s				
	Strain rate	1.0	m/s				
	Sample length	100	mm				
	Sample width	20	mm				
	Grammage of samples	60	g/m^2				
	Wet pressing	50	kPa				
Dryness [%]			48.4	52.6	57.8	52.8	48.7
Trial point			**Distilled water**	**TMP filtrate**	**Surfactant**	**Oleaic acid**	**Defoamer**
Test rig			Impact	Impact	Impact	Impact	Impact
Average values	Initial tension	[N/m]	160.35	185.96	232.70	181.83	168.20
	Residual tension	[N/m]	82.46	94.30	117.09	94.36	86.69
Deviations	Initial tension	[N/m]	12.22	19.18	32.87	23.90	10.16
(95% confidence)	Residual tension	[N/m]	6.21	8.23	16.82	13.09	5.34
	Strips	[-]	10	10	10	11	10

Relaxation measurement with Impact test rig (2% strain)

	Strain	2	%				
	Relaxation time	0.475	s				
	Strain rate	1.0	m/s				
	Sample length	100	mm				
	Sample width	20	mm				
	Grammage of samples	60	g/m^2				
	Wet pressing	50	kPa				
Dryness [%]			61.7	62.5	65.0	63.0	60.6
Trial point			**Distilled water**	**TMP filtrate**	**Surfactant**	**Oleaic acid**	**Defoamer**
Test rig			Impact	Impact	Impact	Impact	Impact
Average values	Initial tension	[N/m]	348.30	344.16	368.10	354.84	327.43
	Residual tension	[N/m]	175.51	173.52	177.81	171.89	163.24
Deviations	Initial tension	[N/m]	12.62	20.93	30.23	34.58	20.93
(95% confidence)	Residual tension	[N/m]	5.23	12.21	15.96	15.41	11.46
	strips	[-]	10	10	10	10	10

Some additional results

Trial point			**Distilled water**	**TMP filtrate**	**Surfactant**	**Oleaic acid**	**Defoamer**
Test rig			Impact	Impact	Impact	Impact	Impact
Average values	Grammage	[g/m2]	57.8	58.2	63.7	59.2	59.0
	Density (dry)	[kg/m3]	632	596	613	622	631
	Density (50 kPa)	[kg/m3]	382	379	412	384	374
	Density (350 kPa)	[kg/m3]	501	492	553	482	512
	Light scattering coefficient	[m^2/kg]	26.0	33.3	25.2	25.8	26.0
	pH of white water	[-]	6.9	7.2	6.7	6.5	6.8
	Shrinkage potential	[%]	3.1	3.0	3.0	3.1	3.4
Deviations	Grammage	[g/m2]	0.7	0.7	3.1	0.7	0.9
(95% confidence)	Density	[kg/m3]	2.7	3.4	7.8	3.6	2.4
	Density (50 kPa)	[kg/m3]	3.2	2.5	6.0	5.3	3.8
	Density (350 kPa)	[kg/m3]	3.5	3.6	3.1	2.3	2.4
	Light scattering coefficient	[m^2/kg]	0.5	0.5	1.0	0.3	0.3
	pH of white water	[-]	0.2	0.1	0.3	0.4	0.2
	Shrinkage potential	[%]	0.1	0.2	0.0	0.1	0.1

Extractive type	Content in white water	STDEV
in TMP filtrate	[mg/l]	[mg/l]
Fattyacids	22.7	2.6
Resin acids	47.2	0.8
Lignans	3.7	0.5
Sitosterol	7.2	1.0
Steryl esters	95.2	12.7
Triglyserides	196.2	23.7
Total lipophilic extractives	368.5	40.8

Appendix V: Results from Chapter 12 in table form

Dynamic tensile strength measurement with Impact test rig

	Strain rate	1.0	m/s								
	Sample length	100	mm								
	Sample width	20	mm								
	Grammage of samples	60	g/m^2								
	Wet pressing	50	kPa								
Dryness [%]				50.0	50.2	50.2	51.0	47.3	47.8	50.9	52.1	51.1
Trial point				**Reference**	**CMC 1 g/m2**	**CMC 2 g/m2**	**Chitosan 2 g/m2**	**CMC + Chitosan 1 g/m2 + 1 g/m2**	**PVA 1 g/m2**	**CMC + C-PAM 1 g/m2 + 0.5 g/m2**	**A-PAM + C-PAM 0.5 g/m2 + 0.5 g/m2**	**A-PAM + C-PAM 0.5% + 0.5 % to pulp**
Test rig				Impact	Impact	Impact	Impact	Impact	Impact	Impact	Impact	Impact
Average values	Tensile strength	[kN/m]		0.19	0.22	0.18	0.19	0.25	0.22	0.33	0.44	0.22
	Strain at break	[%]		7.38	6.88	6.71	6.61	6.67	7.29	7.37	7.11	7.42
	Dynamic modulus	[kN/m]		2.75	3.26	2.68	2.98	3.78	3.06	4.45	6.15	2.99
	Elastic modulus	[kN/m]		13.36	14.87	13.21	12.58	12.92	12.46	14.01	15.80	11.60
	T.E.A.	[mJ]		22.19	22.32	17.77	19.25	23.46	22.51	31.00	38.60	22.76
Deviations	Tensile strength	[N/m]		0.01	0.03	0.01	0.01	0.02	0.02	0.03	0.01	0.02
(95% confidence)	Strain at break	[%]		0.3	0.5	0.5	0.60	0.47	0.22	0.57	0.29	0.20
	Dynamic modulus	[kN/m]		0.13	0.50	0.29	0.30	0.30	0.24	0.22	0.29	0.26
	Elastic modulus	[kN/m]		0.91	1.92	1.07	0.64	1.41	0.68	1.26	0.87	0.83
	T.E.A.	[mJ]		1.30	3.27	1.77	2.22	2.94	2.04	3.91	2.15	1.96
	Strips	[-]		10	10	10	10	10	10	10	10	10

Dynamic tensile strength measurement with Impact test rig

	Strain rate	1.0	m/s								
	Sample length	100	mm								
	Sample width	20	mm								
	Grammage of samples	60	g/m^2								
	Wet pressing	350	kPa								
Dryness [%]				59.3	55.8	56.5	57.7	59.7	61.2	58.2	60.6	58.7
Trial point				**Reference**	**CMC 1 g/m2**	**CMC 2 g/m2**	**Chitosan 2 g/m2**	**CMC + Chitosan 1 g/m2 + 1 g/m2**	**PVA 1 g/m2**	**CMC + C-PAM 1 g/m2 + 0.5 g/m2**	**A-PAM + C-PAM 0.5 g/m2 + 0.5 g/m2**	**A-PAM + C-PAM 0.5% + 0.5 % to pulp**
Test rig				Impact	Impact	Impact	Impact	Impact	Impact	Impact	Impact	Impact
Average values	Tensile strength	[kN/m]		0.47	0.45	0.46	0.50	0.95	0.79	0.77	0.96	0.54
	Strain at break	[%]		7.30	6.91	7.04	6.85	8.43	7.07	7.53	8.41	7.11
	Dynamic modulus	[kN/m]		6.39	6.54	6.60	7.33	11.29	11.17	10.31	11.40	8.05
	Elastic modulus	[kN/m]		23.06	19.39	20.50	20.41	23.76	27.93	24.18	22.70	23.76
	T.E.A.	[mJ]		45.55	41.35	44.00	45.56	95.38	68.19	69.81	94.49	51.29
Deviations	Tensile strength	[N/m]		0.01	0.03	0.01	0.01	0.02	0.02	0.03	0.01	0.03
(95% confidence)	Strain at break	[%]		0.3	0.6	0.4	0.40	0.43	0.18	0.43	0.37	0.3
	Dynamic modulus	[kN/m]		0.13	0.50	0.29	0.30	0.30	0.24	0.22	0.29	0.7
	Elastic modulus	[kN/m]		0.91	1.92	1.07	0.64	1.41	0.68	1.26	0.87	1.5
	T.E.A.	[mJ]		1.30	3.27	1.77	2.22	2.94	2.04	3.91	2.15	3.3
	Strips	[-]		10	10	10	10	10	10	10	10	10

Dynamic tensile strength measurement with Impact test rig

	Strain rate	1.0	m/s								
	Sample length	100	mm								
	Sample width	20	mm								
	Grammage of samples	60	g/m^2								
	Dry samples										
Dryness [%]				Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry
Trial point				**Reference**	**CMC 1 g/m2**	**CMC 2 g/m2**	**Chitosan 2 g/m2**	**CMC + Chitosan 1 g/m2 + 1 g/m2**	**PVA 1 g/m2**	**CMC + C-PAM 1 g/m2 + 0.5 g/m2**	**A-PAM + C-PAM 0.5 g/m2 + 0.5 g/m2**	**A-PAM + C-PAM 0.5% + 0.5 % to pulp**
Test rig				Impact	Impact	Impact	Impact	Impact	Impact	Impact	Impact	Impact
Average values	Tensile strength	[kN/m]		3.29	3.96	3.92	3.62	4.29	3.45	3.24	3.78	3.20
	Strain at break	[%]		3.52	4.40	4.48	4.18	4.49	3.89	4.16	4.39	3.52
	Dynamic modulus	[kN/m]		94.10	90.13	87.97	87.02	96.22	88.89	78.05	86.19	91.93
	Elastic modulus	[kN/m]		225.90	239.74	233.37	240.86	249.86	247.65	209.18	222.41	201.57
	T.E.A.	[mJ]		124.61	186.08	188.01	164.44	202.82	147.24	146.07	176.49	118.94
Deviations	Tensile strength	[N/m]		0.07	0.15	0.10	0.10	0.12	0.09	0.05	0.01	186.16
(95% confidence)	Strain at break	[%]		0.2	0.1	0.2	0.19	0.28	0.14	0.14	0.20	0.40
	Dynamic modulus	[kN/m]		5.17	3.94	3.45	2.97	4.91	3.64	2.72	2.42	9.41
	Elastic modulus	[kN/m]		3.60	10.60	8.18	8.60	9.03	9.43	7.51	11.07	15.96
	T.E.A.	[mJ]		8.07	10.15	13.47	11.42	17.41	7.25	6.65	14.93	20.74
	Strips	[-]		10	10	10	10	10	10	10	10	10

Relaxation measurement with Impact test rig (2% strain)

	Strain	2	%
	Relaxation time	0.475	s
	Strain rate	1.0	m/s
	Sample length	100	mm
	Sample width	20	mm
	Grammage of samples	60	g/m^2
	Wet pressing	50	kPa

Dryness [%]			50.0	50.2	50.2	51.0	47.3	47.8	50.9	52.1
Trial point			**Reference**	**CMC 1 g/m2**	**CMC 2 g/m2**	**Chitosan 2 g/m2**	**CMC + Chitosan 1 g/m2 + 1 g/m2**	**PVA 1 g/m2**	**CMC + C-PAM 1 g/m2 + 0.5 g/m2**	**A-PAM + C-PAM 0.5 g/m2 + 0.5 g/m2**
Test rig			Impact	Impact	Impact	Impact	Impact	Impact	Impact	Impact
Average values	Initial tension	[N/m]	60.17	64.32	57.61	61.37	57.05	50.60	69.40	82.27
	Residual tension	[N/m]	23.65	24.39	20.06	20.85	19.02	19.54	23.58	27.52
Deviations	Initial tension	[N/m]	3.43	4.78	3.46	3.09	4.27	4.30	4.69	5.20
(95% confidence)	Residual tension	[N/m]	2.3	2.6	1.6	1.68	0.92	1.85	1.69	1.13
	Strips	[-]	10	10	10	10	9	10	6	10

Relaxation measurement with Impact test rig (2% strain)

	Strain	2	%
	Relaxation time	0.475	s
	Strain rate	1.0	m/s
	Sample length	100	mm
	Sample width	20	mm
	Grammage of samples	60	g/m^2
	Wet pressing	350	kPa

Dryness [%]			59.3	55.8	56.5	57.7	59.7	61.2	58.2	60.6
Trial point			**Reference**	**CMC 1 g/m2**	**CMC 2 g/m2**	**Chitosan 2 g/m2**	**CMC + Chitosan 1 g/m2 + 1 g/m2**	**PVA 1 g/m2**	**CMC + C-PAM 1 g/m2 + 0.5 g/m2**	**A-PAM + C-PAM 0.5 g/m2 + 0.5 g/m2**
Test rig			Impact	Impact	Impact	Impact	Impact	Impact	Impact	Impact
Average values	Initial tension	[N/m]	113.48	103.40	108.05	116.54	125.98	129.02	120.45	142.38
	Residual tension	[N/m]	47.75	40.08	42.40	43.82	49.33	50.74	45.70	55.19
Deviations	Initial tension	[N/m]	2.87	11.73	4.66	7.97	10.37	7.46	12.35	6.73
(95% confidence)	Residual tension	[N/m]	2.2	5.8	3.1	3.18	3.88	2.50	4.88	3.92
	Strips	[-]	10	10	10	10	10	10	10	10

Some paper technical properties

Trial point			**Reference**	**CMC 1 g/m2**	**CMC 2 g/m2**	**Chitosan 2 g/m2**	**CMC + Chitosan 1 g/m2 + 1 g/m2**	**PVA 1 g/m2**	**CMC + C-PAM 1 g/m2 + 0.5 g/m2**	**A-PAM + C-PAM 0.5 g/m2 + 0.5 g/m2**
Test rig			Impact	Impact	Impact	Impact	Impact	Impact	Impact	Impact
Average values	Density	[N/m]	585	581	573	594	585	588	600	600
	Grammage	[g/m2]	62	60	61	60	62	59	62	60
	Air permeance	[ml/min]	1436	1858	2504	2218	2058	2054	2129	2129
Deviations	Density	[N/m]	4	4	12	3	6	6	7	5
(95% confidence)	Grammage	[g/m2]	0.5	0.6	1.1	0.5	0.5	0.7	0.8	0.7
	Air permeance	[ml/min]	68	97	312	204	133	253	80	83

Appendix VI: Results from Chapter 13 in table form

Dynamic tensile strength measurement with Impact test rig

	Strain rate	1.0	m/s		
	Sample length	100	mm		
	Sample width	20	mm		
	Grammage of samples	60	g/m²		
	Wet pressing	50	kPa		
Dryness [%]			40.7	41.5	38.9
Trial point			**Original furnih with no chemicals**	**Original furnish + starch & polymer**	**Long fibres+starch / short fibre+polymer**
Test rig			Impact	Impact	Impact
Average values	Tensile strength	[kN/m]	0.21	0.20	0.20
	Strain at break	[%]	6.03	7.00	7.07
	Dynamic modulus	[kN/m]	3.42	2.87	2.85
	Elastic modulus	[kN/m]	8.91	6.66	6.36
	T.E.A.	[mJ]	16.64	18.97	18.79
Deviations	Tensile strength	[N/m]	5.32	8.38	3.08
(95% confidence)	Strain at break	[%]	0.2	0.5	0.2
	Dynamic modulus	[kN/m]	0.17	0.20	0.12
	Elastic modulus	[kN/m]	1.08	0.99	0.61
	T.E.A.	[mJ]	0.85	1.79	0.55
	Strips	[-]	10	10	10

Dynamic tensile strength measurement with Impact test rig

	Strain rate	1.0	m/s		
	Sample length	100	mm		
	Sample width	20	mm		
	Grammage of samples	60	g/m²		
	Wet pressing	350	kPa		
Dryness [%]			51.4	54.6	52.1
Trial point			**Original furnih with no chemicals**	**Original furnish + starch & polymer**	**Long fibres+starch / short fibre+polymer**
Test rig			Impact	Impact	Impact
Average values	Tensile strength	[kN/m]	0.43	0.58	0.60
	Strain at break	[%]	6.91	7.73	7.88
	Dynamic modulus	[kN/m]	6.28	7.52	7.68
	Elastic modulus	[kN/m]	17.98	14.53	14.78
	T.E.A.	[mJ]	40.37	55.08	60.13
Deviations	Tensile strength	[N/m]	23.65	37.45	37.45
(95% confidence)	Strain at break	[%]	0.50	0.51	0.51
	Dynamic modulus	[kN/m]	0.33	0.72	0.72
	Elastic modulus	[kN/m]	2.74	1.12	1.12
	T.E.A.	[mJ]	5.18	5.27	5.27
	Strips	[-]	10	10	10

Relaxation measurement with Impact test rig (1% strain)

	Strain	1	%		
	Relaxation time	0.475	s		
	Strain rate	1.0	m/s		
	Sample length	100	mm		
	Sample width	20	mm		
	Grammage of samples	60	g/m²		
	Wet pressing	50	kPa		
Dryness [%]			40.7	41.5	38.9
Trial point			**Original furnih with no chemicals**	**Original furnish + starch & polymer**	**Long fibres+starch / short fibre+polymer**
Test rig			Impact	Impact	Impact
Average values	Initial tension	[N/m]	74.72	74.88	68.41
	Residual tension	[N/m]	28.03	24.98	24.71
Deviations	Initial tension	[N/m]	6.21	4.96	8.87
(95% confidence)	Residual tension	[N/m]	1.62	1.92	2.69
	Strips	[-]	11	10	10

Relaxation measurement with Impact test rig (1% strain)

	Strain	1	%		
	Relaxation time	0.475	s		
	Strain rate	1.0	m/s		
	Sample length	100	mm		
	Sample width	20	mm		
	Grammage of samples	60	g/m^2		
	Wet pressing	350	kPa		
Dryness [%]			51.4	54.6	52.1
Trial point			**Original furnih with no chemicals**	**Original furnish + starch & polymer**	**Long fibres+starch / short fibre+polymer**
Test rig			Impact	Impact	Impact
Average values	Initial tension	[N/m]	158.21	170.96	162.83
	Residual tension	[N/m]	64.44	69.42	67.94
Deviations	Initial tension	[N/m]	4.16	5.44	8.63
(95% confidence)	Residual tension	[N/m]	4.36	2.60	3.37
	strips	[-]	10	10	10

Relaxation measurement with Impact test rig (2% strain)

	Strain	2	%		
	Relaxation time	0.475	s		
	Strain rate	1.0	m/s		
	Sample length	100	mm		
	Sample width	20	mm		
	Grammage of samples	60	g/m^2		
	Wet pressing	50	kPa		
Dryness [%]			40.7	41.5	38.9
Trial point			**Original furnih with no chemicals**	**Original furnish + starch & polymer**	**Long fibres+starch / short fibre+polymer**
Test rig			Impact	Impact	Impact
Average values	Initial tension	[N/m]	118.99	108.74	111.14
	Residual tension	[N/m]	43.26	36.96	41.34
Deviations	Initial tension	[N/m]	10.59	9.80	9.64
(95% confidence)	Residual tension	[N/m]	4.84	4.16	4.31
	Strips	[-]	10	10	10

Relaxation measurement with Impact test rig (2% strain)

	Strain	2	%		
	Relaxation time	0.475	s		
	Strain rate	1.0	m/s		
	Sample length	100	mm		
	Sample width	20	mm		
	Grammage of samples	60	g/m^2		
	Wet pressing	350	kPa		
Dryness [%]			51.4	54.6	52.1
Trial point			**Original furnih with no chemicals**	**Original furnish + starch & polymer**	**Long fibres+starch / short fibre+polymer**
Test rig			Impact	Impact	Impact
Average values	Initial tension	[N/m]	261.62	238.72	245.49
	Residual tension	[N/m]	114.06	100.09	100.65
Deviations	Initial tension	[N/m]	18.39	12.97	15.32
(95% confidence)	Residual tension	[N/m]	6.55	10.36	15.88
	Strips	[-]	10	10	10

Dewatering properties

Trial point			**Original furnih with no chemicals**	**Original furnish + starch & polymer**	**Long fibres+starch / short fibre+polymer**
Test rig			Filtration device	Filtration device	Filtration device
Average values	Drainage time	[s]	108.5	45.5	38.0
	Drainage resistance, 10s	[kg/m^{2}s]	3532000	1087000	809400
	Drainage resistance, 20s	[kg/m^{2}s]	2626000	756800	559600
	Drainage resistance, 30s	[kg/m^{2}s]	3398000	1026000	802850

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