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The effect of chemical additives on the strength, stiffness and elongation potential of paper

Anders Strand, Alexey Khakalo, Jarmo Kouko, Antti Oksanen, Annika Ketola, Kristian Salminen, Orlando Rojas, Elias Retulainen, Anna Sundberg

KEYWORDS: Tensile index, tensile stiffness, stretch, paper shrinkage, cationic starch, carboxymethyl cellulose, unrestrained drying, extendable fiber network

ABSTRACT: The effects of wet-end additions of cationic starches and/or carboxymethyl cellulose (CMC) on paper properties was determined by papermaking trials. The aim of this study was to mitigate the distinctive decrease in strength and stiffness due to unrestrained drying by addition of wet-end additives, while maintaining the extraordinarily high stretch potential of papers after unrestrained drying.

Addition of the different polysaccharides increased the tensile index and density of the paper. The largest increases in tensile index and stiffness were seen when combining cationic starches with CMC. With certain combinations of cationic starch and CMC, it was possible to increase the tensile index and stiffness of the paper, while maintaining the high elongation at break after unrestrained drying.

To complement the results from the papermaking trials, adsorption of cationic starches and CMC onto cellulose nanofibril model surfaces was studied by QCM-D and SPR techniques. The adsorbrates adsorbed onto cellulose surfaces as soft gels, containing a large amount of coupled water. Adsorption of soft and malleable polysaccharide layers in the fiber-fiber joints enhanced the paper properties significantly on a macroscopic level. The softest and most swollen polysaccharide layers resulted in the largest increases in tensile index and stiffness of paper.

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Introduction
A great deal of research has lately been aimed at finding novel bio-based alternatives to available fossil-based products, and towards opening up new packaging applications. Recently published studies have shown the possibilities of creating highly extendible networks from wood fibers that can be molded by available forming techniques into 3D shapes (Svensson et al. 2013; Vishtal et al. 2014; Vishtal, Retulainen 2014). Highly extendible networks of wood fibers have been produced by the means of mechanical treatments and/or various chemical additives combined with unrestrained drying (Seth 2005; Zeng et al. 2013; Khakalo et al. 2014, 2017b; Vishtal et al. 2015). Formation of micro-crepes in the longitudinal direction of fibers caused by fiber shrinkage in transversal direction has been described as the mechanism behind paper shrinkage during unrestrained drying (Page, Tydeman 1962). The largest shrinkages occur in papers that are highly beaten. Stretching a shrunken fiber network is to a certain extent a reversal of shrinkage, as the applied forces tend to pull out the kinks and micro-compressions, both between and within the bonds. As hydrogen bonds slowly break, the micro-compressions are released, allowing for a greater extension of the fiber network before it breaks due to actual failure of fiber-fiber bonds.
Unrestrained drying of paper sheets lowers their tensile stiffness quite significantly, and reported values are therefore usually quite low (Page, Tydeman 1962; Zeng et al. 2013). To increase the tensile stiffness of paper sheets after unrestrained drying, a closer investigation of the properties of the fiber-fiber joint, and the contributors to fiber-fiber joint strength, is needed.

The fiber-fiber bonds are usually the limiting factor for the strength of paper, and the highest recorded tensile strengths of paper are far below the values obtained for single fibers (Page 1969; Davison 1972). In order to form strong contact between fibers, it is important to have a large molecular contact area between the fibers (Torgnysdotter Wågberg, 2004). The softness of the surface layer will have a large influence on the joint strength between fibers, while the bulk properties will affect the possibility for fibers to form contact points with other fibers. Cellulose has a strong affinity to itself, and to other hydroxyl-containing materials. Hydrogen bonding between fibers requires close proximity, in the size range of 0.25-0.35 nm (McKenzie 1984; Hubbe 2006; Gardner et al. 2008; Forne et al. 2011). Cellulosic surfaces are thought to be covered by nano-width cellulosic hair-like features, in addition to water-swollen hemicellulose and other associated colloidal material (Kibblewhite 1973; Pelton 1993; Hubbe et al. 2009). The adhesion properties of cellulose surfaces vary with different degree of crystallinity; a surface with a lower degree of crystallinity provides a more effective surface for reorientation of its surface groups, meaning that these can participate in specific and non-specific interactions to a higher degree (Gardner et al., 2008). Greater mobility of the surface segments and their hydroxyl groups seems to be a very important parameter for the development of fiber-fiber joint strength (Hubbe, 2006). Water acts as a solvent for segments of macromolecules, such as hemicelluloses or microfibrils, which extend from the surface of each fiber (Kibblewhite
Hydrophilic polymers, both native in pulp and added, are known to improve the adhesion between cellulose fibers and to improve fiber-fiber bonding (Fornue et al. 2011). The most commonly used dry strength agent is cationic starch. Addition of polyelectrolytes, such as cationic starch, is a promising way to enhance bonding between fibers (Hubbe 2006). Additives that enhance strength successfully should be of sufficiently high molar mass to remain on the fiber surface, hydrophilic, retainable to the fiber network, and able to form hydrogen bonds (Pelton 2004; Hubbe 2006; Fornue et al. 2011). It is suggested that cationic starch mainly increases the bond strength per unit area of bonded area. Even though dry strength additives are widely used, innovation is still needed in order to better understand and optimize their effects.

CMC acts as a bonding agent and reduces the flocculation tendency of pulp, increases the water retention value of pulp, and increases the tensile strength, tear strength, and surface strength of paper (Beghello et al. 1997; Laine et al. 2002; Hubbe 2006). Adsorbed CMC is believed to extend outwards from the fiber surfaces due to repulsion between the anionic charges in its chain, and this may facilitate more efficient interdiffusion of macromolecules at the fiber surfaces (Hubbe 2006; Duker, Lindström 2008). It is generally known that inter-fiber bond strength increases as fibers become more swollen with water by refining, chemical treatment or adsorption of swollen polymeric material on the fiber surfaces.

The aim of this study was to enhance the tensile strength and stiffness of fiber networks after unrestrained drying by wet-end addition of modified polysaccharides, whilst maintaining the extraordinarily high stretch potential distinctive for unrestrained drying.

Materials and Methods

Materials

The fibers used in the papermaking experiments were ECF bleached once dried softwood kraft pulp, which was received from a Finnish pulp mill. The pulp used for the adsorption studies was a bleached softwood kraft pulp (cellulose 80.3%, xylan 10.4%, glucomannan 8.4% and total lignin <0.9%) provided by a Finnish pulp mill.

Three different cationic starches were received from Chemigate as pre-boiled slurries. One cationic starch was received from Chemigate in dry form. The cationic starch slurries were dissolved in cold tap water, which had been pre-adjusted to pH 8 with 2 M NaOH and to 1 mS/cm conductivity with 2 M CaCl₂, under agitation. The dry cationic starch was diluted with tap water, which had been pre-adjusted to pH 8 and 1 mS/cm conductivity, under agitation and heating to its boiling point until clearly dissolved.

Sodium carboxymethyl cellulose (CMC), M₆ 700 kDa and DS 0.80-0.95, was obtained from Aldrich as dry powder. The pH and conductivity of cold tap water was adjusted as described above. The CMC was dissolved in the pre-adjusted tap water, with agitation and heating to its boiling point.

Polydiallyldimethylammonium chloride (poly-DADMAC) was obtained from Aldrich. The poly-DADMAC was received as a viscous solution with a dry content of 26% and a molar mass of 200-350 kDa. The polyDADMAC was diluted with deionized water under agitation. Poly(vinyl sulfate) potassium salt (KPVS) was obtained from Wako. The KPVS salt was dissolved in deionized water under agitation. Hexadimethrine bromide (Polybrene) was obtained from Sigma. The molar mass of the polybrene was approximately 8 kDa (Sundberg et al. 2000; Fardim et al. 2002). The Polybrene was dissolved in deionized water.

Methods

Refining: The refining of the pulp was performed with a ProLab™ refining station (Valmet, Finland) at Åbo Akademi University, Finland (Lundin 2008). Mechanical refining of the pulp was used to reverse the adverse effect of drying, increase fiber flexibility, to expand the microfibrillar structure of the pulp and to enhance the entanglement between fibrils and fibers in suspension (Mayhood et al 1961; Kibblewhite 1973; Scallan, Tigerström 1992; Koskenhely 2008; Belle et al. 2016). Kraft pulp, 2 kg o.d., was diluted to 20 kg with cold tap water and wetted overnight. The suspension was afterwards diluted to 40 kg and poured into the mixing chest of the ProLab™ refiner. The suspension was disintegrated for 15 min at 600 rpm before the refining. Another 10 kg of cold tap water was used to clean the slushing station, and was mixed with the rest of the pulp, resulting in a pulp consistency of 4% during the refining. The refining was performed using conical fillings at 3000 rpm. During the refining, the pulp suspension was continuously circulated through the system with a speed of 100 L/min by the stock pump. Samples of the pulp were taken at refining intensities of 50, 100, 150, 200, 250 and 300 kWh/ton. The Schopper-Riegler (°SR) values of the pulp samples were measured according to ISO 5267-1. The °SR values were plotted against refining intensity (kWh/ton) (Fig 1). The refining intensity 135 kWh/ton, which corresponded to °SR 25, was chosen for the tests.

Pulp characterization: The pulp was characterized using a Kajaani FiberLab optical fiber analyzer (Metso Automation, Finland). The determined values before and after refining are shown in Table 1. The refining caused an increase in fines content, and a slight increase in fiber width and cell wall thickness. The average fiber length remained unchanged, while the curl factor of the fibers decreased slightly.
Fig 1 - The measured dewatering resistance of kraft pulp at different refining intensities.

Table 1 - Properties of the kraft pulp before and after refining to 135 kWh/ton. The fiber length and amount of fines are reported as length weighted averages.

<table>
<thead>
<tr>
<th>Property</th>
<th>Unrefined pulp</th>
<th>ProLab™ refined pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td>°SR</td>
<td>12</td>
<td>25</td>
</tr>
<tr>
<td>Fiber length, l(), mm</td>
<td>1.83</td>
<td>1.83</td>
</tr>
<tr>
<td>Fines (l), %</td>
<td>2.45</td>
<td>2.90</td>
</tr>
<tr>
<td>Fiber width, µm</td>
<td>28.5</td>
<td>29.7</td>
</tr>
<tr>
<td>Cell wall thickness, µm</td>
<td>6.2</td>
<td>7.6</td>
</tr>
<tr>
<td>Curl, %</td>
<td>15.3</td>
<td>14.5</td>
</tr>
</tbody>
</table>

**Charge titration:** The charge of the refined kraft pulp was analyzed by polyelectrolyte back titration using a particle charge detector (Mütek PCD 03, Mütek Analytic GmbH, Germany) coupled to a titration device (736 GP Coulometric titrator, Titrino, Metrohm Ltd., Switzerland). Polybrene was added in excess to diluted samples of refined pulp, and was allowed to react for 20 min. The suspension was afterwards filtered through a glass fiber filter (GF 50), and the filtrate was titrated using KPVS. The amount of titrand needed for neutralization was used to calculate the total anionic charge of the kraft pulp. The procedure was repeated with different additions of polybrene to vary the excess concentration of the polymer. The determined values were compiled into an isotherm, from which the total charge of the kraft pulp was estimated.

PolyDADMAC was added in excess to pulp samples and was allowed to react for 20 min. The suspension was afterwards filtered through a glass fiber filter, and the filtrate was titrated using KPVS. The amount of titrand needed for neutralization was used to calculate the “surface” anionic charge of the kraft pulp. Different amounts of polyDADMAC were added to pulp samples, filtered and titrated. The determined values were compiled into an isotherm, from which the “surface” charge of the kraft pulp was estimated.

The cationic charge of the starches were determined by polyelectrolyte titration against KPVS. The anionic charge of the carboxymethyl cellulose was determined by polyelectrolyte titration against polybrene. The determined charge densities are shown in Table 2. The determined value of total charge in the refined kraft pulp (40 µeq/g) was very close to other reported values of anionic charge content in elemental chlorine free bleached kraft pulp from pine (Fardim et al. 2002).

**Table 2 - Some properties of the cationic starches and CMC.**

<table>
<thead>
<tr>
<th>Charge density µeq/g</th>
<th>Molar mass</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Classic 135</td>
<td>+193</td>
<td>Very high</td>
</tr>
<tr>
<td>Raifix 01015 SW</td>
<td>+831</td>
<td>Low</td>
</tr>
<tr>
<td>Raisabond 15</td>
<td>+882</td>
<td>Medium</td>
</tr>
<tr>
<td>Raifix 25035</td>
<td>+1870</td>
<td>Medium</td>
</tr>
<tr>
<td>Carboxymethyl cellulose (CMC)</td>
<td>-4176</td>
<td>700 kDa</td>
</tr>
<tr>
<td>Refined kraft pulp</td>
<td>-40</td>
<td>-10*</td>
</tr>
</tbody>
</table>

*The measured “surface” charge of the kraft pulp.

**Papermaking procedure:** The conductivity of cold tap water was adjusted to 1 mS/cm with 2 M CaCl₂, and to pH 8.0 with 2 M NaOH. The pre-adjusted water was used to dilute set amounts of refined pulp, and the suspensions were further diluted with pre-adjusted water the following day and their pH and conductivity were again adjusted to pH 8 with 2 M NaOH and to 1 mS/cm with CaCl₂. Dissolved carboxymethyl cellulose (pH 8, 1 mS/cm) was in some cases added to the suspension. Dissolved cationic starch was added afterwards under vigorous agitation. The components were allowed to interact under agitation for 20 min before the sheet formation. The final consistency of the pulp suspension was 0.3%.

Paper sheets were formed on a 125 mesh wire in a 16.5 x 16.5 cm laboratory sheet former. The water was recirculated during the papermaking procedure. The aimed grammage of the papers was 100 g/m².

The formed sheets were dried between blotters on a 60°C drying cylinder (restrained drying), or on a drying frame between two pieces of polyamide fabric to allow for paper shrinkage during drying (unrestricted drying). None of the sheets were wet-pressed.

**Paper testing:** The grammage and thickness of the papers were measured. The mechanical properties (tensile index, stretch, work, tensile stiffness, and breaking length) of the paper sheets were measured with a Lorentzen & Wettre, L&W tensile strength tester. The straining speed was 12 mm/min in the tensile measurements, and at least 25 samples were tested. The air permeability of the papers was determined with a Lorentzen & Wettre, L&W Air Permeance tester. All paper tests were performed at 23°C and at 50% relative humidity.

**Preparation of cellulose nanofibrils (CNF) for adsorption studies:** First, wood fibers were washed to Na-form in order to ease the defibrillation process, according to a previously described procedure (Swerin et al. 1990). The charge density of the fibers used was measured by conductometric titration, and was determined to be 27 µeq/g. The pulp was mechanically refined in a Valley beater at °SR 85. This ensured fiber accessibility and fibrillation efficiency. Finally, diluted fibers (solids contents <1 wt-%) were further disintegrated (at least 12 passes) by a high-pressure microfluidizer (M110P, Microfluidics corp., Newton, MA, USA) equipped with...
200 and 100 μm chambers and operated at 2000 bar pressure. The prepared aqueous dispersions of CNF were stored at 4°C until used.

Preparation of CNF model surface for adsorption studies: CNF-polsaccharide interactions were investigated by QCM-D and SPR using gold coated sensors. The sensors (SPR gold chips or QCM crystals) were first cleaned with UV/ozone treatment for 20 min to remove any organic contaminants. The CNF thin films were prepared according to previously established techniques (Ahola et al. 2008). In short, CNF gel was diluted (0.190 wt % CNF in water) and tip-ultrasonicated for 10 min at 25% amplitude setting and consecutively centrifuged at 10400 rpm for 45 min. Individual nanofibrils were obtained from the resultant clear supernatant. The nanofibrils were spin-coated (Model WS-650SX-6NPP, Laurell Technologies, PA, USA) onto UV/ozoneized QCM-D or SPR crystals with a pre-adsorbed thin anchor layer of PEI at 3000 rpm with 90 s spinning time. After spin-coating, the CNF films were dried at 80°C for 10 min and stored in desiccator until further use. Success of coating was verified by AFM imaging.

Polymer solution preparation for adsorption studies: Solutions of CMC and cationic starches (0.5 mg/mL) were prepared using distilled water, with the aid of heating and magnetic stirring. The pH and conductivities of prepared polysaccharide solutions are summarized in Table 3. The polymer solutions were degassed and passed through syringe filters (0.45 μm, Acrodisc syringe GHP filter, Sigma-Aldrich, U.S.A.) to remove any solid or undissolved particles prior to QCM-D and SPR analyses.

Polsaccharide affinity with CNF model surfaces: The adsorption of polysaccharides on CNF films and the properties of the adsorbed layers were investigated by using a QCM-D instrument (model E4, QSense AB, Sweden) and a multiparametric surface plasmon resonance unit (MP-SPR Model Navi 200, Oy BioNavis Ltd., Ylöjärvi, Finland). An experimental protocol similar to the one used by Khakalo et al. (2017a) was applied for calculating the properties of adsorbed layers as well as the extent of their hydration. Both QCM-D and SPR experiments were performed at a constant flow rate of 100 μl/min and the temperature was maintained at 23°C until adsorption plateau was reached. Thereafter, rinsing with polymer-free solution was applied to ascertain the irreversible binding of polysaccharides to CNF surfaces deposited on the (QCM-D/SPR) sensors. Each set of experiments was performed at least in duplicate.

Table 3 - The pH and conductivities of the solutions used for adsorption studies.

<table>
<thead>
<tr>
<th>Solutions</th>
<th>pH</th>
<th>Conductivity (μS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milli-Q water</td>
<td>5.1</td>
<td>0.8</td>
</tr>
<tr>
<td>CMC</td>
<td>6.7</td>
<td>116.7</td>
</tr>
<tr>
<td>Classic 135</td>
<td>6.0</td>
<td>5.4</td>
</tr>
<tr>
<td>Raifix 01015 SW</td>
<td>6.7</td>
<td>60.2</td>
</tr>
<tr>
<td>Raisabond 15</td>
<td>6.5</td>
<td>62.8</td>
</tr>
<tr>
<td>Raifix 25035</td>
<td>6.0</td>
<td>95.8</td>
</tr>
</tbody>
</table>

Results and discussion

Cationic starches or CMC – Tensile index and stretch

Papers were prepared with addition of four different commercially available starches or CMC, and reference sheets without additives. The measured tensile indexes of the paper sheets are shown in Fig 2 and in Table 4. All of the additives increased the tensile index above the original value, which was 68 kNm/kg.

A linear increase in tensile index was found when increasing the dosage of Classic 135 from 2% to 5%. The maximum coverage of Classic 135 on the fiber surfaces, when only taking the cationic charge of the starch and the anionic charge of the pulp into account, should be at an addition of 5.2%. All of the added cationic starch in the experiments with Classic 135 could have been retained in the paper sheet due to attraction between cationic and anionic charges. The highest determined tensile index was 82.5 kNm/kg, which was obtained with addition of 5% Classic 135, i.e. the cationic starch with a low charge density and very high molar mass. This was in agreement with previous findings (Hubbe 2006).

Addition of Raisabond 15 and Raifix 01015 SW, i.e. cationic starches with a higher charge density, also increased the tensile index of the paper. The maximum coverage of Raisabond 15 on the fiber surfaces, when only taking cationic and anionic charge into account, is at an addition of 1.1%, while the value for Raifix 01015 SW is calculated to 1.2%. The maximum coverage of these cationic starches on the fibers was achieved below addition of 2%, hence increasing the dosage from 2 to 4% did not increase the tensile index of the paper.

Addition of Raifix 25035, i.e. a cationic starch with a very high charge density, also increased the tensile index of the paper. The increase in strength was, however, lower than for the other cationic starches; addition of 1% only caused an increase of about 0.5 kNm/kg. The calculated maximum coverage of Raifix 25035 was a dosage of 0.5%, indicating that the maximum coverage level was achieved below the first experimental point. Further addition of Raifix 25035 causes a small increase in tensile index, indicating that only a small amount of additional cationic starch can be retained physically in the sheets during forming.

Addition of 1% CMC to the suspension caused a quite large increase in tensile index on its own; about 11.6 kNm/kg. It has been shown that wet-end addition of CMC increases the tensile, tear, and surface strength of paper, as well as decreases its roughness (Beghello et al 1997). It has also been reported that adsorption of CMC on fibers reduces flocculation and has a positive effect on the formation of paper (Beghello et al 1997; Yan et al 2006; Duker, Lindström 2008). A wet-end addition of 1% CMC resulted a similar tensile index as addition of 4% of Classic 135, i.e. about 80 kNm/kg. Decreasing the dosage of CMC from 1% to 0.5% lowered the tensile index only slightly. The small difference between 1% and 0.5% indicated that not all CMC could be retained in the sheets due to mutual repulsion between anionic charges on the CMC and the fibers. It has been reported that ionized groups in the external part of the fiber surface increases the strength of the fiber-fiber joint, which is probably due to a more...
swollen surface layer on the fibers and a higher relative bonded area between fibers (Torgnysdotter, Wågberg 2003, 2004; Duker, Lindström 2008; Myllytie et al. 2009). A similar increase in tensile index would be expected if some of the added CMC had adsorbed onto the fibers in suspension. It has previously been reported that CMC, cationic starch and micro-fibrillated cellulose mainly increases the relative bonded area between fibers, resulting in stronger fiber networks (Lindström et al. 2016).

Addition of the cationic starches or CMC to the suspension resulted in only slight increases in stretch for the sheets dried under restrain (Table 4). In tensile tests performed at traditional paper testing conditions, the increase in stretch was only between 0.1 and 0.8% compared to the reference sheets. Enhanced fiber-fiber bonding by addition of cationic starch or CMC have been shown to allow for greater use of the stretch potential of the fiber network before it breaks (Seth 2005). The measurable increases in stretch potential by additives were quite limited in these experiments, since the mechanical refining procedure had already increased the fiber-fiber bonding in the pulp quite extensively. It has previously been reported that refining of pulp increases the strength of individual fiber-fiber joints (Mayhood et al. 1961). However, the authors attributed most of the increase in paper strength from refining to plastization of fibers, which increased the number of fiber contacts per unit fiber length.

**Cationic starches with CMC – Tensile index and stretch**

Papers were prepared with addition of the four different cationic starches combined with 1% CMC. The measured tensile indexes of the paper sheets are shown in Fig 3, as well as reported in Table 4. All of the additives increased the tensile index above the original value, which was 68 kNm/kg. Also in these experiments, the increases in tensile index differed depending on the added starch. Addition of 1% or 0.5% CMC on its own already caused quite a significant increase in tensile index, which was discussed in the previous section. Combinations of the cationic starches with CMC resulted in values far surpassing the values of the individual components.

The largest increases in tensile index were seen when Classic 135 and CMC were combined. Addition of 2% Classic and 1% CMC resulted in a tensile index of 90.4 kNm/kg, i.e. 22 kNm/kg higher than papers without additives. The tensile index increased further with higher additions of Classic 135 and reached its maximum value, 98.2 kNm/kg, at addition of 4% starch with 1% CMC. The addition of highly anionic CMC to the suspension meant that a dosage of about 26.8% Classic 135 would be needed in order to completely neutralize all accessible anionic charges, which meant that more additives could easily have been retained.

The combination of Raisabond 15 or Raifix 01015 SW with 1% CMC also resulted in increased paper strength (Fig 3). These increases were, however, not as large as in the case of Classic 135. Changing the dosage of these two cationic starches between 2 and 4% resulted in only minor differences in tensile index. It was noted that the introduction of 1% CMC resulted in significant increases in tensile index with Raisabond 15 and Raifix 01015 SW. The addition of highly anionic CMC to the suspension means that a dosage of about 5.9% Raisabond 15, or 6.2% Raifix 01015 SW, would be needed in order to completely neutralize all accessible anionic charges.

The combination of Raifix 25035 with 1% CMC also resulted in increased values of tensile index. Addition of 1% of the cationic starch resulted in a modest increase in paper strength compared to 1% CMC alone; 82.2 compared to 80 kNm/kg. However, more noticeable increases in strength was seen when increasing the dosage above 3%. The addition of highly anionic CMC to the suspension means that a dosage of about 2.8% Raifix 25035 is needed in order to completely neutralize all accessible anionic charges.

For three of the four cationic starches, the highest tensile index was obtained by combination of 4% cationic starch with 1% CMC, i.e. a ratio of 4:1. The tensile index of the papers even resulted in very similar values for three of the cationic starches at a ratio of 4:1, i.e. 88.1-89.1 kNm/kg. Aiming for fiber saturation by cationic polymers before addition of anionic CMC has been shown to be an effective strategy for increasing the dry strength of paper (Hubbe 2006). However, it has also been reported that in-situ formation of polyelectrolyte complexes between...
polyanions and polycations may form non-equilibrium structures that can interact with fibers in a beneficial way before becoming deactivated (Chen et al. 2003; Hubbe et al. 2005; Lofton et al. 2005; Hubbe 2006). In-situ formation on non-stoichiometric complexes between CMC and cationic starch could explain why these three cationic starches increased the tensile index to the same extent at a ratio of 4:1, regardless of their charge density. The uptake of water-soluble polyanions and polycations to fibers and fines can be described in a few step-wise mechanisms; mixing and/or complexation of the added polysaccharides with dissolved and colloidal carbohydrates in the pulp suspension, adsorption onto fibers or fines, and association of fines and related aggregates to fibers (Rojas, Neuman 1999). It is theorized that when a sticky and long-chained molecule (cationic starch in this case) is introduced to a pulp suspension, it is unlikely to first hit a pulp fiber, since the fibers occupy a very minute fraction of the total volume (Davison 1983). According to this theory, the cationic starch in these experiments may have come into contact with the highly anionic CMC, forming in-situ polyelectrolyte complexes, before coming into contact with fines or fibers. These colloidal polyelectrolyte complexes have been reported as irreversible, kinetically frozen structures (Dautzenberg, Karibyants 1999; Feng et al. 2008; Hubbe et al. 2009). It has also been reported that additions of polyelectrolytes before polyanions to the pulp suspension resulted in higher paper strength, while the formation was better when the polyanion was added before the polycation (Ankerfors, Wågberg 2013). The total effect of these mechanisms may be quite complex to calculate, but it seems like sequential addition of polyelectrolytes is an effective way to improve paper properties (Hubbe 2006).

The highest tensile index was achieved by combination of the cationic starch with the highest molar mass and the lowest charge density, Classic 135, with CMC. Similar trends have previously also been reported at a slightly different ratio of cationic starch to CMC (Retulainen, Nieminen 1996).

Addition of the cationic starches in combination with CMC to the suspension resulted in only slight increases in elongation at break for the sheets dried under restraint (Table 4). In tensile tests performed at traditional paper testing conditions, the increase in stretch was only between 0.1 and 0.8% compared to the reference sheets. Enhanced fiber-fiber bonding by addition of cationic starch in combination with CMC allows for greater use of the stretch potential of the fiber network before it breaks (Seth, 2005). However, it seems that not even large increases in fiber-fiber bond strength is sufficient to increase the stretch potential of the fiber network in these experiments.

### Tensile stiffness, air permeability and surface charge

For packaging applications, the tensile stiffness is also of utmost importance (Hubbe 2006). The tensile stiffness of the paper sheets with cationic starch and/or CMC, and reference sheets was measured (Table 4). The values were plotted versus tensile index and can be seen in Fig 4. The tensile stiffness of the reference sheets was 5.4 MNm/kg. Addition of the different cationic starches on their own increased or decreased the stiffness of the paper only slightly, regardless of dose. It was thereby concluded that addition of cationic starch does not increase the tensile stiffness of paper significantly on its own, which was in agreement with previous findings (Myllytie et al., 2009).

Addition of CMC increased the stiffness of paper significantly. Adsorption of CMC onto fibers has previously been shown to increase the stiffness, or sheet modulus, of paper (Laine et al. 2002; Myllytie et al. 2009). Wet-end addition of 1%, or even 0.5%, CMC to the lead to increased stiffness of the papers. The stiffness of the paper could be increased even higher by combining CMC with the different cationic starches. The highest measured stiffness was obtained when combining 5% Classic 135 and 1% CMC. It was shown that Classic 135 leads to no significant increases in stiffness on its own. The trend in these experiments shows that the stiffness increased with increasing addition of Classic 135 in the presence of CMC. It is therefore logical to assume that this cationic starch, with low charge density and very high molar mass, was quite effective at retaining CMC in the fiber network during sheet forming. Very high molar mass, hydrophilic nature, and generally a linear structure has previously been identified as desired properties of an effective retention aid (Hubbe et al. 2009).

The determined tensile stiffness values for combinations of cationic starches and CMC were 5.7-6.4 MNm/kg. However, very few combinations resulted in stiffness values above 6.0 MNm/kg. By using these different additives, and combinations of them, paper can be tailored to a broad range in tensile index, 68-98 kN/m/kg, and in tensile stiffness, 5.3-6.4 MNm/kg.

The air permeability of the paper sheets with cationic starch and/or CMC, and reference sheets were measured. The measurements showed that the air permeability of the papers decreased at almost all measurement points when cationic starch or CMC was added to the pulp (Table 4). The observed decrease in air permeability indicated that the additives caused the fiber network to become less porous to some extent. This is in agreement with the suggestion that cationic starch may draw fibers together during drying to form more dense structures, even increasing the relative bonded area between fibers (Hubbe 2006).

The results showed that the cationic starches with higher charge density caused denser fiber networks compared to the cationic starch with low charge density (Table 4). However, the largest decrease in air permeability was obtained by addition of 1% CMC, which lowered the value from 886 mL/min to 431 mL/min on its own. Even 0.5% CMC was enough to lower the air permeability of the papers to 572 mL/min. Combinations of the cationic starches with the CMC caused larger variations in the results. The air permeability of the sheets did not necessarily decrease due to addition of cationic starch in combination with CMC, but increased quite significantly in some cases.

Since the anionic charge of CMC, the surface charge of the pulp, and the cationic charge of the different starches have been determined, it was possible to calculate the net charge of the pulp suspension with additives. The air permeability was plotted versus the net charge in the pulp suspensions, and a correlation was seen (Fig 5).
Table 4 - The mechanical properties of laboratory sheets after restrained drying. The sheets have been prepared with wet-end additions of cationic starch and/or CMC. The average values, as well as their confidence level intervals (cl 95%) or standard deviations (s), are reported. The additions are calculated as wt-% of o.d. pulp.

<table>
<thead>
<tr>
<th></th>
<th>Density kg/m³</th>
<th>Tensile index kNm/kg</th>
<th>Tensile stiffness MN/m²</th>
<th>Stretch % cl 95%</th>
<th>Air permeability mL/min s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft pulp</td>
<td>466</td>
<td>68.4</td>
<td>1.6</td>
<td>5.4</td>
<td>4.1</td>
</tr>
<tr>
<td>0.5% CMC</td>
<td>477</td>
<td>77.2</td>
<td>1.8</td>
<td>5.7</td>
<td>0.1</td>
</tr>
<tr>
<td>1% CMC</td>
<td>487</td>
<td>80.0</td>
<td>1.5</td>
<td>5.9</td>
<td>0.1</td>
</tr>
<tr>
<td>2% Classic 135</td>
<td>477</td>
<td>75.3</td>
<td>1.9</td>
<td>5.5</td>
<td>0.1</td>
</tr>
<tr>
<td>3% Classic 135</td>
<td>491</td>
<td>77.7</td>
<td>1.7</td>
<td>5.3</td>
<td>0.1</td>
</tr>
<tr>
<td>4% Classic 135</td>
<td>480</td>
<td>79.8</td>
<td>1.7</td>
<td>5.4</td>
<td>0.1</td>
</tr>
<tr>
<td>5% Classic 135</td>
<td>484</td>
<td>82.5</td>
<td>1.3</td>
<td>5.5</td>
<td>0.1</td>
</tr>
<tr>
<td>1% CMC + 1% Raifax 25035</td>
<td>488</td>
<td>68.9</td>
<td>1.1</td>
<td>5.6</td>
<td>0.1</td>
</tr>
<tr>
<td>1% CMC + 2% Raifax 25035</td>
<td>490</td>
<td>78.1</td>
<td>1.5</td>
<td>5.6</td>
<td>0.1</td>
</tr>
<tr>
<td>1% CMC + 3% Raifax 25035</td>
<td>490</td>
<td>76.3</td>
<td>2.0</td>
<td>5.6</td>
<td>0.1</td>
</tr>
<tr>
<td>1% CMC + 4% Raifax 25035</td>
<td>488</td>
<td>75.5</td>
<td>1.7</td>
<td>5.6</td>
<td>0.1</td>
</tr>
<tr>
<td>1% CMC + 5% Raifax 25035</td>
<td>476</td>
<td>72.9</td>
<td>1.1</td>
<td>5.4</td>
<td>0.1</td>
</tr>
<tr>
<td>1% CMC + 2% Classic 135</td>
<td>509</td>
<td>90.4</td>
<td>2.1</td>
<td>6.2</td>
<td>0.1</td>
</tr>
<tr>
<td>1% CMC + 3% Classic 135</td>
<td>522</td>
<td>95.0</td>
<td>2.0</td>
<td>6.3</td>
<td>0.1</td>
</tr>
<tr>
<td>1% CMC + 4% Classic 135</td>
<td>531</td>
<td>98.2</td>
<td>1.3</td>
<td>6.3</td>
<td>0.1</td>
</tr>
<tr>
<td>1% CMC + 5% Classic 135</td>
<td>532</td>
<td>97.7</td>
<td>2.0</td>
<td>6.4</td>
<td>0.1</td>
</tr>
<tr>
<td>1% CMC + 2% Raifax 01015 SW</td>
<td>488</td>
<td>86.1</td>
<td>1.7</td>
<td>6.1</td>
<td>0.1</td>
</tr>
<tr>
<td>1% CMC + 3% Raifax 01015 SW</td>
<td>497</td>
<td>86.8</td>
<td>1.9</td>
<td>5.9</td>
<td>0.1</td>
</tr>
<tr>
<td>1% CMC + 4% Raifax 01015 SW</td>
<td>496</td>
<td>88.1</td>
<td>1.3</td>
<td>6.0</td>
<td>0.1</td>
</tr>
<tr>
<td>1% CMC + 2% Raisabond 15</td>
<td>499</td>
<td>89.0</td>
<td>1.6</td>
<td>5.7</td>
<td>0.1</td>
</tr>
<tr>
<td>1% CMC + 3% Raisabond 15</td>
<td>485</td>
<td>86.6</td>
<td>2.3</td>
<td>5.9</td>
<td>0.1</td>
</tr>
<tr>
<td>1% CMC + 4% Raisabond 15</td>
<td>485</td>
<td>88.5</td>
<td>2.1</td>
<td>5.9</td>
<td>0.1</td>
</tr>
<tr>
<td>1% CMC + 1% Raifax 25035</td>
<td>487</td>
<td>82.2</td>
<td>2.2</td>
<td>5.8</td>
<td>0.1</td>
</tr>
<tr>
<td>1% CMC + 2% Raifax 25035</td>
<td>462</td>
<td>80.4</td>
<td>2.7</td>
<td>5.7</td>
<td>0.2</td>
</tr>
<tr>
<td>1% CMC + 3% Raifax 25035</td>
<td>501</td>
<td>85.0</td>
<td>2.0</td>
<td>5.8</td>
<td>0.1</td>
</tr>
<tr>
<td>1% CMC + 4% Raifax 25035</td>
<td>501</td>
<td>89.1</td>
<td>1.7</td>
<td>6.0</td>
<td>0.1</td>
</tr>
<tr>
<td>1% CMC + 5% Raifax 25035</td>
<td>505</td>
<td>87.6</td>
<td>1.8</td>
<td>5.8</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Fig 4 - The tensile stiffness (MN/m²) versus the tensile index (kNm/kg) of paper sheets made with wet-end additions of CMC and/or cationic starches. The average values with their confidence level intervals (95%) are shown.

Fig 5 - The air permeability (mL/min), with standard deviation, versus the calculated “surface” charge in the pulp suspension (µeq) at different additions of CMC and/or cationic starches.
High air permeability values were found between net charges of -1463 and +474 µeq, indicating that fiber networks formed within this region were less dense due to flocculation compared to fiber networks formed at higher cationic or anionic net charge. Increasing the charge on fibers leads to additional electrostatic repulsion between them, which results in less flocculation (Torgnysdotter and Wågberg, 2004). The fact that the curve is shifted towards the anionic side may because of screening effects by the abundant calcium ions, which had been added to adjust the background conductivity of the suspensions.

Adsortion onto CNF model surfaces – QCM-D and SPR

The adsorption behavior of CMC and the different cationic starches onto model surfaces of cellulose nanofibrils (CNF) was studied by QCM-D and SPR techniques. The CNF films can be considered similar to the hydrated surface of refined fibers in an aqueous suspension. The sensograms recorded upon adsorption of the polysaccharides from aqueous solution on CNF-coated QCM-D crystals are illustrated in Fig 6. It should be noted that the observed shift in QCM-D frequency (Δf) is directly related to the amount of adsorbed polysaccharide at the interface.

The films were allowed to swell in water to an equilibrium state before any of the additives were introduced to the system. The order of addition was the same as in the papermaking experiments; i.e. first addition of CMC and then addition of cationic starch. Adsorption of CMC onto the CNF film took place, which was seen as a decrease in frequency of the oscillating quartz crystal (Fig 1a). The adsorption took place quite slowly and negligible amounts were deposited over 30 min, due to the fact that both CMC and the cellulose carry anionic charges. The measured dissipation of the adsorbed CMC showed that the layer acted like a hydrated gel, containing 98.8% of coupled water (Fig 6b, Table 5). Adsorbed layers of CMC have previously been reported to contain a high amount of coupled water (Laine et al. 2002). Rinsing of the films for about 20 min with ion-exchanged water after adsorption removed most of the adsorbed CMC, and the softness of the surface layer was lowered considerably. However, according to the QCM-D and SPR measurements, some CMC did remain on the CNF surface after rinsing (Fig 6a, b, c).

The different cationic starches were introduced to the system after the CMC adsorption and rinsing cycle was completed. All of the cationic starches adsorbed quickly onto the CNF film, indicating an adsorption mechanism driven by electrostatic attraction between cationic charges on the starches and anionic charges on the CNF with residual CMC (Fig 6a). The attraction between cationic and anionic groups as a driving force for adsorption has been heavily utilized in a wide array of studies (Decher 1997; Kekkonen et al. 2001; Gårdlund et al. 2005; Renneckar, Zhou 2009; Lundström-Hämälä et al. 2010; Marais et al. 2014). The largest decrease in frequency, or the highest adsorption, was seen for Classic 135, which was the cationic starch with very high molar mass and low charge density. The adsorbed layer of Classic 135 was very soft and gel-like, which was evident from the high

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Table 5 - Viscoelastic properties of the polysaccharide layers adsorbed on films of CNF. SPR data and the Voigt modeling results from QCM-D are shown after rinsing with Milli-Q water. Surface concentration (M_{SPR}), hydrodynamic surface concentration (M_{QCM-D}), layer thickness (h), shear viscosity (η), and elastic shear modulus (μ).

<table>
<thead>
<tr>
<th>Polysaccharide</th>
<th>M_{SPR}</th>
<th>M_{QCM-D}</th>
<th>Coupled water</th>
<th>h_{SPR}</th>
<th>h_{QCM-D}</th>
<th>η × 10^{-3}</th>
<th>μ × 10^{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMC</td>
<td>0.33</td>
<td>26.7 ± 1.3</td>
<td>98.76</td>
<td>0.2</td>
<td>22.2 ± 0.9</td>
<td>0.86 ± 0.02</td>
<td>0.74 ± 0.1</td>
</tr>
<tr>
<td>Classic 135</td>
<td>8.07</td>
<td>46.1 ± 1.7</td>
<td>82.49</td>
<td>4.94</td>
<td>38.4 ± 1.5</td>
<td>1.49 ± 0.1</td>
<td>0.97 ± 0.1</td>
</tr>
<tr>
<td>Raifax 01015</td>
<td>1.03</td>
<td>2.53 ± 0.3</td>
<td>59.29</td>
<td>0.63</td>
<td>2.1 ± 0.2</td>
<td>2.76 ± 0.5</td>
<td>92.7 ± 3</td>
</tr>
<tr>
<td>Raisabond 15</td>
<td>0.75</td>
<td>2.22 ± 0.2</td>
<td>66.22</td>
<td>0.46</td>
<td>1.9 ± 0.1</td>
<td>4.57 ± 0.2</td>
<td>31.0 ± 1.7</td>
</tr>
<tr>
<td>Raifax 25035</td>
<td>0.66</td>
<td>1.37 ± 0.1</td>
<td>51.82</td>
<td>0.40</td>
<td>1.1 ± 0.1</td>
<td>0.35 ± 0.05</td>
<td>152.55 ± 4</td>
</tr>
</tbody>
</table>
dissipation values (Fig 6b), and by the fact that the layer contained 82.5% of coupled water (Table 5). This is in agreement with previous findings that very hydrated multilayers of polyelectrolytes are soft and malleable (Lundström-Hämälä et al. 2010). It has been reported that the softness of the surface layer will have a large effect on the strength of fiber-fiber joints (Torgnyssdotter, Wågberg 2004; Rohm et al. 2013), which is confirmed by the fact that CMC + Classic 135 gave the highest values of tensile index. The adsorption of Classic 135 was rather irreversible, since negligible desorption was detected during the subsequent rinsing procedure. During the rinsing, however, the adsorbed layer of Classic 135 became less rigid due to reordering of the polysaccharide chains.

The three other cationic starches also adsorbed onto the residual CMC on the CNF surface (Fig 6a), but the shifts in frequency were much lower than for Classic 135. This indicated that the adsorbed amount of these starches was much lower. The measured dissipation of the adsorbed cationic starches also showed that they adsorbed as stiffer and more rigid layers due to their high charge densities and low-medium \( M_w \) (Fig 6b). This was in agreement with previous findings; polymers with a high substitution of cationic groups tend to conform to the anionic fiber surface as dense and flat layers, while polymers with a low content of cationic groups tend to adsorb as softer layers (Rojas, Neuman 1999; Hubbe 2006; Kontturi et al. 2008; Hubbe et al. 2009).

The adsorption of Raifix 01015 SW, Raifix 25035 and Raisabond 15 was rather irreversible, since negligible desorption was detected during the subsequent rinsing procedure. The adsorbed layer of these cationic starches became more rigid during the rinsing, which indicated that the polysaccharide chains were able to conform to the CNF-CMC surface in a very dense fashion.

The results from the papermaking trials, previously presented, can now be re-examined with new insights in combination with the results from the adsorption studies with CNF model surfaces. The CMC used in this study, with high \( M_w \) and high charge density, moderately absorbs onto cellulosic fibers in a pulp suspension to some extent, given enough time. The cationic charges on the added starch targets the anionic charges of CMC and fibers, resulting in adsorption of starch on fibers where it may retain additional CMC from the water phase. The cationic starch that resulted in the largest increase in tensile index and tensile stiffness was the same cationic starch that had the highest retention to CNF films, and formed the softest and thickest surface layer in the adsorption studies. High molar mass of the polysaccharide chains, coupled with a low charge density seems to be the optimal properties for retention of highly anionic CMC to fibers.

Unrestrained drying of sheets - Impact of cationic starches and CMC

Some laboratory sheets were dried between two polyamide fabrics, allowing for shrinkage during the drying process. The unrestrained drying technique altered the properties of the papers quite significantly, compared to the ones dried under restraint between blotters. The 1D shrinkage of the reference sheets during unrestrained drying were 5.3% which increased the stretch significantly; from 4.9% (Table 4) to 9.6% (Table 6). However, unrestrained drying lowered the tensile index from 68.4 to 52.9 kN/m/kg, as well as the tensile stiffness from 5.4 to 2.1 MNm/kg of the reference sheets. It has previously been reported that drying under limited restrain lowers the stiffness of paper and increases the elongation potential (McKenzie, Higgins 1955). Experiments were performed to investigate if the decrease in strength and stiffness due to unrestrained drying could be mitigated to some extent by addition of cationic starches and CMC, while maintaining the shrinkage and the high elongation at break. The approach is quite logical, since addition of dry-strength additives in paper are used to compensate for the debonding effect of e.g. mineral fillers (Hubbe 2006).

Addition of 1% CMC to the pulp suspension resulted in slight increases in tensile index and stiffness of the papers, while the shrinkage and stretch were kept on par with the values for the reference sheets (Table 6). Addition of cationic starches and CMC at a ratio of 4:1 was chosen based on the previously reported results in this study. The combinations of cationic starches with CMC gave mixed results. Classic 135 in combination with CMC once again gave the highest values of tensile index and tensile stiffness; 78.7 kN/m/kg and 3.2 MNm/kg, respectively, while the stretch of the papers were similar to the reference sheets after unrestrained drying and the shrinkage was only slightly decreased. This combination of additives could thus possibly be useful to mitigate some of the decrease in tensile index and stiffness due to the unrestrained drying. Combination of the three other cationic starches with CMC also increased the tensile index and the tensile stiffness of the sheets (Table 6). However, these combinations also seemed to cause a slight decrease in paper shrinkage and also a noticeable decrease in stretch. When comparing these values (Table 6) with the reference sheets after restrained drying (Table 4), is clear that addition of CMC and cationic starches can completely compensate for the decrease in tensile index from unrestrained drying, while maintaining the high stretch potential. These additives could also mitigate some of the decrease in tensile stiffness from unrestrained drying, however, not completely.

It is evident that merely increasing the strength of the fiber-fiber bonds does not necessarily increase the stretch potential of sheets after unrestrained drying, unlike sheets after restrained drying (Seth 2005). The ability of similar surfaces to adhere to each other by a diffusion-like mechanism is possessed by all amorphous high polymers in the plastic state (McKenzie 1984). Self-adhesion is favored by the presence of solvents or plasticizers, and adversely affected by strongly interacting polar groups between chains and by crosslinking of chains. If water acts as a plasticizer for the macromolecular segments on fiber surfaces, it seems logical that the presence of water would lubricate the fiber network during unrestrained drying. It was shown that adsorbed layers of CMC and Classic 135 form soft layers that contain a very high amount of coupled water (Table 5), and that these two additives do not adversely affect the shrinkage of paper during unrestrained drying (Table 6). It is therefore suggested that a soft layer, containing a large amount of coupled water, may act as a plasticizer during unrestrained drying. This mechanism
Table 6 - Measured mechanical properties of laboratory sheets after unrestrained drying. The average values, as well as their confidence interval (cl 95%) or standard deviation (s), are reported.

<table>
<thead>
<tr>
<th>Shrinkage</th>
<th>Density</th>
<th>Tensile index</th>
<th>Tensile stiffness</th>
<th>Stretch</th>
<th>Air permeability</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>kg/m³</td>
<td>kN/m²</td>
<td>kg/m² cl 95%</td>
<td>MN/m² cl 95%</td>
<td>% cl 95% mL/min</td>
</tr>
<tr>
<td>Kraft pulp</td>
<td>5.3</td>
<td>379</td>
<td>52.9 0.6</td>
<td>2.1 0.1</td>
<td>9.6 0.2</td>
</tr>
<tr>
<td>1% CMC</td>
<td>5.3</td>
<td>418</td>
<td>61.9 0.9</td>
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<td>9.8 0.2</td>
</tr>
<tr>
<td>1% CMC + 4% Classic 135</td>
<td>5.1</td>
<td>463</td>
<td>78.7 1.0</td>
<td>3.2 0.1</td>
<td>9.7 0.1</td>
</tr>
<tr>
<td>1% CMC + 4% Raifix 01015 SW</td>
<td>4.6</td>
<td>421</td>
<td>67.5 1.8</td>
<td>2.8 0.1</td>
<td>8.9 0.2</td>
</tr>
<tr>
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<td>4.6</td>
<td>444</td>
<td>73.6 1.3</td>
<td>3.0 0.1</td>
<td>9.2 0.1</td>
</tr>
<tr>
<td>1% CMC + 4% Raifix 25035</td>
<td>4.7</td>
<td>432</td>
<td>72.3 1.7</td>
<td>3.0 0.1</td>
<td>8.9 0.2</td>
</tr>
</tbody>
</table>

has been suggested earlier (Pelton 2004). During drying, the fiber web loses water continuously until it reaches a dry content where the hydrogel surfaces of the fibers begin to adhere to each other, and bonds start to develop vigorously (Fornue et al. 2011). It has been reported that cationic starches start to increase the tensile strength of paper at around 75% solids content, while CMC starts to increase the paper strength at 50% dry content (Myllytyie et al. 2009). The strength increases at different dry content during unrestrained drying is perhaps not the most vital aspect, but instead the fact that the properties of the cationic starch, and its ability to bind water, will cause different end results.

Conclusions

The effect of wet-end additions of cationic starches and/or carboxymethyl cellulose (CMC) on the tensile index, tensile stiffness, stretch, and paper shrinkage during unrestrained drying, was determined by papermaking trials. Addition of the different cationic starches increased the tensile index of paper and resulted in more dense fiber networks, but had very limited effects on the tensile stiffness of the paper. Addition of CMC increased the tensile index and tensile stiffness of paper noticeably, and also resulted in more dense fiber networks. The largest increase in tensile index and tensile stiffness was seen when combining a cationic starch with high molar mass and low charge density with CMC. It was seen that not even large increases in fiber-fiber bond strength can overcome, or significantly increase, the stretch potential of the fiber network after restrained drying.

Combinations of CMC with the tested cationic starches also increased the tensile index and stiffness of papers after unrestrained drying. With certain combinations of CMC and cationic starch, the high elongation at break after unrestrained drying was preserved, while the tensile index and stiffness of the paper were significantly increased. It was shown that addition of CMC and cationic starches can completely compensate for the decrease in tensile index from unrestrained drying, while maintaining the high stretch potential. These additives could also mitigate some of the decrease in tensile stiffness from unrestrained drying.

To complement the results from the papermaking trials, adsorption of CMC and cationic starches onto cellulose nanofibril (CNF) surfaces was studied by QCM-D and SPR techniques. CMC adsorbed slowly on the cellulose surface as a very soft layer, containing a large amount of coupled water. Desorption of CMC was seen during the subsequent rinsing procedure, which indicated that the CMC adsorption was mostly reversible. The cationic starches adsorbed very quickly onto the CNF/CMC surface, due to attraction of cationic and anionic charges. The adsorbed amount of cationic starch varied as a function of molar mass and charge density. The cationic starches with high charge densities adsorbed as rigid and thin layers with a low content of coupled water. The cationic starch with very high molar mass and low charge density formed the thickest and softest adsorbed layer, which contained a high amount of coupled water. A polysaccharide chain with very high molar mass and low charge density seems to be optimal for retention of highly anionic CMC to fibers.

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