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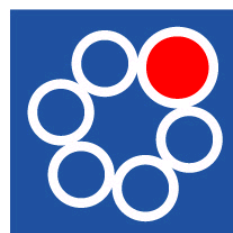
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Chemical Routes for Improving Z-Strength on Laboratory Sheets

Master of Science Thesis, 20 Credits

by

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Abstract

Paper hand sheets have been manufactured from mainly pure CTMP (Chemi Thermo-mechanical Pulp), but also in mixture with Kraft Pulp (Chemical pulp). The manufacture was performed in two different sheet formers, the Finnish sheet former and the Rapid Köhten sheet former, investigating the effect in z-strength of some chemical additives. The used chemical additions were cationic starch, cationic and anionic polyacrylamides and microfibrillated cellulose. Measurements of the delamination resistance (z-strength) was done on all sheets, and the formation was analysed in some of the sheets. The effect of different counter ion-forms of the pulp and varied pulp concentration have also been studied.

The z-strength was increased by all types of additions. The addition of cationic starch combined with anionic polyacrylamide gave the highest z-strength values. There was a difference in z-strength between the two forming methods, where the Rapid Köhten apparatus gave higher sheet density and higher z-strength than the Finnish sheet former. In this work z-strength was found to be not connected to the formation of the paper.

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Chapter 1

Introduction and Purpose

Liquid carton board is used as package for liquids, and it is produced in a multi-layered structure, where each layer has specific properties in order to protect the liquid and the package.

The paper board is produced in layers. The surface layers often consist of Kraft Pulp (Chemical pulp) separated by a the middle layer that often consist of Chemimechanical pulp (CTMP). CTMP is used due to its high bulk (low density) that is preferred in the paper board in order to obtain a high bending stiffness. One problem is the low z-strength in CTMP (the strength in the thickness direction of the paper). That has to be improved in order to achieve the wanted stability, strength and convertability (creasing) of the board. The z-strength can be increased by increasing the fibre-fibre bond. The formation of the paper could also be a factor that affects the z-strength. The influence of different additions such as polymer additives and microfibrillated cellulose were investigated in this work.

The aim with this work was to study different chemical routes to improve z-strength in laboratory sheets, mainly made of CTMP. Further on, that could hopefully be applied in the production of paper board to achieve a decrease in the raw material use.

Chapter 2

Background

2.1 The Wood Fibre

Wood is the most commonly used raw material for paper production. The properties of wood fibres are prescribed by the structure and chemical composition. Wood mainly consists of the polymeric substances cellulose, hemicelluloses and lignin. The relative composition varies between different types of wood. Some information about the structure in the cell wall and in the fibre is given in this section.

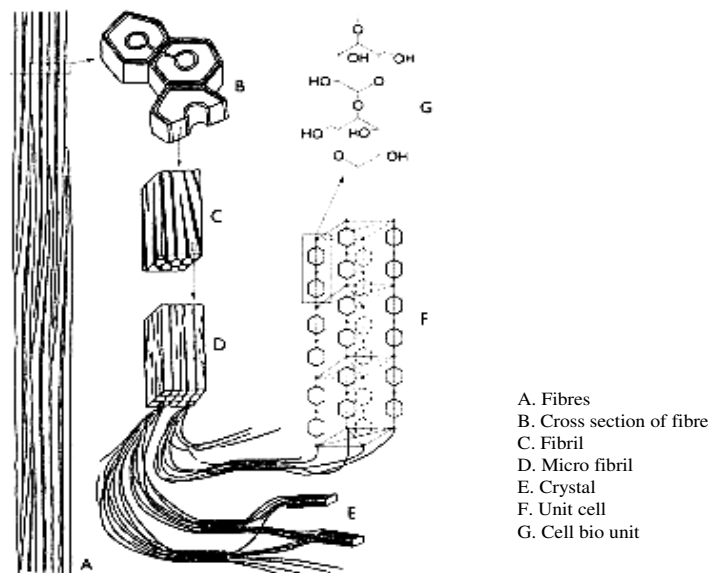


Figure 2.1: *The organisation of cellulose in the fibre [5].*

2.1.1 Cellulose

Cellulose is synthesised by most plant species. The cellulose content differs between, for example, wood and cotton, and is 40-50 % and 95-99 %, respectively. Cellulose consists of covalently connected glucose monomers creating linear polysaccharides. The degree of polymerisation (DP) is high, around 10 000. The chains are arranged in microfibril elements by hydrogen bonding between neighbouring cellulose chains. These microfibrils have amorphous and crystalline segments alternating where the crystalline cellulose is very strong and has a modulus around 140 GPa. The microfibrils build up the cellulose fibres (see Figure 2.1). The microfibrils vary in size and cross sectional shape depending on the source of the cellulosic material. Because of the high strength, the cellulose works as a skeleton in the wood fibre walls. [5], [7]

2.1.2 Hemicelluloses

Hemicelluloses occur together with cellulose in plant cell walls as a supporting structure. The type and amount of hemicelluloses vary widely. Wood consists of 20-35 % hemicelluloses. The hemicelluloses are a group of polysaccharides consisting of different monomers depending on type of wood. The most common monomers are mannose, glucose, xylose, arabinose and galactose. Hemicelluloses are often branched, unlike cellulose and it is easily decomposed, which results in lower degree of polymerisation than for cellulose after pulping, (DP is between 150 and 200). The function of hemicelluloses in wood is to contribute to flexibility and it works as linkage between cellulose and lignin as well as between fibres. [5], [7]

2.1.3 Lignin

Most of the lignin is situated in the fibre cell wall (in the middle lamella (M) in Figure 2.2) and the biological functions of lignin is to improve the stiffness of the cell walls, to glue different cells together, to make the cell wall less hydrophilic and to protect wood against microbiological degradation. Lignin is a polymer built up by aromatic hydrocarbons connected to a complicated three-dimensional structure. The structure and concentration of lignin varies through the wood regarding different species and different parts of the tree. [5], [7]

2.1.4 The Cell Wall Structure

The wood cell wall is built up by different layers with varied chemical composition and fibrillar structure. In Figure 2.2, the different layers are shown. The pattern of the layers shows the fibril orientation in the fibre cell wall. The middle lamella (M) consists of 40-60 % lignin. The cellulose fibrils are disordered in the primary wall (P). The secondary wall consists of three layers (S1, S2 and S3) and the cellulose fibrils are ordered differently in each layer. S2 is the thickest layer. It constitutes 80 % of the fibre and most of the wood fibre strength is given by that layer. [5]

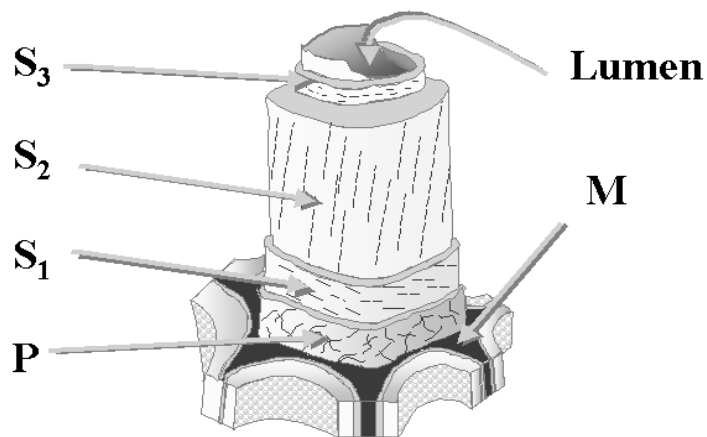


Figure 2.2: *The layers in the wood cell wall.*[18]

2.2 Pulping

The purpose of pulping is to set the wood fibres free. There are four main pulping techniques that are used; Mechanical pulping, Chemical pulping, Chemi Mechanical pulping and Semi Chemical pulping, [5], [8]. The methods are chosen depending on aimed properties of the paper. These methods are described below (except the Semi Chemical method).

2.2.1 Mechanical Pulping

In mechanical pulping, the principle is to disintegrate the wood mechanically. There are different methods that give different properties of pulp. The oldest method is the production of Stone Ground Wood (SGW) where wood is pressed against a rotating grindstone. Another technique is Thermo Mechanical Pulp (TMP), where preheated chips pass in between two rotating discs. This results in a higher share of whole fibres than in the grindstone method. The yield of the TMP-method is more than 90 %. Mechanical pulp has a high opacity which makes it suitable for newspaper production. [5], [8]

2.2.2 Chemical Pulping

In the chemical pulping method as much lignin as possible is chemically dissolved from the wood. The process involves cooking the chips with inorganic compounds until the fibres easily can be separated from each other. During cooking some degradation of hemicelluloses and cellulose also occurs. There are basically two chemical pulping methods, sulphite pulping and Kraft pulping. The cooking chemicals used in kraft cooking are sodium hydroxide and sodium sulphide. Approximately half of the wood material is dissolved in chemical pulping. The yield of the process is rather low, 48-60 %, but it gives the greatest paper strength due to fibre flexibility. [5], [8]

2.2.3 Chemi Mechanical Pulp (CMP)

CMP or CTMP (Chemical Thermo Mechanical Pulp) are mechanical pulps that are modified with small amounts of chemicals in order to facilitate the disintegration by softening of the lignin and get a greater extent of whole fibres than in mechanical pulps. This results in higher strength than mechanical pulps and better yield than the chemical pulps. The yield of wood in this process is 85-90 %. [5], [8]

2.2.4 Comparison of Pulping Methods

The differences between mechanical pulping and chemical pulping are large. The greatest paper strength is attained from chemical pulp since the average fibre length is much larger and the fibre flexibility is better. These properties increase the joint strength between the fibres. The brightness is also higher for papers made from bleached chemical pulp. But there are some disadvantages with the chemical pulp. The yield is much lower

than for mechanical pulps (approximately 50 % compared to 90 %) as well as a lower opacity. The mechanical pulping gives the highest yield, but it results in more damaged fibres which give less strong papers. Another disadvantage with the mechanical pulping is lower brightness of the papers. The opacity and the bending stiffness is, however greater for papers produced of mechanical pulp. The chemi mechanical pulp lies in between the mechanical and the chemical pulp regarding strength and yield. It has both high strength and high yield. [5], [8]

2.3 Paper

There are many different qualities of paper but there is no strict definition of what a paper is. Paper can be said to consist of hydrophilic fibres bonding to each other. Hydrogen bonding holds the fibres together after drying and give mechanical strength of paper. Paper is a heterogenous material and its mechanical properties is more similar to plastic materials than metals. Paper has viscoelastic behavior (the mechanical properties are time dependent) and they are also dependent of the relative humidity. The fibre characteristics of interest for paper production are many. Properties like fibre length, fibre form and flexibility, chemical composition and optical properties are some factors that influence the final product. Different types of fibres are used in order to make different types of paper. The demands are different for different paper qualities and thereby some properties are more important than others depending on area of use. If, for example, printing paper and carton board are compared, there are some differences. The optical properties are very important for papers that are used for printing where a good contrast is preferred. But in carton board other properties like, for example, bending stiffness are desired. [6], [5]

2.4 Liquid Carton Board

Liquid carton board is used as package for liquids, and usually consists of a multi-layered structure, where each layer has specific properties. One example is the TBA material from Tetra Pack. The material consists of one outer layer of polyethylene as protection from outside moisture, a paper board layer for stability and strength, and an aluminium foil that protects the content from oxidation, that is covered on both sides by adhesive polyethylene. The innermost polyethylene layer seals the liquid.

The paper board is produced in layers, where the surface layers often consist of Kraft Pulp and the middle layer often consists of Chemimechanical pulp. CTMP is used due to its high bulk (low density) which is preferred in the middle layer. One problem is the low fibre-fibre bond strength in CTMP, that has to be improved in order to achieve the desired stability and strength in the paper board. One way of doing that is to increase the z-strength. There should be noted that high z-strength could lead to problems in creasing operations. [6], [16], [17]

2.5 Z-Strength

The z-strength is a measure of the strength in the thickness direction of the paper. The definition of it is the force required to produce a unit area of fracture (kPa) [6]. According to Aaltio [1], the delamination strength is controlled by the fibre-to-fibre bonding and the z-orientation of the fibres, while the influence of mean fibre length and single fibre strength is very small in hand sheet papers [3]. Therefore, there are different ways to improve the z-strength. The bond improvement can be accomplished by different additions in the production stage, and the z-orientation is changed with changed formation of the sheet.

2.6 Ways to Improve Z-Strength

2.6.1 Formation

The formation describes the local distribution of basis weight [5]. The formation of paper is affected by several factors in the production. Factors such as chemical additions, pulp concentration and forming principle are some of them. Some mechanical effects of formation have been investigated by Fellers [12] and Norman [10]. In a sheet with bad formation, more fibres are oriented in the z-direction, which results in an increased z-strength according to Aaltio [1].

Formation can be measured by monitoring the mass distribution in paper using beta radiography. The resulting photograph is then scanned as a formation spectrum, showing basis weight variations of the paper at different scales. In this investigation a simplified method was used for formation analysis. [15]

2.6.2 Chemical Additives

In paper production, different types of paper chemicals are used. Process chemicals are used to improve processibility and functional chemicals give the paper product specific properties. The additives used in this work are described in this section.

Polyacrylamide

Polyacrylamides are soluble in water and have the ability to form hydrogen bonds. Anionic polyacrylamide (A-PAM) is used as retention agent for cationic particles and as a formation aid. Cationic polyacrylamide (C-PAM) is used as retention and dry strength agent. The conformation of the polymer in a solution and the interaction with the fibre depends to a great extent on the charge of the polymer, the surface charge density of fibres and the electrolyte concentration. [5], [4]

Starch

Starch (usually cationic) is used in paper production as a retention and dry strength agent. It is a polysaccharide extracted from potatoes, corn or wheat. Native starch is uncharged but can be made cationic or anionic by chemical derivatisation. The retention of cationic starch is almost complete at levels under 1 %, and the retention can be improved by co-addition of A-PAM. [4], [5]

Microfibrillated Cellulose (MFC)

Microfibrillated cellulose (MFC) is a material that consists of microfibrils that are produced by splitting pulp fibres in some kind of homogeniser. MFC was first produced by Albin F. Turbak in the 1980's [13]. Since then, several improved methods have been developed. STFI-Packforsk has developed improved methods for manufacture of MFC. This microfibrillated cellulose consists of microfibril aggregates with the dimensions 20-30 nm in width and a length of 100-1000 nm [11]. Two types of MFC are produced at STFI-Packforsk with different reactivity. One low charged MFC, where residues of hemicelluloses on the surface decreases the reactivity, and one high charged MFC with a clean cellulose surface. MFC has properties that makes it suitable in many differently applications.

Since the bonding properties are good for MFC, it can be used as an additive in paper production to increase the paper strength. MFC can be attached on the fibres and thereby create a larger and more reactive surface area. This results in a stronger linkage between the fibres and the paper strength is improved.

Chapter 3

Experimental

3.1 Materials

3.1.1 Pulps

In this work, two pulps were used, one CTMP and one Kraft Pulp.

- The CTMP contained 24.6 % lignin and the polysaccharide composition was 48.1 % Cellulose, 17.5 % Glucomannan and 8.2 % Xylan.
- Pine Kraft Pulp (from Stora Enso Kaukopää mill) contained 83 % Cellulose, 8.3 % Glucomannan and 8.5 % Xylan, and was refined to 30-35 SR.

3.1.2 Chemical Additives

- Cationic Starch (Amylofax PW, AVEBE, DS: 0.035)
- Anionic Polyacrylamide (A-PAM PL156, Ciba, charge density: 40 mole%).
- Cationic Polyacrylamide (C-PAM, PL1520, EKA Chemicals, charge density: 20 mole%)
- Two types of Microfibrilled Cellulose (MFC, manufactured at STFI-Packforsk). Low charged MFC and high charged MFC with charges of approximately 40 $\mu\text{ekv/g}$ and 600 $\mu\text{ekv/g}$, respectively.

3.2 Methods

Preparation of pulps and additions were performed the same way in nearly all parts of this work and the methods are described below. The exception is the set of sheets with mixed pulps where the washing step was not included in the preparation.

3.2.1 Preparation of Pulps

The CTMP was prepared in two steps. First, the hot disintegration of pulp according to ISO 5263-2:2004 followed by washing it to a desired counter ion-form. The Kraft Pulp was prepared by washing before usage.

3.2.2 Washing to Different Counter ion-forms

The washing method consists of several steps as follows:

- First the pulp was immersed in 0.01 M HCl-solution at pH 2 for 30 minutes in order to clean it from adsorbed metal ions (its H⁺-form), followed by washing of the pulp with deionised water until the conductivity of the filtrate was less than 5 μ S/cm.
- The next step was to leach out dissolved substances from the pulp by transferring it to 0.001 M NaHCO₃ for 30 minutes and convert it into its Na⁺-form. The pH was adjusted to 9 with NaOH. This was followed by washing the pulp with deionised water until the conductivity of the filtrate was less than 5 μ S/cm.
- The washing to Ca²⁺-form was performed by immersing the Na⁺-form of the pulp in 0.05 M CaCl₂ for 30 minutes, followed by washing of the pulp with deionised water until the conductivity of the filtrate was less than 5 μ S/cm.
- The washing from Ca²⁺- to Na⁺-form has to be done via the H⁺-form since Na⁺-ions do not have enough affinity to replace the Ca²⁺-ions on the fibres.
- The pulp ended up at a dryness of approximately 20 % after the washing, and was stored in that condition before use.

3.2.3 Preparations of Solutions

Polyacrylamides

The anionic and the cationic polyacrylamide solutions were prepared in several steps. First 0.125 g of the polyacrylamide (A-PAM or C-PAM) was soaked in 1.5 ml ethanol for 2 minutes. After an addition of 50 ml water the mixture was mixed thoroughly for 2 minutes. Then the mixture was stirred for 2 hours and left over night without stirring in order to swell the granules.

Starch

Preparation of the C-Starch solution was done by adding 3 grams of potato starch (Amylofax PW) to 200 ml deionised water. The solution was heated (in a water bath) to 90 °C while stirred and it was kept at that temperature for 15 minutes in order to gelatinise the C-Starch. Then the solution was cooled down to room temperature. Finally, the solution was diluted to the volume of 1 liter.

Microfibrillated Cellulose (MFC)

Two types of microfibrillated cellulose, with approximately 2 % dry content, were diluted with deionised water into solutions of 0.15 % dryness. The disintegration was done in a high intensity blender (Polytron PT 3000, Kinematica AG) at 10 000 RPM for approximately 1 minute.

3.2.4 Hand Sheet Methods

In this work two different hand sheet methods were used, Finnish sheet forming and Rapid Köhten sheet forming.

Finnish Hand Sheet Former

The Finnish hand sheets were made according to SCAN-C 26:76 using a 120 mesh metal wire. The mixing of pulp and additions were performed using a Britt Dynamic Drainage Jar (BDDJ) at 1000 RPM. The basis weight was 100 or 120 g/m² (specified in Chapter 3.3). The pressing of Finnish sheets did not exactly follow the SCAN-C 26:76. They were pressed to two different densities. The sheets with lower final density were pressed according to the first pressing step described in the SCAN-method (400 kPa for 5 minutes), while the higher-density-sheets were subjected to two additionally pressing steps, each equal to the first (totally 3 x 400 kPa for 5 min). All Finnish sheets were dried in room temperature according to the method.

Rapid Köhten Hand Sheet Former

The other sheet forming method used was a Rapid Köhten-apparatus (placed at the Department of Fibre and Polymer technology at the Royal Institute of Technology (KTH) in Stockholm) in which the stirring procedure as well as the drying and pressing differed from the Finnish sheet forming method. There were three vacuum dryers included. The wet sheets were pressed in the driers by vacuum suction, and dried at a temperature of 93 °C, at the same time. All Rapid Köhten sheets were produced according to ISO 5269-2:2004. The drying time was 15 minutes.

3.3 Sheet Production for Different Systems

Several chemical systems were investigated in this work. These are divided into parts describing used method and other circumstances. In most of the parts, the description consists of one table concerning used conditions followed by a description of the method that was used.

3.3.1 Reference Sheets

Reference sheets were made in both sheet forming methods without any chemical additions. Different counter ion-forms of the CTMP were tested in the Finnish former, and two different pulp ratios of CTMP and Kraft Pulp were tested in the Rapid Köhten former (RK). The influence of off-line pressing in the Rapid Köhten method was also investigated.

Table 3.1 *Conditions used in production of reference sheets without any chemical additions.*

	Finnish sheet former	RK sheet former
Pulp:	CTMP (Ca ²⁺)	CTMP (Ca ²⁺)
	CTMP (Na ⁺)	Kraft Pulp (Ca ²⁺)
Chemical environment:	Deionised water with 0.002 M CaCl ₂ resp. 0.002 M NaCl	Tap water
Basis weight :	120 g/m ²	150 g/m ²
BDDJ volume:	300 ml	500 ml

The sheet forming procedure was as follows:

- The pulp was stirred in water (see BDDJ volume in Table 3.1) for 1 minute in a specified chemical environment. The environment is the same in the BDDJ and in the sheet former.
- The mixture was then poured into the sheet former and sheets were made according to the hand sheet methods described in Chapter 3.2.4.
- Each type of Finnish sheets were pressed to two different sheet densities. The RK-sheets were produced with pure CTMP (Ca²⁺) and with 75 % CTMP (Ca²⁺) / 25 % Kraft Pulp (Ca²⁺).

Off-line Pressing of Rapid Köhten Sheets

Since z-strength is connected to sheet density, it was of interest to investigate if the sheet density could be altered using different pressing procedures of the wet Rapid Köhten sheets before they were pressed and dried according to the method in chapter 3.2.4. The influence of such off-line pressing was investigated for the Rapid Köhten sheets made of 100 % CTMP (Ca²⁺). This was done by using different pressing methods. The sheets were produced as the reference Rapid Köhten sheets above. The different off-line pressing methods were as follows:

- Reference: no off-line pressing.
- Low: off-line pressing at 100 kPa for 5 minutes.
- Medium: off-line pressing 3 times at 400 kPa for 5 minutes.
- High: off-line pressing 3 times at 400 kPa for 5 minutes, plus additionally 5 minutes at 1200 kPa.

3.3.2 Pulp Mixture in Rapid Köhten.

One set of sheets was made by mixing CTMP and Kraft Pulp in different ratios in Rapid Köhten (RK). The used CTMP/Kraft Pulp ratios were 100/0, 75/25, 50/50, 25/75, and 0/100. The specific conditions are presented in Table 3.2.

Table 3.2 *Conditions used in production of RK-sheets with mixed pulps.*

	RK sheet former
Pulp:	CTMP and Kraft Pulp
Environment:	Tap water
Basis weight :	80 g/m ²

These sheets were made as follows:

- Stock solutions of the two pulps were made with the concentration of 3 g/l.
- The pulps were then mixed in the CTMP/Kraft Pulp ratios 100/0, 75/25, 50/50, 25/75, and 0/100.
- The mixtures were then used in the sheet production in the RK-apparatus (see Chapter 3.2.4)

3.3.3 Effect of Pulp Concentration

A set of Finnish hand sheets was produced with varied pulp concentration, using the conditions in Table 3.3. The total volume of water in the sheet former was varied between 0.5 and 10 liters to give a range of pulp concentrations between 0.3 g/l and 5.4 g/l (see Table 3.4).

Table 3.3 *Conditions used in the production of Finnish handsheets with varied pulp concentration in the sheet former.*

	Finnish sheet former
Pulp:	CTMP (Ca ²⁺)
Environment:	Tap water
Basis weight:	100 g/m ²

Table 3.4 *Used volumes giving different pulp concentrations.*

Pulp conc. (g/l)	0.3	0.4	0.5	0.6	0.8	1	2	3	4	5.4
Total vol. (l)	10	6.8	5.4	4.5	3.4	2.7	1.4	0.9	0.7	0.5

The sheet forming procedure was as follows:

- The pulp was stirred in 500 ml tap water for 1 minute in the BDDJ.
- The mixture was then poured into the sheet former and the sheets were made according to the methods in Chapter 3.2.4.
- The sheets were then pressed to one density (3 x 400 kPa for 5 minutes).

3.3.4 Effect of A-PAM Addition

Finnish sheets were made with a pulp concentration of 3 g/l and three different additions of A-PAM (PL 156) were investigated, see Table 3.5.

Table 3.5 *Conditions used when adding A-PAM to the pulp.*

	Finnish sheet former
Pulp:	CTMP (Ca ²⁺) at 3 g/l
Environment:	Tap water
Basis weight:	100 g/m ²
Addition:	A-PAM (1, 2, 3 mg/l)

The sheet forming procedure was as follows:

- The pulp was stirred in 500 ml tap water for 1 minute in the BDDJ.
- A-PAM was added to the BDDJ and the mixture was stirred for 30 seconds.
- The mixture was then poured into the sheet former and the sheets were made according to the methods in Chapter 3.2.4.
- The sheets were then pressed to one density (3 x 400 kPa for 5 minutes).

3.3.5 Addition of C-PAM

This addition was done using both sheet forming methods. Used conditions are tabulated in Table 3.6.

Table 3.6 *Conditions used when adding C-PAM in sheet production.*

	Finnish sheet former	Rapid Köhten sheet former
Pulp:	CTMP (Ca ²⁺)	CTMP (Ca ²⁺) Kraft Pulp (Ca ²⁺)
Chemical: environment	Deionised water with 0.002 M CaCl ₂	Tap water
Basis weight :	120 g/m ²	150 g/m ²
BDDJ volume:	200 ml	500 ml
Addition:	0.05 % and 0.10 % C-PAM	0.05 % and 0.10 % C-PAM

The sheet forming procedure was as follows:

- The pulp was stirred in water (see BDDJ volume in Table 3.6) for 1 minute in a specified chemical environment. The chemical environment is the same in the BDDJ as in the sheet former.
- Addition of C-PAM was made to the BDDJ and the stirring proceeded for 30 seconds.
- The mixture was then poured into the sheet former and the sheets were made according to the methods in Chapter 3.2.4.
- The Finnish sheets were pressed to two different densities and the Rapid Köhten sheets were made from two pulp compositions, 100 % CTMP (Ca²⁺) as well as a mixture of 75 % CTMP (Ca²⁺) and 25 % Kraft Pulp (Ca²⁺).

3.3.6 Addition of C-Starch and C-Starch/A-PAM

The addition of C-Starch (cationic starch) and A-PAM was tested in both the Finnish sheet former and the RK-sheet former. The used conditions are presented in Table 3.7. The description of sheet production with only C-Starch addition is followed by the description of adding both C-Starch and A-PAM.

Table 3.7 Conditions used in sheet production with addition of C-Starch and A-PAM.

	Finnish sheet former	Rapid Köhten sheet former
Pulp:	CTMP (Ca ²⁺)	CTMP (Ca ²⁺) Kraft Pulp (Ca ²⁺)
Environment:	Tap water	Tap water
Basis weight :	120 g/m ²	150 g/m ²
BDDJ volume:	500 ml	500 ml
Addition 1:	1 %, 2 % and 5 % C-Starch	1 %, 2 % and 5 % C-Starch
Addition 2:	0.10 % A-PAM	0.10 % A-PAM

Two sets of sheets were made. One set with C-Starch addition only, and another set with C-Starch and A-PAM added.

The sheet forming procedure for C-Starch addition only was as follows:

- The pulp was stirred in water (see BDDJ volume in Table 3.7) for 1 minute.
- Addition of C-Starch solution was made into the BDDJ and the stirring proceeded for 10 minutes. (10 minutes in order to get adsorption equilibrium)
- The mixture was then poured into the sheet former and the sheets were made according to the methods in Chapter 3.2.4.
- The Finnish sheets were pressed to two different densities and the Rapid Köhten sheets were made of two pulp compositions, 100 % CTMP (Ca²⁺) as well as a mixture of 75 % CTMP (Ca²⁺) and 25 % Kraft Pulp (Ca²⁺).

The sheet forming procedure for C-Starch and A-PAM added was as follows:

- The pulp was stirred in water (see BDDJ volume in Table 3.7) for 1 minute.
- Addition of C-Starch solution was made to the BDDJ and the stirring proceeded for 9.5 minutes.
- The addition of A-PAM was made and the mixture was stirred for another 30 seconds in the BDDJ.
- The mixture was then poured into the sheet former and the sheets were made according to the methods in Chapter 3.2.4.

- The Finnish sheets were pressed to two different densities and the Rapid Köhten sheets were made of two pulp compositions, 100 % CTMP (Ca²⁺) as well as a mixture of 75 % CTMP (Ca²⁺) and 25 % Kraft Pulp (Ca²⁺).

3.3.7 Addition of Microfibrillated Cellulose (MFC)

Two kinds of MFC were used in sheet production in the Finnish sheet former, one high charged MFC and one low charged MFC. The addition of high charged MFC was performed as shown in Table 3.8 and the addition of low charged MFC is described in Table 3.9.

Table 3.8 *Conditions used in sheet production with added high charged MFC.*

	Finnish sheet former
Pulp:	CTMP (Ca ²⁺)
Chemical environment:	Deionised water with 0.002 M resp 0.01 M CaCl ₂
Basis weight:	120 g/m ²
BDDJ volume:	300 ml
Addition:	2 % and 5 % high charged MFC

The sheet forming procedure was as follows:

- The pulp was stirred in a specified chemical environment (see BDDJ volume in Table 3.8) for 1 minute. The environment was the same in the BDDJ and in the sheet former.
- Addition of MFC-dispersion (dryness 0.15 %) was made and the stirring proceeded for 1 minute in the BDDJ.
- The mixture was then poured into the sheet former and the sheets were made according to the methods in Chapter 3.2.4.
- The sheets were pressed to two different densities.

Table 3.9 *Conditions used in sheet production with added low charged MFC.*

	Finnish sheet former
Pulp:	CTMP (Ca ²⁺)
Chemical environment:	Deionised water with 0.002 M CaCl ₂
Basis weight:	120 g/m ²
BDDJ volume:	300 ml
Addition 1:	0.05 % and 0.10 % C-PAM
Addition 2:	2 % and 5 % low charged MFC

The sheet forming procedure was as follows:

- The pulp was stirred in a specified chemical environment (see BDDJ volume in Table 3.9) for 1 minute . The environment is the same in the BDDJ and in the sheet former.
- The pulp was set aside in a beaker.
- MFC-dispersion (dryness 0.15 %) and C-PAM were mixed in BDDJ in specified chemical environment for 30 seconds, in order to flocculate MFC separately.
- The two dispersions (pulp and flocculated MFC) were poured into the BDDJ and stirred for another 30 seconds.
- The final mixture was then poured into the sheet former, with the same chemical environment as in the BDDJ, and the sheets were made according to the methods in Chapter 3.2.4.
- The sheets were pressed to two different densities.

3.4 Sheet Analysis

3.4.1 Density

The density of the sheets was established by the basis weight and measurements of the structural thickness according to SCAN P 88:01. The sheet dimensions were 16.5 x 16.5 cm for the Finnish hand sheets and 20 cm in diameter for the Rapid Köhten sheets.

3.4.2 Z-Strength

The measurement of z-strength was performed using the Z-directional tensile test according to SCAN-P 80:98. The paper is clamped between two specimen holders with adhesive tape and then pulled apart by a force perpendicular to the plane of the paper. The working velocity was chosen depending on expected z-strength according to the method. Four measurements were done on each paper sheet. The standard deviations of the measurements are presented in connection with the z-strength in the tables in Appendix A.

3.4.3 Formation

The formation was evaluated optically by the STFI-Formation method. The sheets were scanned, and then the pictures were analysed with a computer program. Every sheet was scanned with scanner Agfa ARCUS II, with settings; greyscale, transparent and 300 dpi. The computer programme used for analysis was STFI Mottling v2.7. By using this method, information about the occurrence of flocs of different sizes is obtained. The sizes are presented in a Power Spectra by wavelengths, where the floc size is half the wavelength. The spectrum is also summarised giving three different formation numbers, small-scale formation (wavelength 0.3-3 mm), large-scale formation (wavelength 3-30 mm) and total formation (wavelength 0.3-30 mm). The total formation is used to compare the formation of the laboratory sheets.

Chapter 4

Results and Discussion

The results are presented and discussed from diagrams in the figures below, and all tables (A.1-A.13) are found in Appendix A. The sections are arranged in the same order as in Chapter 3.3.

4.1 Reference Sheets

The results from z-strength measurements of the reference sheets are shown in Figure 4.1 (and presented in Table A.1 and A.2 in Appendix A). The Finnish sheets were pressed to two densities and are presented as two points connected by a line. The Rapid Köhten (RK) sheets are only pressed to one density. The reason for this is the relatively small differences in sheet density that are presented in Table 4.1.

Table 4.1 *Effect of different off-line pressings on density and z-strength for Rapid Köhten sheets made of 100 % CTMP.*

	Density (kg/m ³)	Z-strength (kPa)
Reference:	545	256
Low:	520	212
Medium:	573	170
High:	593	172

Table 4.1 shows that the off-line pressing procedure slightly increases the density of the sheet, while the z-strength actually decreases, compared to the reference sheet. The deterioration of the z-strength is due to the higher solids content going into the Rapid Köhten drier. (All sheets in this investigation are dried according to the method described in chapter 3.2.4, 15 minutes and 93 °C) A higher solids content means that the time, while the fibres are plasticised during drying will decrease if they are prepressed off-line. This is also reflected in the difference between RK-procedure and the Finnish sheet forming procedure, where the sheets are dried at room temperature.

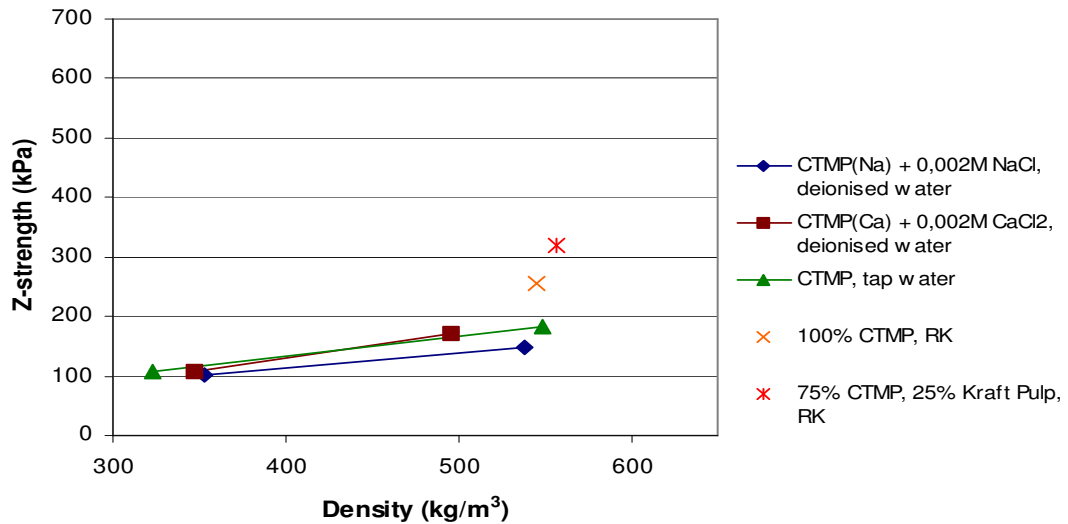


Figure 4.1: The z-strength of reference sheets made in both sheet formers. Finnish sheets have two densities in each environment and the RK-sheets have two different pulp contents of CTMP and Kraft Pulp.

Fibres in different ionic forms have slightly different swelling values (WRV). One set of experiments was therefore conducted with fibres in their Na^+ and Ca^{2+} -forms and in tap water. Table A.1, however, reveals that there are no discernible difference between the different ionic forms, therefore this aspect can be ignored.

The different pressing levels for the Finnish sheets show that the z-strength is improved by a higher density in all three ion-forms. The higher density results in narrower contact between the fibres, which increases contact surface, and in turn increases the z-strength.

The z-strength in the RK-sheets is higher than in the Finnish sheets at approximately the same density. The reason for this, as discussed above, is the drying and pressing methods. Evidently the warm drying and vacuum pressing in the RK-apparatus improves the z-strength. Besides the higher density, the reason for this is the drying temperature which is higher than the softening temperature for lignin. The fibre walls soften and get more flexible, which increases the fibre bonding in the paper.

The higher z-strength for sheets made of 25 % Kraft Pulp and 75 % CTMP is caused by the influence of Kraft Pulp. That will be discussed further in the next section.

4.2 Pulp Mixture in Rapid Köhten

Further investigations on the pulp mixture of CTMP and Kraft Pulp were also conducted. The results from different CTMP/Kraft Pulp ratios (0/100, 25/75, 50/50, 75/25, and 100/0) in Rapid Köhten (RK) are presented in the figures below (and in Table A.3 in Appendix A).

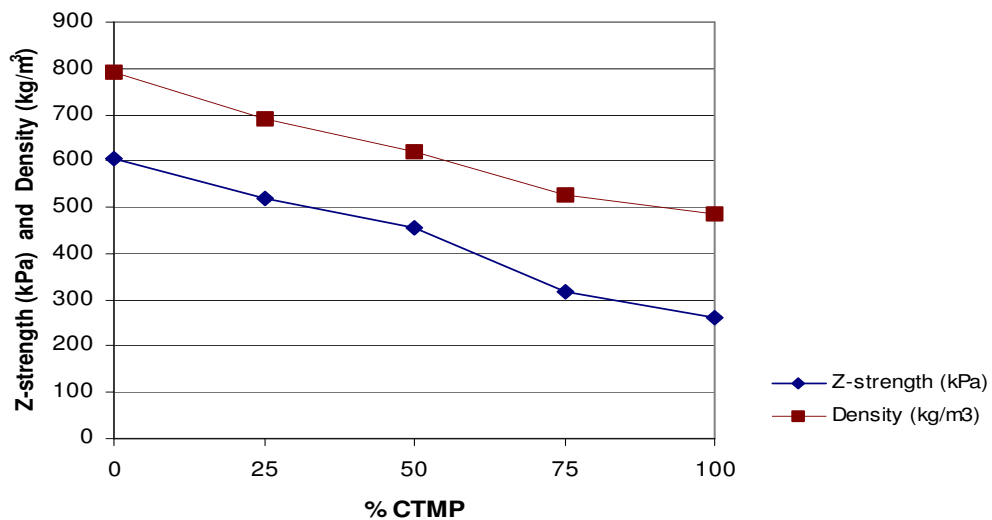


Figure 4.2: The effect on density and z-strength in RK-sheets by mixing CTMP and Kraft Pulp in different ratios (0/100, 25/75, 50/50, 75/25, and 100/0).

Both z-strength and density decreases, as the content of CTMP increases, as can be seen in Figure 4.2. Kraft Pulp is a chemical pulp which enables a more efficient fibre-fibre binding and higher strength in the paper due to more flexible fibres. The density changes since the Kraft Pulp fibres have a higher density than the CTMP fibres have. This also results in a proportional increase in z-strength with density (see Figure 4.3) where the pure Kraft Pulp sheet has the highest z-strength and density.

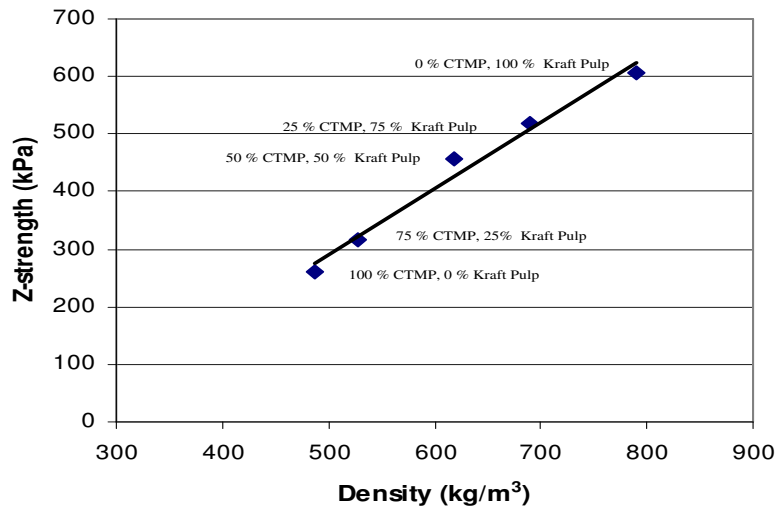


Figure 4.3: The relation between z-strength and density for RK-sheets when mixing CTMP and Kraft Pulp.

4.3 Effect of Pulp Concentration

In the Finnish sheet former, the pulp concentration can be varied by changing the total volume of water in the sheet former. This affects fibre flocculation, which results in changed formation. The formation and z-strength was analysed of the produced sheets. (the complete results from the measurements are found in Table A.4 in Appendix A)

The results of formation measurements of the sheets produced at different pulp concentrations are shown in Figure 4.4. A higher pulp concentration in the sheet former results in an increased fibre flocculation giving a worse formation of the sheet.

Figure 4.5 shows that the z-strength is not changed by a higher pulp concentration in the forming procedure (the blue squares in the figure), in the interval between 0.3 and 5 g/l, despite the worse formation. According to mentioned theories (see Chapter 2.6.1) there should be an increase in z-strength with worsen formation, because of more fibres are oriented in the z-direction in sheets with worse formation.

The reason why a worse formation did not result in increased z-strength is most likely that it is difficult to orient long fibres in the z-direction. With a higher fraction of fines material a different picture may have emerged.

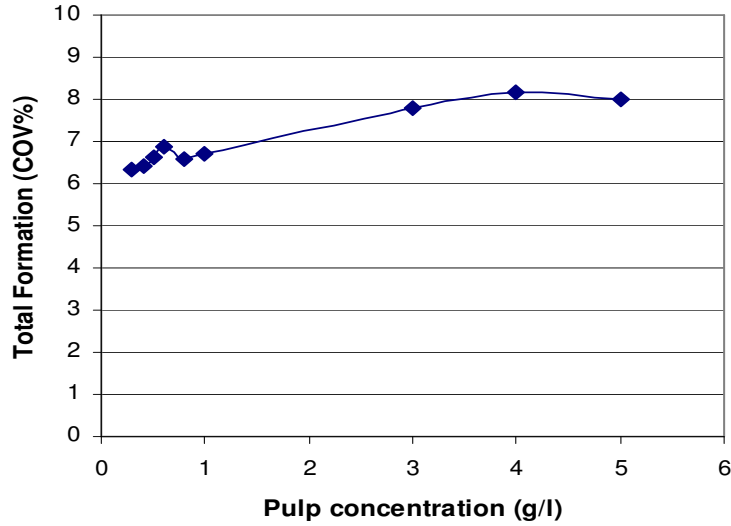


Figure 4.4: Results from formation measurements of sheets produced with different pulp concentration in the Finnish sheet former.

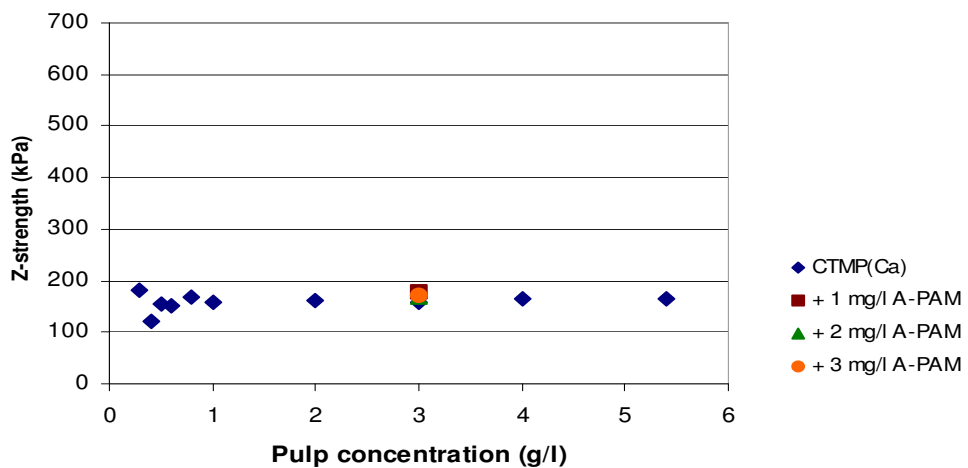


Figure 4.5: Results of z-strength with varied pulp concentration in the Finnish sheet former and effects of A-PAM addition.

4.4 Addition of A-PAM to High Pulp Concentration

An addition of A-PAM should decrease the flocculation and should thereby improve the formation, according to [14]. But the results from formation measurements of adding A-PAM to pulp concentration of 3 g/l shows very little difference in formation (see Figure 4.6). It is also seen from Figure 4.5 that the z-strength is not effected either by A-PAM addition.

The reason for this is most likely that the used amount of A-PAM was not enough to affect the formation. A higher dose would thus have been investigated.

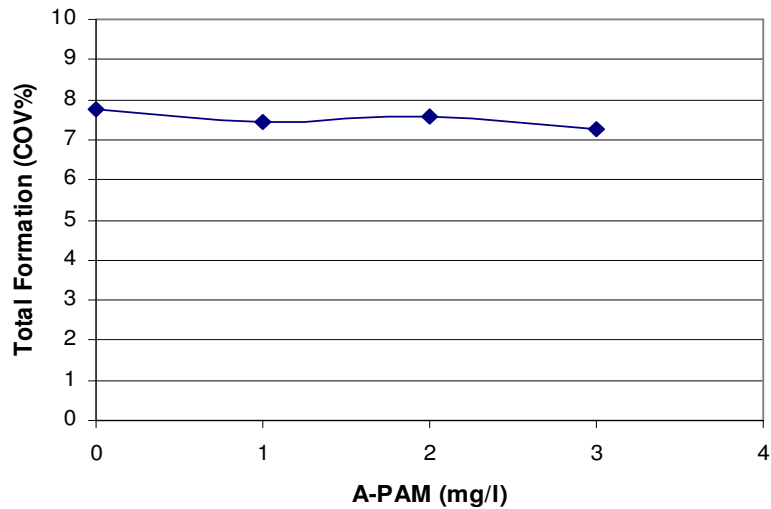


Figure 4.6: Results in total formation measured on Finnish sheets produced in 3 g/l pulp concentration and different amounts of A-PAM added.

4.5 Addition of C-PAM

The effect of adding C-PAM in both forming methods are shown in Figure 4.7 (and presented in Table A.5 in Appendix A). The reference points representing pure pulp are included in the figure. As can be seen from the figure, this addition was done to Finnish sheets produced in two densities and Rapid Köhten sheets with two pulp contents (RK, 100 % CTMP and 75 % CTMP/25 % Kraft Pulp).

The z-strength was not affected in the Finnish sheets by the C-PAM addition nor in the RK- sheets with 100 % CTMP. The RK-sheets with 100 % CTMP have slightly higher strength than the Finnish sheets with approximately the same density due to drying and pressing methods as discussed in chapter 4.3.

The greatest improvement in z-strength as well as the highest density was achieved by the pulp mixture of 25% Kraft Pulp and 75% CTMP.

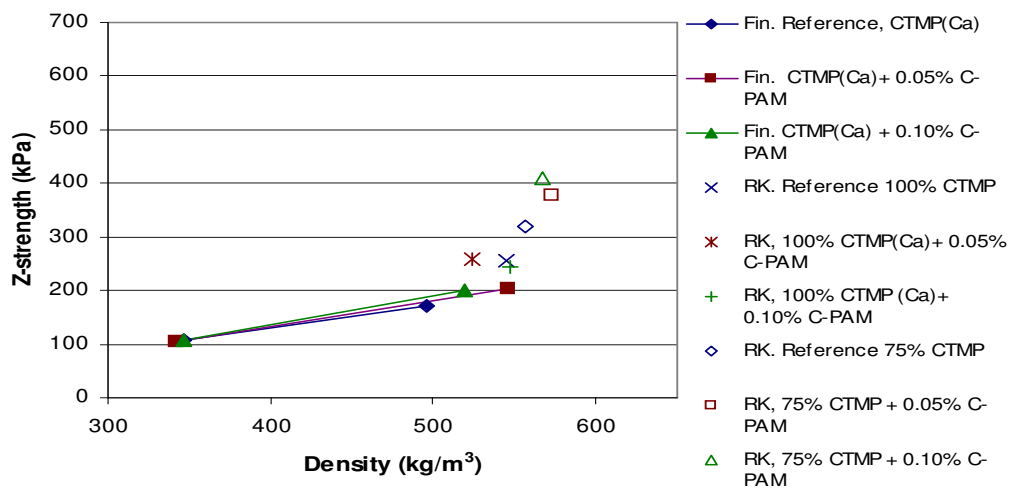


Figure 4.7: The effects of adding C-PAM to sheets produced in the Finnish sheet former (two densities) and the Rapid Köhten (RK) apparatus (two pulp mixtures of CTMP and Kraft Pulp).

As C-PAM is a flocculant it would have been expected that worsened sheet formation would increase z-directional strength as discussed earlier. Obviously, the z-directional strength is not sensitive to sheet formation, in conformity with the results presented when the pulp concentration was changed. The increased z-strength in the presence of Kraft Pulp may be attributed to the fibre fraction in this pulp, either by retaining the fines or directing the fines in the z-direction.

4.6 Addition of C-Starch and C-Starch/A-PAM

The results concerning the z-strength of these additions made in the Finnish sheet former (two densities) and the Rapid Köhten former (RK, two pulp mixtures) are shown in Figures 4.8 and 4.9 (and in Tables A.6, A.7, A.8 and A.9 in Appendix A). Formation analyses have also been done on the Finnish sheets.

4.6.1 Effect of C-Starch Addition

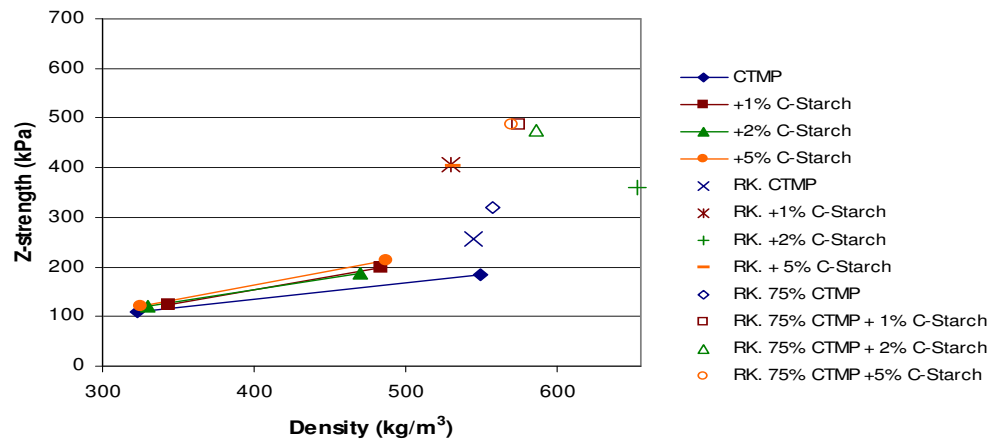


Figure 4.8: Results from addition of C-Starch to sheets produced in the Finnish sheet former (two densities) and the Rapid Köhten (RK) sheet former (two pulp mixtures of CTMP and Kraft Pulp).

The z-strength in the Finnish sheets were not affected by the starch addition, probably caused by uncomplete retention in that sheet former (see Figure 4.8). The RK-sheets do, however get an improved z-strength by most likely the C-Starch addition. But there are no difference between the three added amounts. There is a limit for the starch retention in the paper.

The interaction between fibre-starch-fibre becomes more efficient by the drying and pressing method in the RK-apparatus. The cationic starch interacts better with the pulp mixture (25 %Kraft Pulp and 75 % CTMP) than with CTMP, as for the cationic polyacrylamide mentioned earlier. But there are no difference by changing the amount of C-Starch from 1 % to 2 % and 5 %. The system needs some help to get any effect of the higher starch additions. The difference between the two forming situations is interesting, but remains to be explained.

4.6.2 Effect of Addition of C-Starch and A-PAM

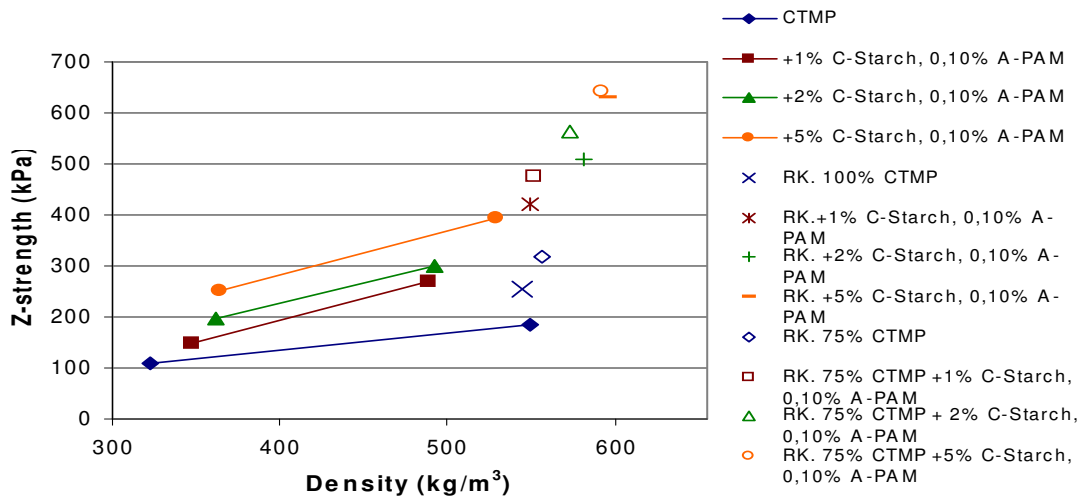


Figure 4.9: Results from adding C-Starch and A-PAM to sheets produced in the Finnish sheet former (two densities) and the Rapid Köhten (RK) sheet former (two pulp mixtures of CTMP and Kraft Pulp).

The difference by adding both C-Starch and A-PAM can be seen by comparing Figures 4.8 and 4.9. The z-strength in the sheets was highly affected by the addition of C-Starch and A-PAM, reaching values up to twice as high as with only C-Starch added. By adding both C-Starch and A-PAM, there is also a significant improvement by increasing the C-Starch addition. The A-PAM provides a more efficient retention of C-Starch, by precipitating the non-adsorbed C-Starch as a polyelectrolyte complex onto the fibre, which improves the z-strength. The pulp mixture still reaches the highest z-strengths but the difference to CTMP (100 %) is not as large as in Figure 4.8.

The increase in z-strength is caused by an increased sheet density, but mainly by the amount of starch precipitated together with A-PAM, and the choice of drying and pressing method.

4.6.3 Effect on Formation

The formation was measured on the Finnish sheets with additions of C-Starch and A-PAM. In Figure 4.10 the total formation of the Finnish sheets with lower density are plotted in comparison with the z-strength (Table A.10 in Appendix A presents the complete results).

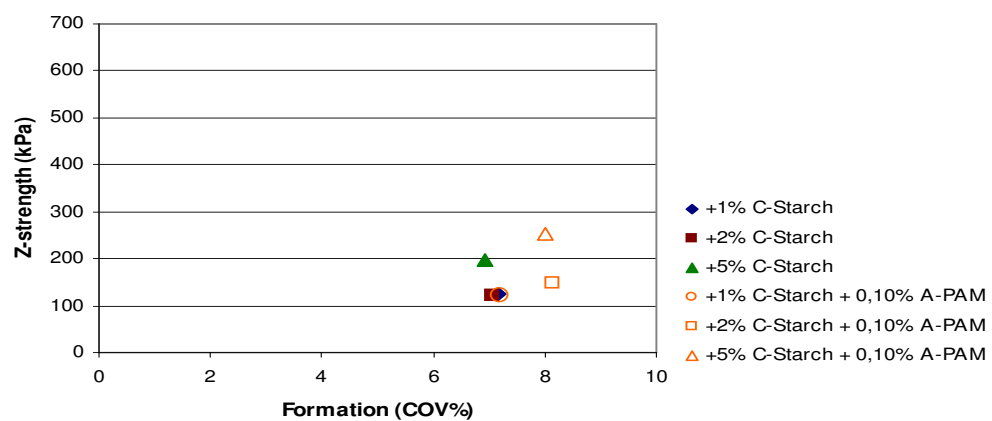


Figure 4.10: Results from formation measurements on Finnish sheets with additions of C-Starch and A-PAM.

C-Starch/A-PAM has only a minor influence on formation while the z-strength is improved to a larger extent. The z-strength is however, not connected to the formation, which the results in chapter 4.3 also shows. Here, it is the chemical properties of C-Starch and A-PAM that improves the z-strength by interacting with the paper fibres.

4.7 Addition of Microfibrillated Cellulose (MFC)

4.7.1 Addition of High Charged MFC

The addition of high charged MFC was made in the Finnish sheet former at two different salt concentrations. Here the salt is added as a coagulating agent of MFC. The results are plotted in Figure 4.11 (and presented in Table A.11 in Appendix A). The additions improved the z-strength, but not very much. There is also a slight difference in z-strength by changing salt concentration. At higher electrolyte concentration the retention of MFC increases and the z-strength is improved.

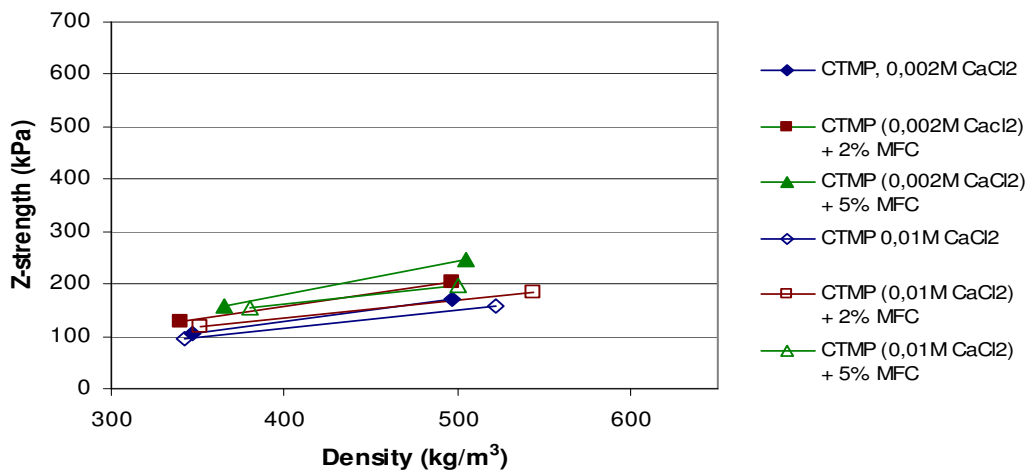


Figure 4.11: Effects on z-strength of Finnish sheets (two densities) by adding high charged MFC at two different salt concentrations.

4.7.2 Addition of Low Charged MFC and C-PAM

The additions of low charged MFC and C-PAM were made in the Finnish sheet former giving two densities at each addition, see results in Figure 4.12 (and Table A.13 in Appendix A).

A greater improvement of the z-strength was achieved in this case than by adding the highly charged MFC (compare with 0.002 M salt concentration in Figure 4.11).

C-PAM was added to MFC in order to flocculate MFC and retain it better in the sheet. Since low charged MFC is not as reactive as high charged MFC, salt addition do not work as a coagulation agent in this case (because the MFC is sterically stabilised).

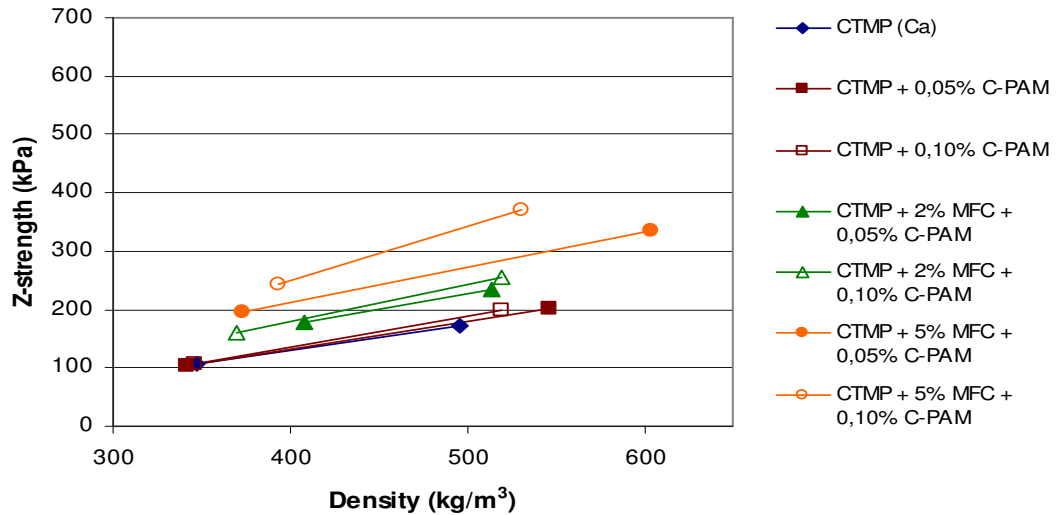


Figure 4.12: Effects in z-strength of Finnish sheets (two densities) by adding low charged MFC and C-PAM in 0.002 M CaCl₂.

Evidently, the C-PAM addition improved the z-strength of the sheet to a greater extent together with low charged MFC than the high charged MFC did alone.

The retention of MFC increased by using C-PAM as retention agent. A higher amount of C-PAM gives a higher z-strength due to better MFC- retention. The amount of MFC added increases the strength and makes the effects of C-PAM more differentiated. With no MFC added there are no difference in strength between the two amounts of C-PAM. MFC is necessary to get the strength improvement, which proves that MFC can be used as a dry strength agent.

4.7.3 Effect on Formation by Adding MFC

Measurements of formation of the sheets with added MFC in 0.002 M CaCl₂ were done and these results are shown in Figures 4.13 and 4.14 (and in Tables A.12 and A.13 in Appendix A).

The total formation was not affected by the addition of high charged MFC. The additions of low charged MFC and C-PAM results in slightly higher (worse) formation. Figure 4.14 gives a good picture of how the z-strength and formation is related in the case of adding MFC. Here it is seen that the differences in formation are smaller than the differences in z-strength. As in chapter 4.3 and 4.6.3 that means that the interactions in the paper are results of higher bonding strength rather than worse formation.

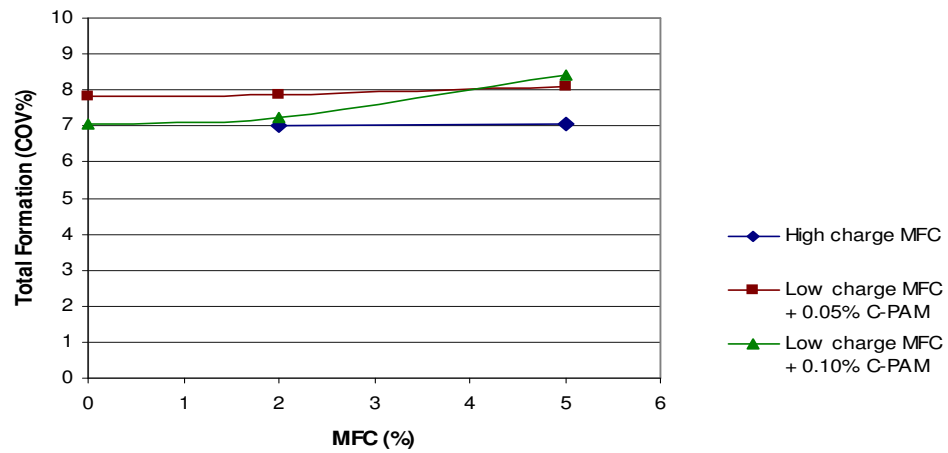


Figure 4.13: The total formation measured on Finnish sheets with addition of high charge and low charged MFC.

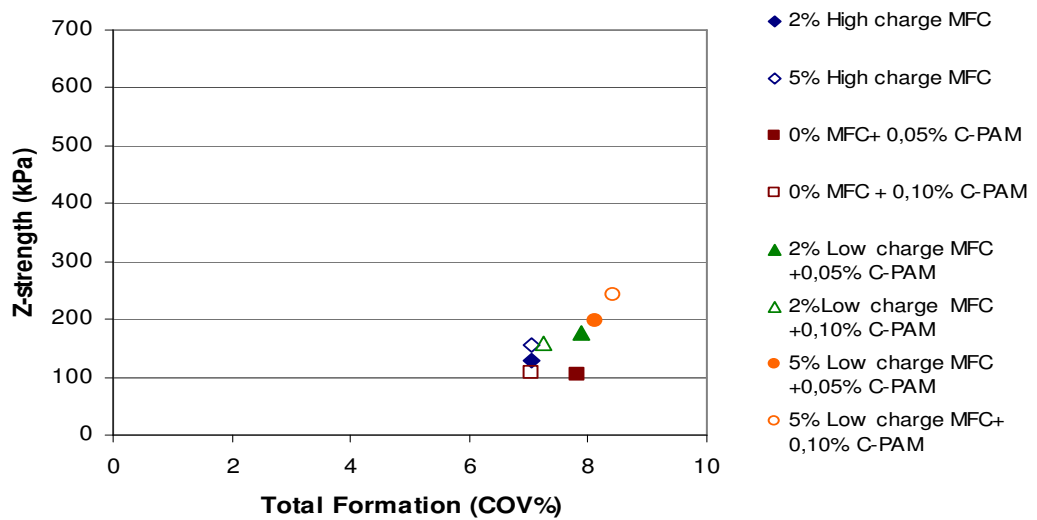


Figure 4.14: The relation between z-strength and total formation for Finnish sheets produced with additions of high charge and low charged MFC.

Chapter 5

Conclusions

Conclusions that can be made from this work is the following:

- There is no difference in z-strength for sheets produced of CTMP in different counter ion-form.
- The z-strength is improved by all additions investigated in this work. The largest effect was gained with additions of C-Starch combined with A-PAM.
- The z-strength and density are improved by mixing Kraft Pulp with CTMP compared to sheets with pure CTMP.
- The Rapid Köhten apparatus produces sheets with higher densities and higher z-strength than the Finnish sheet former, probably due to the vacuum pressing and warm drying method.
- The z-strength is neither affected by change in pulp concentration (in the range of 0.3-5 g/l) nor addition of A-PAM to a high pulp concentration (3 g/l).
- The results in this work shows that the z-strength is not connected to formation.

Chapter 6

Suggestions for Future Work

There are much further work that can be done in order to develop a better understanding in z-strength and formation.

- Investigate the influence of other chemical additions.
- Use other types of Microfibrillated cellulose.
- Measurements of retention of MFC, C-PAM and C-Starch.
- Change the environmental conditions.
- Further experimentals concerning the relationship between z-strength and formation.

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Appendix A

Table A .1 Results in z-strength from measurements of reference Finnish sheets (two densities) made in different environment, without any additions.

	Density [kg/m ³]	Z-strength [kPa] (stddv %)
CTMP(Na), 0.002 M NaCl	353	102 (2.8)
	537	147 (3.5)
CTMP(Ca), 0.002 M CaCl ₂	347	106 (2.7)
	496	172 (9.5)
CTMP, tap water	323	109
	549	183

Table A .2 Results in z-strength for reference Rapid Köhten sheets of two different pulp mixtures (CTMP and Kraft Pulp), without additions.

	Density [kg/m ³]	Z-strength [kPa] (stddv %)
100 % CTMP	545	256 (18.8)
75 % CTMP	557	319 (2.5)

Table A .3 Results of Rapid Köhten sheets with varied pulp contents of CTMP and Kraft Pulp.

% CTMP	Density [kg/m ³]	Z-strength [kPa] (stddv %)
100	487	261 (4.8)
75	528	316 (1.5)
50	619	456 (5.1)
25	690	518 (0.8)
0	790	607 (1.8)

Table A .4 Results from sheets produced with different pulp concentrations in the Finnish sheet former. A-PAM is added to pulp concentration of 3 g/l.

Pulp conc. (g/l)	Total vol. [l]	Density [kg/m ³]	Z-strength [kPa] (stddv %)	Small scale formation COV%	Large scale formation COV%	Total formation COV%
0.3	10	532	182 (3.4)	5.6	2.7	6.3
0.4	6.8	418	123 (2.8)	5.7	2.8	6.4
0.5	5.4	521	153 (2.8)	5.8	3.1	6.6
0.6	4.5	516	152 (4.3)	6.0	3.2	6.8
0.8	3.4	514	169 (4.2)	5.8	3.0	6.5
1	2.7	536	157 (4.2)	5.9	3.2	6.7
2	1.4	526	161 (5.0)			
3	0.9	553	158 (3.1)	6.5	4.2	7.7
4	0.7	535	166 (3.8)	6.6	4.6	8.1
5.4	0.5	544	165 (1.8)	6.3	4.8	8.0
A-PAM						
1 mg/l		546	179 (7.4)	6.3	3.8	7.4
2 mg/l		527	169 (8.2)	6.4	4.0	7.5
3 mg/l		524	172 (5.9)	6.2	3.6	7.2

Table A .5 Results of z-strength for sheets made in both formers with addition of C-PAM. The Finnish sheets (two densities) are produced in 0.002 M CaCl₂. The Rapid Köhten consists of CTMP and Kraft Pulp.

	Density [kg/m ³]	Z-strength [kPa] (stddv %)
Finnish sheets		
0.05 % C-PAM	342	104 (3.3)
	547	203 (2.9)
0.10 % C-PAM	346	107 (3.7)
	520	200 (5.6)
Rapid Köhten sheets		
100 % CTMP		
0.05 % C-PAM	524	258 (4.2)
0.10 % C-PAM	548	245 (1.5)
75 % CTMP		
0.05 % C-PAM	573	377 (4.2)
0.10 % C-PAM	567	409 (6.5)

Table A .6 Results of z-strength for Finnish sheets (two densities) with C-Starch addition.

	Density [kg/m ³]	Z-strength [kPa] (stddv %)
Reference	347	106 (2.7)
	466	172 (9.5)
1 % C-Starch	343	123 (3.4)
	483	197 (2.7)
2 % C-Starch	329	121 (3.9)
	470	187 (0.4)
5 % C-Starch	325	121 (6.2)
	487	214 (3.0)

Table A .7 Results of z-strength for Rapid Köhten sheets (CTMP and Kraft Pulp mixture) with C-Starch additions.

	Density [kg/m ³]	Z-strength [kPa] (stddv %)
100 % CTMP		
Reference	545	256 (18.8)
1 % C-Starch	530	405 (1.9)
2 % C-Starch	653	361 (10.6)
5 % C-Starch	531	403 (8.9)
75 % CTMP		
Reference	557	319 (2.5)
1 % C-Starch	487	474 (3.4)
2 % C-Starch	570	486 (1.4)
5 % C-Starch	551	476 (2.8)

Table A .8 Results of z-strength for Finnish sheets (two densities) with addition of C-Starch and A-PAM.

	Density [kg/m ³]	Z-strength [kPa] (stddv %)
Reference	347	106 (2.7)
	466	172 (9.5)
1 % C-Starch + 0.10 % A-PAM	347	149 (4.8)
	489	270 (1.2)
2 % C-Starch + 0.10 % A-PAM	362	197 (7.5)
	492	299 (4.0)
5 % C-Starch + 0.10 % A-PAM	364	252 (2.7)
	529	393 (4.1)

Table A .9 Results of z-strength for Rapid Köhten sheets (CTMP and Kraft Pulp mixture) with addition of C-Starch and A-PAM.

	Density [kg/m ³]	Z-strength [kPa] (stddv %)
100 % CTMP		
Reference	545	256 (18.8)
1 % C-Starch + 0.10 % A-PAM	550	420 (2.8)
2 % C-Starch + 0.10 % A-PAM	582	508 (3.0)
5 % C-Starch + 0.10 % A-PAM	596	631 (2.1)
75 % CTMP		
Reference	557	319 (2.5)
1 % C-Starch + 0.10 % A-PAM	573	563 (1.4)
2 % C-Starch + 0.10 % A-PAM	592	643 (2.3)
5 % C-Starch + 0.10 % A-PAM	575	487 (1.7)

Table A .10 Formation results of Finnish sheets (two densities) with addition of C-Starch and A-PAM.

	Density [kg/m ³]	Z-strength [kPa]	Small scale formation COV%	Large scale formation COV%	Total formation COV%
1 % C-Starch	343	123	6.3	3.2	7.1
	483	197	5.7	3.1	6.5
2 % C-Starch	329	121	6.2	3.1	7.0
	470	187	5.5	2.8	6.2
5 % C-Starch	325	121	6.2	3.0	6.9
	487	214	5.5	2.8	6.2
1 % C-Starch + 0.10 % A-PAM	347	149	6.3	3.3	7.2
	489	270			
2 % C-Starch + 0.10 % A-PAM	362	197	6.9	4.2	8.1
	492	299	5.7	3.3	6.6
5 % C-Starch + 0.10 % A-PAM	364	252	6.6	4.3	8.0
	529	393	7.1	5.9	3.9

Table A .11 Results of z-strength from Finnish sheets (two densities) with additions of high charged MFC made in 0.002 M CaCl₂ and 0.01 M respectively

	0.002 M CaCl ₂		0.01 M CaCl ₂	
	Density [kg/m ³]	Z-strength [kPa] (stddv %)	Density [kg/m ³]	Z-strength [kPa] (stddv %)
No MFC	347	106 (2.7)	343	95 (3.4)
	496	172 (9.5)	522	159 (2.8)
2 % high charged MFC	340	128 (2.2)	351	117 (2.4)
	496	204 (2.2)	544	185 (1.9)
5 % high charged MFC	365	157 (3.4)	380	153 (1.7)
	504	247 (2.5)	500	199 (2.1)

Table A .12 Results from formation measurements of Finnish sheets (two densities) with additions of high charged MFC made in 0.002 M CaCl₂

	Density [kg/m ³]	Z-strength [kPa]	Small scale formation COV%	Large scale formation COV%	Total formation COV%
2 % high charged MFC	340	128	6.2	3.3	7.0
	496	204	5.3	2.8	6.0
5 % high charged MFC	365	157	6.1	3.4	7.0
	504	247	5.3	3.1	6.1

Table A .13 Results of z-strength and formation for Finnish sheets (two densities) with addition of low charged MFC and C-PAM in 0.002 M CaCl₂.

	Density [kg/m ³]	Z-strength [kPa]	Small scale formation COV%	Large scale formation COV%	Total formation COV%
No MFC					
0.05 % C-PAM	342	104	6.6	4.1	7.8
	547	203	5.3	2.8	6.0
0.10 % C-PAM	346	107	6.2	3.3	7.0
	520	200	5.2	3.0	6.0
2 % low charged MFC					
0.05 % C-PAM	408	177	6.5	4.4	7.8
	513	234	5.7	3.7	6.8
0.10 % C-PAM	370	160	6.0	3.9	7.2
	519	257	5.9	3.8	7.1
5 % low charged MFC					
0.05 % C-PAM	373	196	6.4	4.8	8.1
	603	335	5.7	4.2	7.1
0.10 % C-PAM	393	243	6.5	5.3	8.4
	531	370			