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**FORMATION OF POLYELECTROLYTE MULTILAYERS AND
POLYELECTROLYTE COMPLEXES IN DUAL POLYMER
TREATMENT OF PAPERMAKING PULP**

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ABSTRACT

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Formation of polyelectrolyte multilayers and polyelectrolyte complexes in dual polymer treatment of papermaking pulp

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The goal of this study was to find a new approach to modify chemically the properties of paper by improving fiber quality.

This Master's thesis includes the multiple polymer treatment in general and the measurement methods with which the formation of multilayers and complexes can be noticed.

The treatment by an oppositely charged dual polymer system is a good approach to increase paper strength. In this work, starch, a cationic polymer, and carboxymethyl cellulose (CMC), an anionic polymer, were used step-by-step to improve paper strength. The adsorption of cationic starch and CMC on cellulose fibers were analyzed via polyelectrolyte titration. The results showed that paper strength was enhanced slightly with a layer-by-layer assembly of the polymers. However, if the washing stage, which was required for layer-by-layer assembly, was eliminated, the starch/CMC complex was deposited on fibers more efficiently, and the paper strength was improved more significantly.

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Lappeenranta

Olga Birichevskaya

LIST OF KEY ABBREVIATIONS

ccc	critical coagulation concentration
CD	charge density
CMC	carboxymethyl cellulose
cnp	charge neutralization point
CPAM	polyacrylamide
DLVO	Derjaguin, Landau, Verwey and Overbeek
D.S.	degree of substitution
L&W	Lorentzen&Wettré
PE	polyelectrolyte
PEC	polyelectrolyte complex
PEM	polyelectrolyte multilayer
ML	middle lamella
P	primary cell wall
S1, S2, S3	secondary cell wall
TMP	thermomechanical pulp
W	warty layer

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1 Introduction

1.1 Background knowledge

Paper is occurred from fibers in water suspension. The fibers are obtained usually from wood, by a chemical or a mechanical process. At first, during paper production, the fiber suspension is dewatered by elements such as blades, suction boxes, foils, suction rolls, press nips, and then dried on cylinders (steam-heated) and only a little amount of water is left to the final paper /1/.

At low concentration of fibers, the fiber web is held together first of all by mechanical entanglement. The fibers are took into such close contact, at a high dry content, that strong forces can develop acting at the molecular level, giving its high strength for the final paper. There are some forces that may possibly act to hold the fibers together in the dry paper: mechanical entanglement of fibers and fiber surface fibrils, covalent bonds, inter-diffusion of polymers across the fiber/fiber interface, hydrogen bonds, polar interactions, ionic bonds, and van der Waals interactions /1/. Since the process water in the paper machine is circulated again and again to a big extent there is a rather high accumulation of anionic and uncharged polymers emanating from the fiber raw material itself, bleaching chemicals, inorganic salts and so on. To this mixture other cationic and anionic polymers are added to make better paper quality and/or paper machine runnability. A variety of polyelectrolyte complexes will therefore be formed in this complex circulating water system. Few complexes can be advantageous for deleting of dissolved colloidal material from the process water, but not needed phenomenon might occur, where added cationic strength additives are used by the anionically charged substances in the fibre water mixture, instead of increasing the strength of the paper /2/.

Nevertheless this usual occurrence of polyelectrolyte complexes in the paper industry, surprisingly little is known about the build of the most usual complexes and the factors manipulating their formation. It is therefore quest to learn more about the complex formation in order to prevent not needed reactions where polymer efficiency is lower and to promote reactions that can give extra beneficial effects /2/.

The original idea of the treatment is to produce multilayers, which means that all polymers are adsorbed on the fiber surface. However, in practice it is probably formed both multilayers and polyelectrolyte complexes. The formation of both a multilayer and a complex is not bad. On the contrary, it can have a positive effect on the strength /3/.

1.2 Target of the research

The first objective of the work was to tell how much of the strengthening effect based on multilayers and how much on the formation on polyelectrolyte complexes. The other objectives were to find what is the maximum strength that can be reached with such treatment and to compare with a recent master's thesis /47/ where was noticed a clear increase of paper strength when the pulp was treated with two oppositely charged polymers.

LITERATURE PART

2 Wood fiber structure and composition

Cellulose is the most common organic polymer on earth, produced by biosynthesis in annuals and perennials in huge quantities. The primary molecular structure of cellulose is simple, but its ability to formation of several levels of organization, inter- and intramolecular interactions and its unusual pathways of biosynthesis in nature have constantly research on cellulose /4/.

Cellulose is a linear homopolysaccharide consisting of a repeating anhydroglucose units, namely β -(1 \rightarrow 4) linked D-glucopyranosyl units, as shown on figure 1 /4, 5/.

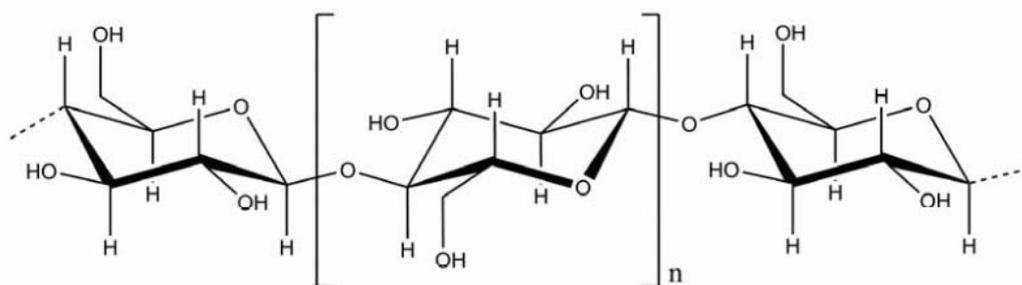


Figure 1. Structure of cellulose /4/.

The wood cell consists of cellulose, hemicellulose and lignin and of small amounts of extractives (table I, figure 2a) /6/.

Table I. Natural composition of pine and birch and the kraft pulps derived from them /6/.

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

Wood fibers contain about 15% to 30% of lignin. Lignin is a glue of wood, which holds the wood cells together /7/.

The cell walls consist of several layers: middle lamella (ML), primary cell wall (P), secondary cell wall (S1, S2, S3) (figure 2) and warty layer (W). These layers have different structure and chemical composition /6/.

The cell wall consists of cellulose microfibrils which are integrated in an amorphous matrix of hemicellulose and lignin. Figure 2b illustrates how cellulose and hemicellulose are distributed in the secondary cell wall between the microfibrils /8/.

The primary cell wall is a thin layer, consisting of cellulose, hemicellulose, protein, and pectin completely integrated in lignin /6/. The microfibrils (figure 2c) in the middle lamella form an irregular network. The middle lamella with primary layer during refining are removed completely (ML+P) /8/.

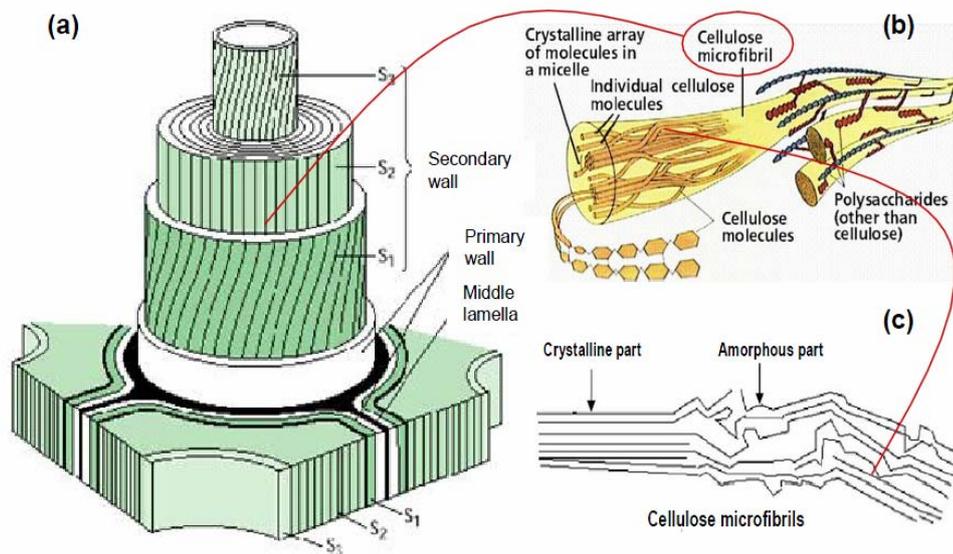


Figure 2. (a) Simplified composition of the wood cell wall. The cell wall is divided into a primary (P) and secondary (S1, S2, S3) cell wall. The lines in the secondary cell wall represent the microfibrillar alignment. (b) A schematic representation of the cellulosic microfibrils. Amorphous hemicellulose and some lignin are located between the crystalline cellulose microfibrils. (c) Schematics of a cellulose microfibril /8/.

The softwoods consist of two types of cell: long tracheids or fibers (90-95%) and a small number (less than 10%) of ray cells. Thickness of the softwood cellwall is typically 2 to 4 μm for earlywood and 4 to 8 μm for latewood. The structure of hardwood is more varied compared with softwood. Hardwoods consist of several cell types: fiber tracheids (30-70%), vessels (15-40%) and parenchyma cells (5-30%). Cell wall thickness 3 to 4 μm /6, 8/.

3 Factors affecting paper strength

The most important factors affecting paper strength are the following;

- properties of fibers (fiber strength, charge of fibers and fiber wall porosity, chemical composition of fibers, fiber deformation and fiber dimensions, cellulose microfibril angle etc.);
- extent of fiber-to-fiber bonding (beating, wet pressing etc.). Amount of bonding is a function of the density of paper, because both beating and wet pressing affect density;
- fiber orientation and distribution (sheet formation, density, machine direction etc.);
- shrinkage restrictions during drying (restraint drying, residual stresses etc.) /8/.

3.1 Effect of fiber charge on paper strength

The fiber charge has a great importance for the paper properties /8/.

Cellulosic fibers contain various ionizable groups such as carboxylic, sulphonic acidic, phenolic and hydroxyl groups. Because of these groups the fibers to carry a negative charge. The charges are important for various properties, such as paper strength, rate of beating, cell wall flexibility and swelling /8, 9/.

The charged groups are located either inside the cell wall or on the fiber surface, due to that they are called as surface- and bulk charges, respectively. Surface charges are important for fiber- and paper strength /10/.

There are some approaches to increase the amount of charged groups on the fibers, such as carboxymethylation, sulfonation or oxidation. Carboxymethylation is used as a method for increasing the swelling of fibers by introduction of charges. This increases the strength of paper /8/.

3.2 Effect of beating degree of fibers on paper strength

Properties of fibers changes due to refining, fibers swell more and shrink more than unrefined pulp. Refining leads to straightening of fibers, resulting in higher tensile stiffness as well as higher tensile strength /11/.

The effect of beating on the increase of fiber swelling has been attributed to internal fibrillation of the wall of fiber. Figures 3 and 4 show effect of beating on fibers and fibrillated structure of fibers. The increased fiber swelling, due to fiber fibrillation, increases drying stresses which are useful to tensile index and elastic modulus of the fiber restraint dried fiber network /12/.

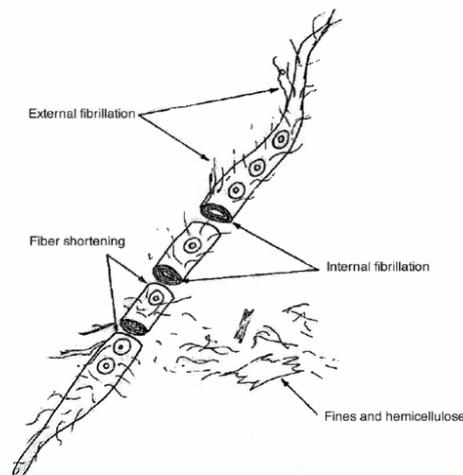


Figure 3. Effect of beating on fibers /13/.



Figure 4. Fibrillated structure of cellulose fibers /14/.

Surfaces of cellulosic fibers are rough on a scale of 0.01 to 10 μm . Refined fibers indicate the presence of fibrils and microfibrils extending on the fiber surfaces. Dimensions can range from about 2-5 μm in the case of primary microfibrils to much larger fibrils resulting from partial delamination of the outer layers of the cell wall. Roughness can severely reduce molecular contact between adjacent surfaces /15/.

3.3 Effect of fines on paper strength

Fiber fines have two main natures. Figure 5 shows the main types of fiber fines. Primary fines consist of parenchyma cells and chunky parts of fiber. Secondary fines are produced by refining. They are more fibrillar /16/.

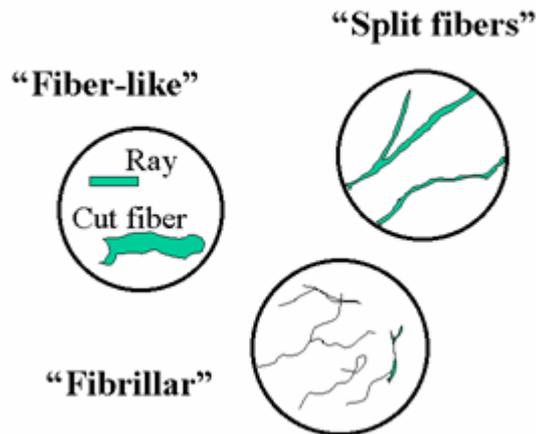


Figure 5. Types of fiber fines /17/.

Fines contribute to consolidation of sheet, interfiber bonding and to wet web strength. Interfiber bonds can be strengthened by adding strength chemicals and fines /8/. Fines have large specific area and their capacity to adsorb polymers is therefore higher than for whole fibers /10/.

Presence of fines have a positive effect on tensile and internal strength, tensile stiffness and light scattering (some mechanical pulp fines), but they also have a negative effect on density (usually low density is good) and tear strength /8/.

3.4 Effect of adding polyelectrolytes on paper strength

The effect of polymer strength additives on bond strength between cellulosic fibers has been studied by several researchers. Traditionally, paper strength additives have been divided by purpose into wet and dry strength additives /4/.

Most strength additives are polymers - natural, synthetic, or chemically modified natural polymers. Their interactions with the pulp components in water are very important for effect on paper strength /4/.

Polymeric strength additives promote fiber–fiber interactions through covalent or ionic bonds, increasing fiber–fiber bond strength /18/.

Adsorption of strength additives is used in many industrial applications. A strong polymer-surface interaction is the driving force. Most cationic additives have the ability to adsorb to the anionic fiber surface. That is why polymer additives used in papermaking often are cationic. The distribution and density of charges are also very important. Other factors that affect the adsorption are the molecular weight of the polymer and the presence of fiber segments called "fines" /10/.

Refining is an energy-intensive mechanical process which considerably improves fiber bonding and as a result improves strength of paper. The mechanism of refining as an improving fiber bonding and paper strength has been linked to fiber swelling, plasticization, fines generation, external fibrillation.

However, paper strength additives have always been important in papermaking /4/.

4 Use of polyelectrolytes in papermaking

4.1 *Acting of polyelectrolytes*

Polyelectrolytes are charged polymers. A positively or negatively charged polyelectrolyte is called a polycation (polybase) or a polyanion (polyacid), respectively. If positive and negative charges are on the same chain, the polyelectrolyte is called a polyampholyte (e.g. proteins) /19/.

Experimentally, the adsorption of charged polymers on charged or neutral substrate has been characterized to be a function of the polymer charge, chemical composition of the substrate, pH and ionic strength of the solution /20/.

It is very important to control the surface interactions between cellulose fibers in papermaking. It can be done by adding cationic polyelectrolytes to change the surface interactions. “They can introduce attractive forces, such as bridging, or diminish the electrostatic repulsion by neutralizing the surface charges of fiber, thereby increasing the importance of the attractive van der Waals forces. In these cases, polyelectrolytes act as flocculants. They can also act as a stabilizer, if their adsorption changes the forces between the surfaces to repulsive, such as steric repulsion or electrostatic repulsion due to charge reversal. The role of polyelectrolyte is a matter of dosage” /21/.

The polyelectrolyte properties impact the mechanism behind flocculation and strength of flocs. High charged, low molecular mass polyelectrolytes cause flocculation due to charge neutralization or patchwise attraction. The flocs are sensitive to polymer amount and break easily due to shear force.

High molecular weight and low charged polyelectrolyte molecules can bind more quantity of particles together from a larger distance than high charged, low molecular weight polyelectrolytes /22/.

Two systems, polyelectrolyte multilayers and complexes, positively impact the strength properties of fibres in papermaking process. PEM treatment of wood fibres significantly enhances adhesion between fibres which further on increases paper strength. In treating fibres with polyelectrolyte complexes, the increase in paper strength is most likely made by the increased fibre/fibre joint strength, which in turn arises from the enhanced fibre contact part properties. An interesting thing is that by

applying PECs, it is possible to improve sheet forming, retention and dewatering at the same moment /38/.

4.2 Types of polyelectrolytes

“Polyelectrolytes are a sample of group of macromolecules with many practically and interesting useful properties. Being both polymers and electrolytes, they have both the properties of a macromolecule and the charge possibilities of an electrolyte. Various combinations of polyelectrolytes, for example, cationic starches and carboxymethyl cellulose, are used today to enhance paper properties, such as wet or dry strength” /23/. There are two types of strength additives: natural and synthetic /24/.

4.2.1 Natural polymers

Starches, cellulose derivatives, xyloglucans, galactomannans, and chitosan are concerning to strength additives. Usually for increasing of tensile strength cationic starch and polyacrylamide are used. Molecular structures of the polysaccharides (natural strength additives) are collected in Figure 6 /4/.

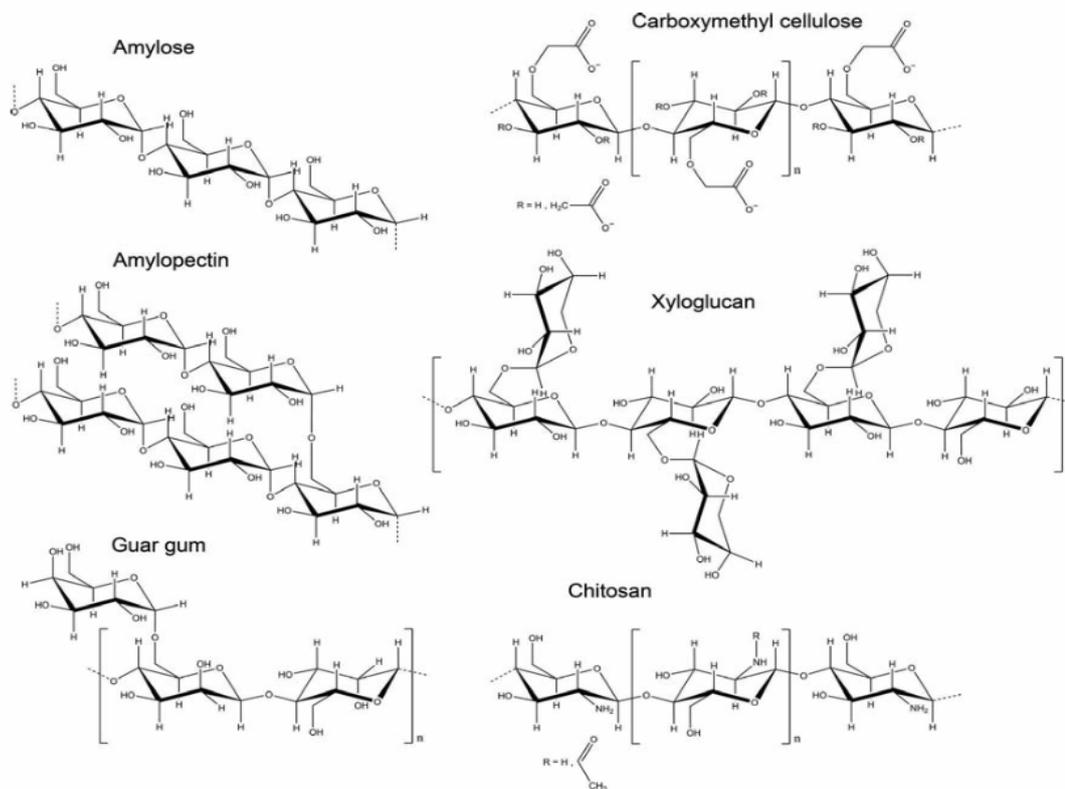


Figure 6. The molecular structures of polysaccharides /4/.

Starch is one of the oldest and currently the most widely used strength additive in papermaking /25/. Starch consists of two main polysaccharides: amylose and amylopectin, on a macromolecular level (figure 6). Amylose is a linear polymer of 1-4 linked α -D-glucopyranosyl units, whereas amylopectin is a highly branched polymer with the same D-glucopyranosyl units with 1-4 linked α -D-glucopyranosyl chains branched by 1-6 linkages. The molecular weights of native amylose and amylopectin are in the range of 0.25 to 1 Mg/mol and 10-500 Mg/mol, respectively. Depending on the plant (potato, corn etc.), starch generally contains 75 to 80% amylopectin and 20 to 25% amylose. Grades of starch additives for different purposes are prepared by other chemical modifications like oxidation and hydrolysis. Before use, starch needs to be cooked in order to obtain the required solution properties. The properties of the starch solution further will influence paper properties /4/.

After the saturation level of adsorption has been reached, starch no longer adheres to wet end components. It has been assumed that the hydrodynamic surface area best corresponds to the places where starch can be adsorbed. Table II presents data for the hydrodynamic surface area and saturation value of some wet end components /26/.

Table II. Hydrodynamic surface area and saturation values for cationic starch adsorption. D.S. = 0.042 /26/.

Adsorbent	Hydrodynamic surface area, m ² /g	Saturation value, mg/g
Fiber fraction	1.2	16
Pulp blend	2.1	42
Fines fraction	8.0	65
Filer clay	2.0	17
Coating clay	12.0	59

Carboxymethyl cellulose (CMC) (figure 7) was first prepared in 1918 and was produced commercially in the early 1920's at the IG Farbenindustrie AG in Germany. However, since then, significant improvements in process technology, in

product quality, and in production efficiency have been made. Today CMC of different quality is applied in many areas of industry and human life /27/.

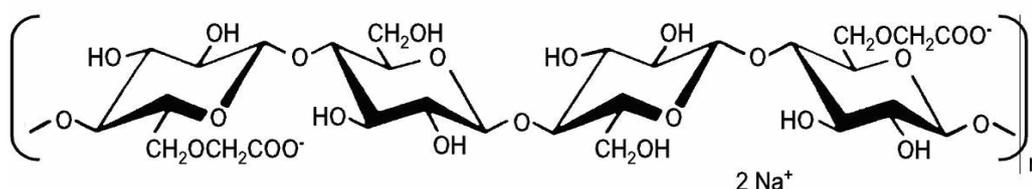


Figure 7. Spatial structure of CMC /2/.

Carboxymethyl cellulose is prepared by etherification of cellulose. CMC is produced in variety of molecular weights and degrees of substitution. CMC along with several other cellulose derivatives can be adsorbed irreversibly onto cellulose fibers. Fibers modified by CMC have shown excellent dry strength properties in unfilled paper sheets /4/.

Carboxymethylated polysaccharides are based on renewable resources. They are biodegradable and non-toxic materials that are used in an increasing number of applications. There are various grades of CMC (table III). Especially the highly purified products, i.e., of low salt content have done the CM polysaccharides to an expensive additive in many applications including the food and pharmaceutical area. CMC is known to be applied in more than 200 applications today /2/.

Table III. Carboxymethyl cellulose (CMC) grades and typical applications (adopted from /27/).

Quality of CMC	Examples of application area	Content of CMC (%)	Content of salt (%)
Technical	Detergents, mining flotation	< 75	> 25
Semi-purified	Oil and gas drilling muds	75-85	15-25
Purified	Paper coating, textile sizing and printing, ceramic glazing, oil drilling muds	> 98	< 2
Extra purified (Cellulose gum)	Food, toothpaste, pharmaceuticals	> 99.5	< 0.5

4.2.2 Synthetic polymers

Synthetic polymers as strength additives that are used in papermaking include e.g. poly(acrylamide), polyvinylamine, and different wet strength resins: ureaformaldehyde (UF), melamine-formaldehyde (MF), and poly(amideamine) epichlorohydrin (PAE) resins /4/.

Cationic poly(acrylamides) (C-PAM) are prepared by radical co-polymerization of an acrylamide monomer with a cationic charge carrying co-monomer (figure 8). The polymers can be prepared with different molecular weights and charge densities depending on the use (strength, retention). Synthetic polyampholytes and polyelectrolyte complexes of poly(acrylamides) and other polyelectrolytes have also shown potential as strength additives. Polyvinylamine (PVAm) is a linear amine functional polymer (figure 8) known to improve both the wet and dry strength of paper. Wet strength resins are chemically reactive condensation products of ureaformaldehyde, melamine-formaldehyde, and poly(amideamine) epichlorohydrin (figure 8), that gives wet strength to paper after drying and curing /4/.

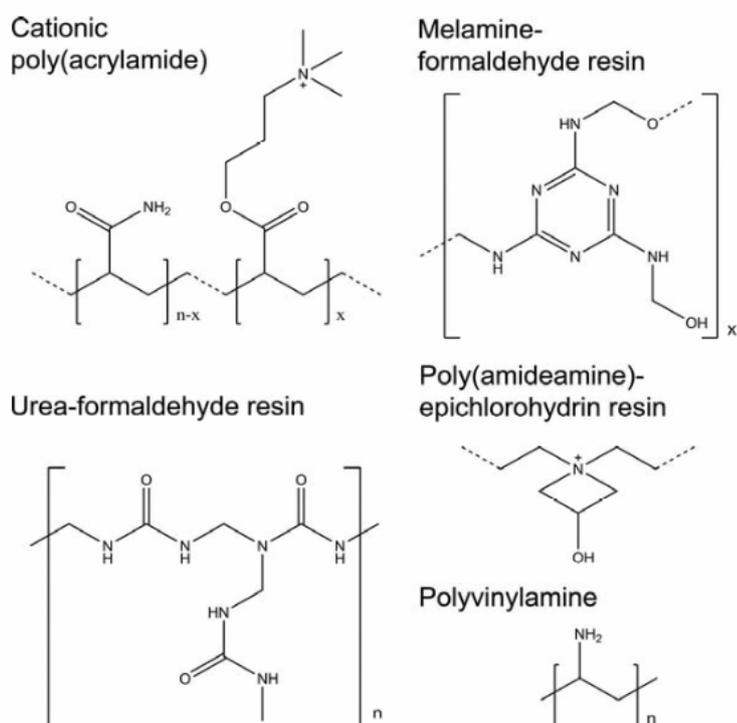


Figure 8. The molecular structures of synthetic polymers /4/.

5 Interaction between cellulosic surface and polyelectrolyte

5.1 DLVO – theory

The theory of the stability of colloidal systems was developed in 1940s by Deryagin, Landau, Vewey and Overbeek.

DLVO theory is a good explanation of the interaction between two approaching particles. The theory shows determination of the colloidal stability by the potential energy of the particles (V_T) /28/.

$$V_T = V_A + V_R,$$

where:

V_A - potential energy of the attractive interaction due to van der Waals force;

V_R - potential energy of the repulsive electrostatic interaction.

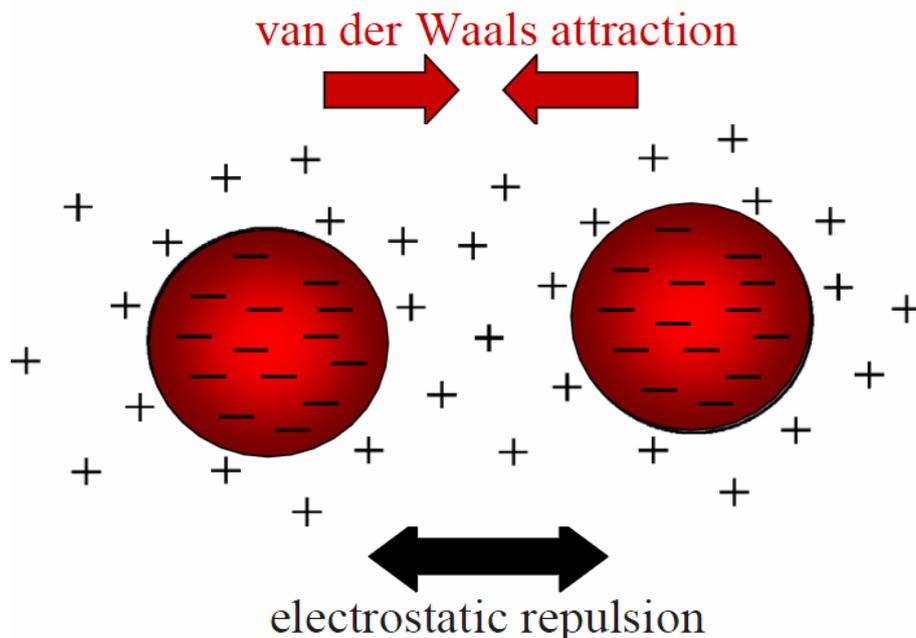


Figure 9. Representation of DLVO theory /29/.

If repulsive forces overwhelm attractive forces, it means stability of the system. But if attractive forces overwhelm repulsive forces, it leads to coagulation.

Figure 10 shows conditions for colloid stability. Where: X – distance between two particles, V_T - potential energy of the particles.

Electrolyte concentration increases from curve 1 to curve 5.

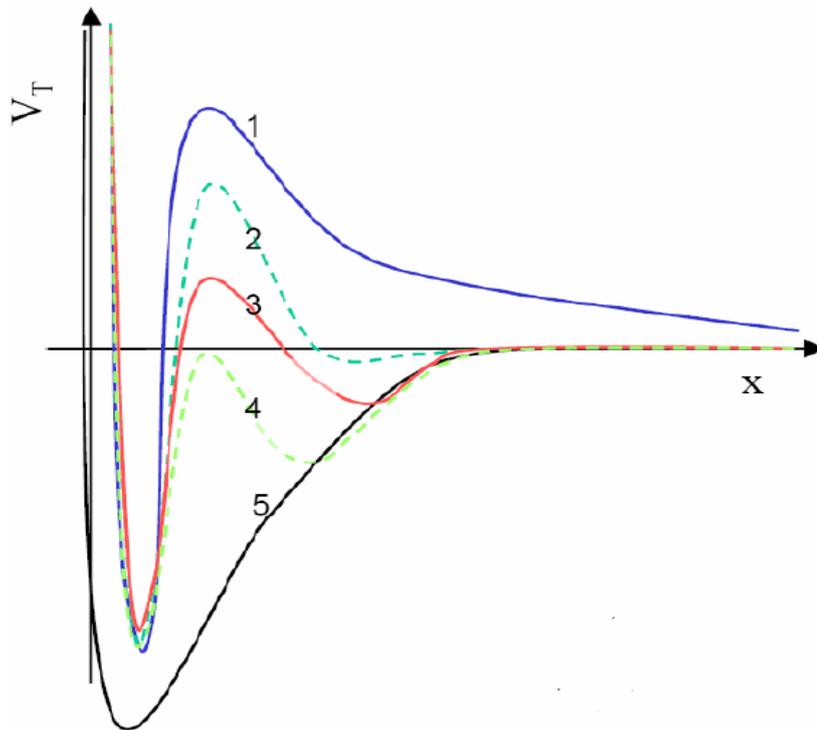


Figure 10. Conditions for colloid stability /29/.

Description of the curves:

- 1) Surface charge density is high, electrolyte concentration is low, potential barrier is high → colloid stability;
- 2) Secondary minimum may appear ($x > 3$ nm), potential barrier is still high → kinetically stable colloid;
- 3) Potential barrier is small → slow coagulation;
- 4) Potential barrier < 0 , fast coagulation at the ccc (critical coagulation concentration) → unstable colloid;
- 5) No potential barrier, strong attraction potential → (very) fast coagulation /29/.

To maintain the colloidal system stable, the repulsive forces must be dominant. The stability of colloidal system can be achieved by two fundamental mechanisms that affect dispersion stability (figure 11): steric stabilization of colloids and electrostatic or charge stabilization.

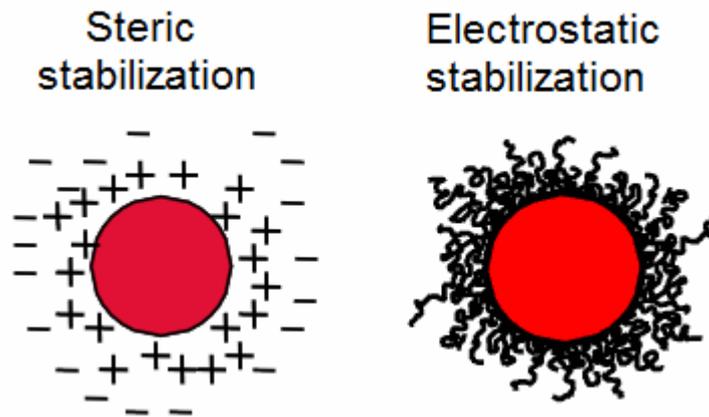


Figure 11. Types of colloidal system stability /29/.

- Steric stabilization of colloids is achieved by forming a coating at the particle surface by attaching of polymer molecules, which separates the particle from another particle by creating a repulsive force.
- Electrostatic or charge stabilization involves free polymeric molecules creating repulsive forces between the approaching particles.

5.2 Adsorption of polyelectrolytes on cellulosic fibers

Surface charges are very important as they affect the interactions between fibers and chemical additives, such as cationic polyelectrolytes, as well as fiber-fiber interactions. The fiber-fiber interactions are important for the formation of the paper web. It is desirable to form a web as uniform as possible. However, different chemical and mechanical forces create local fiber concentrations higher than the average, as a result fiber flocs are formed. Flocs are undesirable due to their negative impact on various paper properties, such as formation, strength, opacity and printability. The mechanisms responsible for fiber flocculation are illustrated in figure 12. They can be divided into colloidal interactions, mechanical surface linking and elastic fiber bending /30/.

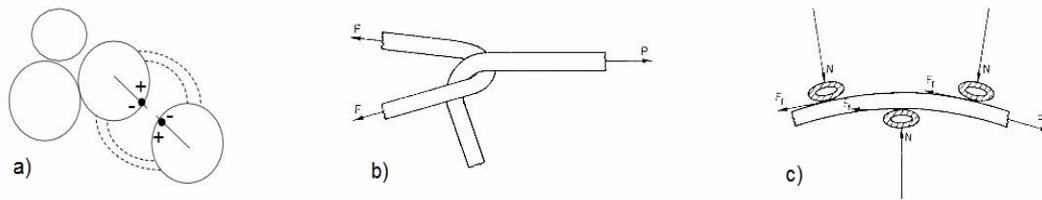


Figure 12. Illustration of the forces responsible for fiber flocculation. a) colloidal interactions, b) mechanical surface linking, c) elastic fiber bending /30/.

Between pure cellulose surfaces the surface forces are repulsive. Two force regions are usually observed for cellulose surfaces, steric and electrostatic /21/. The range of electrostatic repulsion decreases with increasing ionic strength as predicted in DLVO theory. The range of the steric force for cellulose depends on the cellulose used in the experiments /31/.

Water-soluble polymers, i.e. polyelectrolytes, are used as retention chemicals, and also for draining, fixing and increasing paper strength. They adsorb on the negatively charged surface of fibers and fines, and so they change the surface forces between these particles. Adsorption is mainly electrostatically driven. Electrostatic interactions are important for adsorption of polyelectrolytes on a surface with oppositely charge /32, 33/.

At first, the electrostatic repulsion between cellulose surfaces decreases, when polyelectrolytes are adsorbed on cellulose surfaces /21/. Close to the charge neutralization point (cnp), attractive forces like van der Waals forces are dominating. Further adsorption leads to reversal of charge and thus electrostatic repulsion increases again. If the charge density of polyelectrolyte is decreased, the polyelectrolyte adsorbs in a looser conformation. These can introduce a repulsive steric contribution to interactions even at large distances. The range of steric interaction can be several hundred nanometers. Close to charge neutralization, the bridging attraction can be seen. This attraction is usually lower, but it ranges further than with high charged polyelectrolytes because of the lower affinity of the low charged polyelectrolyte to the surface. On separation, pull-off forces are highest when surfaces are partly covered, i.e. close to cnp. When more polyelectrolyte adsorbs, the pull-off force decreases /31/.

Adsorption depends on the properties of polymer (molecular weight, charge density, crosslinking, branching, structural restrictions), solution conditions and the surface properties of the particles (surface area, surface charge, surface chemical

composition and porosity) /30/. Due to these factors, polymer may adsorb in different conformations on fibers and fines surfaces. High charged polyelectrolytes tend to adsorb in a flat conformation, and low charged polyelectrolytes adsorbs in a loose conformation, containing more loops and tails. The polymer with long chain can form a bridge between fibers, to prevent its sliding /34/.

Polyelectrolyte adsorption on cellulosic fibers is complicated by the porous nature of the fiber /30/. It was shown by Alinec and van de Ven that fibers contain macro pores ~75 nm in diameter and micro pores having a diameter of about 4 nm /48/. Due to the porous nature of the fiber, the extent the polyelectrolyte adsorption into the fiber cell wall will be dependent on the molecular conformation of the polyelectrolyte in solution. Adsorbed amount of polyelectrolyte increases as the molecular mass decreases through penetration into the fiber wall. To neutralize for the fiber charges, a high charge density polyelectrolyte will adsorb to a lower amount compared to a low charge density polyelectrolyte having similar molecular mass /30/.

5.3 Polyelectrolyte multilayers

The polyelectrolyte multilayer (PEM) treatment is a relatively new method for changing a surface by treating a charged surface consecutively with oppositely charged polyelectrolytes. This layer-by-layer technique has become popular over the last ten years. Applying this technique to fibers has been used to make better paper strength or to tailor this surface with high quantity of additives to meet definite end-use properties. Wagberg et al. /36/ used polyallylamine (PAH) and polyacrylic acid (PAA), but because of their high cost they are restricted in the papermaking industry. With this, it is a considerable interest to research if the polyelectrolyte multilayer technique could be applied to make better paper strength using two already well known polyelectrolytes for the paper making industry, starch and CMC /35/.

The polyelectrolyte multilayers concept could preferably be used to furnish typical of a centre ply in a liquid packaging board, i.e., a mixture of chemimechanical pulp

(CTMP) and unbleached chemical pulp, to both get high bulk from the CTMP and improve the paper strength with the polyelectrolyte multilayers /35/.

Regarding dry strength additives in papermaking, cationic starch is the most usually applied additive. Due to the combination of a relatively low cost and a rather high efficiency in making better paper properties. Cationic starch gives the best (10-15%) strength increase when adsorbed as a single layer, which is often too little for certain applications. It is rather well established that there is a correlation between the adsorbed quantity and the strength-enhancing effect of the additive and so different approaches, apart from changing the charge of the strength-enhancing additive, have been applied to increase the adsorption. Combinations of cationic and anionic polyelectrolytes and cationic polyelectrolytes, inorganic complexes and anionic polyelectrolytes have been used in order to increase the adsorbed amount of the strength additives. It has been shown, according Stratton /37/ that the combination of cationic and anionic polyelectrolytes in the wet end of papermaking is much more efficient than a treatment of the dry paper, and furthermore it was also shown that the additives were made efficient via an increase in the fiber/fiber contact.

To understand adsorption of Pes on the fiber surface there are following processes occur during the adsorption:

- Transport of the polyelectrolytes to the fiber surface from the solution (molecular mass of the polyelectrolyte evaluates the available fiber surface);
- Registration of the Pes on the fiber surface;
- Reconfiguration of the Pes on the fiber surface;
- Detachment of the Pes from the fiber surface /39/.

The excess adsorbed amount oversaturated the fiber surface, making it possible to adsorb an anionic polyelectrolyte on top of the starch layer /35/.

The polyelectrolytes adsorbed in the furthestmost layer have a huge influence on the internal structure of the PEM and the net surface charge of the multilayer is determined by the final layer, with the preceding layers being neutral /38/.

5.4 Polyelectrolyte complexes

Polyelectrolyte complex (PEC) formation is a usual phenomenon happening when cationic Pes react with anionic Pes and/or other anionic substances (figure 13). Mixing of solutions of cationic and anionic polyelectrolytes leads to a spontaneous formation of complexes /41/. The research of the interactions between oppositely charged Pes is of increasing interest, since the use of PECs is increased in many industrial applications, e.g., in biotechnology, in medicine and in papermaking. The interactions between different additives, in papermaking process waters, are not constantly and can make formation of undesirable deposits in the paperweb and on the surfaces, and can also make undesirable consumption of added chemicals /38/.

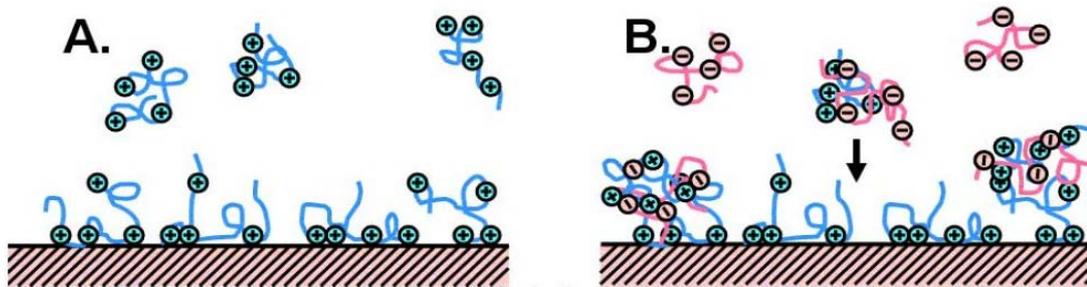


Figure 13. Concept of a two-step treatment, starting with an excess of cationic polyelectrolyte, followed by anionic polyelectrolyte, creating polyelectrolyte complex, which subsequently deposit onto fiber surfaces, where they can contribute to paper strength: A-first step – treatment with cationic polyelectrolyte; B-second step – treatment at first with cationic polyelectrolyte and then with anionic polyelectrolyte /15/.

In controlled conditions, PECs and PEMs can be viewed as a new and useful chemical concept for papermaking.

In some cases the efficiency of PECs is improved than in the single PE systems and usually as well the amount needed is smaller because of synergistic effects arising between two Pes /38/.

Polyelectrolyte complexes impact the bonding and structure of the fiber network in the papermaking process. The complexes have been found to change the molecular contact area in the fiber–fiber joint, which strengthens the joint and promote significantly increases the strength properties of papers made from the treated fibres. Also sheet making, retention and dewatering have been seen to improve if polyelectrolyte complexes are used in papermaking applications /38/.

6 Strengthening effect of multilayers and complexes

6.1 Single polymer system

Single polymer system can be formed by adding charged polyelectrolyte.

It was shown that increase in the paper strength by PEs occurs due to increased degree of contact between fibers, an increase in the number of fiber/fiber contacts and the introduction of covalent bonds /1/.

6.2 Dual polymer system

Dual polymer systems can be formed by adding oppositely charged polyelectrolytes. Because of charge reversal, cationic polyelectrolyte with high charge and low molecular weight is added first. Polyelectrolytes form bilayer structures, which resembles the polyelectrolyte multilayer. After influence of the shear forces and multiple collisions, the multilayer structure is partly mixed towards the less ordered structure of a complex. PECs form more stable flocs than single polymer systems. Positive effects of PECs have been reported on paper strength /4/. In PEC treatment the increase in paper strength is most likely caused by the increased fiber-to-fiber joint strength /41/.

Also, PEMs increases paper strength, when compared to single polyelectrolyte systems /36/. PEM addition enhances significantly the adhesion between fibers which further increases paper strength /41/. Dual polyelectrolyte systems are able to increase the polymer amount in the fiber web making the fiber surface smoother, and thus increasing the bonded area between fibers. This, however, only partly explains why the paper strength is increased. In addition, PECs have been reported to yield better retention and strength properties than the sequential addition of polymer /23/. Only by increasing the layer number of PEM, i.e. the amount of the polymer, could similar levels of strength be achieved /23, 31, 41/.

Surface forces between multilayer structures mostly depend from the outer layer of the system, whereas the effect of PECs is depending on the properties of PEC /31/. Treating the fibers with PECs also improves sheet forming, retention and dewatering /41/, as were mentioned in chapter 5.4.

7 Measurement methods to detect formation of multilayers and complexes

The properties of the complexes made in aqueous solutions by oppositely charged PEs have been characterised by numerous instruments, such as turbidimetry, atomic force microscopy and electrophoretic mobility. The reaction stoichiometry has been found out by polyelectrolyte titration, in the mean time the adsorption kinetics and the structural parameters of the PECs have been explained by static light scattering and by reflectometry /38/.

Some methods for detecting adsorption on cellulosic fibers:

- Electron Spectroscopy for Chemical Analysis (ESCA) can be used to measure content of the nitrogen on the surface and then compare it with adsorbed amount of nitrogen determined by adsorption of polyelectrolyte /49/;

- Stagnation point adsorption reflectometry (SPAR). A unique speciality of the SPAR setup is that the measurement of adsorption is made in the stagnation point itself. A beam of linearly polarised light is focused on the stagnation point, over the surface on which it is reflected, and further guided into the detector. The parallel and perpendicular components of the polarised light are separated by a beam splitter and the intensity of each component is registered as a voltage by two photo diodes. The ratio of the two signals constitutes the instrumental output, which is proportional to the reflectivity ratio on the wafer /23, 50/.

- Quartz crystal microbalance with dissipation (QCM-D) monitoring.

In the quartz crystal microbalance with dissipation monitoring the frequency of the resonating crystal decreases when a polyelectrolyte is adsorbed to it /23, 50/.

The QCM-D technique enables simultaneous measurement of both the adsorbed amount of polymer on a sensor surface and the viscoelastic properties of the adsorbed polymer layer /4, 31/.

- Dynamic contact angle (DCA) analysis.

The adsorption of polyelectrolyte complexes on individual fibers can be analysed using a Dynamic Contact Angle analyser. A fiber is mounted between two pieces of tape, which is glued to a holder. The solvent or the PEC solutions are placed on a table directly underneath the mounted fiber, so that the angle between the fiber and

the solution is close to 90° when the fiber is immersed. The fiber is immersed and withdrawn at a rate of $20 \mu\text{m/s}$.

The fiber need to be washed 2–3 times in order to study the repeatability of the measurement, before the fiber is partly treated for 10 minutes in the solution. As the last step – washing of the fiber in order to study the influence of treatment /23/.

- Environmental scanning electron microscopy (ESEM).

To analyse and compare modified and untreated fibers, a field emission gun environmental scanning electron microscope also can be used. The measurements are made in the back scattering emission (BSE) mode using an acceleration current of 8-10 kV and a pressure of 0.6-0.7 torr /23/.

EXPERIMENTAL PART

8 Objective of the study

The first objective of the work was to tell how much of the strengthening effect was based on multilayers and how much on the formation of polyelectrolyte complexes. The other objective was to find what is the maximum strength that can be reached with such treatment.

9 Materials

9.1 Fibers

Fibers used in this study were bleached baled pine and birch pulp. The pine pulp was beaten in Valley Hollander up to degrees of SR 20 and SR 35 and the birch pulp up to degree SR 20. The zeta-potential and conductivity of the pulps were measured with zeta-potential meter SZP-06 (Mutek) and are shown in table IV.

Table IV. Zeta-potential of the softwood (pine) and hardwood (birch) cellulose beaten in Valley-Hollander up to degrees of SR 20⁰ and 35⁰.

Fiber type	The target degree of ⁰ SR	Zeta-potential, mV.	Conductivity, mS.
Pine (bleached, baled)	20	-39,3 ± 1,3	0,130 ± 0,002
Pine (bleached, baled)	35	-40,4 ± 2,0	0,117 ± 0,003
Birch (bleached, baled)	20	-58,0 ± 0,5	0,097 ± 0,005

Obtained degree of beating coincides with target degree.

9.2 Polyelectrolytes

The starch grades used in this study were cationic potato starches Raisamyl 115 (DS 0,015) and Raisamyl 150 (DS 0,05). To obtain the solution of starch ready for use, the starch had to be cooked. The starch was dispersed in cool water (5 %) and then warmed by mixing continuously since it started to boil. The temperature was kept

around 95-100 °C about 30 minutes. After cooking the starch solution was diluted with water to solid content of 1%.

The CMC grades used in this study were Finnfix WRM, Finnfix 2 and Finnfix 10G. The 5 g of dry CMC was dispersed in 500 ml of water (1 %) and stirred until it was complete dissolved.

The charges of polyelectrolytes were measured with Mutek PDC-02 device.

After measurements the charge of polyelectrolytes was calculated in accordance with equation 1.

$$CD_{\text{polyelectrolyte}} = \frac{V_{\text{titr}} \cdot CD_{\text{titr}}}{V \cdot C} \quad (1)$$

where:

V_{titr} – used amount of titrant, ml;

CD_{titr} – charge of the titrant, mekv/l (for 0.001 N poly-DADMAC or PES-Na the charge is 1 mekv/l);

V – volume of the titrated sample, l;

C – concentration of the sample, g/l.

The results are presented in table V.

Table V. Characteristics of polyelectrolytes.

Trade name	Polyelectrolyte	Charge of PE, mekv/g.
Raisamyl 150	Cationic starch (DS 0,05)	0,35
Raisamyl 115	Cationic starch (DS 0,015)	0,10
Finnfix WRM	CMC (DS 0,56)	-3,35
Finnfix 2	CMC (DS 0,76) M = 30 000	-4,57
Finnfix 10G	CMC (DS 0,76) M = 66 000	-9,12

10 Methods

Pulp was refined in Valley-Hollander beater (Valley Laboratory beater, ISO 5264/1) up to required degree of beating. Then pulp was analyzed with Shopper-Riegler (determination of rate of drainage by Shopper-Riegler method, ISO 5267/1).

After that, the following methods were used for this work:

- polyelectrolyte treatment of the fibers (one and two layers);
- determination of the Zeta-potential of the fibers;
- determination of the charge of the filtrate.

10.1 Polyelectrolyte treatment

Polyelectrolyte treatment happened according to the scheme shown in figure 13.

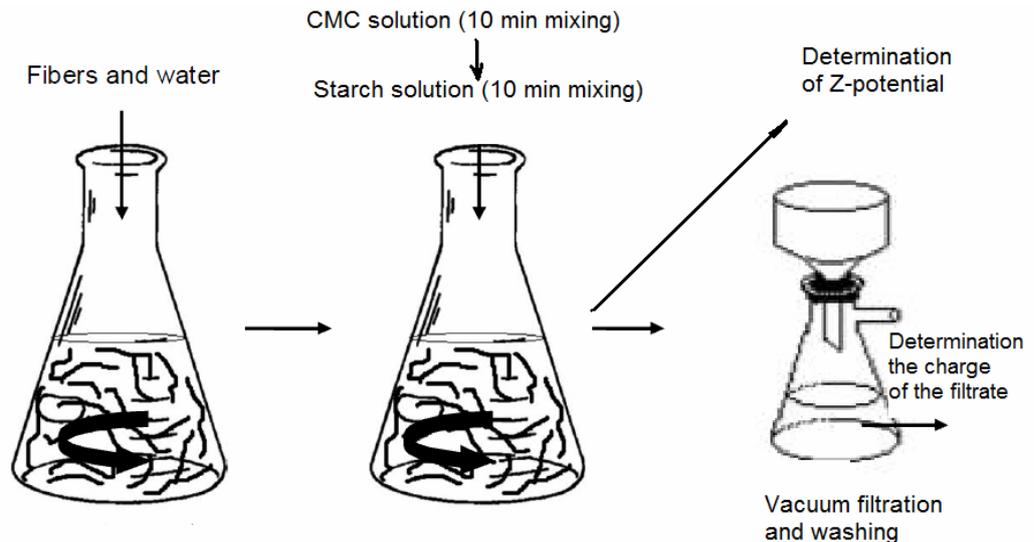


Figure 13. Simplified scheme of the experiments /8/.

Fiber suspension after Valley-Hollander was diluted till concentration 2 g/l. Tap water was used for diluting. The temperature was maintained on a constant level at 20⁰C. It was controlled by thermometer.

Fibers were treated during 10 minutes of continuous mixing, at first with cationic starch and then, in case of two layer treatment, with anionic CMC. Some part of the sample went to the determination of Z-potential and some part to the vacuum

filtration or/and washing to determine the charge of the filtrate. Washing was done only after starch addition (before CMC addition) by vacuum filtration of fiber suspension through the wire. Then fibers from wire were diluted in the same amount of pure water.

10.2 Determination of the Zeta-potential of the fibers

Surface charges play an important role in many industrial processes. And the surface charge of the product is often used as a parameter of quality control. Efficiency of the selected additive can be determined by examining a sample before and after contact with a chemical additive. Determination of the Z-potential of the surface of fibers was done by Streaming Potential method on System Zeta Potential, SZP 06 BTG Mütek GmbH (figure 14).



Figure 14. System Zeta Potential, SZP 06 BTG Mütek GmbH /42/.

The determination of the zeta potential was done using the standard screen electrode (308 μm).

It should be mentioned that all samples were tested under the same conditions, because the installation is sensitive to temperature changes. There was washing of the measuring cell after each measurement. Each pulp sample was measured five times for increasing accuracy of the results of Zeta potential. As the results were used average value and standard errors of the mean /43/.

10.3 Determination of the charge of the filtrate

Determination of the charge of the filtrate was done by Mutek PCD-02 (figure 15).

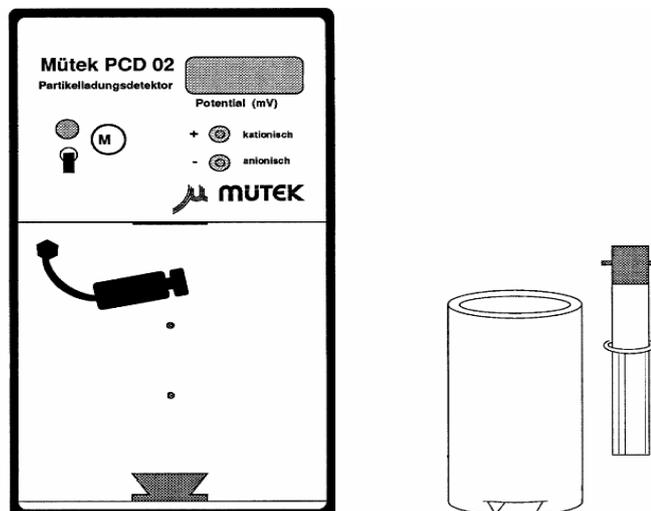


Figure 15. System Mutek PCD-02.

Polyelectrolyte titration was used to determine the charge of the solution. Figure 16 shows spatial structure of polyelectrolytes used in titration.

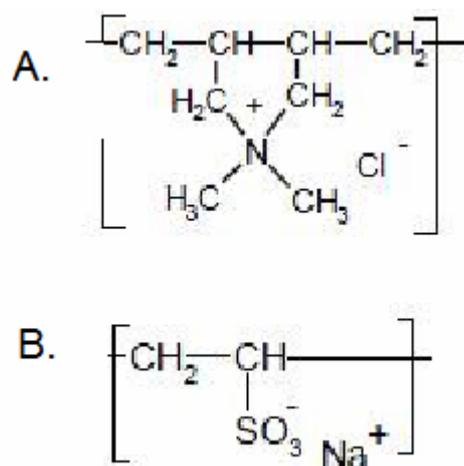


Figure 16. Polyelectrolytes used in titration:
 A. poly-(dimethyldiallylammonium)chloride, PDADMAC and
 B. polyetehylene sulphonate (PES-Na) /44/.

Each filtrate sample was measured minimum three times. For results were used average values and standard errors of the mean.

The charge of the filtrate was calculated from titration result by using equation (2):

$$CD_{\text{filtrate}} = \frac{V_{\text{titr}} \cdot CD_{\text{titr}}}{V} \quad (2)$$

where:

V_{titr} – used amount of titrant, ml;

CD_{titr} – charge of the titrant, mekv/l (for 0.001 N poly-DADMAC or PES-NA the charge is 1 mekv/l;

V – volume of the titrated sample, l.

10.4 Preparation and testing of the laboratory sheets

The target basis weight of the laboratory sheets was $60 \pm 3 \text{ g/m}^2$. Laboratory sheets for the trials were made with the KCL Laboratory Sheet former from bleached baled pine and birch. Air bubbles barbotage was used for fibers slurry agitating. The sheets were made quite soon after the polyelectrolyte treatment (in 30 minutes).

For testing of dry strength, samples were dried on the drying drum for 6 hours. Then, handsheets were conditioned for 8 hours (23°C, 50% Relative Humidity), (SCAN-P2).

First of all some general properties were measured, such as grammage, thickness (with Lorentzen&Wettré Thickness Tester) and density. Before cutting of handsheets also air permeability and roughness were measured by Bendtsen tester Lorentzen&Wettré (L&W).

For thickness, each sample in 5 points was measured with L&W Thickness tester. Six handsheets with similar basis weight were cut into strips with standard width - 15 mm, and 10 of them were tested on L&W Tensile Tester and 6 strips were tested on Stiffness Measurement Tester L&W.

Instructions for measurements are based on standards:

- grammage (SCAN-P 6:75);
- thickness (SCAN-P 7:75);
- air permeability (SCAN-P 21:67);
- roughness (SCAN-P 60:87);
- tensile strength (SCAN-P 38:80);
- bending stiffness (SCAN-P 64:90).

11 Test point matrix

With each polyelectrolyte additions 11 test series were made according to table VI.

Table VI. Test point matrix.

test serie	meaning of the test	fiber	SR	Starch	CMC	CMC : Starch
Ref.	reference	pine	20	Raisamyl 150	-	-
1	Starch grade	pine	20	Raisamyl 115	-	-
2	Beating degree	pine	35	Raisamyl 150	-	-
3	Fiber	birch	20	Raisamyl 150	-	-
4	CMC	pine	20	Raisamyl 150	WRM	1:10
5	CMC-dosage	pine	20	Raisamyl 150	WRM	1:20
6	Starch grade	pine	20	Raisamyl 115	WRM	1:20
7	Beating degree	pine	35	Raisamyl 150	WRM	1:20
8	Fiber	birch	20	Raisamyl 150	WRM	1:20
9	D.S. of CMC	pine	20	Raisamyl 150	Finnfix 2	1:20
10	M of CMC	pine	20	Raisamyl 150	Finnfix 10	1:20

Four series with one layer treatment and seven with two layers treatment. The variables in testseries with one layer treatment were DS of the starch (Raisamyl 115, DS 0,015 and Raisamyl 150, DS 0,05), beating degree of the pulp (pine SR 20 and SR 35) and type of pulp (pine and birch SR 20).

In series with two layer treatment type of pulp, beating degree, the grade of CMC and dosage of CMC was changed.

Each series was done with four addition level of polyelectrolytes which are shown in tables VII and VIII. Also, there was one extra point in each series with washing at the starch dosage 100 mg/g and respectively dosage of CMC. Tables VII and VIII show proportional dosage of starch and CMC.

Table VII. Dosage of polyelectrolyte for one layer treatment.

Polyelectrolyte	Dosage, mg/g.
Starch C=1 g/l.	0
	10
	25
	100

Table VIII. Dosage of polyelectrolytes for two layers treatment.

Proportion CMC/starch	Starch, mg/g. (C=1 g/l.)	CMC, mg/g. (C=0,1 g/l.)
1:10	0	0
	10	1
	25	2,5
	100	10
1:20	0	0
	10	0,5
	25	1,25
	100	5

The selected dosages of CMC were based on the measured charge of CMC (WRM Finnfix) and starch (Raisamyl 150). The dosages were chosen so that either equal amount of anionic and cationic charge was added with CMC and Raisamyl 150 (CMC:starch 1:10) or only half so much anionic charge was added with CMC than cationic charge with starch (CMC:starch 1:20).

12 Results and discussions

12.1 The Zeta-potential and the charge of the filtrate

12.1.1 One layer application

Consider the influence of one layer application of cationic starch with/without washing after treatment on Zeta-potential. Figure 16 shows the changing of Zeta-potential with starch application. There are 4 curves on Figure 6, according to the Table VI, with one extra point with washing for each curve. Values of the results of Zeta-potential and the charge of the filtrate are presented in tables in Appendix I.

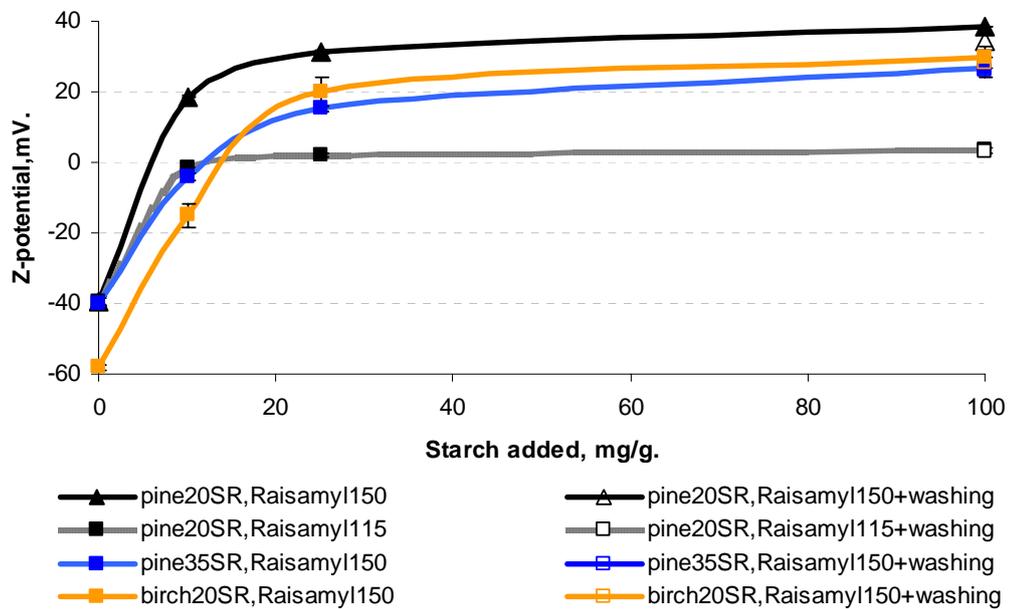


Figure 17. The Z-potential as a function of only starch (mg/g.) added to the fiber suspension. The starch grades were Raisamyl 150 (DS 0,05) and Raisamyl 115 (DS 0,015).

The change of the zeta-potential is quite linear with starch additions 0-10 mg/g. With further addition of starch the Zeta-potential of fibers still increase until the addition was a bit under 25 mg/g. Adding starch above this amount does not change any more the zeta-potential of the fibers. This means that no more than this amount of starch can adsorb on the fiber (so called saturation point).

Consider the influence of one layer application of cationic starch with/without washing after treatment on the charge of the filtrate (results are presented on figure 18), next conclusions can be done:

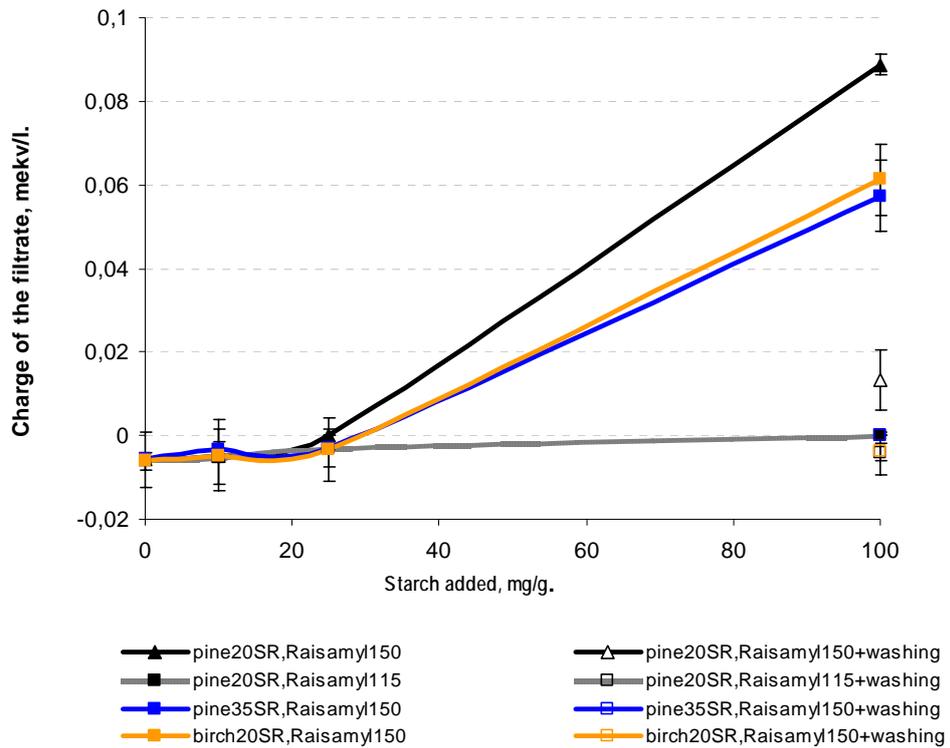


Figure 18. Charge of the filtrate as a function of only starch added (mg/g.) to the fiber suspension. The starch grades were Raisamyl 150 (DS 0,05) and Raisamyl 115 (DS 0,015).

Before dosage of starch 25 mg/g. there is no starch in the solution and charge of the filtrate is still negative. But after saturation point some starch left in the solution and since that point charge of filtrate becomes positive.

In case with series pine20⁰SR with different types of starches, suspension with Raisamyl 115 did not reach even zero point, while another series has the charge almost +0.1 mekv/l. in the highest point of dosage. This is because of higher charge density of cationic starch Raisamyl 150, compared with Raisamyl 115.

In case with washing almost all starch from the solution was removed. There is no capability to form complexes with another polyelectrolyte.

From figures 17 and 18 can be made the following conclusions:

- below the saturation point part of the fibers are covered with starch, there is no starch in solution (only multilayer will be formed);
- at the saturation point the fibers are totally covered by starch but there is no starch in the solution (only multilayer will be formed);

- above the saturation point the fibers are covered by starch and there is starch left in the solution to be able to form polyelectrolyte complexes with the second added polyelectrolyte (both multilayer and polyelectrolyte complexes will be formed).

In case of pine 35⁰SR, more starch is needed to achieve the saturation point in case of more beaten pulp. If we look at the charge of the filtrate, it turns towards positive with less amount of starch in case of pine 20⁰SR (figure 18).

Fines have a large influence on the saturation adsorption of the polyelectrolyte.

Figures 17 and 18 show that the series pine 20⁰SR/Raisamyl150 have a very good adsorption capacity and a higher degree of beating would probably result in a too high densification of the sheets.

The curves from pine 20⁰SR and birch 20⁰SR have no big difference in behavior.

In case of no CMC addition the washing does not decrease the Z-potential so much.

It means that the starch adsorbed on the fiber remains on the fibers despite of the washing.

12.1.2 Two layers application

Influence of two layers application of cationic starch and CMC with and without washing after starch treatment on Zeta-potential is shown in figure 19.

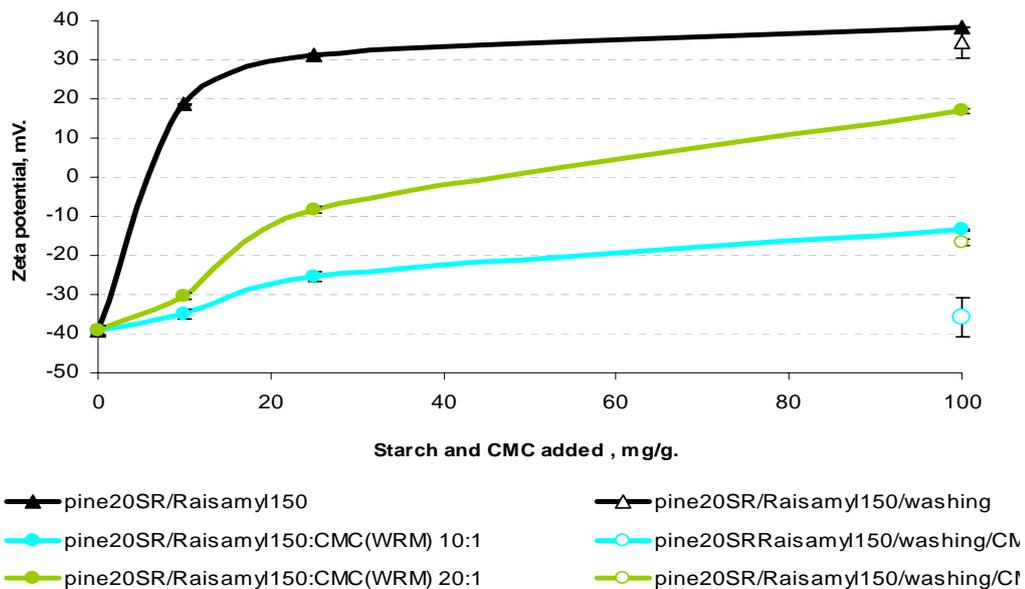


Figure 19. The Z-potential as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:10 or 1:20 of starch addition.

To compare series of pine 20⁰ SR and series with adding CMC, we can see that Zeta-potential lower in series with two layers treatment, because fibers become covered by anionic CMC.

The CMC amount adsorbed on pulps depends on several factors: charge of CMC, DS of CMC, pH, degree of beating of the pulp and so on. Blomstedt presents in her dissertation /33/ that the amount of adsorbed CMC increased strongly for CMC with a lower degree of substitution and for beaten fibers.

Pettersson et. al. were observed saturation points of different pulp samples with different degree of beating with three layers of polyelectrolyte treatment (cationic starch/CMC/cationic starch). In case of beating of fibers up to 22⁰SR it was observed a linear increase in adsorption for each layer compared to unbeaten pulp. Further beating of the fibers up to 33⁰SR only increased the adsorption of cationic starch in the first adsorbed layer, while in the second and third layers the adsorption of polyelectrolytes was similar. It can also indicate that the cationic starch will decrease available surface for the CMC in the second layer. This could be, for instance, due to an aggregation of fines and collapsing of fibrils on the fiber surface by the cationic starch. There is no obvious reason why for the differently treated fibers the adsorption conformation of the starch should be different /21/.

Comparing dosages of starch/CMC (20:1 and 10:1), we can say that suspension of series with dosage starch/CMC 10:1 has lower Zeta-potential, because concentration of CMC higher, it means that more than 20:1 (starch:CMC) CMC can adsorb. The zeta-potential stays quite stable with higher amount of CMC (added amount of cationic and anionic charge is same). This probably means that the layer with two polyelectrolytes is quite neutral. However the CMC could not totally neutralize the charge of the starch layer (zeta-potential of treated fibers is less than of untreated fibers, figure 19) although the added charge amounts were quite the same. Maybe some part on CMC does not adsorb on the starch layer but stays in the solution. This could explain why the charge of the filtrate is a bit more negative with high PE additions (figure 20).

During washing starch from solution and partly from the fiber surface is removed, and capability to form complexes is lower compared to unwashed sample. It means that after washing there are no possibilities to form polyelectrolyte complexes. And

if there is no starch in the solution with which the CMC could form complexes the CMC more preferably adsorbs on the layer of starch on the fibers. That is why the zeta-potential is more negative when the washing stage was included.

Figure 20 shows the dependence of two layers application of cationic starch and CMC with/without washing after treatment on the charge of the filtrate.

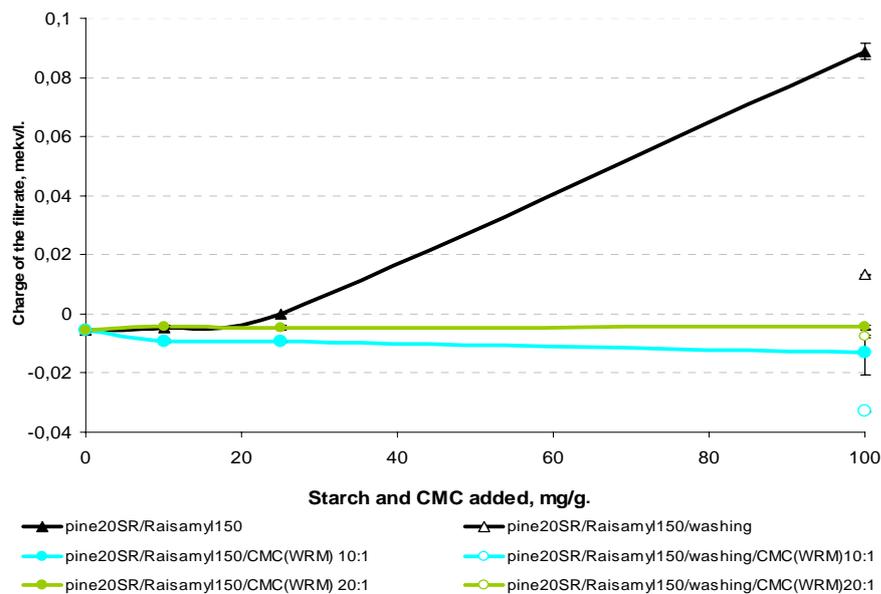


Figure 20. The charge of the filtrate as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:10 or 1:20 of starch addition.

From figure 20 with charge of filtrate after adding CMC to the sample there is no reversion of the charge to positive. It means that before saturation point no complex formation and after saturation point formation of PECs occurs and the charge becomes negative.

Concentration of CMC also has influence on the charge of the filtrate. Due to the pulp beaten up to degree 20⁰SR, pulp has a linear increase of adsorption in each layer of polyelectrolyte /21/. But in case with higher concentration of CMC the charge of the filtrate is more negative compared to lower concentration of CMC. It means that part of the CMC does not adsorb on the fiber surface.

In case of two layers application the results could also be examined as function of CMC addition. From figures 21 and 22, we can see how it affects if there is starch available in the solution or not (starch additions 10, 25 and 100 mg/g vs. starch addition 100 mg/g with washing). In cases of starch additions 10 and 25 mg and 100 mg with washing stage there is not (much) starch in the solution.

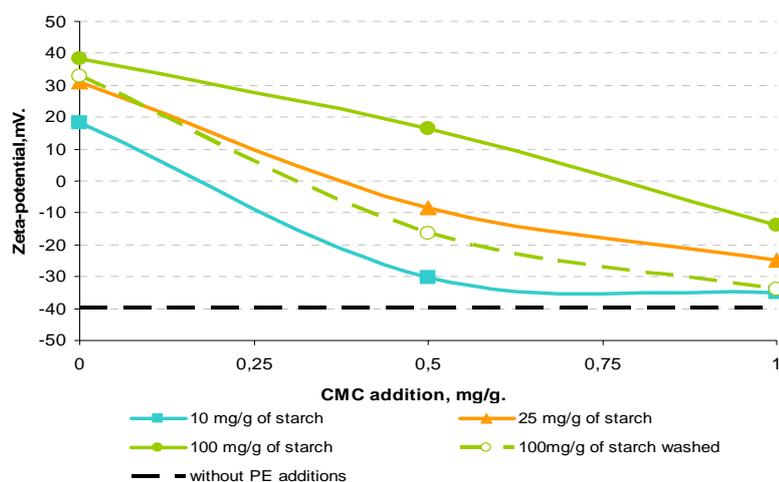


Figure 21. The Z-potential as a function of CMC addition (mg/g.) to the fiber suspension. The added amount of CMC was 1:20 and 1:10 of starch addition.

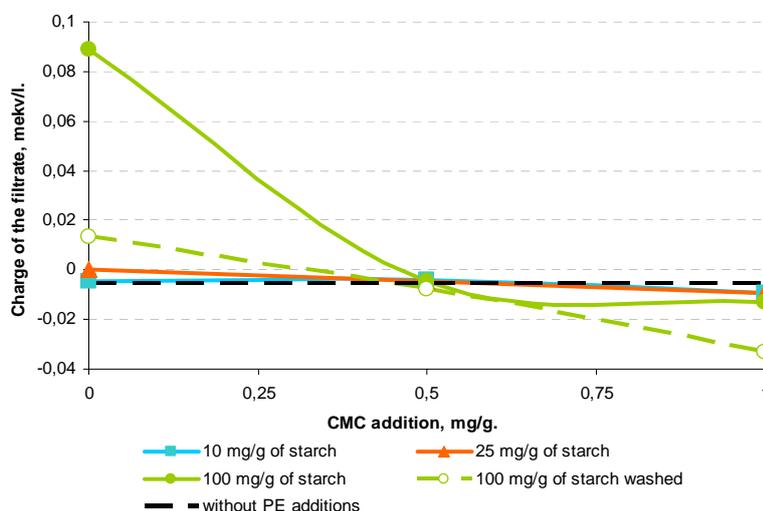


Figure 22. The charge of the filtrate as a function of CMC addition (mg/g.) to the fiber suspension. The added amount of CMC was 1:20 and 1:10 of starch addition.

From figure 22 it can be concluded that CMC reacts preferably with the starch in the solution than with the adsorbed starch, because we see (the results with starch addition 100 mg/g) a sharp decrease in the charge of filtrate, it means that most of the CMC has passed into the solution.

In addition we can see that the zeta-potential change caused by CMC addition is quite the same in cases of 25 mg/g addition (saturation point) and 100 mg/g with washing. In both cases the fibers are fully covered by starch before CMC addition and there will not form PE complexes because there is no (much) starch left in the solution.

12.2 The properties of handsheets

12.2.1 Consider the effect of starch grade and starch /CMC ratio

This chapter considered influence of starch grade and starch/CMC ratio on properties of handsheets. Here we can see dependences of properties such as density, tensile index, tensile energy adsorption index, elongation, tensile stiffness, bending stiffness, air permeability and roughness from starch and CMC addition (mg/g). There are five curves, on figures 24-30, with different dosages of starch and CMC in accordance with table VI. Also, there is one addition point in each series with washing in dosage of starch 100 mg/g.

When considering paper consolidation, it is also important to clarify how the different additives increase density of sheets. Density is the ratio between basis weight and thickness of the material in kg/m^3 . Figure 23 illustrates that series with only starch addition have higher density compare with series with starch and CMC addition.

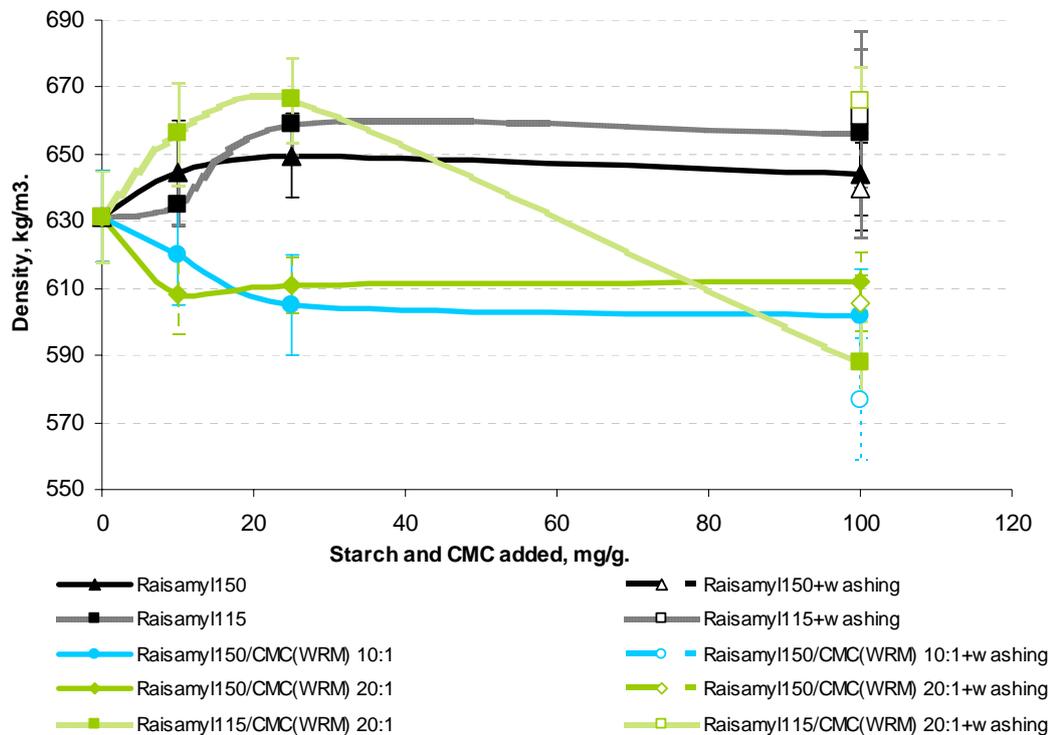


Figure 23. The density of the sheets made from pine pulp (SR 20) as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:10 or 1:20 of starch addition.

For series with Raisamyl 115 and CMC (WRM) we can see increasing in density after washing. It means that PECs have negative effect on density. On the contrary, for other series PECs have positive impact on density.

As were mentioned in chapter 6.2, there are two mechanisms for single polymer system that leads to flocculation - polymer bridging and patch-wise flocculation. The starch with lower charge density (Raisamyl115) adsorbs in an extended conformation with many loops and tails. These loops and tails “adsorb” to another surface forming bridges. The flocs formed by Raisamyl 115 are looser compared with flocs formed by Raisamyl 150. Stronger flocs have negative impact on properties of paper such as formation and strength properties. Particles connected with long and flexible polyelectrolyte bridges stay together even in shear. It can partly explain that series with Raisamyl 115 have higher results in tensile index (fig. 24), tensile energy adsorption (figure 25) and tensile stiffness (figure 27).

The coiled conformation of the adsorbed chains gives a higher deviation from the 1:1 charge stoichiometry in the first layer and makes it possible to adsorb more polyelectrolyte in the PEM /45/. It means that in case with Raisamyl115 and CMC(WRM) (with starch/CMC ratio 20:1) adsorbed amount of CMC in the second layer higher compare with series with Raisamyl150. It's indicates that the more adsorbed of CMC then higher strength properties.

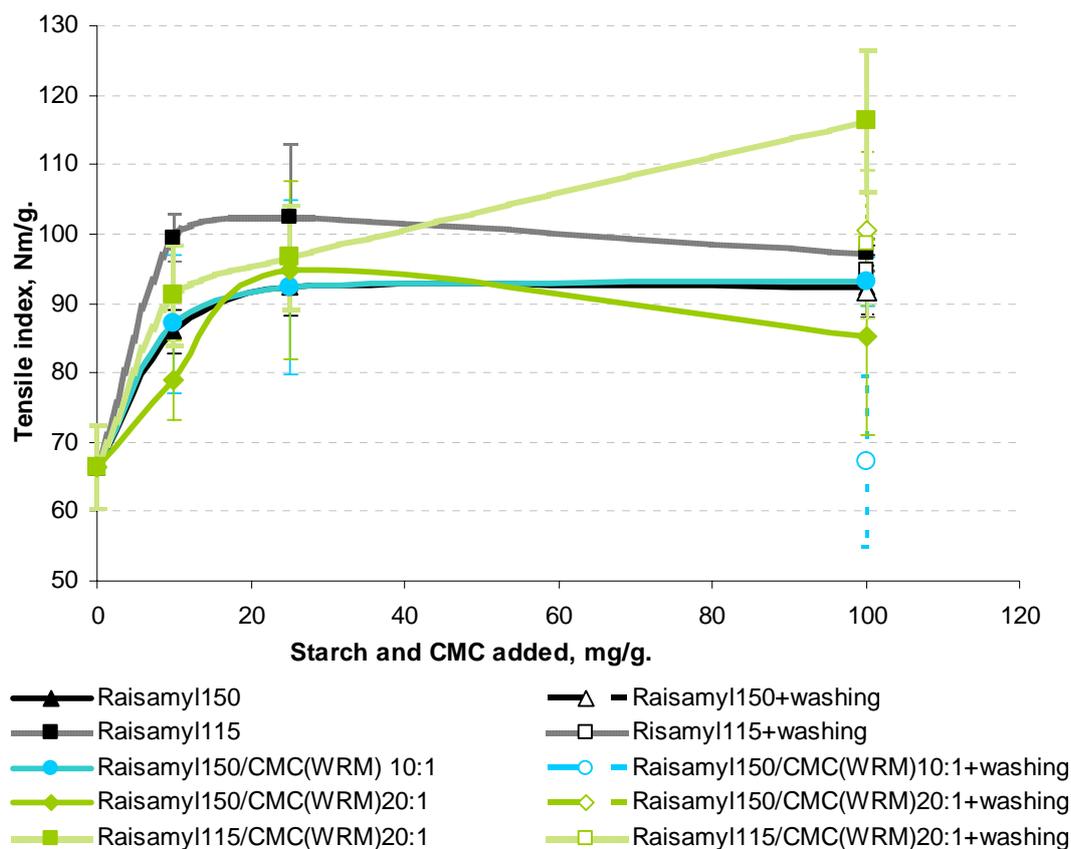


Figure 24. The tensile index of sheets made from pine pulp (SR 20) as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:10 or 1:20 of starch addition.

In other studies, the influence of PECs on paper strength has been investigated using a sequential addition of polyelectrolytes to the pulp suspension, forming PECs. This procedure probably makes it difficult to draw any conclusions, how much of these results that can be applied to a system with pre-formed PECs /23/. However, the effects on the tensile strength and stiffness of paper with sequential addition of cationic polyacrylamide (CPAM) and CMC to a mixture of bleached softwood Kraft pulp and bleached thermomechanical pulp (TMP) were investigated /46/. That study showed that adding polyanions after adding polycations gave better results than adding polycations only.

Figure 24 shows that it also impact from starch grade (DS of starch and charge density).

The formation of starch/CMC PECs and PEMs improved the paper strength more effectively than the layer-by-layer assembly of starch and CMC. Because if we take

a look on results with washing, where no possibilities to form complexes, they are lower compare with results without washing. Also if we compare results with 25 mg/g starch addition + CMC (theoretically only PEM will form) the tensile index is better with 100 mg/g starch + CMC addition (both PEM and PECs will form).

The tensile strength of the fiber network was more significantly improved after forming the complexes of starch/CMC than one or two layers application of polyelectrolytes, especially such combination as pine 20⁰SR/Raisamyl 115/CMC WRM (20:1), pine 20⁰SR/Raisamyl 150/CMC Finnfix 10 (20:1) and maybe pine 20⁰SR/Raisamyl 150/CMC WRM (10:1), except series with pine 20⁰SR/Raisamyl150, where we can see decreasing in tensile index after second polyelectrolyte edition. If we look at the added cationic/anionic charge ratio at testpoints where additions of starch/CMC - 20:1 is the lowest compared to 10:1 (starch/CMC ratio). It can be assumed that the charge ratio is important.

Tensile index with one layer application:

- In case with pine20⁰SR and Raisamyl150, tensile index was increased on 26%;
- For pine 20⁰SR and Raisamyl115 on 30%.

Tensile index for two layers application:

- For pine20⁰SR/Raisamyl150/CMC, tensile index was increased by PEMs on 33% and by PEMs+PECs on 22%;
- For pine20⁰SR/Raisamyl115/CMC, by PEMs on 32% and by PEMs+PECs on 42% (it means that strengthening effect of PECs only 10%).

In case with higher dosage of CMC, there are similar results for one and two layers application, only after washing (where no capabilities to form PECs) we can see decreasing in tensile index.

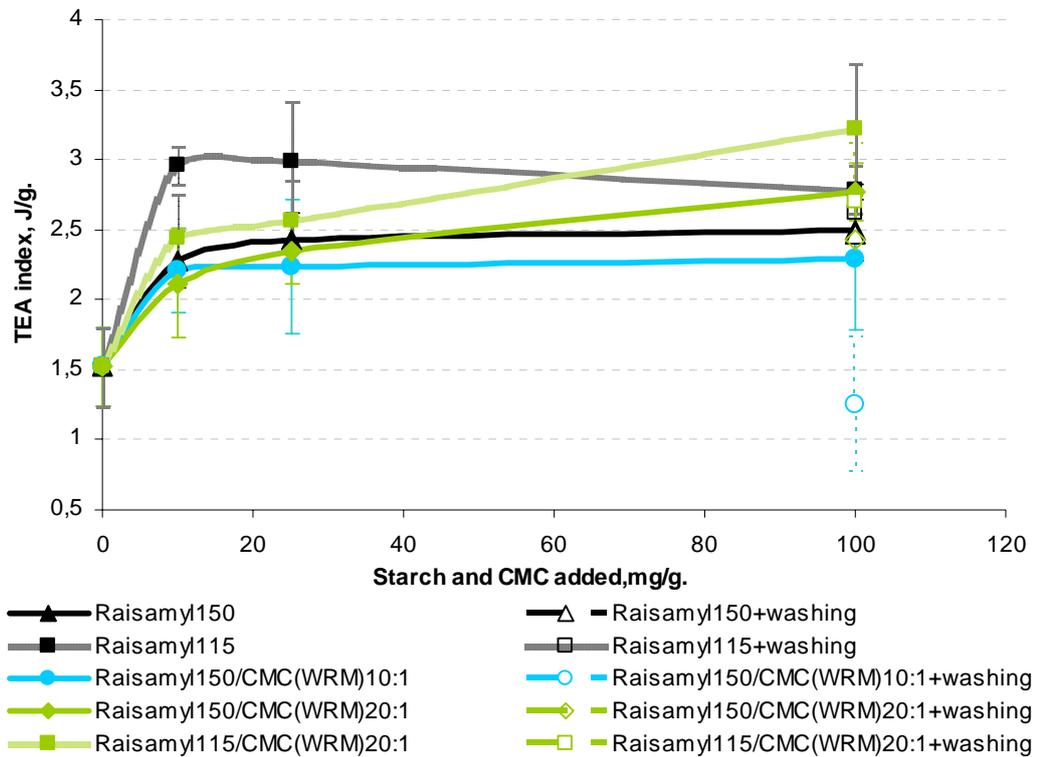


Figure 25. The tensile energy adsorption index of sheets made from pine pulp (SR 20) as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:10 or 1:20 of starch addition.

Tensile index and tensile energy absorption (figure 25) could be improved considerably when sheets were made from two layers (PEMs + PECs) treated pulp rather than from pulp with only one added layer of starch.

The maximum tensile force the test piece can withstand before it breaks and the corresponding elongation of the strip was measured and recorded. Dependences of elongation from polyelectrolyte additions can be seen on figure 26.

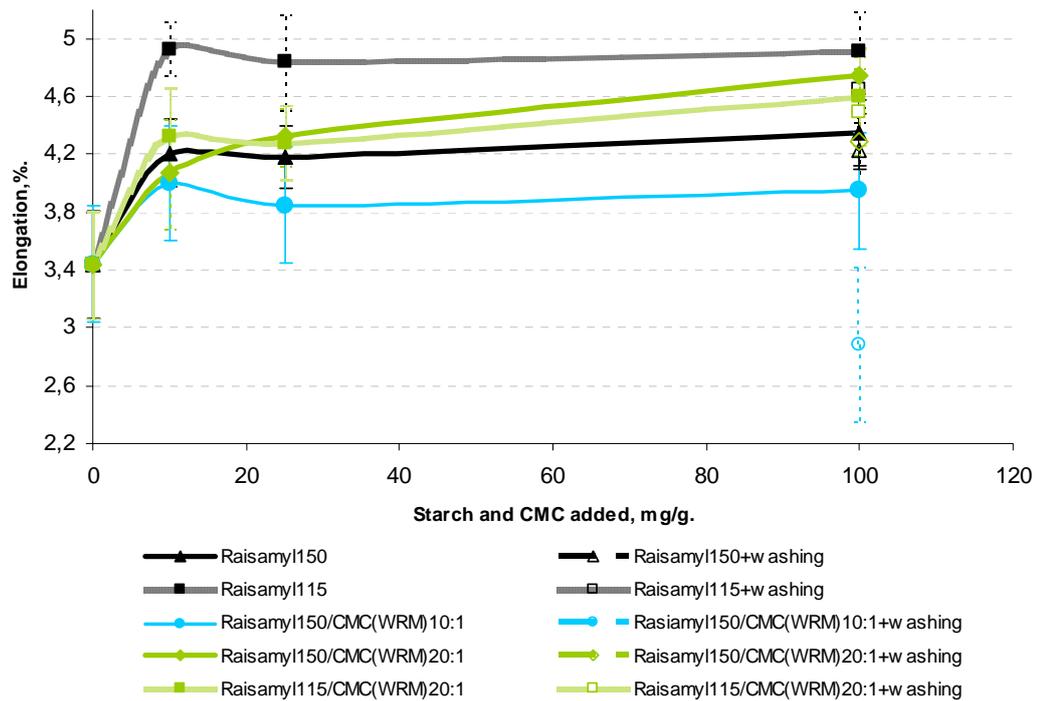


Figure 26. Elongation of sheets made from pine pulp (SR 20) as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:10 or 1:20 of starch addition.

The ability to form longer and more flexible bridges, in case with Raisamy115, leads to higher elongation (figure 26). With increasing of dosage of CMC (starch/CMC ratio 10:1) decreasing in elongation can be detected. May be it can be explain by formation of more strong flocs, compare with another dosage (20:1). Stiffness relates to the elastic properties of the material. It refers to the resistance the material gives when deformed by an external load. For paper and board, two aspects of stiffness are usually measured: tensile stiffness and bending stiffness. Tensile stiffness is the ratio of the stretching force per unit cross-sectional area to the elongation per unit length. Figures 27 and 28 corresponding present results of measurements.

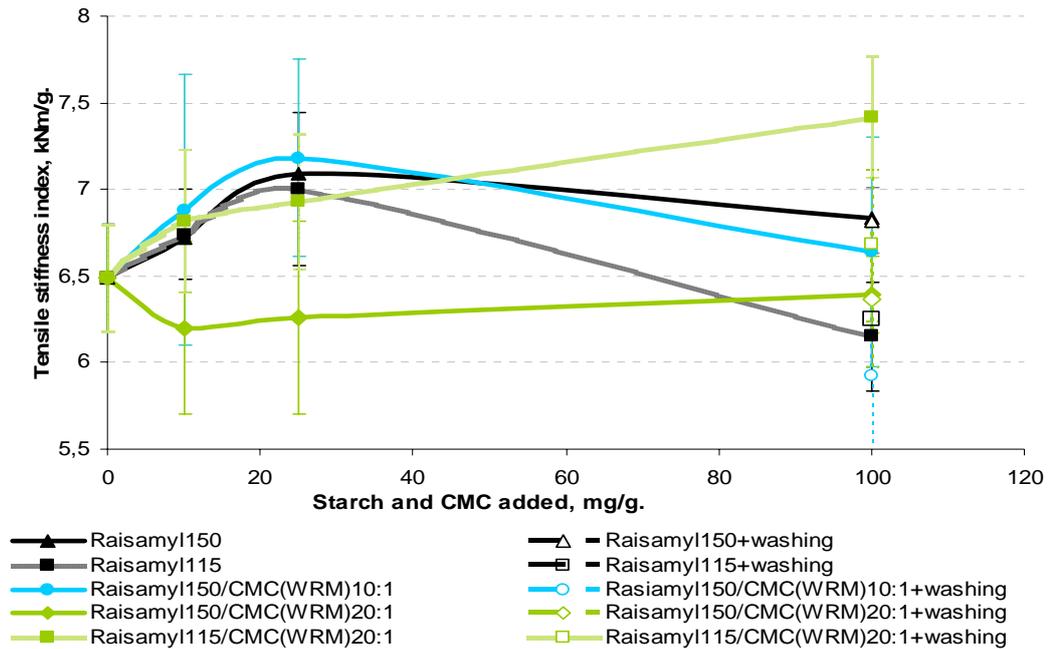


Figure 27. Tensile stiffness index of sheets made from pine pulp (SR 20) as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:10 or 1:20 of starch addition.

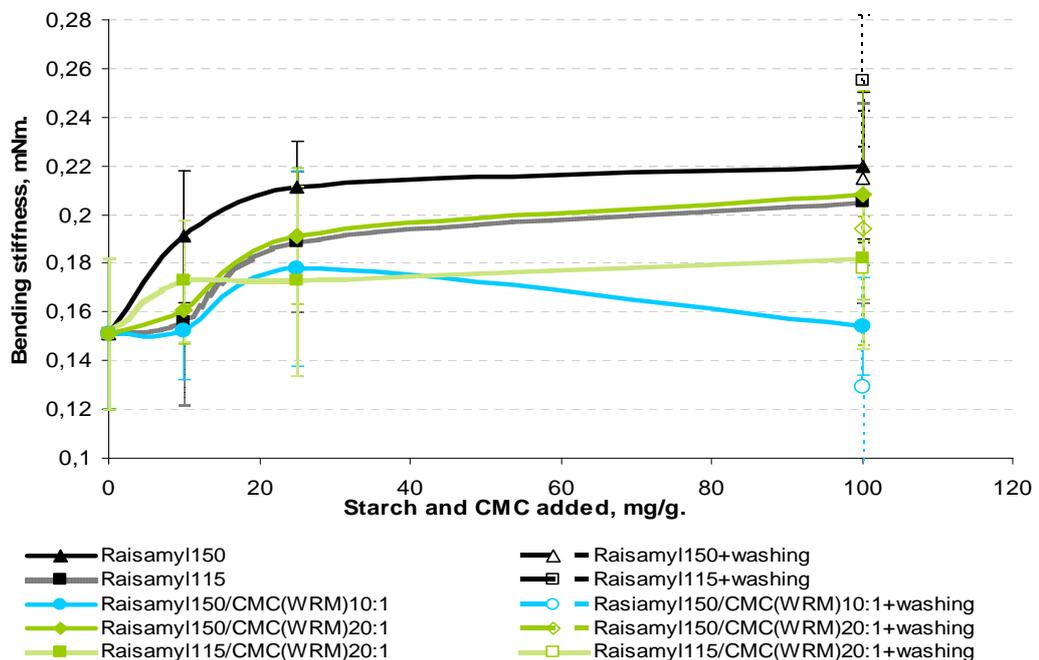


Figure 28. Bending stiffness of sheets made from pine pulp (SR 20) as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:10 or 1:20 of starch addition.

Better effect on bending stiffness gives one layer treatment, compared with tensile stiffness where no clear answer.

The air permeability (figure 29) is the flow of air through a defined area of paper. The air permeability and roughness measured using the Bendtsen tester.

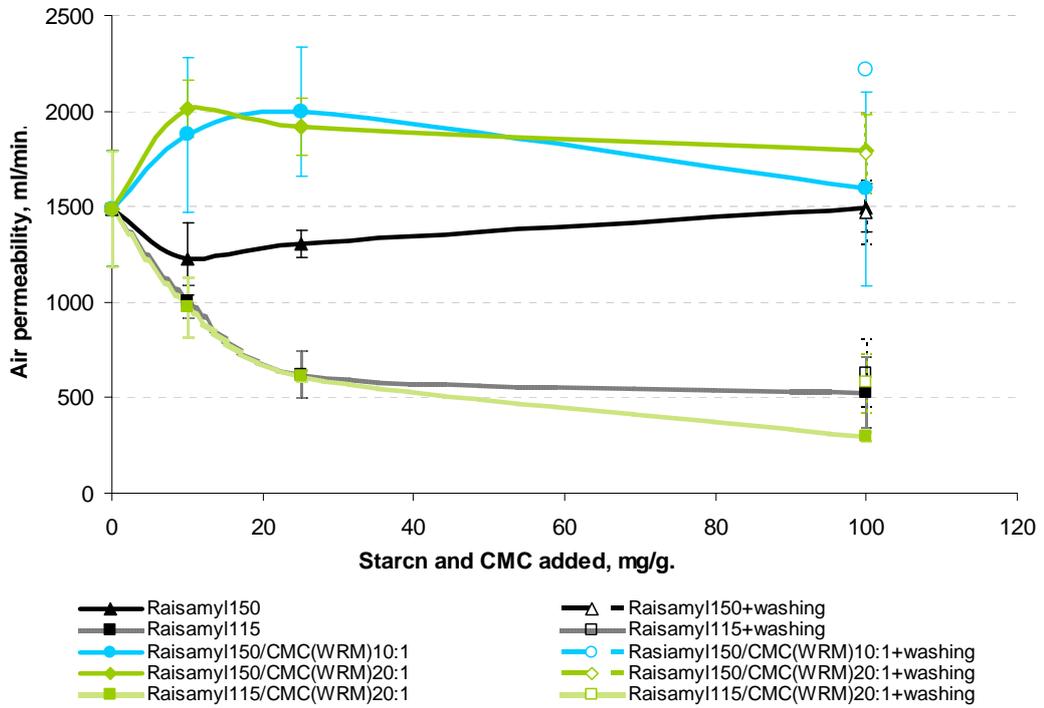


Figure 29. Air permeability of sheets made from pine pulp (SR 20) as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:10 or 1:20 of starch addition.

After two layers application of polyelectrolytes, air permeability (figure 29) decreases due to decreasing of pore sizes. Sheets become more rough (figure 30), it even felt to the touch.

Roughness (figure 30) of the paper is the amount of the air that flows through the paper surface and the metal ring that is set to the paper when the pressure differences are set toward unit of time. It should be noted that measurement were made from not calendered sheets.

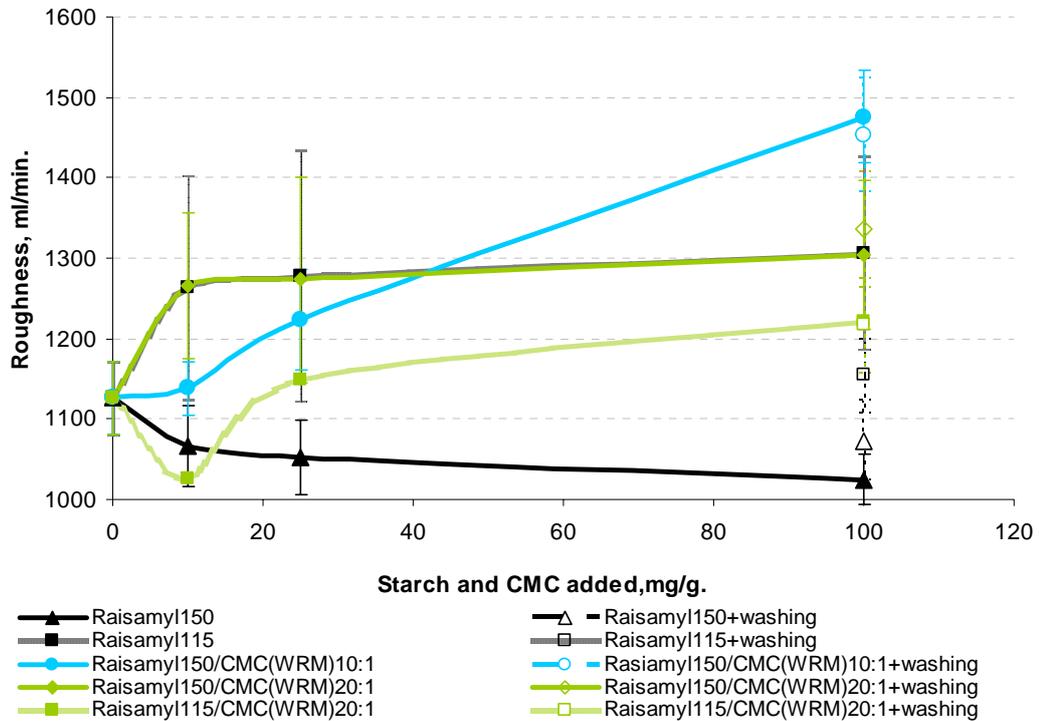


Figure 30. Roughness of sheets made from pine pulp (SR 20) as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:10 or 1:20 of starch addition.

There is no significant difference in comparing dosages of CMC (10:1 and 20:1), except elongation and roughness. It can be concluded that in economy of production of paper will be rational to use lesser ratio starch/CMC, to be exact 20:1.

In case of washing situation is not unique. There are three cases: washing has negative impact on paper properties, positive impact and no impact.

12.2.2 Consider the effect of pulp sample

Pulp sample (hardwood, softwood) and degree of beating play an important role for all properties of paper.

The amount of CMC adsorbed depends on several factors, including DP (degree of polymerization) and DS of CMC, charge of CMC, pH and degree of beating of the pulp and so on.

Figure 31 shows dependences of density to polyelectrolyte additions.

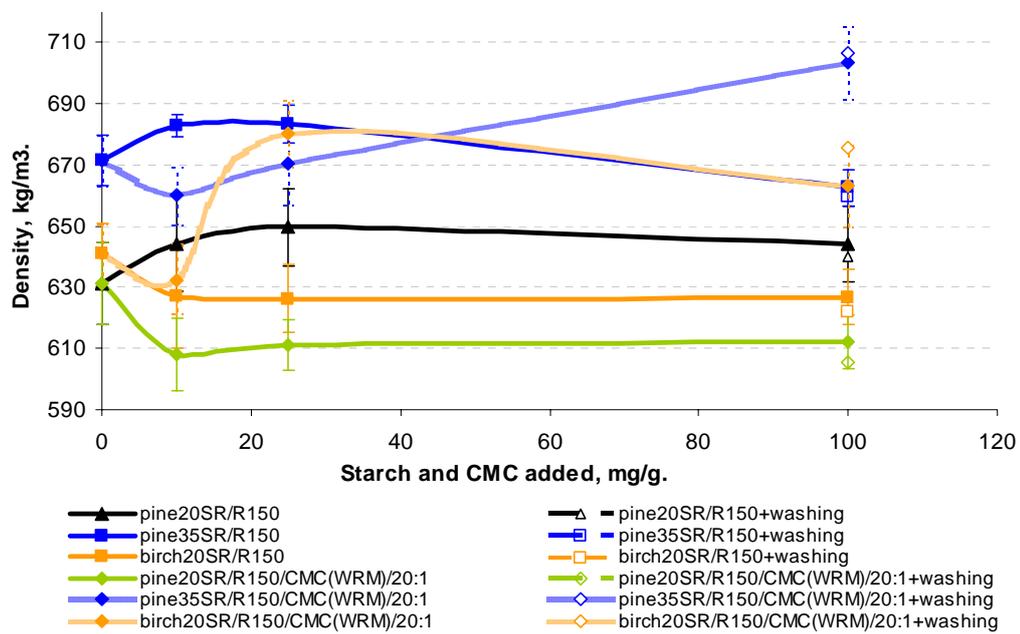


Figure 31. The density as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:20 of starch addition.

Generally, it can be said that fines have a positive effect on density, tensile and internal strength, tensile stiffness and light scattering have a negative effect on tear strength /8/.

The higher density of birch can partly be explained by the higher hemicellulose content, which has been shown to improve fiber bonding and swelling (shrinkage).

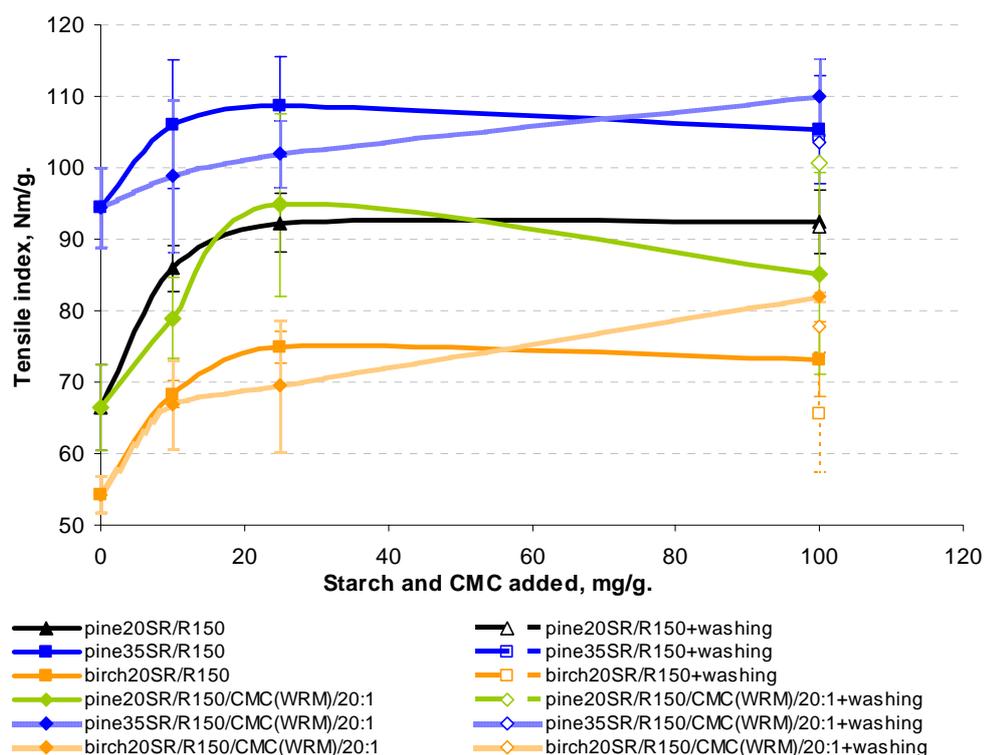


Figure 32. The tensile index as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:20 of starch addition.

The strength properties such as tensile index and tensile energy adsorption index (figures 32 and 33 respectively) were improved when they were treated by oppositely charged polyelectrolytes, especially when the pulps were beaten. Softwood pulp had in most cases better strength properties than hardwood pulp. This can be partly explained by the fact that softwood fibers are longer than hardwood fibers and that more of polyelectrolytes are adsorbed onto the softwood fibers than hardwood fibers.

After beating and polyelectrolytes treatment of the pulp the tensile and internal strengths develop faster than those of the untreated pulps /8/. An increase in TEA index (figure 33) was also observed after CMC modification, but only in higher dosage of polyelectrolytes. In addition, microfibrillation of the external fiber surface is one of the most important factors in the formation of interfiber bonds.

Tensile index with one layer application:

- In case with pine35⁰SR and Raisamy1150, tensile index was increased on 10%, for birch 20⁰SR and Raisamy1150 on 26%.

Tensile index for two layers application:

- For pine35⁰SR/Raisamyl150/CMC, tensile index was increased by PEMs on 9% and by PEMs+PECs on 13%.
- For birch20⁰SR/Raisamyl150/CMC, by PEMs on 30% and by PEMs+PECs on 34%.
- Strengthening effect of PECs for both cases about 4%.

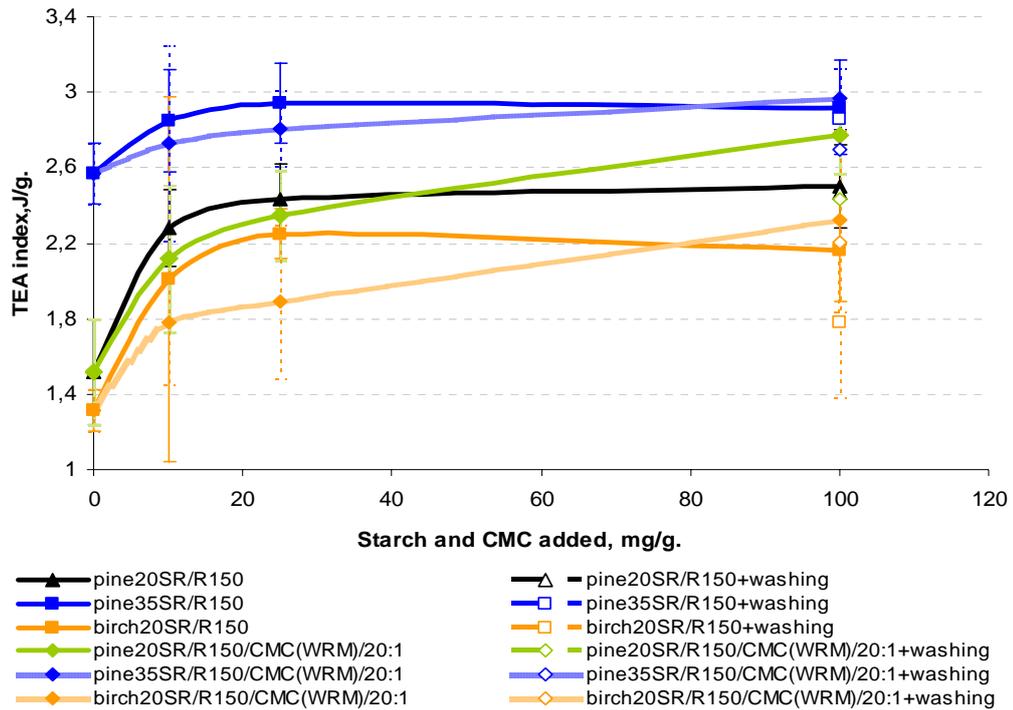


Figure 33. The tensile energy adsorption index as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:20 of starch addition.

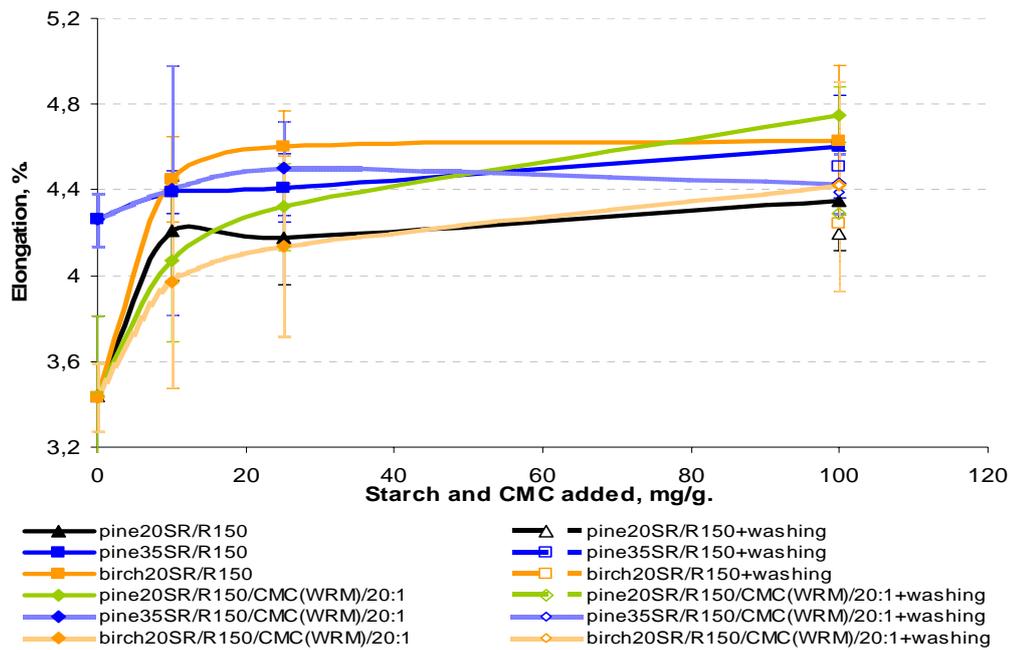


Figure 34. Elongation as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:20 of starch addition.

From figure 34 can be seen increasing of elongation for all series of pulp, especially after formation of PECs. Elongation was more increased for birch pulp, this effect partly depends on a more flexible fiber and larger surface area of the fibers, which increase the contact area in fiber/fiber joint.

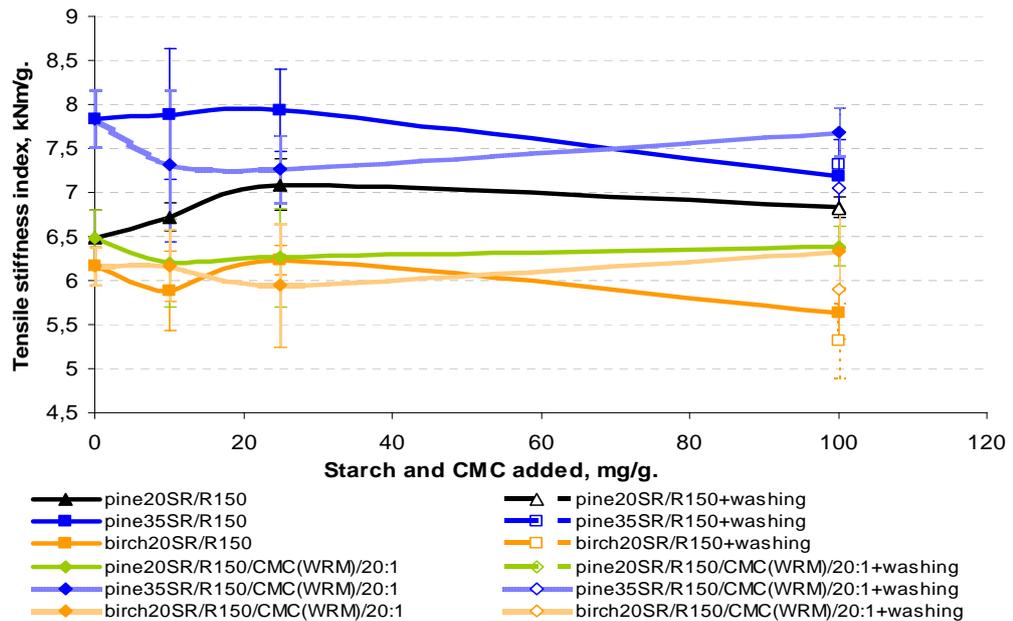


Figure 35. Tensile stiffness index as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:20 of starch addition.

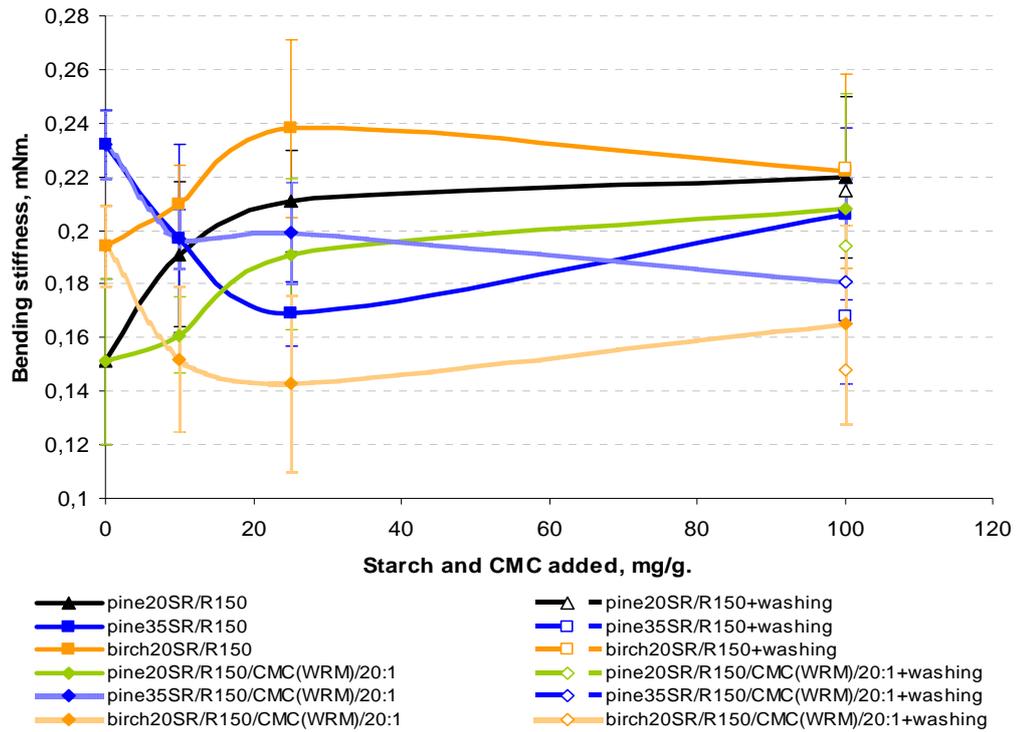


Figure 36. Bending stiffness as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:20 of starch addition.

An increased bending stiffness (figure 36) should prevent the formation layer of polyelectrolyte. So polyelectrolyte treatment has a negative impact on bending stiffness for more beaten pulp and for birch pulp.

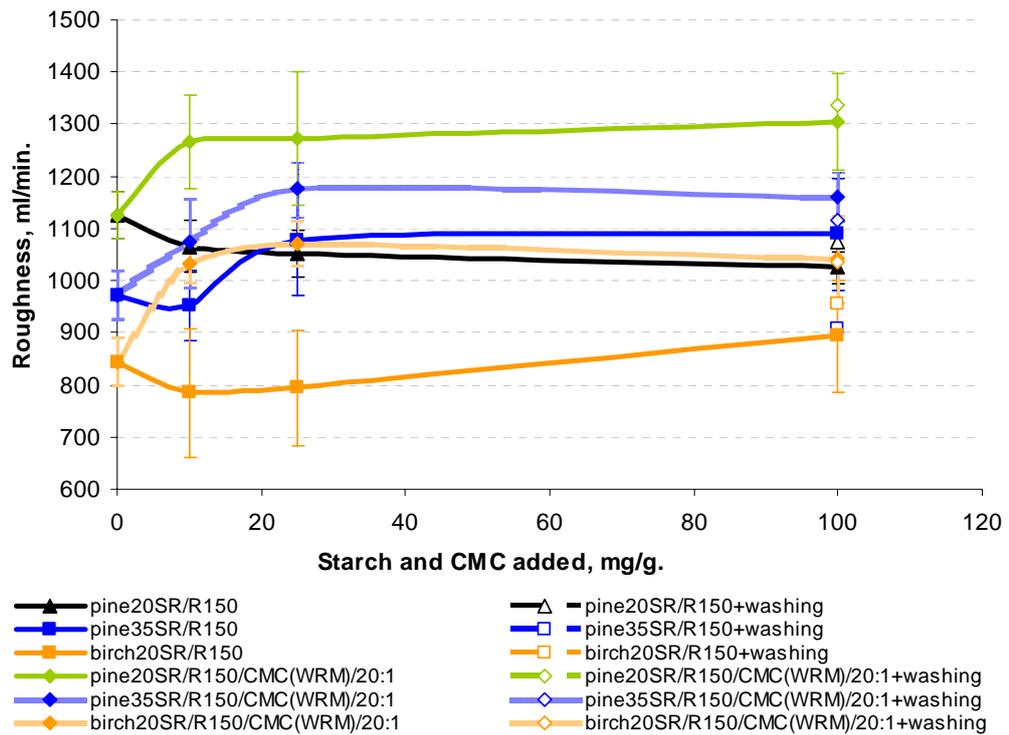


Figure 37. Roughness as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:20 of starch addition.

As can be seen from figure 37, the birch pulp and more beaten pulp have the lowest values of roughness. Should be noted that CMC treatment gives the highest results. It means that formation of PEMs and PECs has impact also on roughness of the sheets.

Air permeability (figure 38) is a common indirect method to describe the pore structure of paper.

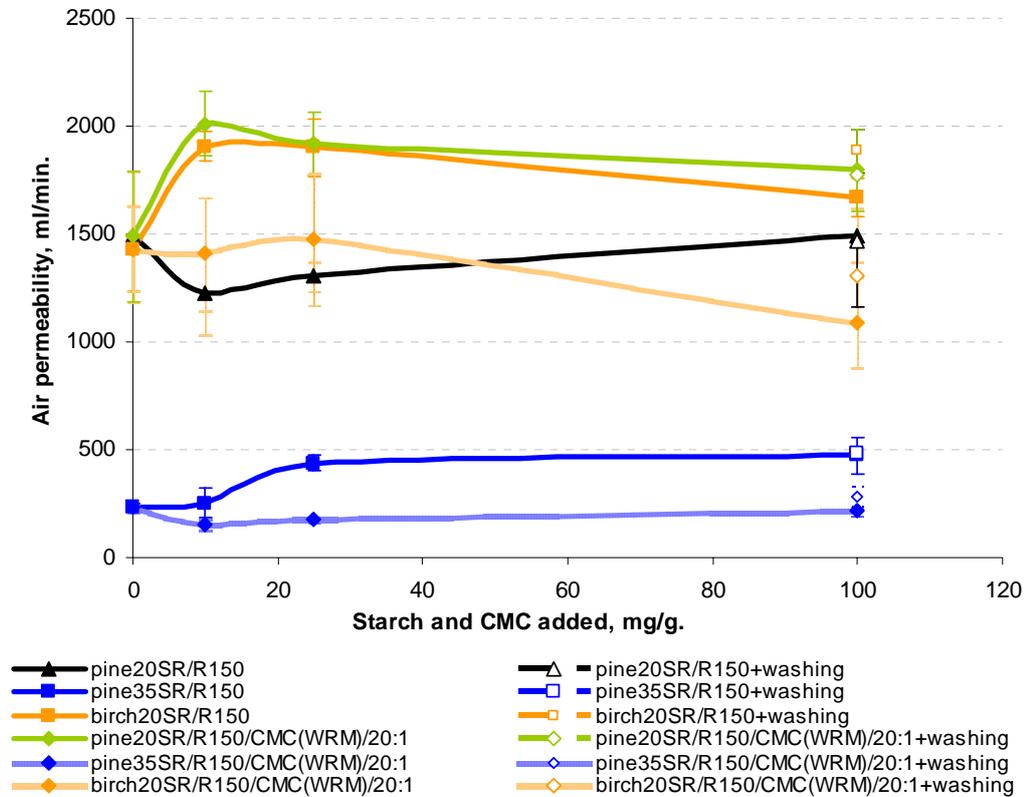


Figure 38. Air permeability as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:20 of starch addition.

Sheets made from highly beaten fibers have small pores, thus lower air permeability (pine 35⁰SR with one and two layers application). From figure 38 can be concluded that after polyelectrolyte treatment air permeability becomes lower. Also formation of PECs has a negative impact on air permeability.

Formation of PEMs and PECs have better effect on tensile properties for highly beaten pulp, because of more amount of polyelectrolytes can adsorb on the fiber surface, except tensile stiffness index (figure 35). This effect partly depends on a more flexible fiber and larger surface area of the beaten fibers, which increase the contact area in fiber/fiber joint.

12.2.3 Consider the effect of CMC grade

This chapter considered influence of CMC grade on properties of handsheets. Here we can see dependences of properties such as density, tensile index, tensile energy adsorption index, elongation, tensile stiffness, bending stiffness, air permeability and roughness from starch and CMC addition (mg/g). There are four curves, in accordance with table VI, on figures 39-46, with different dosages of starch and CMC (tables VII, VIII). Also, there is one addition point in each series with washing in dosage of starch 100 mg/g.

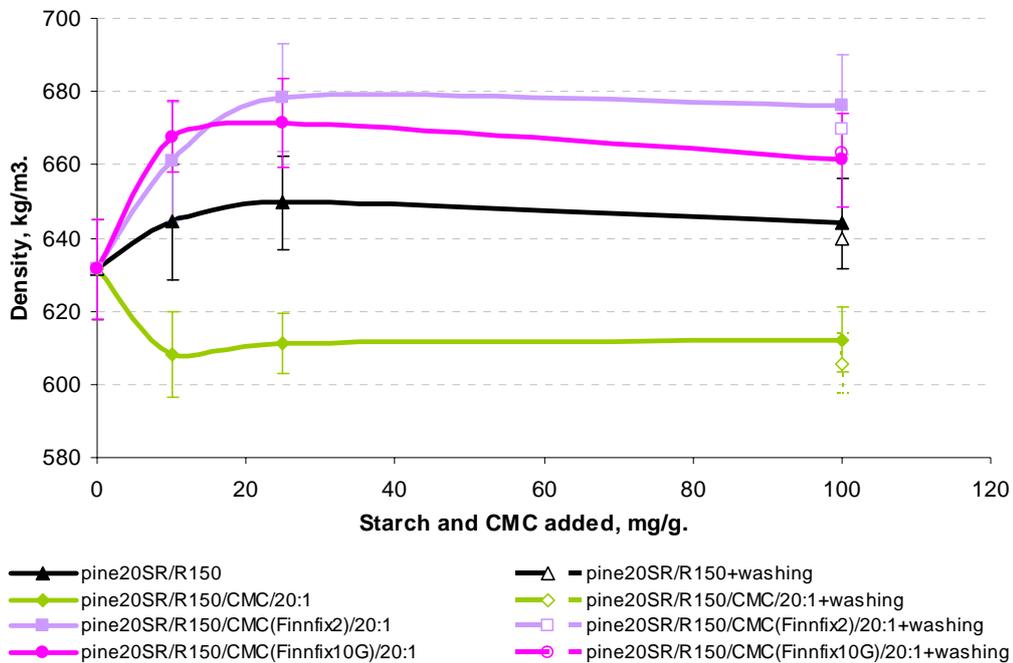


Figure 39. The density as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:20 of starch addition.

Figure 39 shows that washing have a decreasing effect on density. It means that PECs have an increasing effect on density of handsheets.

With an increasing of charge density of CMC, density of the sheets increases.

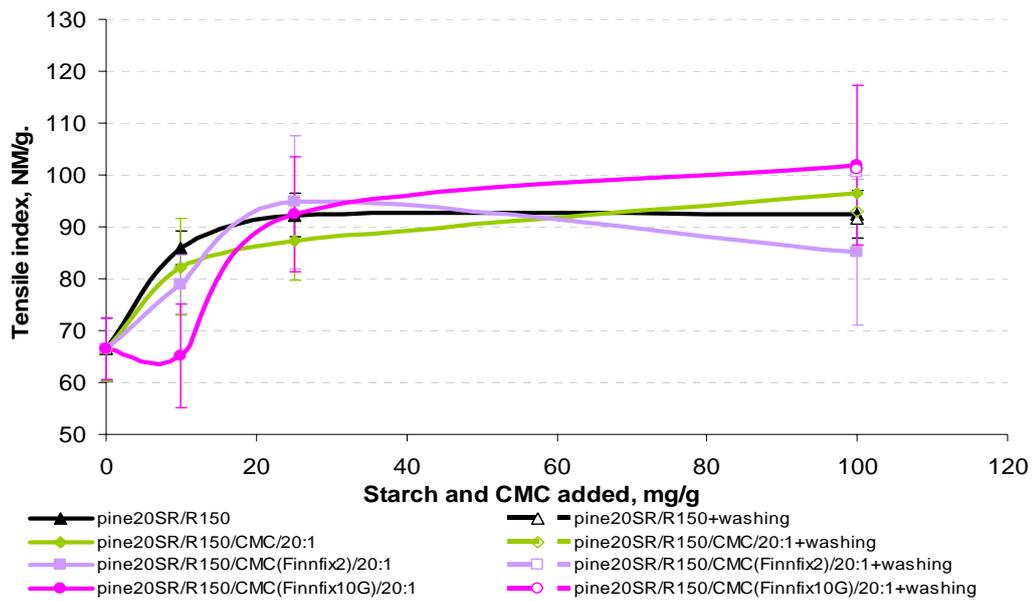


Figure 40. The tensile index as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:20 of starch addition.

The attachment of CMC to pulp is known to have strong impact on tensile strength properties. Not so good effect, compared to other series, on tensile index have only serie with grade of CMC Finnfix2. But after washing (where no capability to form PECs) results are high. In another series we can see increasing in tensile index (figure 40), TEA index (figure 41) and elongation (figure 42). Better strengthening effect give formation both PEMs and PECs.

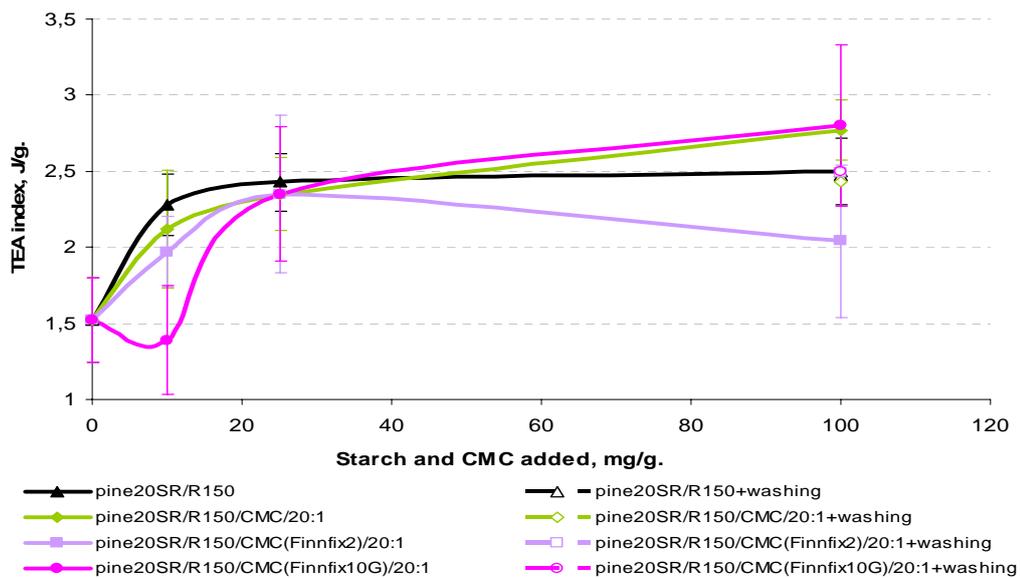


Figure 41. The tensile energy adsorption index as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:20 of starch addition.

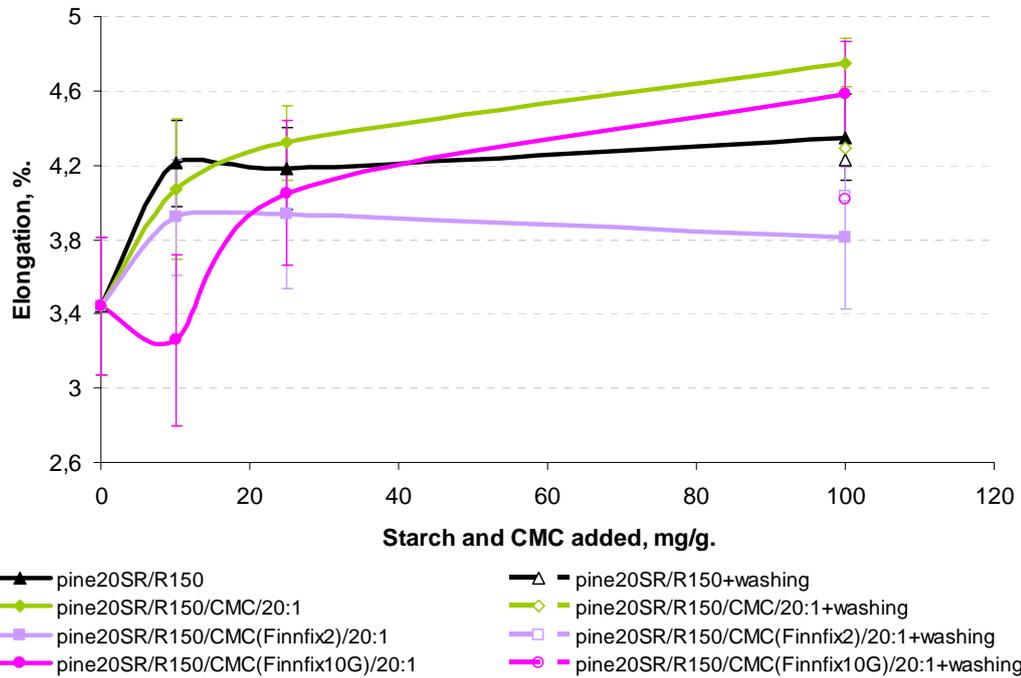


Figure 42. Elongation as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:20 of starch addition.

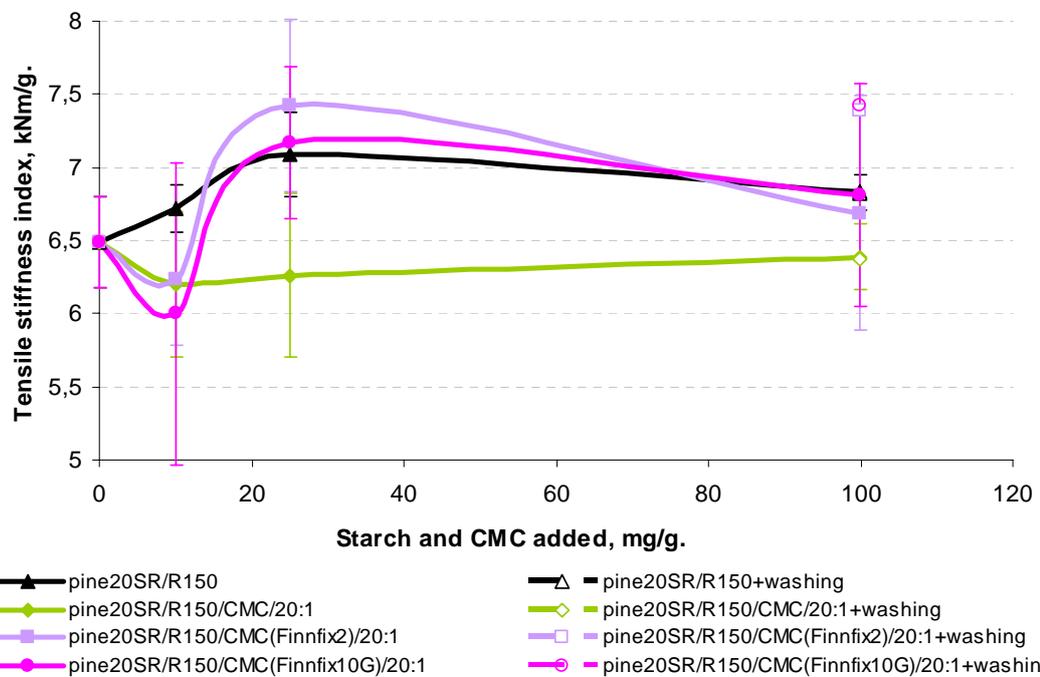


Figure 43. Tensile stiffness index as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:20 of starch addition.

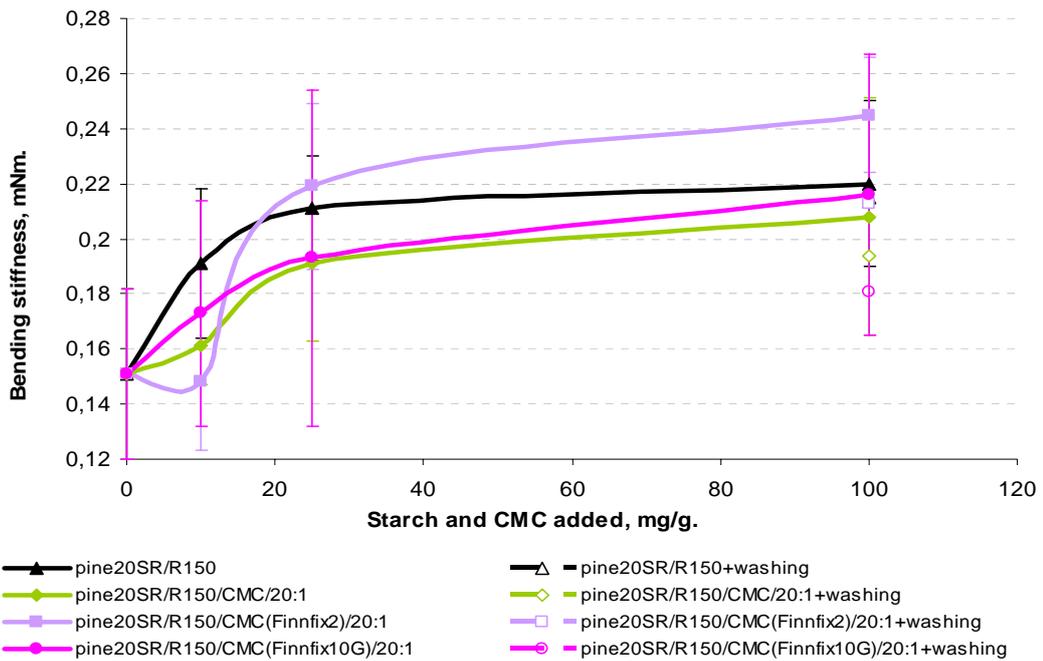


Figure 44. Bending stiffness as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:20 of starch addition.

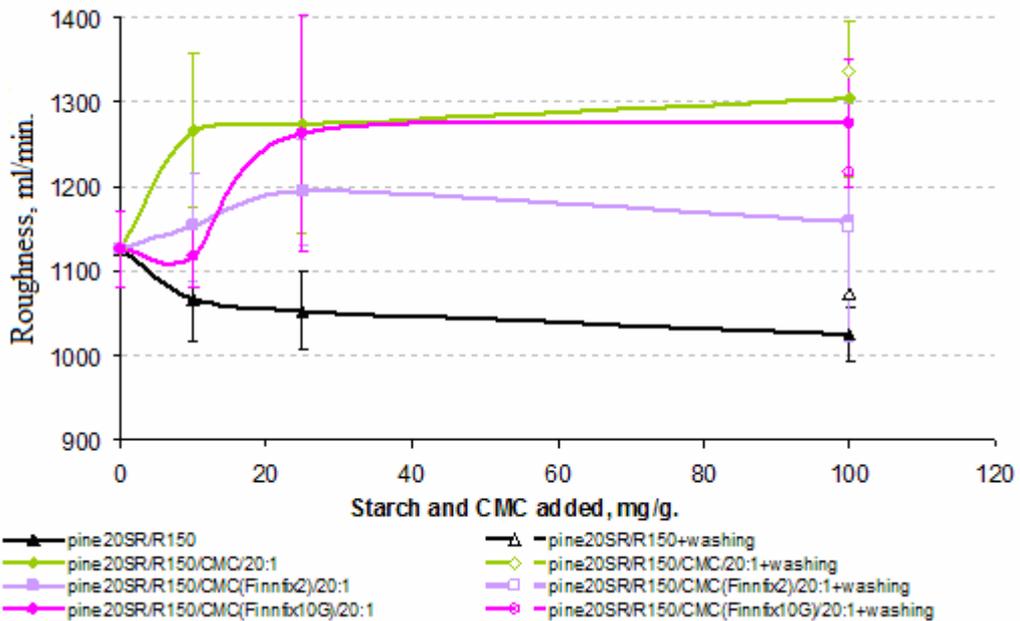


Figure 45. Roughness as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:20 of starch addition.

The higher charge density of CMC, the more stable roughness (figure 45).

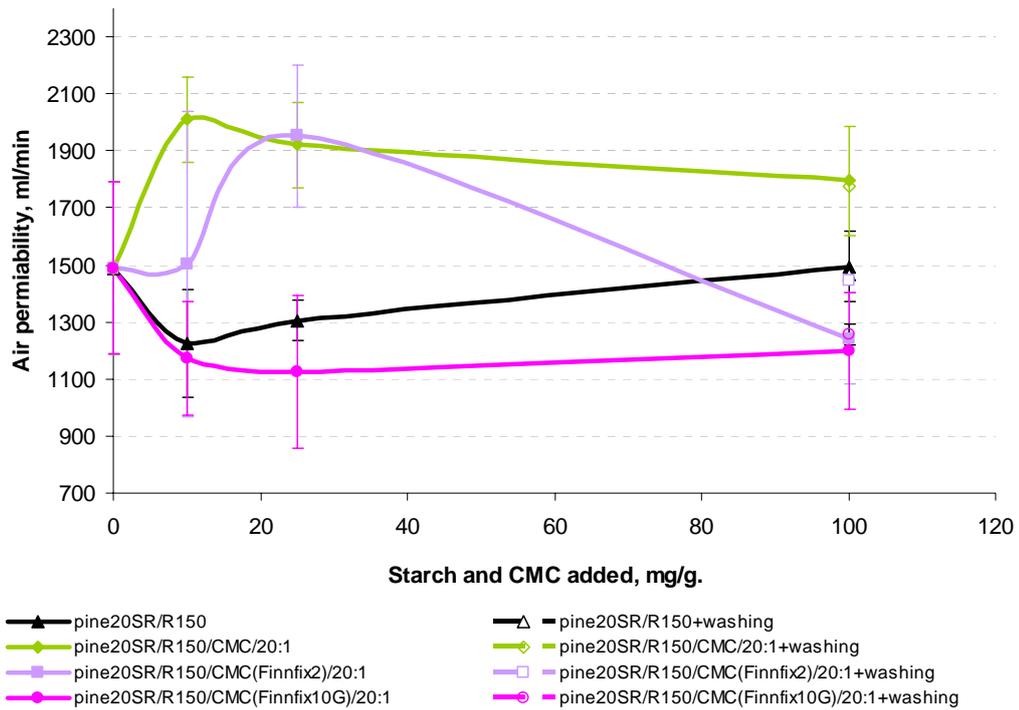


Figure 46. Air permeability as a function of starch and CMC added (mg/g.) to the fiber suspension. The added amount of CMC was 1:20 of starch addition.

Serie with added CMC grade Finnfix 2 (with higher charge density, compared with Finnfix WRM), has better tensile properties than series with CMC grade Finnfix WRM. To be exact, tensile index (figure 40), tensile energy adsorption index (figure 41) and tensile stiffness index (figure 43). But the lowest values of bending stiffness (figure 44) and air permeability (figure 46).

Serie with added CMC grade Finnfix 10G (with the highest charge density) have the lowest results in tensile properties. From figures in this chapter can be concluded that charge density plays important role on tensile properties of paper.

13 Comparison and analysis with previously made work

This chapter consists of comparison and analysis with previously made work at Lappeenranta University of Technology by Maria Frolova: “Adsorption of polyelectrolytes on fiber surfaces, to modify paper properties”.

Consider the Z-potential, were noted that number of SR has no influence on Z-potential values /47/.

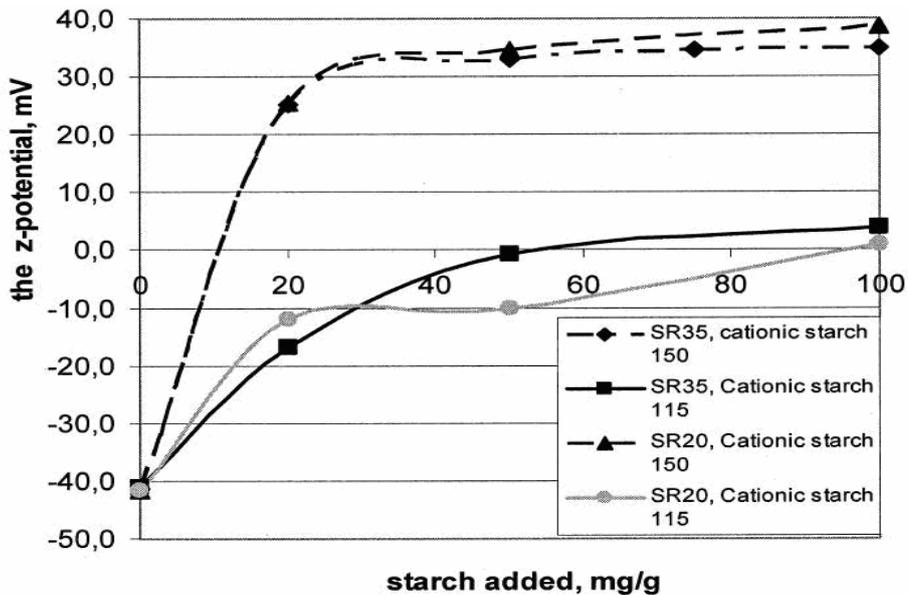


Figure 47. The Z-potential as a function of only starch (mg/g.) added to the fiber suspension. The pulp samples were pine 20⁰SR and pine 35⁰SR. The starch grades were Raisamyl 150 (DS 0,05) and Raisamyl 115 (DS 0,015) /47/.

But from figure 17 can be seen that more starch is needed to achieve the saturation point in case of more beaten pulp.

If we look at the charge of the filtrate, it turns towards positive with less amount of starch in case of pine SR 20 (figure 18).

In case with charge of the filtrate results did not reach even zero point (figure 48), compare with present work where were detected reversal point of the charge of the filtrate (figure 18).

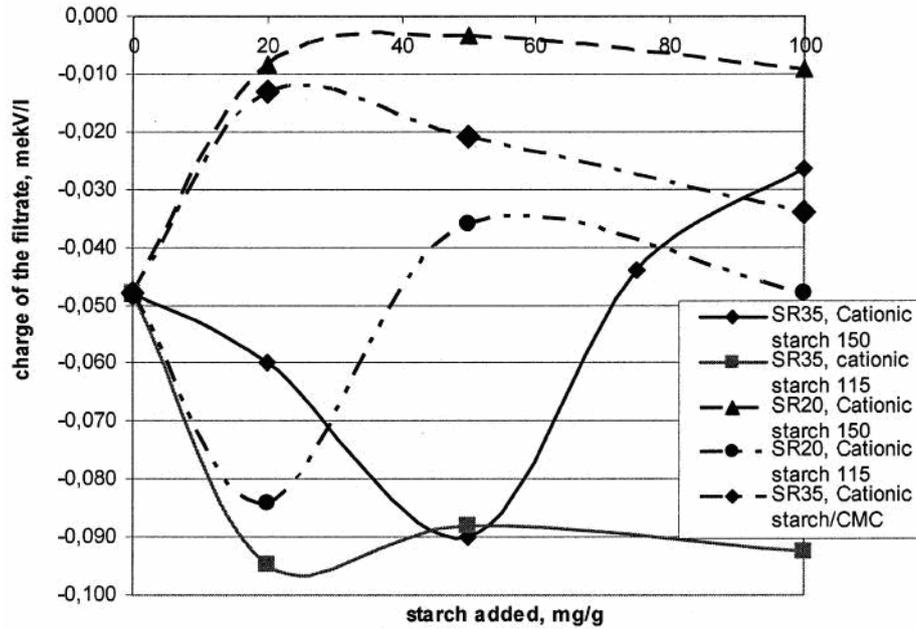


Figure 48. Charge of the filtrate as a function of starch and CMC added (mg/g.) to the fiber suspension. The pulp samples were pine 20⁰SR and pine 35⁰SR. The starch grades were Raisamyl 150 (DS 0,05) and Raisamyl 115 (DS 0,015). The CMC grade was Finnfix WRM (DS 0,56) /47/.

Consider tensile index with one layer application should be noted that increasing in tensile index for series with pine20⁰SR and Raisamyl150 have the similar results (increasing approximately on 26%). But in case with series pine20⁰SR and cationic starch Raisamyl115, increasing in tensile index comes to 20% (figure49), but in present work 30% (figure 24).

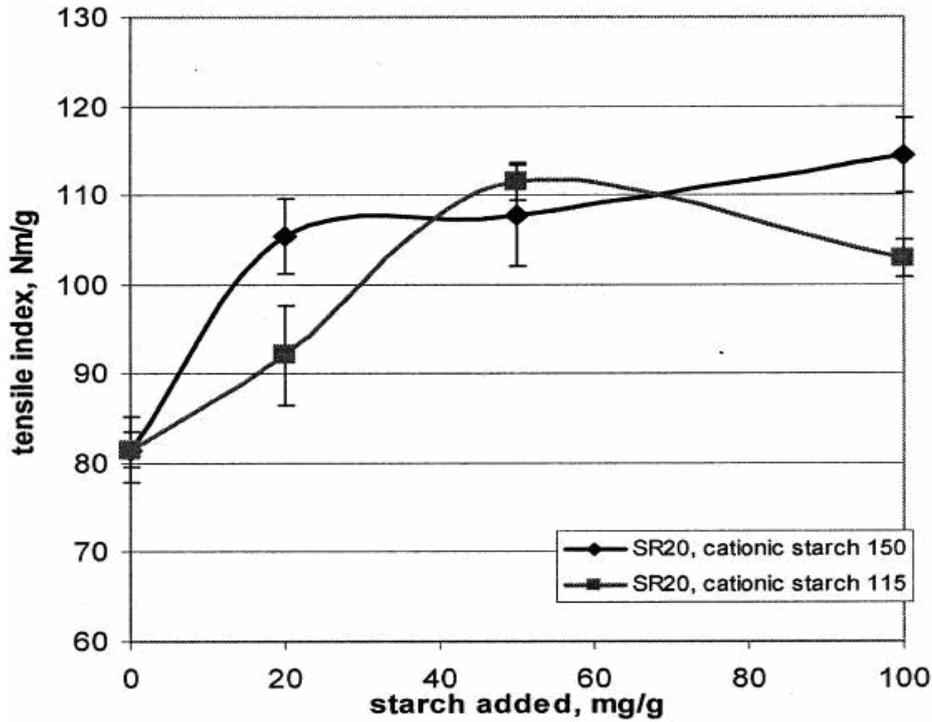


Figure 49. The tensile index as a function of only starch added (mg/g.) to the fiber suspension. The pulp sample was pine 20⁰SR. The starch grades were Raisamyl 150 (DS 0,05) and Raisamyl 115 (DS 0,015) /47/.

For two layers application situation was more different. It can be seen from figure 50, that increasing in tensile index approx. 30% compare with results shown on figure 32, in 13%. Also, tensile index values were higher for the CMC modified pulp, especially when the pulps were beaten (figure 32).

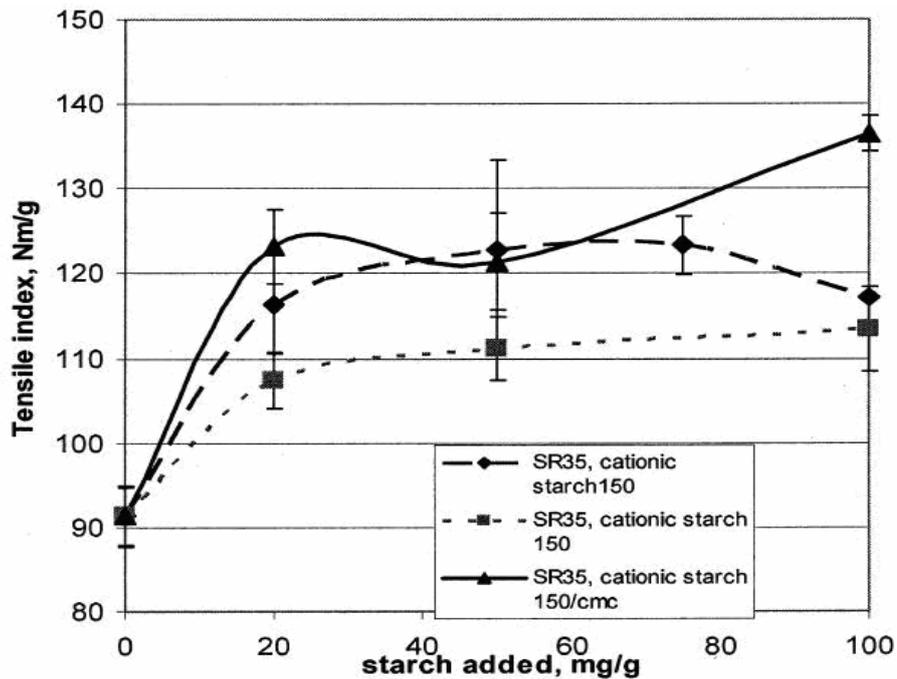


Figure 50. The tensile index as a function of only starch added (mg/g.) to the fiber suspension. The pulp sample was pine 35⁰SR. The starch grade was Raisamyl 150 (DS 0,05). The CMC grade was Finnfix WRM (DS 0,56) /47/.

CONCLUSIONS

The objectives of the work were to tell how much of the strengthening effect was based on multilayers and how much on the formation of polyelectrolyte complexes and to find what is the maximum strength that can be reached with such treatment.

There were two types of application of polyelectrolytes in this work. One layer and two layers application. Fibers were treated during 10 minutes of continuous mixing, at first with cationic starch and then with anionic CMC. Some part of the sample went to determination of Zeta-potential and some part was directed to the vacuum filtration or/and washing to determine the charge of the filtrate. Washing was done only after starch addition (before CMC addition). Handsheets were done after analysing the pulp samples.

The following conclusions can be done after analysing the pulp samples:

When saturation point will be reached, this means that no more than this amount of starch can adsorb on the fiber. There will be formation of polyelectrolyte complexes with second added polyelectrolyte.

It means that:

- below the saturation point part of the fibers are covered with starch, there is no starch in solution (only multilayer will be formed);
- at the saturation point the fibers are totally covered by starch but there is no starch in the solution (only multilayer will be formed);
- above the saturation point the fibers are covered by starch and there is starch left in the solution to be able to form polyelectrolyte complexes with the second added polyelectrolyte (both multilayer and polyelectrolyte complexes will be formed).

The CMC amount adsorbed on pulps depends on several factors: charge of CMC, DS of CMC, concentration of CMC, pH, degree of beating of the pulp and so on.

During washing starch from solution and partly from the fiber surface was removed, and capability to form complexes with second added polyelectrolyte were less compared with unwashed sample. It means that after washing no possibilities to form polyelectrolyte complexes exist.

In this work were investigated three effects (effect of starch grade and starch/CMC ratio, effect of pulp sample and effect of CMC grade) on mechanical properties of the handsheets, such as density, tensile index, tensile energy adsorption index, elongation, tensile stiffness, bending stiffness, air permeability and roughness.

It can be concluded that there is no significant difference in comparing dosages of CMC (10:1 and 20:1), except elongation and roughness. Thus, in economy of production of paper will be rational to use lesser ratio starch/CMC, to be exact 20:1. Formation of PEMs and PECs have better effect on tensile properties for highly beaten pulp, because of more amount of polyelectrolytes can adsorb on the fiber surface, except tensile stiffness index. This effect partly depends on a more flexible fiber and larger surface area of the beaten fibers, which increase the contact area in fiber/fiber joint.

The charge density of polyelectrolytes plays important role on strength properties of paper.

The formation of starch/CMC PECs and PEMs improved the paper strength more effectively than the layer-by-layer assembly of starch and CMC. Results with washing (where no possibilities to form complexes) are lower compared with results without washing. The tensile strength of the fiber network was more significantly improved after forming the complexes of starch/CMC than one or two layer application of polyelectrolytes.

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LIST OF APPENDICES

- Appendix I:** The effect of the additives on Z-potential and the charge of the filtrate
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APPENDIX I (1/2)

The effect of the additives on Z-potential and the charge of the filtrate

Table I: The Z-potential and the charge of the filtrate (\pm standard deviation) of the suspension of fibers, prepared from pine (SR 20⁰) and one layer of cationic starch (Raisamyl 150).

Amount of PE, mg/g. Starch	Z-potential, mV.	The charge of the filtrate, mekv/l.
0	-39,3 \pm 1,3	-0,0055 \pm 0,0003
10	18,6 \pm 0,1	-0,0048 \pm 0,0002
25	31,2 \pm 0,4	0 \pm 0
100	38,4 \pm 0,1	0,0888 \pm 0,0026
100 (washed)	34,4 \pm 3,8	0,0133 \pm 0,0073

Table II: The Z-potential and the charge of the filtrate (\pm standard deviation) of the suspension of fibers, prepared from pine (SR 20⁰) and one layer of cationic starch (Raisamyl 115).

Amount of PE, mg/g. Starch	Z-potential, mV.	The charge of the filtrate, mekv/l.
0	-39,3 \pm 1,3	-0,0055 \pm 0,0003
10	-1,7 \pm 0,1	-0,0051 \pm 0,0065
25	1,9 \pm 0,6	-0,0031 \pm 0,0045
100	3,3 \pm 0,6	0 \pm 0
100 (washed)	3,1 \pm 0,6	0,0042 \pm 0,0051

Table III: The Z-potential and the charge of the filtrate (\pm standard deviation) of the suspension of fibers, prepared from pine (SR 35⁰) and one layer of cationic starch (Raisamyl 150).

Amount of PE, mg/g. Starch	Z-potential, mV.	The charge of the filtrate, mekv/l.
0	-39,9 \pm 1,3	-0,0058 \pm 0,0064
10	-3,9 \pm 1,0	-0,0032 \pm 0,0018
25	15,2 \pm 0,6	-0,0030 \pm 0,0004
100	26,9 \pm 3,0	0,0572 \pm 0,0085
100 (washed)	25,9 \pm 4,3	0 \pm 0

Table IV: The Z-potential and the charge of the filtrate (\pm standard deviation) of the suspension of fibers, prepared from birch (SR 20⁰) and one layer of cationic starch (Raisamyl 150).

Amount of PE, mg/g. Starch	Z-potential, mV.	The charge of the filtrate, mekv/l.
0	-58,1 \pm 0,6	-0,0061 \pm 0,0020
10	-15,0 \pm 3,1	-0,0048 \pm 0,0085
25	19,9 \pm 4,0	-0,0035 \pm 0,0076
100	29,7 \pm 3,2	0,0613 \pm 0,0085
100 (washed)	28,2 \pm 1,3	-0,0038 \pm 0,0020

APPENDIX I (2/2)

Table V: The Z-potential and the charge of the filtrate (\pm standard deviation) of the suspension of fibers, prepared from pine (SR 20⁰) and two layers: inner layer - cationic starch (Raisamyl 150) and the outer layer - CMC (Finnfix WRM). Ratio starch:CMC – 10:1.

Amount of PEs, mg/g. Starch/CMC	Z-potential, mV.	The charge of the filtrate, mekv/l.
0/0	-39,3 \pm 1,3	-0,0055 \pm 0,0003
10/1	-35,1 \pm 1,2	-0,0091 \pm 0,0007
25/2,5	-25,3 \pm 1,2	-0,0094 \pm 0,0003
100/10	-13,5 \pm 0,3	-0,0132 \pm 0,0075
100/10(washed)	-35,7 \pm 4,9	-0,0330 \pm 0,0075

Table VI: The Z-potential and the charge of the filtrate (\pm standard deviation) of the suspension of fibers, prepared from pine (SR 20⁰) and two layers: inner layer - cationic starch (Raisamyl 150) and the outer layer - CMC (Finnfix WRM). Ratio starch:CMC – 20:1.

Amount of PEs, mg/g. Starch/CMC	Z-potential, mV.	The charge of the filtrate, mekv/l.
0/0	-39,3 \pm 1,3	-0,0055 \pm 0,0003
10/0,5	-30,5 \pm 0,7	-0,0042 \pm 0,0005
25/1,25	-8,2 \pm 0,9	-0,0047 \pm 0,0007
100/5	16,9 \pm 0,8	-0,0044 \pm 0,0006
100/5(washed)	-16,7 \pm 0,9	-0,0077 \pm 0,0010

APPENDIX II (1/3)

Paper properties, thickness and density

Handsheets were made according to series from table VI.

Table I: Properties of the serie of handsheets (\pm standard deviation), prepared from pine (SR 20⁰) and one layer of cationic starch (Raisamyl 150).

Amount of PE, mg/g. Starch	Basis weight, g/m ² .	Thickness, μ m.	Density, kg/m ³ .
0	63,9 \pm 0,9	101,2 \pm 3,9	631,4 \pm 13,5
10	66,7 \pm 0,7	103,5 \pm 7,1	644,4 \pm 15,7
25	67,5 \pm 0,9	103,9 \pm 5,2	649,6 \pm 12,7
100	67,5 \pm 1,1	104,8 \pm 5,3	644,0 \pm 12,3
100 (washed)	65,2 \pm 0,8	101,9 \pm 4,1	639,8 \pm 13,1

Table II: Properties of the serie of handsheets (\pm standard deviation), prepared from pine (SR 20⁰) and one layer of cationic starch (Raisamyl 115).

Amount of PE, mg/g. Starch	Basis weight, g/m ² .	Thickness, μ m.	Density, kg/m ³ .
0	63,9 \pm 0,9	101,2 \pm 3,9	631,4 \pm 13,5
10	64,0 \pm 0,3	100,7 \pm 0,5	634,9 \pm 5,7
25	70,0 \pm 0,7	106,2 \pm 1,1	659,1 \pm 9,1
100	72,0 \pm 0,9	109,8 \pm 5,1	656,1 \pm 30,7
100 (washed)	71,0 \pm 0,8	107,5 \pm 3,3	661,0 \pm 20,7

Table III: Properties of the serie of handsheets (\pm standard deviation), prepared from pine (SR 35⁰) and one layer of cationic starch (Raisamyl 150).

Amount of PE, mg/g. Starch	Basis weight, g/m ² .	Thickness, μ m.	Density, kg/m ³ .
0	68,0 \pm 0,6	101,3 \pm 1,3	671,3 \pm 8,3
10	68,0 \pm 0,5	99,6 \pm 0,5	682,9 \pm 3,4
25	68,0 \pm 0,7	99,5 \pm 0,9	683,4 \pm 6,2
100	65,3 \pm 0,5	98,5 \pm 0,9	662,6 \pm 5,9
100 (washed)	66,7 \pm 0,8	101,1 \pm 1,4	659,6 \pm 7,4

Table IV: Properties of the serie of handsheets (\pm standard deviation), prepared from birch (SR 20⁰) and one layer of cationic starch (Raisamyl 150).

Amount of PE, mg/g. Starch	Basis weight, g/m ² .	Thickness, μ m.	Density, kg/m ³ .
0	68,0 \pm 0,7	106,0 \pm 1,4	641,3 \pm 9,6
10	68,0 \pm 0,6	108,4 \pm 1,1	627,1 \pm 17,1
25	68,9 \pm 0,7	110,0 \pm 1,0	626,2 \pm 11,1
100	69,0 \pm 0,6	110,1 \pm 1,1	626,8 \pm 8,9
100 (washed)	67,6 \pm 0,7	108,7 \pm 1,7	621,8 \pm 12,5

APPENDIX II (2/3)

Table V: Properties of the serie of handsheets (\pm standard deviation), prepared from pine (SR 20⁰) and two layers: inner layer - cationic starch (Raisamyl 150) and the outer layer - CMC (Finnfix WRM). Ratio starch:CMC – 10:1.

Amount of PEs, mg/g. Starch/CMC	Basis weight, g/m ² .	Thickness, μ m.	Density, kg/m ³ .
0/0	63,9 \pm 0,9	101,2 \pm 3,9	631,4 \pm 13,5
10/1	64,6 \pm 0,8	104,7 \pm 9,3	620,0 \pm 15,1
25/2,5	63,9 \pm 0,7	105,9 \pm 5,2	605,1 \pm 14,9
100/10	66,8 \pm 0,8	111,0 \pm 9,9	601,8 \pm 13,7
100/10(washed)	62,2 \pm 0,6	107,8 \pm 10,8	576,7 \pm 18,3

Table VI: Properties of the serie of handsheets (\pm standard deviation), prepared from pine (SR 20⁰) and two layers: inner layer - cationic starch (Raisamyl 150) and the outer layer - CMC (Finnfix WRM). Ratio starch:CMC – 20:1.

Amount of PEs, mg/g. Starch/CMC	Basis weight, g/m ² .	Thickness, μ m.	Density, kg/m ³ .
0/0	63,9 \pm 0,9	101,2 \pm 3,9	631,4 \pm 13,5
10/0,5	62,4 \pm 1,0	108,1 \pm 8,1	608,7 \pm 11,7
25/1,25	66,0 \pm 1,2	108,0 \pm 7,6	611,1 \pm 8,3
100/5	64,9 \pm 0,6	106,0 \pm 7,9	612,2 \pm 9,0
100/5 (washed)	65,4 \pm 0,7	108,0 \pm 6,8	605,5 \pm 8,3

Table VII: Properties of the serie of handsheets (\pm standard deviation), prepared from pine (SR 20⁰) and two layers: inner layer - cationic starch (Raisamyl 115) and the outer layer - CMC (Finnfix WRM). Ratio starch:CMC – 20:1.

Amount of PEs, mg/g. Starch/CMC	Basis weight, g/m ² .	Thickness, μ m.	Density, kg/m ³ .
0/0	63,9 \pm 0,9	101,2 \pm 3,9	631,4 \pm 13,5
10/0,5	65,3 \pm 0,7	99,5 \pm 3,6	656,2 \pm 15,3
25/1,25	67,0 \pm 0,7	100,5 \pm 5,2	666,4 \pm 12,6
100/5	67,0 \pm 0,4	114,0 \pm 4,8	588,1 \pm 12,1
100/5 (washed)	68,0 \pm 0,3	102,0 \pm 2,7	666,0 \pm 9,9

Table VIII: Properties of the serie of handsheets (\pm standard deviation), prepared from pine (SR 35⁰) and two layers: inner layer - cationic starch (Raisamyl 150) and the outer layer - CMC (Finnfix WRM). Ratio starch:CMC – 20:1.

Amount of PEs, mg/g. Starch/CMC	Basis weight, g/m ² .	Thickness, μ m.	Density, kg/m ³ .
0/0	68,0 \pm 0,6	101,3 \pm 1,3	671,3 \pm 8,3
10/0,5	64,4 \pm 0,4	97,5 \pm 1,7	660,0 \pm 9,7
25/1,25	67,5 \pm 0,3	100,7 \pm 3,2	670,3 \pm 13,1
100/5	66,8 \pm 0,5	95,1 \pm 4,3	703,4 \pm 11,8
100/5 (washed)	66,2 \pm 0,4	93,7 \pm 2,9	706,5 \pm 7,9

APPENDIX II (3/3)

Table IX: Properties of the serie of handsheets (\pm standard deviation), prepared from birch (SR 20⁰) and two layers: inner layer - cationic starch (Raisamyl 150) and the outer layer - CMC (Finnfix WRM). Ratio starch:CMC – 20:1.

Amount of PEs, Starch/CMC, mg/g.	Basis weight, g/m ² .	Thickness, μ m.	Density, kg/m ³ .
0/0	68,0 \pm 0,7	106,0 \pm 1,4	641,3 \pm 9,6
10/0,5	68,0 \pm 0,8	107,5 \pm 2,3	632,5 \pm 11,2
25/1,25	66,8 \pm 0,5	98,2 \pm 2,9	680,2 \pm 10,8
100/5	64,6 \pm 0,5	97,4 \pm 1,8	663,2 \pm 13,4
100/5 (washed)	65,2 \pm 0,3	96,5 \pm 1,2	675,6 \pm 11,8

Table X: Properties of the serie of handsheets (\pm standard deviation), prepared from pine (SR 20⁰) and two layers: inner layer - cationic starch (Raisamyl 150) and the outer layer - CMC (Finnfix 2). Ratio starch:CMC – 20:1.

Amount of PEs, Starch/CMC, mg/g.	Basis weight, g/m ² .	Thickness, μ m.	Density, kg/m ³ .
0/0	63,9 \pm 0,9	101,2 \pm 3,9	631,4 \pm 13,5
10/0,5	65,7 \pm 0,4	99,4 \pm 4,3	660,9 \pm 16,2
25/1,25	63,7 \pm 0,3	93,9 \pm 2,9	678,4 \pm 14,8
100/5	65,2 \pm 0,4	96,4 \pm 4,1	676,3 \pm 13,7
100/5 (washed)	63,6 \pm 0,5	95,0 \pm 5,0	669,5 \pm 11,7

Table XI: Properties of the serie of handsheets (\pm standard deviation), prepared from pine (SR 20⁰) and two layers: inner layer - cationic starch (Raisamyl 150) and the outer layer - CMC (Finnfix 10G). Ratio starch:CMC – 20:1.

Amount of PEs, Starch/CMC, mg/g.	Basis weight, g/m ² .	Thickness, μ m.	Density, kg/m ³ .
0/0	63,9 \pm 0,9	101,2 \pm 3,9	631,4 \pm 13,5
10/0,5	64,3 \pm 0,2	96,3 \pm 3,7	667,7 \pm 9,9
25/1,25	66,0 \pm 0,2	98,3 \pm 3,9	671,4 \pm 12,1
100/5	66,0 \pm 0,4	99,8 \pm 4,1	661,3 \pm 12,8
100/5 (washed)	62,0 \pm 0,2	93,5 \pm 3,8	663,1 \pm 13,3

APPENDIX III (1/4)

Testing of strength properties of paper

Handsheets were made according to series from table VI.

There are ten parallel measurements in each point.

Table I: Properties of the serie of handsheets (\pm standard deviation), prepared from pine (SR 20⁰) and one layer of cationic starch (Raisamyl 150).

Amount of PE, mg/g. Starch	Basis weight, g/m ² .	Tensile index, Nm/g.	TEA index, J/g.	Elongation, %.	Tensile stiffness index, kNm/g.
0	63,9 \pm 0,9	66,46 \pm 6,06	1,52 \pm 0,28	3,44 \pm 0,37	6,49 \pm 0,31
10	66,7 \pm 0,7	85,92 \pm 3,18	2,28 \pm 0,20	4,21 \pm 0,23	6,72 \pm 0,16
25	67,5 \pm 0,9	92,28 \pm 4,10	2,43 \pm 0,19	4,18 \pm 0,22	7,09 \pm 0,29
100	67,5 \pm 1,1	92,41 \pm 4,50	2,50 \pm 0,22	4,35 \pm 0,23	6,83 \pm 0,12
100 (washed)	65,2 \pm 0,8	91,72 \pm 3,6	2,47 \pm 0,21	4,2 \pm 0,28	6,82 \pm 0,19

Table II: Properties of the serie of handsheets (\pm standard deviation), prepared from pine (SR 20⁰) and one layer of cationic starch (Raisamyl 115).

Amount of PE, mg/g. Starch	Basis weight, g/m ² .	Tensile index, Nm/g.	TEA index, J/g.	Elongation, %.	Tensile stiffness index, kNm/g.
0	63,9 \pm 0,9	66,46 \pm 6,06	1,52 \pm 0,28	3,44 \pm 0,37	6,49 \pm 0,31
10	64,0 \pm 0,3	99,5 \pm 3,4	2,96 \pm 0,14	4,93 \pm 0,19	6,74 \pm 0,26
25	70,0 \pm 0,7	102,5 \pm 10,5	2,99 \pm 0,42	4,84 \pm 0,33	7,00 \pm 0,44
100	72,0 \pm 0,9	97,16 \pm 2,38	2,79 \pm 0,17	4,91 \pm 0,28	6,15 \pm 0,31
100 (washed)	71,0 \pm 0,8	94,73 \pm 3,72	2,62 \pm 0,20	4,65 \pm 0,23	6,25 \pm 0,11

Table III: Properties of the serie of handsheets (\pm standard deviation), prepared from pine (SR 35⁰) and one layer of cationic starch (Raisamyl 150).

Amount of PE, mg/g. Starch	Basis weight, g/m ² .	Tensile index, Nm/g.	TEA index, J/g.	Elongation, %.	Tensile stiffness index, kNm/g.
0	68,0 \pm 0,6	94,37 \pm 5,57	2,57 \pm 0,16	4,26 \pm 0,12	7,84 \pm 0,33
10	68,0 \pm 0,5	106,1 \pm 9,0	2,85 \pm 0,27	4,39 \pm 0,10	7,89 \pm 0,74
25	68,0 \pm 0,7	108,56 \pm 7,1	2,94 \pm 0,21	4,41 \pm 0,16	7,93 \pm 0,47
100	65,3 \pm 0,5	105,34 \pm 7,55	2,92 \pm 0,25	4,60 \pm 0,24	7,18 \pm 0,42
100 (washed)	66,7 \pm 0,8	104,38 \pm 3,85	2,86 \pm 0,18	4,51 \pm 0,22	7,32 \pm 0,31

APPENDIX III (2/4)

Table IV: Properties of the serie of handsheets (\pm standard deviation), prepared from birch (SR 20⁰) and one layer of cationic starch (Raisamyl 150).

Amount of PE, mg/g. Starch	Basis weight, g/m ² .	Tensile index, Nm/g.	TEA index, J/g.	Elongation, %.	Tensile stiffness index, kNm/g.
0	68,0 \pm 0,7	54,25 \pm 2,58	1,31 \pm 0,11	3,43 \pm 0,16	6,17 \pm 0,22
10	68,0 \pm 0,6	68,28 \pm 1,88	2,01 \pm 0,97	4,45 \pm 0,20	5,88 \pm 0,45
25	68,9 \pm 0,7	74,85 \pm 2,29	2,25 \pm 0,13	4,60 \pm 0,17	6,23 \pm 0,17
100	69,0 \pm 0,6	73,17 \pm 5,28	2,16 \pm 0,27	4,63 \pm 0,35	5,63 \pm 0,29
100 (washed)	67,6 \pm 0,7	65,66 \pm 8,37	1,78 \pm 0,41	4,24 \pm 0,52	5,31 \pm 0,43

Table V: Properties of the serie of handsheets (\pm standard deviation), prepared from pine (SR 20⁰) and two layers: inner layer - cationic starch (Raisamyl 150) and the outer layer - CMC (Finnfix WRM). Ratio starch:CMC – 10:1.

Amount of PEs, mg/g. Starch/CMC	Basis weight, g/m ² .	Tensile index, Nm/g.	TEA index, J/g.	Elongation, %.	Tensile stiffness index, kNm/g.
0/0	63,9 \pm 0,9	66,46 \pm 6,06	1,52 \pm 0,28	3,44 \pm 0,37	6,49 \pm 0,31
10/1	64,6 \pm 0,8	87,01 \pm 9,96	2,21 \pm 0,30	4,00 \pm 0,16	6,88 \pm 0,78
25/2,5	63,9 \pm 0,7	92,28 \pm 12,49	2,24 \pm 0,48	3,85 \pm 0,45	7,18 \pm 0,57
100/10	66,8 \pm 0,8	93,21 \pm 13,61	2,29 \pm 0,50	3,95 \pm 0,38	6,64 \pm 0,66
100/10 (washed)	62,2 \pm 0,6	67,23 \pm 12,23	1,25 \pm 0,48	2,88 \pm 0,53	5,92 \pm 0,41

Table VI: Properties of the serie of handsheets (\pm standard deviation), prepared from pine (SR 20⁰) and two layers: inner layer - cationic starch (Raisamyl 150) and the outer layer - CMC (Finnfix WRM). Ratio starch:CMC – 20:1.

Amount of PEs, mg/g. Starch/CMC	Basis weight, g/m ² .	Tensile index, Nm/g.	TEA index, J/g.	Elongation, %.	Tensile stiffness index, kNm/g.
0/0	63,9 \pm 0,9	66,46 \pm 6,06	1,52 \pm 0,28	3,44 \pm 0,37	6,49 \pm 0,31
10/0,5	62,4 \pm 1,0	82,22 \pm 9,29	2,12 \pm 0,39	4,07 \pm 0,38	6,20 \pm 0,50
25/1,25	66,0 \pm 1,2	87,30 \pm 7,62	2,35 \pm 0,24	4,32 \pm 0,20	6,26 \pm 0,56
100/5	64,9 \pm 0,6	96,38 \pm 5,10	2,77 \pm 0,20	4,75 \pm 0,13	6,39 \pm 0,22
100/5 (washed)	65,4 \pm 0,7	92,88 \pm 7,15	2,43 \pm 0,23	4,29 \pm 0,19	6,37 \pm 0,40

APPENDIX III (3/4)

Table VII: Properties of the serie of handsheets (\pm standard deviation), prepared from pine (SR 20⁰) and two layers: inner layer - cationic starch (Raisamyl 115) and the outer layer - CMC (Finnfix WRM). Ratio starch:CMC – 20:1.

Amount of PEs, mg/g. Starch/CMC	Basis weight, g/m ² .	Tensile index, Nm/g.	TEA index, J/g.	Elongation, %.	Tensile stiffness index, kNm/g.
0/0	63,9 \pm 0,9	66,46 \pm 6,06	1,52 \pm 0,28	3,44 \pm 0,37	6,49 \pm 0,31
10/0,5	65,3 \pm 0,7	91,10 \pm 7,32	2,44 \pm 0,31	4,33 \pm 0,33	6,82 \pm 0,41
25/1,25	67,0 \pm 0,7	96,62 \pm 7,50	2,56 \pm 0,29	4,28 \pm 0,26	6,93 \pm 0,39
100/5	67,0 \pm 0,4	116,3 \pm 10,27	3,22 \pm 0,46	4,60 \pm 0,34	7,42 \pm 0,35
100/5 (washed)	68,0 \pm 0,3	98,51 \pm 10,64	2,70 \pm 0,41	4,49 \pm 0,30	6,68 \pm 0,48

Table VIII: Properties of the serie of handsheets (\pm standard deviation), prepared from pine (SR 35⁰) and two layers: inner layer - cationic starch (Raisamyl 150) and the outer layer - CMC (Finnfix WRM). Ratio starch:CMC – 20:1.

Amount of PEs, mg/g. Starch/CMC	Basis weight, g/m ² .	Tensile index, Nm/g.	TEA index, J/g.	Elongation, %.	Tensile stiffness index, kNm/g.
0/0	68,0 \pm 0,6	94,37 \pm 5,57	2,57 \pm 0,16	4,26 \pm 0,12	7,84 \pm 0,33
10/0,5	64,4 \pm 0,4	98,83 \pm 10,71	2,73 \pm 0,52	4,40 \pm 0,58	7,31 \pm 0,86
25/1,25	67,5 \pm 0,3	102,05 \pm 4,66	2,81 \pm 0,20	4,50 \pm 0,22	7,27 \pm 0,38
100/5	66,8 \pm 0,5	109,98 \pm 5,37	2,97 \pm 0,16	4,43 \pm 0,14	7,69 \pm 0,28
100/5 (washed)	66,2 \pm 0,4	103,47 \pm 11,42	2,77 \pm 0,50	4,39 \pm 0,52	7,05 \pm 0,80

Table IX: Properties of the serie of handsheets (\pm standard deviation), prepared from birch (SR 20⁰) and two layers: inner layer - cationic starch (Raisamyl 150) and the outer layer - CMC (Finnfix WRM). Ratio starch:CMC – 20:1.

Amount of PEs, mg/g. Starch/CMC	Basis weight, g/m ² .	Tensile index, Nm/g.	TEA index, J/g.	Elongation, %.	Tensile stiffness index, kNm/g.
0/0	68,0 \pm 0,7	54,25 \pm 2,58	1,31 \pm 0,11	3,43 \pm 0,16	6,17 \pm 0,22
10/0,5	68,0 \pm 0,8	66,88 \pm 6,18	1,78 \pm 0,33	3,97 \pm 0,49	6,17 \pm 0,41
25/1,25	66,8 \pm 0,5	69,48 \pm 9,42	1,89 \pm 0,41	4,14 \pm 0,42	5,95 \pm 0,70
100/5	64,6 \pm 0,5	82,03 \pm 10,66	2,32 \pm 0,48	4,42 \pm 0,49	6,34 \pm 0,44
100/5 (washed)	65,2 \pm 0,3	77,88 \pm 9,27	2,20 \pm 0,42	4,42 \pm 0,40	5,90 \pm 0,47

APPENDIX III (4/4)

Table X: Properties of the serie of handsheets (\pm standard deviation), prepared from pine (SR 20⁰) and two layers: inner layer - cationic starch (Raisamyl 150) and the outer layer - CMC (Finnfix 2). Ratio starch:CMC – 20:1.

Amount of PEs, mg/g. Starch/CMC	Basis weight, g/m ² .	Tensile index, Nm/g.	TEA index, J/g.	Elongation, %.	Tensile stiffness index, kNm/g.
0/0	63,9 \pm 0,9	66,46 \pm 6,06	1,52 \pm 0,28	3,44 \pm 0,37	6,49 \pm 0,31
10/0,5	65,7 \pm 0,4	78,96 \pm 5,64	1,97 \pm 0,23	3,92 \pm 0,31	6,24 \pm 0,45
25/1,25	63,7 \pm 0,3	94,79 \pm 12,81	2,35 \pm 0,52	3,94 \pm 0,40	7,42 \pm 0,59
100/5	65,2 \pm 0,4	85,17 \pm 14,09	2,04 \pm 0,50	3,81 \pm 0,38	6,69 \pm 0,80
100/5 (washed)	63,6 \pm 0,5	100,63 \pm 11,11	2,49 \pm 0,35	4,03 \pm 0,23	7,39 \pm 0,81

Table XI: Properties of the serie of handsheets (\pm standard deviation), prepared from pine (SR 20⁰) and two layers: inner layer - cationic starch (Raisamyl 150) and the outer layer - CMC (Finnfix 10G). Ratio starch:CMC – 20:1.

Amount of PEs, mg/g. Starch/CMC	Basis weight, g/m ² .	Tensile index, Nm/g.	TEA index, J/g.	Elongation, %.	Tensile stiffness index, kNm/g.
0/0	63,9 \pm 0,9	66,46 \pm 6,06	1,52 \pm 0,28	3,44 \pm 0,37	6,49 \pm 0,31
10/0,5	64,3 \pm 0,2	65,17 \pm 10,64	1,39 \pm 0,36	3,26 \pm 0,46	6,00 \pm 1,03
25/1,25	66,0 \pm 0,2	92,46 \pm 11,07	2,35 \pm 0,44	4,05 \pm 0,39	7,17 \pm 0,52
100/5	66,0 \pm 0,4	101,88 \pm 15,33	2,80 \pm 0,53	4,58 \pm 0,29	6,81 \pm 0,76
100/5 (washed)	62,0 \pm 0,2	100,97 \pm 20,13	2,50 \pm 0,67	4,02 \pm 0,41	7,42 \pm 1,07

APPENDIX IV (1/4)

Roughness, air permeability and bending stiffness

Table I: Roughness, air permeability and bending stiffness (\pm standard deviation) of handsheets, prepared from pine (SR 20⁰) and one layer of cationic starch (Raisamyl 150).

Amount of PE, mg/g. Starch	Roughness, ml/min.	Air permeability, ml/min.	Bending stiffness, mNm.
0	1126 \pm 45	1488 \pm 302	0,151 \pm 0,031
10	1066 \pm 50	1225 \pm 190	0,191 \pm 0,027
25	1052 \pm 46	1304 \pm 71	0,211 \pm 0,019
100	1025 \pm 31	1494 \pm 124	0,220 \pm 0,035
100 (washed)	1073 \pm 49	1468 \pm 167	0,215 \pm 0,027

Table II: Roughness, air permeability and bending stiffness (\pm standard deviation) of handsheets, prepared from pine (SR 20⁰) and one layer of cationic starch (Raisamyl 115).

Amount of PE, mg/g. Starch	Roughness, ml/min.	Air permeability, ml/min.	Bending stiffness, mNm.
0	1126 \pm 45	1488 \pm 302	0,151 \pm 0,031
10	1263 \pm 139	1007 \pm 88	0,156 \pm 0,034
25	1278 \pm 156	624 \pm 122	0,189 \pm 0,029
100	1307 \pm 120	530 \pm 183	0,205 \pm 0,041
100 (washed)	1155 \pm 47	631 \pm 175	0,255 \pm 0,027

Table III: Roughness, air permeability and bending stiffness (\pm standard deviation) of handsheets, prepared from pine (SR 35⁰) and one layer of cationic starch (Raisamyl 150).

Amount of PE, mg/g. Starch	Roughness, ml/min.	Air permeability, ml/min.	Bending stiffness, mNm.
0	973 \pm 47	230 \pm 19	0,232 \pm 0,013
10	952 \pm 67	254 \pm 72	0,197 \pm 0,035
25	1077 \pm 104	436 \pm 236	0,169 \pm 0,012
100	1089 \pm 107	473 \pm 84	0,206 \pm 0,032
100 (washed)	907 \pm 103	486 \pm 160	0,168 \pm 0,016

APPENDIX IV (2/4)

Table IV: Roughness, air permeability and bending stiffness (\pm standard deviation) of handsheets, prepared from birch (SR 20⁰) and one layer of cationic starch (Raisamyl 150).

Amount of PE, mg/g. Starch	Roughness, ml/min.	Air permeability, ml/min.	Bending stiffness, mNm.
0	845 \pm 46	1430 \pm 199	0,194 \pm 0,015
10	785 \pm 123	1906 \pm 68	0,210 \pm 0,014
25	794 \pm 110	1902 \pm 133	0,238 \pm 0,033
100	894 \pm 107	1668 \pm 91	0,222 \pm 0,036
100 (washed)	957 \pm 92	1885 \pm 100	0,223 \pm 0,040

Table V: Roughness, air permeability and bending stiffness (\pm standard deviation) of handsheets, prepared from pine (SR 20⁰) and two layers: inner layer - cationic starch (Raisamyl 150) and the outer layer - CMC (Finnfix WRM) (10:1).

Amount of PEs, mg/g. Starch/CMC	Roughness, ml/min.	Air permeability, ml/min.	Bending stiffness, mNm.
0/0	1126 \pm 45	1488 \pm 302	0,151 \pm 0,03
10/1	1138 \pm 33	1876 \pm 402	0,152 \pm 0,02
25/2,5	1224 \pm 62	1995 \pm 337	0,178 \pm 0,04
100/10	1476 \pm 57	1593 \pm 509	0,154 \pm 0,02
100/10 (washed)	1453 \pm 71	2217 \pm 277	0,129 \pm 0,05

Table VI: Roughness, air permeability and bending stiffness (\pm standard deviation) of handsheets, prepared from pine (SR 20⁰) and two layers: inner layer - cationic starch (Raisamyl 150) and the outer layer - CMC (Finnfix WRM) (20:1).

Amount of PEs, mg/g. Starch/CMC	Roughness, ml/min.	Air permeability, ml/min.	Bending stiffness, mNm.
0/0	1126 \pm 45	1488 \pm 302	0,151 \pm 0,031
10/0,5	1266 \pm 91	2011 \pm 150	0,161 \pm 0,014
25/1,25	1273 \pm 128	1920 \pm 148	0,191 \pm 0,028
100/5	1304 \pm 93	1795 \pm 190	0,208 \pm 0,043
100/5(washed)	1337 \pm 219	1776 \pm 214	0,194 \pm 0,005

APPENDIX IV (3/4)

Table VII: Roughness, air permeability and bending stiffness (\pm standard deviation) of handsheets, prepared from pine (SR 20⁰) and two layers: inner layer - cationic starch (Raisamyl 115) and the outer layer - CMC (Finnfix WRM) (20:1). .

Amount of PEs, mg/g. Starch/CMC	Roughness, ml/min.	Air permeability, ml/min.	Bending stiffness, mNm.
0/0	1126 \pm 45	1488 \pm 302	0,151 \pm 0,031
10/0,5	1026 \pm 68	972 \pm 157	0,173 \pm 0,025
25/1,25	1149 \pm 163	615 \pm 29	0,173 \pm 0,039
100/5	1222 \pm 122	302 \pm 23	0,182 \pm 0,037
100/5 (washed)	1217 \pm 58	578 \pm 157	0,178 \pm 0,031

Table VIII: Roughness, air permeability and bending stiffness (\pm standard deviation) of handsheets, prepared from pine (SR 35⁰) and two layers: inner layer - cationic starch (Raisamyl 150) and the outer layer - CMC (Finnfix WRM).

Amount of PEs, mg/g. Starch/CMC	Roughness, ml/min.	Air permeability, ml/min.	Bending stiffness, mNm.
0/0	973 \pm 47	230 \pm 19	0,232 \pm 0,013
10/0,5	1073 \pm 84	153 \pm 26	0,197 \pm 0,011
25/1,25	1175 \pm 53	174 \pm 13	0,199 \pm 0,019
100/5	1162 \pm 45	214 \pm 22	0,181 \pm 0,038
100/5 (washed)	1117 \pm 25	284 \pm 44	0,181 \pm 0,016

Table IX: Roughness, air permeability and bending stiffness (\pm standard deviation) of handsheets, prepared from birch (SR 20⁰) and two layers: inner layer - cationic starch (Raisamyl 150) and the outer layer - CMC (Finnfix WRM).

Amount of PEs, Starch/CMC, mg/g.	Roughness, ml/min.	Air permeability, ml/min.	Bending stiffness, mNm.
0/0	845 \pm 46	1430 \pm 199	0,194 \pm 0,015
10/0,5	1032 \pm 35	1408 \pm 262	0,152 \pm 0,027
25/1,25	1072 \pm 44	1474 \pm 305	0,143 \pm 0,033
100/5	1042 \pm 82	1087 \pm 210	0,165 \pm 0,037
100/5 (washed)	1034 \pm 38	1310 \pm 150	0,148 \pm 0,019

APPENDIX IV (4/4)

Table X: Roughness, air permeability and bending stiffness (\pm standard deviation) of handsheets, prepared from pine (SR 20⁰) and two layers: inner layer - cationic starch (Raisamyl 150) and the outer layer - CMC (Finnfix 2).

Amount of PEs, Starch/CMC, mg/g.	Roughness, ml/min.	Air permeability, ml/min.	Bending stiffness, mNm.
0/0	1126 \pm 45	1488 \pm 302	0,151 \pm 0,031
10/0,5	1153 \pm 64	1502 \pm 737	0,148 \pm 0,025
25/1,25	1194 \pm 62	1952 \pm 967	0,219 \pm 0,03
100/5	1158 \pm 141	1243 \pm 160	0,245 \pm 0,021
100/5 (washed)	1152 \pm 77	1447 \pm 174	0,213 \pm 0,037

Table XI: Roughness, air permeability and bending stiffness (\pm standard deviation) of handsheets, prepared from pine (SR 20⁰) and two layers: inner layer - cationic starch (Raisamyl 150) and the outer layer - CMC (Finnfix 10G).

Amount of PEs, Starch/CMC, mg/g.	Roughness, ml/min.	Air permeability, ml/min.	Bending stiffness, mNm.
0/0	1126 \pm 45	1488 \pm 302	0,151 \pm 0,031
10/0,5	1117 \pm 35	1171 \pm 198	0,173 \pm 0,041
25/1,25	1263 \pm 139	1126 \pm 267	0,193 \pm 0,061
100/5	1275 \pm 76	1199 \pm 205	0,216 \pm 0,051
100/5 (washing)	1217 \pm 41	1257 \pm 36	0,181 \pm 0,030