

Petri Myllytie, Jihui Yin, Susanna Holappa, and Janne Laine. 2009. The effect of different polysaccharides on the development of paper strength during drying. *Nordic Pulp and Paper Research Journal*, volume 24, number 4, pages 469-477.

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The effect of different polysaccharides on the development of paper strength during drying

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KEYWORDS: Paper strength, Fiber bonding, Wet web strength, Dry strength, Polymers

SUMMARY: The effect of different polysaccharides like cationic starch, guar gum, xyloglucan, chitosan, and carboxymethyl cellulose on the development of sheet tensile properties (tensile strength, breaking strain, tensile energy adsorption) and drying tension was studied with a method that resembled reasonably well the real drying process. The simplified model system, which was designed to emphasize the interactions between fiber and polymers, helped to distinguish the observed effect of polymers on the rheological behavior of paper. Each polymer and adsorption condition showed very characteristic development of tensile properties as a function of dry solids. The specific interactions between the polysaccharides and cellulose fibrils on fiber surfaces influenced adsorption, as well as the development of bonding and tensile properties during drying. Significant improvements in the development of tensile properties were attained with most of the tested polymers. Superior wet web strength and tensile properties through the drying range was achieved with carboxymethyl cellulose-chitosan bilayer adsorption technique. The development of drying tension was different to the development of tensile properties, suggesting that the mechanisms how polymers influence these properties are different.

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The strength properties of paper are extremely important for manufacturers and end-users, as well as in recycling. To achieve the desired strength properties of a paper product, dry and wet strength additives are commonly applied in papermaking. Paper strength and the effect of different additives on it have been recently comprehensively reviewed (Hubbe 2006; Lindström et al. 2005). Also, the different mechanisms of action of dry and wet strength additives have been discussed in many publications (Espy 1995; Wågberg and Björklund 1993; Yamauchi and Hatanaka 2002). As most strength additives are polymers; synthetic, natural, or chemically modified natural polymers, some studies have focused on resolving the most important polymer properties regarding paper strength (Pelton et al. 2000; Pelton 2004; Zhang et al. 2001).

Regardless of innumerable studies on the effects of strength additives on paper properties with a variety of pulps (chemical/mechanical), conditions (pH, salinity), additives (fillers, sizes), and processes (beating, drying), the underlying mechanisms of paper strength development and the function of strength additives are still

somewhat unclear. When real paper stocks have been studied, the effect of a certain polymer is easily masked by the overall change in the system resulting from interdependence of adsorption, retention, formation, etc. Thus, it has been difficult to draw straightforward conclusions from such results. Systematic studies of well defined model systems, where the number of variables has been reduced, have helped to explore the elementary properties and interactions. Controlled adsorption of additives (Wågberg et al. 2002), fiber pretreatment (Laine et al. 2000; Swerin et al. 1990), absence of fillers and fines (Enarsson and Wågberg 2007; Hubbe et al. 2007), constant sheetmaking conditions (Hubbe et al. 2007; Laine et al. 2002), and controlled drying conditions (Blomstedt et al. 2007; Pettersson et al. 2007) applied in recent research have all, by their account, contributed to the increased fundamental understanding of paper as a material.

The majority of research has focused on the final strength properties attained with certain polymers at selected conditions. Still, very little information is available on the effects of different polymers on the development of paper strength during drying. Laleg and Pikulik showed that chitosan increases wet web strength throughout the measured solids range (Laleg and Pikulik 1991; Laleg and Pikulik 1992). Work by Mesic (2002) indicated that the strength development depends on the polymer used. Therefore, it could also be possible to develop optimized drying strategies when different additives are applied in paper production. As a part of our previous publication (Myllytie et al. 2009), the development of tensile strength with different polymers as a function of sheet dry matter content was demonstrated. The applied method proved to be an efficient and illustrative way to study the change of sheet properties as a function of drying. As shown by Mesic (2002), we also concluded that the strength development is very specific for different polymers and adsorption conditions, though the ultimate strength can be the same for many polymer treatments (Myllytie et al. 2009).

When strength additives are used, we have proposed that fiber bonding, wet web properties, strength development, and final properties are essentially affected by the molecular level interactions between cellulose and additives. We presumed that addition of polymers into fiber suspension creates a gel-like fiber bonding domain that consists of fiber surface fibrils and adsorbed polymers. The aggregation tendency and interaction with water of the fiber surface fibrils were found to be influenced differently by dispersing (carboxymethyl cellulose) or aggregating (cationic polyacrylamide) polymers. The properties of this bonding domain depended on the mole-

cular level interactions between cellulose fibrils, polymers, and water. The molecular level interactions reflected on bonding and strength development through the drying range (Myllytie et al. 2009).

The aim of this work was to further examine the interactions of certain polysaccharides with the fibrillar structure of fiber surfaces and their effect on the rheological behavior of a drying paper web. The studied polymers were known to have specific interactions with cellulose, i.e. guar gum, xyloglucan, carboxymethyl cellulose, and chitosan. A common dry-strength additive, cationic starch, was included for comparison. In this paper, development of strength properties of paper during drying for different polymers and adsorption conditions are reported. The mechanism of strength development and function of strength additives are discussed in relation to fiber bonding, wet web strength, and dry strength on the basis of the results.

Materials and Methods

Cellulose fibers

Bleached kraft pulp (pine) obtained from Botnia (Äänekoski, Finland) was used in the experiments. The preprocessing of the fiber material was done in such way that the interaction between fiber surface fibrillation and adsorbed polymers would have as clear effect on bonding and strength development as possible. In order to produce intact fibers with even surface fibrillation, a grinding method was chosen for pulp pretreatment. Adapted from procedure by Kang and Paulapuro (2006), the pulp was first soaked in deionized water for 4 hours and disintegrated with cold disintegrator into a suspension with consistency of 2.75%. The pulp suspension was then grinded with a Masuko Supermasscolloider. The clearance between the grinding plates was set to 230 μm and the pulp suspension was passed 12 times through the machine. The consistency of the pulp suspension was the same as in disintegration at first but it decreased slightly during grinding because the machine was rinsed after each pass of the pulp suspension. The grinding produced fines into the pulp suspension mainly from primary wall and S1 cell wall layers.

The fines were removed by flushing the pulp suspension in a stirred tank with 200 mesh wire bottom and constant flow-through of fresh tap water. Flushing time was 45 minutes. The progress of washing was followed by checking the fines content in the outlet water of the tank. After the fines had been washed out, optical microscopy images showed that the fibers were quite intact and no large macrofibrils or ruptured parts of fiber wall were peeled off. Also, the $^{\circ}\text{SR}$ value of the 12 times passed fines-free pulp was approximately the same as $^{\circ}\text{SR}$ of disintegrated (ungrinded) pulp (both around 12°SR). After the removal of the fines the fibers were washed into sodium form according to the procedure by Swerin and Wågberg (1994). At the end, the conductivity of the suspended pulp was below 5 $\mu\text{S}/\text{cm}$. The washed pulp was stored in a refrigerator.

Water-soluble polymers

Wet end grade cationic starch (CS), Raisamyl 50021, with a degree of substitution (D.S.) of 0.035 was received from Ciba Specialty Chemicals (Basel, Switzerland). Carboxymethyl cellulose (CMC), Finnfix WRM, with D.S. of 0.56 was provided by CP Kelco (Äänekoski, Finland). Medium molecular weight chitosan (relative molecular mass of 400000, Prod. no. 22742) was acquired from Fluka BioChemika (Buchs, Switzerland). Guar gum (G4129) was purchased from Sigma-Aldrich Finland (Helsinki, Finland) and tamarind seed xyloglucan from Megazyme (Wicklow, Ireland). All the polymers were used as received.

Chitosan was dissolved in 1% acetic acid solution for 2 hours. Xyloglucan was dissolved in deionized water for 2 hours. Guar gum and starch were dissolved by heating the solution to 95°C and kept at this temperature for 30 min. CMC was dissolved in deionized water at elevated temperature. Centrifugation was used to remove impurities or insoluble particles from chitosan and guar gum solutions. For adsorption experiments, the concentrations of the polymer solutions were adjusted to 5 g/l. Freshly prepared solutions were used in the adsorption experiments.

Polymer adsorption

The polymer adsorption and sheetmaking were carried out consecutively in order to control and determine the polymer adsorption. First the polymers were adsorbed onto the fibers at chosen conditions. Then the fiber suspensions were filtrated and unadsorbed polymers were rinsed off with a small amount (2 l) of 0.5 mM NaHCO_3 solution. Finally the polymer treated fibers were redispersed for sheetmaking. Polymer adsorption (except CMC, see later) and sheetmaking were done at constant ionic strength, 0.5 mM NaHCO_3 . Due to the slow adsorption of the neutral polymers (guar gum and xyloglucan) compared to cationic polymers, the chosen adsorption conditions were a compromise between adsorption time and adsorbed amount. The selected adsorption conditions are collected into Table 1. Fiber consistency (10 g/l), concentration of polymer solutions (5 g/l), and salinity (0.5 mM NaHCO_3) were constant in all adsorption experiments, except for CMC.

During the adsorption and sheetmaking of reference, CS, guar gum, and xyloglucan samples, the pH was not adjusted but it was around 7.5-7.8. Chitosan adsorbed at pH 5 was done by adding acidic chitosan solution into

Table 1. Polymer adsorption conditions.

Sample	Polymer addition [mg/g dry fiber]	Adsorption time [min]	Adsorption pH
Guar gum	20	90	not adjusted
Xyloglucan	20	90	not adjusted
Chitosan 5-10 *	10	30	5
Chitosan 10-10 *	10	30	10
Chitosan 10-20 *	20	30	10
Cationic starch	15	30	not adjusted
CMC	20	120	8
CMC-chitosan bilayer	20+20	120+30	8 and 10

* markings stand for adsorption pH and added amount of polymer, respectively

the pulp and keeping the pH at 5 for 30 min. Chitosan adsorption at pH 10 was carried out by adding acidic chitosan solution into the pulp and mixing for 15 min, then elevating the pH to 10 and mixing for the remaining 15 min. At pH above 6.5 chitosan became insoluble and at pH 10 it was efficiently precipitated onto the fibers. We consider the chitosan adsorption at pH 10 rather as precipitation of colloidal polymer particles onto the fiber surfaces than adsorption in a strict sense. The anionic polymer, CMC, was adsorbed onto the pulp according to method by Laine et al. (2000), with the exception that the fiber consistency was 10 g/l. The sequential adsorption of CMC and chitosan, herein referred as CMC-chitosan bilayer adsorption, was performed by first carrying out the CMC adsorption as above. Then, chitosan was precipitated onto the CMC treated fibers by adding chitosan solution (pH 6.5) into the fiber suspension of which the pH was kept above 10 (10-10.5) during the polymer addition and the adsorption time, in order to avoid excessive flocculation. Then the fibers were filtrated, rinsed, and redispersed for sheetmaking.

The adsorbed amounts of polymers were determined in a separate test series. These adsorption experiments were carried out with 2 g of dry pulp in deionized water at fiber consistency of 10 g/l. After adsorption time, the samples were filtrated through filter paper and the polymer content in the filtrate was determined by sulfuric acid-phenol test or polyelectrolyte titration. The adsorbed amount of CS, xyloglucan, and guar gum was determined with sulfuric acid-phenol test (DuBois et al. 1956). Chitosan adsorption was determined with polyelectrolyte titration (Terayama 1952). The adsorbed amount of CMC was determined by conductometric titration (Katz et al. 1984).

Sheet preparation

Wet handsheets (60 g/m²) were prepared in a laboratory sheet mould according to standard SCAN-C 26:76. Deionized water was used in the mould and NaHCO₃ was added to maintain constant salinity of 0.5 mM. The couching roll was replaced by a 3.355 kg weight plate to attain even moisture distribution in wet sheets. The couching time with the plate was 20 seconds. Handsheets were then wet-pressed according to SCAN-C 26-76, except the number of blotter paper sheets was reduced in order to decrease the initial solids for the measurement of strength development.

Measurement of strength development and drying tension

The development of paper strength during drying was measured with a MTS 400m tensile tester (MTS Systems, USA) combined with 2 kW infra-red (IR) drying module equipped with stepless power control unit (Hedson Technologies, Sweden) and a moisture sensor (MM55E, NDC Infrared Engineering, USA). 50 mm wide strips were cut from wet pressed sheets with moisture content ~40%. Before clamping the samples to the tensile tester, the sample ends were dried, leaving a 70 mm wet section as effective wet testing length. After the

specimen was clamped, all the tests were done as follows. The wet sample was dried from front side with the IR for a chosen time (around 5-120 s). The reading in the moisture sensor was allowed to even out for a moment and tensile test was performed. Tensile test was done according to ISO-1924-2, except that specimen dimensions were 50 mm x 70 mm and crosshead speed was 20 mm/min. Optimum sampling area of the moisture sensor was a spot with diameter of 25 mm, which was obtained at a distance of ~20 cm from the sample. For backscatter mode measurement the sensor was inclined at 20° to the sample surface. The range and accuracy of the sensor in moisture determinations were given as 0-90% and ±0.1%, respectively. The moisture sensor was calibrated with the fiber material (16 points at dry solids between 45% and 95%) and its response was linear ($R^2 = 0.996$) in the calibration range.

The development of drying tension was measured with the same equipment and sample preparation. After clamping the sample to the tensile tester, drying was begun and the tension was recorded as a function of moisture content. Three parallel samples were measured for each material.

Results

In this work the main methods applied were adsorption experiments and the measurements of development of strength properties and drying tension upon drying. The results are presented below. The adsorbed amounts of polymers (at the conditions shown in *Table 1*) are collected into *Table 2*.

The tensile testing setup enabled collection of large amount of stress-strain data. For each sample (*Table 1*), approximately 30 stress-strain curves were recorded at different dry solids between ~40% to ~100%. In addition, the drying tensions at certain dry solids values were determined from around 30 test points per sample. As an example, *Fig 1* shows the stress-strain curves for some of the samples (reference, CS, and CMC-chitosan bilayer samples) at two different dry solids; 70% and 90%. The curves in *Fig 1* were selected just to illustrate how the polymers influence the general viscoelastic behavior of paper and how the following results on the development of tensile properties are manifestation of this behavior.

Development of tensile strength during drying

Figs 2-4 show the strength development of wet pressed sheets as a function of dry matter content through the drying range (~40-100% dryness). The figure insets are magnifications of the curves at high moisture content (45-65% solids), that help to illustrate the polymer effects on wet web strength. The presentation of the results is divided into three groups of polymer adsorptions to clarify the differences and to ease the comparison between the polymers. Results of the first group of polymers; guar gum, xyloglucan, and cationic starch are shown in *Fig 2*. Second group, in *Fig 3*, shows the strength development of chitosan treated sheets at different adsorption conditions. Strength development for the third group, CMC

Table 2. Adsorbed amounts of polymers.

Sample	Polymer addition [mg/g dry fiber]	Adsorption [mg/g dry fiber]	Adsorption efficiency [%]
Guar gum	20	2.3 ^a	12
Xyloglucan	20	9 ^a	45
Chitosan 5-10 *	10	3.8 ^b	38
Chitosan 10-10 *	10	9.4 ^b	94
Chitosan 10-20 *	20	18.8 ^b	94
Cationic starch	15	9.6 ^a	64
CMC	20	15.4 ^c	77
CMC-chitosan bilayer	20+20	15.4 ^c +20 ^b	77 / 100

*) markings stand for adsorption pH and added amount of polymer, respectively

a) acid-phenol test

b) polyelectrolyte titration at pH 5

c) conductometric titration

and CMC-chitosan bilayer samples (20 mg/g chitosan at pH 10 sample is included for comparison), is presented in Fig 4.

The development of sheet tensile strength with different polymers (Figs 2-4) evidently indicated that the polymers had specific effect on strength development and that the polymer properties and adsorption conditions were crucial for the strength effect through the dry solids range. In more detail, Fig 2 shows that in comparison to the reference sheet CS began to increase the sheet strength at solids around 75% and guar gum and xyloglucan increased the strength above 65% solids. At low solids (<65%) CS clearly decreased the sheet strength compared to reference, also with guar gum and xyloglucan the sheet strength below 60% solids was slightly lower compared to reference.

The influence of adsorption conditions on the effect of chitosan as strength additive was obvious (Fig 3). Chitosan adsorbed at pH 5 did not affect the sheet strength at all. When chitosan was adsorbed at pH 10, the wet web strength was above reference at all solids studied and the strength increased with increasing polymer addition. At higher solids, chitosan, adsorbed at pH 10, began to improve the tensile strength at around 65% solids in contrast to reference. Interestingly, the chitosan samples showed a common feature that in nearly dry samples (>90% solids) the increase in strength seemed to level off or decrease slightly.

The effect of CMC adsorption and CMC-chitosan bilayer adsorption on strength development can be seen in Fig 4. CMC began to affect the strength development above ~50% solids. At low solids (<50%) the strength of CMC treated sheets was close to the reference, or even slightly lower. The most prominent effect on strength development was achieved with the CMC-chitosan bilayer adsorption that induced superior wet web strength and strength development through the drying range. The strong increase of strength began already at solids around 50%. Furthermore, the CMC-chitosan bilayer sample also demonstrated similar leveling off or slight decrease in the strength as chitosan samples at solids above 90% (Fig 3).

Change of breaking strain during drying

Fig 5 shows the change of breaking strain as a function of

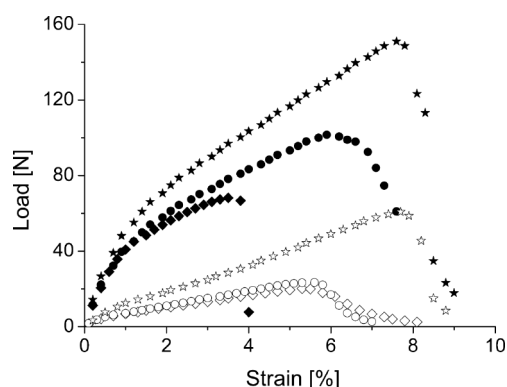


Fig 1. Stress-strain curves of reference (◆), CS (●), and CMC-chitosan bilayer (★) at 70% solids (open symbols) and at 90% solids (filled symbols).

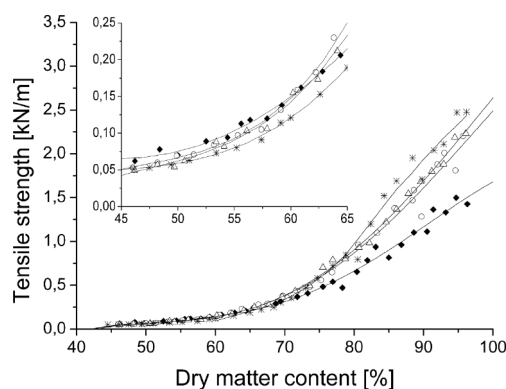


Fig 2. Tensile strength development during drying of reference (◆) sheets and CS (*), guar (○), and xyloglucan (Δ) treated sheets.

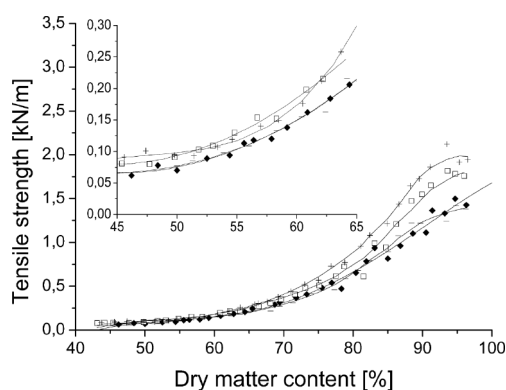


Fig 3. Tensile strength development of chitosan samples at different adsorption conditions: 10 mg at pH 5 (○), 10 mg at pH 10 (□), and 20 mg at pH 10 (△). Reference (◆).

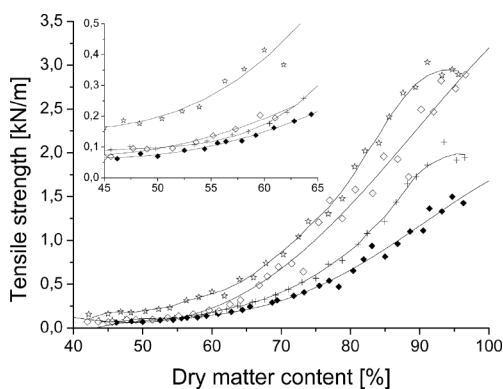


Fig 4. Tensile strength development of CMC (◇) and CMC-chitosan bilayer (★). Chitosan sample 20 mg at pH 10 (+) is included for comparison. Reference (◆).

dry matter content for guar gum, xyloglucan, and cationic starch treated sheets. The same for chitosan samples, adsorbed at different conditions, is shown in Fig 6. The change of breaking strain for CMC and CMC-chitosan bilayer samples is shown in Fig 7 (20 mg/g chitosan at pH 10 sample is included).

Compared to tensile strength data the breaking strain values generally showed more scattering but the effects of polymers on the breaking strain were still appreciable. The breaking strain of reference sample decreased with increasing solids, from ~5.5% to ~2.5%. The decrease was most prominent at solids above 70%. At solids below 70% guar gum, xyloglucan, or CS did not affect breaking strain, but at solids above 70% they improved breaking strain compared to reference (Fig 5). CS increased the breaking strain above the values of the wet sheet, up to 6-7% at solids ~90%. Interestingly, chitosan had minor influence on breaking strain at any adsorption conditions (Fig 6). Only when adsorbed at high pH, chitosan slightly increased breaking strain at solids above 85%. At very low solids (<50%) chitosan seemed to decrease the breaking strain slightly. The most significant effect on breaking strain was achieved with CMC and CMC-chitosan bilayer adsorptions (Fig 7). CMC adsorption first decreased breaking strain at low solids but at solids above 65% it increased breaking strain considerably compared to reference. CMC-chitosan bilayer sample displayed highest breaking strain values of all the samples (above 6%) through the solids range.

Development of other tensile properties during drying

Development of tensile energy absorption (TEA) and modulus (or tensile stiffness) during drying were also acquired from the collected stress-strain data (curves not presented for conciseness). Since polymers influenced tensile strength (Figs 2-4) and breaking strain (Figs 5-7) especially at high solids, TEA showed differences between polymers only at solids around 70% and above. The development of TEA, at high solids, was similar to tensile strength but more pronounced between polymers. The dry solids values where polymers began to increase breaking strain (Figs 5-7) correlated with the points where the TEA began to increase. For CMC and CS, for example, these points of dry solids were 65% and 70%, respectively. The effects of the polymers were more pronounced at high solids because the polymers enhanced both the tensile strength and breaking strain. For instance, at solids around 90%, the CMC-chitosan bilayer adsorption increased the TEA value 7-fold (140 J/m^2) compared to reference (20 J/m^2), while at the same solids the tensile strength and the breaking strain were approximately doubled compared to reference. This was obvious because at higher strength levels (solids) increase in breaking strain strongly affects the area under the stress-strain curve (i.e. TEA).

The development of sheet modulus (or tensile stiffness) during drying did not show appreciable differences between polymers at solids below ~75%. Above that, the development of modulus was similar to tensile strength (mainly) but the differences between polymers were

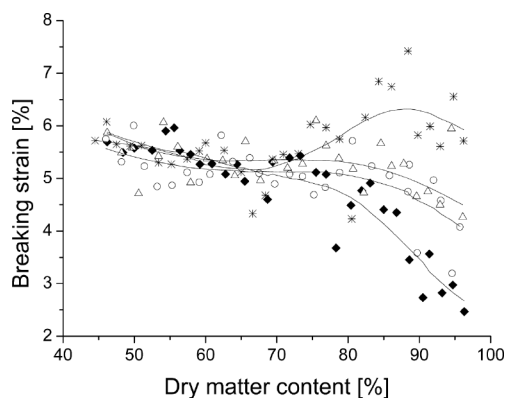


Fig 5. Change of breaking strain during drying of reference (◆) sheets and CS (*), guar (○), and xyloglucan (△) treated sheets.

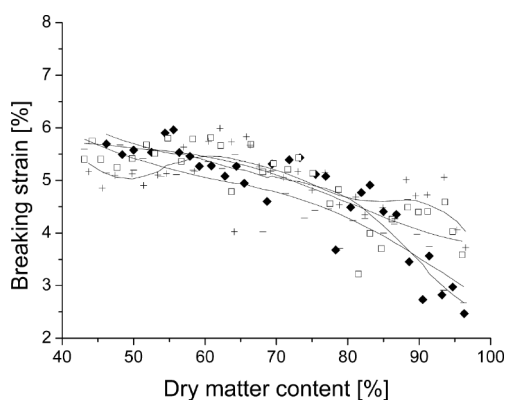


Fig 6. Change of breaking strain of chitosan samples at different adsorption conditions: 10 mg at pH 5 (-), 10 mg at pH 10 (□) and 20 mg at pH 10 (+). Reference (◆).

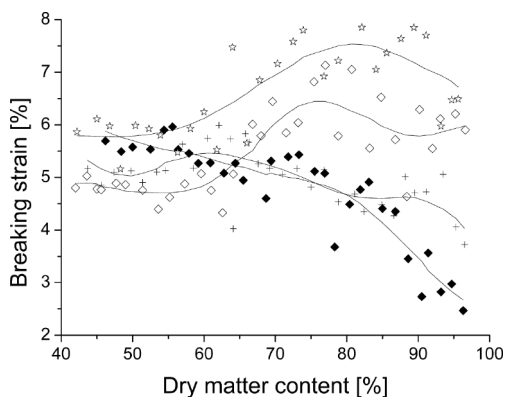


Fig 7. Change of breaking strain of CMC (◇) and CMC-chitosan bilayer (☆). Chitosan sample 20 mg at pH 10 (+) is included for comparison. Reference (◆).

smaller. Guar gum, xyloglucan, CMC, and CMC-chitosan bilayer adsorption increased modulus at high solids. However, CMC adsorption improved modulus the most, in contrast to tensile strength and breaking strain where the CMC-chitosan bilayer adsorption was more efficient. Also, CS did not influence modulus appreciably regardless of considerable improvement in strength.

Development of drying tension during drying

Drying tension was measured with the same equipment and sample preparation as the strength development. It was measured as the tension developed upon drying under longitudinal restraints, i.e. the tension was not allowed to relax by opening the clamps between the points of measurement. At low solids (<60%) the initial drying

tension was very low and the differences between polymers were insignificant. *Figs 8-10* show the development of drying tension as a function of dry matter content in a range of 65-95%. *Fig 8* shows the drying tension for guar gum, xyloglucan, and cationic starch treated sheets. Drying tension of chitosan samples at different adsorption conditions is shown in *Fig 9*. Drying tension for CMC and CMC-chitosan bilayer samples (20 mg/g chitosan at pH 10 sample is included) is shown in *Fig 10*.

In general, the development of drying tension showed different behavior and less marked changes between polymers compared to the development of sheet tensile properties. *Fig 8* shows that xyloglucan slightly increased the drying tension at high solids. The influence of CS or guar gum on the development of drying tension was more uncertain due to scattered results. Interestingly, chitosan, irrespective of adsorption conditions, showed very little influence on the development of drying tension at all (*Fig 9*). The inability of chitosan to affect the development of drying tension was also evident in the case of CMC-chitosan bilayer sample (*Fig 10*). CMC adsorption increased the drying tension the most but subsequent chitosan deposition did not affect the drying tension at all, as it did not either affect drying tension when chitosan was deposited onto reference fibers.

Discussion

Polymer adsorption

For neutral guar gum the adsorption efficiency has been found to be around 20-50% after 2 h adsorption time depending on the beating level (Hannuksela et al. 2002), which is notably higher compared to our result. In our case (*Table 2*) the lower value of 12% may arise from low beating degree and absence of fines. Also, the chosen adsorption time (90 min) was short for a neutral high molecular weight polysaccharide. Native guar gum has a main chain structure similar to that of cellulose (linear β -(1-4)-linked D-mannose) but with dense short chain branching (Lindström et al. 2005). It has been suggested that the similar chain conformation induces the adsorption (Hannuksela et al. 2002; Lindström et al. 2005).

The adsorption efficiency of xyloglucan (45%) was quite close to what was observed by Christiernin et al. (2003) on washed unbeaten fines-free kraft fibers. Clearly lower adsorption efficiencies for xyloglucan (15-30%) were reported in a study where commercial pulp samples were used (Zhou et al. 2006). Apparently, the fiber preprocessing (grinding and washing) facilitates the adsorption of xyloglucan. It has been proposed that xyloglucan adsorbs the better the purer the cellulose fibers are (Zhou et al. 2006). The grinding and washing of fines reveal the S2 wall with clean fibril surfaces, thus making the fibers more susceptible for xyloglucan adsorption.

The adsorption efficiency of CMC was higher compared to CMC adsorption studies by Laine et al. (2000), in which the adsorption efficiency was about 40% with similar polymer and at comparable adsorption conditions. Probably, in our case the fiber preprocessing improved the adsorption of CMC, as suggested for xyloglucan.

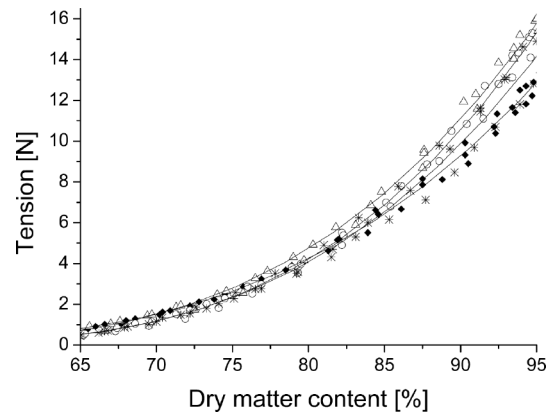


Fig 8. Development of drying tension of reference (◆) sheets and CS (*), guar (○), and xyloglucan (Δ) treated sheets.

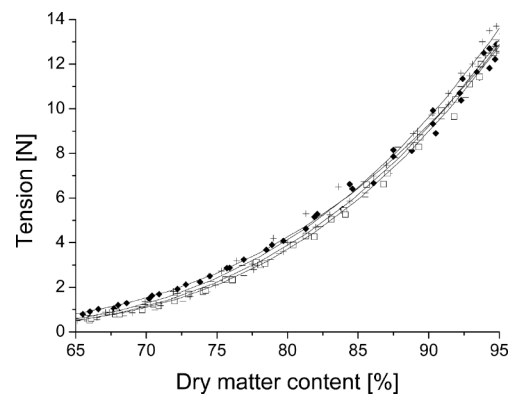


Fig 9. Development of drying tension of chitosan samples at different adsorption conditions: 10 mg at pH 5 (-), 10 mg at pH 10 (□) and 20 mg at pH 10 (+). Reference (◆).

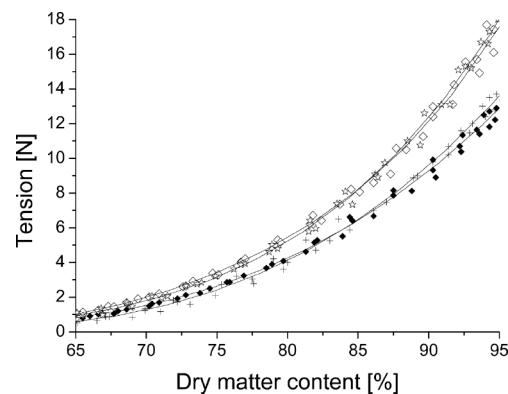


Fig 10. Development of drying tension of CMC (◇) and CMC-chitosan bilayer (☆). Chitosan sample 20 mg at pH 10 (+) is included for comparison. Reference (◆).

Even surface fibrillation on S2 fiber wall should increase the molecular level interactions of CMC with cellulose fibrils, and thus increase the adsorbed amount of CMC.

At pH 10, where chitosan was insoluble and was precipitated as colloidal polymer particles onto fibers, the adsorption efficiency was high (>90%). The high affinity of chitosan towards cellulose may arise from different factors, i.e. residual cationic charges, poor solubility, and structural similarity of cellulose and chitosan molecules. Also, chemical reaction and covalent bonding between cellulose and chitosan has been proposed to occur (Laleg and Pikulik 1992), which could partly influence the adsorption.

Development of tensile strength during drying

When comparing the effects of polymers on the basis of the adsorbed amounts (*Table 1*), guar gum showed high potential to improve tensile strength. The strength development with adsorbed amount of 2.3 mg/g of guar gum was similar to xyloglucan with 9 mg/g adsorbed amount and only somewhat lower compared to cationic starch with 9.6 mg/g of adsorbed amount of polymer (*Fig 2*).

Our results (*Fig 2*) showed that adsorption of CS decreased tensile strength at low solids and began to increase strength only just above solids 72%. The impairment of wet web strength and stretch of bleached kraft sheets by addition of CS has been reported earlier (Laleg and Pikulik 1993; Myllytie et al. 2009). When a cationic polymer is adsorbed and mixed with anionic cellulose fibers or fibrils, charge neutralization (or even reversal) and deswelling takes place in the system (Ahola et al. 2008; Swerin et al. 1990). This reduces the bound water within the fibril layers on fiber surfaces and decreases the chance for molecular level mixing in the fiber bonding domain at wet state, thus decreasing the wet web strength. On the other hand, because adsorption of CS has been proposed to occur as clusters (Shirazi et al. 2003), the structure of the adsorbed layer may become diffuse and the cohesion (strength) of the fiber bonding domain in wet conditions could be weaker.

Excellent dry strength properties can be attained by CMC adsorption onto cellulose (Blomstedt et al. 2007; Laine et al. 2002). It is known that CMC binds water onto fiber surfaces (Laine et al. 2002) and reduces flocculation (better formation) (Yan et al. 2006). In a previous study we showed that CMC disperses fiber surface fibrils and by that way improves fiber bonding and development of sheet strength (Myllytie et al. 2009). The capability of CMC to disperse cellulose fibrils, and thus to promote the fiber surface fibrillation along with the increase of hydration on fiber surfaces, highly advances fiber bonding. Fibril dispersion and hydration increases the mobility of molecules and molecular level mixing in the bonding domain and improves bonding, as suggested in the theory of diffusion adhesion (Voyutskii 1963).

Furthermore, it has been shown that the sodium form of carboxyl group binds more water than the hydrogen form (Berthold et al. 1994), thus the plasticizing effect of Na-CMC may influence the strength properties considerably. Increased plasticization in the fiber bonding domain could enable molecular level orientation as drying tension begins to exert strain to the sheet. For thermo-plastic polymers molecular orientation by straining, when the material is in plasticized state, increases strength and modulus to the direction of strain (van Krevelen 1990). Recently, orientation of cellulose nanowhiskers was found to increase the modulus of nanocomposites to the direction of the orientation (Kvien and Oksman 2007). Analogously, the increased strength and modulus by CMC adsorption could partly derive from molecular level orientation in the fiber bonding domains during drying, as discussed earlier by Salmén et al. (1987). This work does not contradict the view that improved fiber flexibility accounts for the strength effects (Emerton 1957). We

believe that flexibility is an expression of plasticization and further derived from molecular level interactions between fibrillar structure of fibers, polymers, and water.

Xyloglucan and CMC have a similar influence on fiber flocculation (Yan et al. 2006). Also, these polymers are known to disperse cellulose fibrils on adsorption (Ahola et al. 2008; Myllytie et al. 2009). However, though xyloglucan may improve strength development also by dispersing the fiber surface fibrillation, the strength effects were not as prominent as with CMC. Probably, xyloglucan was less efficient because it bound less water to the fiber surfaces. Besides, xyloglucan has been found to change the friction/adhesion properties of cellulose model surfaces (Stiernstedt et al. 2006), and specific interactions between cellulose and xyloglucan (bridge formation) in composites have been suggested (Whitney et al. 1995). Both phenomena can partially influence the behavior of fiber bonding domain and strength development upon drying in the presence of xyloglucan.

Adsorption of chitosan at pH 5 did not affect strength development compared to reference (*Fig 3*). This contradicts results from literature which indicate that at low pH, chitosan improves dry strength (Allan et al. 1978; Lertsutthiwong et al. 2002). Perhaps, the adsorbed amount of chitosan at low pH (3.8 mg/g) was not high enough for a polymer of molecular weight around 400000 g/mol to influence bonding and strength development, especially in the absence of fines in the pulp.

However, at elevated pH, chitosan is one of the few polymers that improves wet web strength (Laleg and Pikulik 1991). Covalent bonding between chitosan and cellulose, i.e. a reaction between primary amine and carbonyl groups, has been suggested as a mechanism for the wet web strengthening (Laleg and Pikulik 1992) but, to our knowledge, direct evidence on covalent bonding between chitosan and cellulose at fiber surfaces has not been introduced. As shown in *Figs 3* and *4*, the observed leveling off of the strength of chitosan containing samples at solids above 90% could originate from chemical reaction and crosslinking, because crosslinking is known to cause brittleness in cellulose sheets (Espy 1995).

It was interesting to see that we could combine the beneficial effect of CMC on strength development and the capability of chitosan to improve wet web strength by controlled bilayer adsorption (*Fig 4*). Especially, the initial wet strength and strength development at low solids were remarkably higher with the CMC-chitosan bilayer sample as a contrast to other samples (inset in *Fig 4*). In fact, we can not at this point prove that the structure of the adsorbed layer on the fibers was, indeed, a bilayer. We rather assume that the fiber bonding domain became a mixed layer of colloidal chitosan particles and CMC stabilized fiber surface fibrils, and that the viscoelastic properties of such bonding domain affected the strength development during drying.

Change of breaking strain during drying

The changes seen in breaking strain with different polymers (*Figs 5-7*) as a function of dry matter content did not coincide with the differences in tensile strength deve-

lopment (Figs 2-4). This might imply that the mechanisms affecting tensile strength and breaking strain were different. All polymers, except chitosan, increased breaking strain at solids above 70%. Again, CMC was the only polymer that clearly decreased breaking strain at low solids (<65%). The observed decrease in breaking strain by CMC can be related to decreased friction between fibers by CMC adsorption (Horvath and Lindström 2007; Zauscher and Klingenberg 2001). Especially, the clear effect of CMC at low solids is in accordance with the proposed important role of entanglement friction for wet web strength in paper (van de Ven 2008).

Though chitosan, adsorbed at high pH, improved tensile strength at all solids (Fig 3) it had only minor effect on breaking strain (Fig 6). Because at high pH chitosan was precipitated onto fiber surfaces as colloidal particles, it is conceivable that the properties of fiber bonding domain could be very different from normal equilibrium adsorption as for e.g. cationic starch or xyloglucan. Interestingly, yet inexplicably, when chitosan was adsorbed onto CMC treated fibers (CMC-chitosan bilayer sample) the breaking strain increased substantially (Fig 7).

The failure mechanisms of the samples, whether the bond breakage was cohesive inside the bonding domain or in the S2 fiber wall, was not examined. However, the fiber material was prepared in a such way that the failure should have occurred at fiber bonds, not as coarse fiber breakage. Thus, we assume it was essentially the mechanical properties of fiber bonding domain that influenced the change of breaking strain during drying.

Development of drying tension during drying

The development of drying tension (Figs 8-10) was quite different to other results. It is generally thought that development of drying tension is related to fiber shrinkage during drying (Wahlström and Fellers 2000). Accordingly, our results implied that the drying tension mainly derived from the swelling/shrinkage tendency of the bulk fiber material but certain adsorbed polymers can affect the development of drying tension as well.

CMC adsorption increased fiber surface swelling, which again improved bonding through molecular level mixing of CMC and fiber surface fibrils. The increased drying tension by CMC adsorption can be partly accounted for the enhanced strength of the fiber bonding domain. Xyloglucan had stronger effect on drying tension than CS or guar gum (Fig 8), while CS had more influence on the development of tensile strength (Fig 2). This could be because xyloglucan, as CMC, has specific interactions with cellulose fibrils due to the similar molecular chain structure and it may change the properties of the fiber bonding domain in a similar way as CMC. The more dispersed structure of fiber surface fibrillation after CMC or xyloglucan adsorption caused swelling of the fiber surfaces, which, added to improved fiber bonding, may have induced the increased drying tension as a contrast to other samples. This seems plausible since the fiber material, and therefore the fiber wall too, was the same for all the samples. The effect of chitosan, or the lack of it, on the development of drying tension is diffi-

cult to explain. Overall, the effect of different polymers and adsorption conditions on the development of drying tension still remains somewhat uncertain.

Conclusions

The effect of different polysaccharides (cationic starch, guar gum, xyloglucan, chitosan, and CMC) on the development of tensile properties of paper as a function of sheet dry matter content was systematically studied. The materials were chosen so that the specific (molecular level) interactions between the polymers and cellulose fibrils on fiber surfaces would reflect to viscoelastic properties of paper as well as possible. The applied method was a reasonable description of the real process because wet pressing was constant and subsequent drying was performed quickly under uniaxially restrained conditions. The development of tensile properties proved to be very characteristic for each polymer and different adsorption conditions. The structural similarity of the polysaccharides to cellulose influenced adsorption and the development of bonding and tensile properties during drying. Significant improvements in the development of tensile properties were attained with most of the tested polymers. Superior wet web strength and tensile properties through drying range was achieved with CMC-chitosan bilayer adsorption technique. The results emphasized the importance of understanding the molecular level interactions taking place in the fiber bonding domain on adsorption and during water removal by pressing and drying. In future, these types of studies might enable optimization of polymer dosing and drying conditions for a certain additive and desired end properties in papermaking processes.

Acknowledgements

The Finnish Funding Agency for Technology and Innovation (TEKES), UPM, M-Real, and Kemira are acknowledged for providing funding for the research project. M.Sc. Jihui Yin is acknowledged for the skillful laboratory work at the Department of Forest Products Technology.

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*Manuscript received March 30, 2009
Accepted August 24, 2009*