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Simplified modification of bleached softwood pulp with carboxymethyl cellulose

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SUMMARY

An ECF-bleached softwood pulp was treated with carboxymethyl cellulose (CMC). The CMC sorptions were carried out under specified conditions (60°C, pH 12.5, CMC addition 1%, pulp consistency 5%) in order to introduce more charged groups on the surface of fibres. The beating of pulp, pH-value, degree of substitution (DS) of CMC and electrolyte concentration had a major impact on the amount of CMC attached. The increase in the water retention values (WRV) of the CMC-treated pulps was very significant, and was associated with improved internal (approximately 50% increase) and tensile strengths of resultant handsheets. These handsheets prepared in water and in electrolyte solution were further studied by electron microscopy (ESEM). As the sorption conditions used are similar to those in papermaking systems, this surface modification method may be advantageous in practice, for example, after the refining stage.

Keywords

Softwood pulp, surface modification, carboxymethyl cellulose (CMC), sorption, water retention value (WRV), degree of substitution (DS), sheet and fibre properties, environmental scanning electron microscopy (ESEM)

Bulk and surface charges have a major impact on paper processing and the properties of the final paper (1,2). The most important functional groups in papermaking are charged carboxyl groups but phenolic, hydroxyl and sulphonic groups are present as well (3). The total acidic or anionic groups can be determined by titration, sorption, chromatographic or spectrometric methods (4). By introducing charged groups, the fibres swell more upon exposure to water, which improves the flexibility of the cell wall, resulting in a greater degree of consolidation and stronger paper. The charged groups also have an important role in enhancing the sorption of cationic paper chemicals and metal cations. More recently, Laine et al. (5) showed that the role of the charged groups on properties of paper is primarily due to an increase in specific bond strength, whereas the role of swelling and fibre flexibilisation is only of secondary importance. Meanwhile, Torgnysdotter and Wågberg found that the surface charge of fibres is the most important factor for the development of both bond strength and paper strength (6).

Different approaches to increase the amount of charged groups into the cell wall of fibres have been used, such as carboxymethylation (7), sulfonation (8,9) or oxidation (10). Barzyl et al. (11,12) carboxymethylated fibres under non-swelling conditions and showed that by introducing carboxyl groups on the surface of fibres the internal and tensile strengths improved. They attributed this to an increase in fibre-to-fibre specific bond strength. The beneficial role of the surface charge on the bonding properties of fibres and further on the properties of paper have been investigated (10,13,14). Previous studies in this laboratory have shown that carboxymethyl cellulose (15) and wood xylans (16,17) can be attached to cellulosic fibres and thus introduce more charged groups on the surface of fibres.

During kraft pulping, hemicelluloses which partially dissolve as individual polymers are sorbed back onto cellulosic fibres (18-20). Significant sorption takes place only at high temperatures and the amount of xylan deposited strongly depends on the nature of the cellulosic fibres (17,21-23). Factors affecting the resorption of xylans are structural changes in xylans, changes in the chemical composition of the fibres (19) and changes in the alkalinity of the cooking liquor (24). The resorbed hemicelluloses have both positive and negative effects on the properties of the pulp, such as increasing bonding within or between the fibres resulting in increased strength properties (25,26) and, disadvantageously, functioning as a physical barrier for diffusion of residual lignin from the fibres (17,27).

Many authors have studied the sorption of wood xylans on cellulosic fibres (16,17,28-30) or cellulose microfibrils (31). Mitikka et al. showed that the sorbed xylan was not concentrated on the external surface of fibres; in contrast, the sorption was evident throughout the cell wall. Furthermore, the sorbed xylan was parallel to cellulosic fibres and tended to adopt the same two-fold axis conformation with cellulose (16). Other investigators have studied the surface properties of CTMP fibres modified with xylans (23). Yllner et al. studied the attachment of xylan on cellulosic fibres during sulphate cooking (21,22). It was shown by Paananen et al. that the improvement of the strength properties for xylan modified pulps must be due to the effect of xylan on fibre bonds during drying of paper (32). Moreover, Hannuksela and co-workers studied the sorption of mannans on different pulps (33,34) and found that the sheet strength properties improved for the mannan modified pulps (26).

Carboxymethyl cellulose (CMC), an anionic polyelectrolyte derived from cellulose, is another useful polymer for introducing more charged groups on the surface of the fibres. In papermaking, CMC is used as a component of coating colour, as a wet end additive and for surface sizing (35,36). The cellulosic surface is negatively charged and therefore anionic polyelectrolytes do not generally adsorb on it (37,38) but previous studies in our laboratory have shown that CMC can be permanently attached on the external surface of ECF-bleached softwood pulp (15). The strength and topology of the sorption of CMC on cellulose can be controlled by the degree of substitution (DS) and polymerisation (DP) of the CMC. Moreover, the charge of fibres, degree of beating of the pulp, pH and ionic strength of the sorption medium and molecular weight of CMC affected the amount of CMC attached on pulp. When the aim is to modify the fibre surfaces, the

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CMC should have a sufficiently high molecular weight in order to be attached only on the external surface of the fibres and to prevent penetration into the cell wall (*8*). Because CMC may adopt a similar chain conformation as crystalline cellulose, the sorption of CMC with low DS is probably enabled by this conformational change, as in the case of wood xylans (*16,17*). It is this similarity in the chain conformations which enables association with cellulose microfibrils (CMFs). It has been shown by Mitikka et al. that microfibrillation of the external fibre surface is the most important factor in the formation of interfibre bonds (*15*). More recently similar studies have been conducted by Laine et al. to show that CMC can be irreversibly attached on the surface of cellulosic fibres at high temperatures and in the presence of calcium (*39*). Laine et al. also studied the effect on papermaking properties by the CMC attachment on a softwood kraft pulp (*40*). Moreover, Watanabe and co-workers have developed an advanced wet-end system with CMC (*41*). Studies with CMC modified pulp have also been carried out by Blomstedt et al. who have investigated the fractionation of CMC modified hardwood pulp (*42*) and the combined effect of CMC and surfactants on the properties of softwood pulp (*43*).

Several authors have recently been exploring the optimal conditions and properties of CMC modified pulps (*15,39,40,42,43*). In the work described here our objective was to develop a method to permanently attach CMC on cellulosic fibres in a simple and industrially practical manner. Thus sorption conditions of pH 12.5, 60°C, pulp consistency 50 g/L, CMC addition 0.5 g/L under which CMC can be attached onto cellulosic fibres were studied. Laine at al. (*39*) have also successfully attached CMC onto cellulosic fibres but only at extreme sorption conditions with high electrolyte concentration and temperature. Thus, the CMC sorption conditions studied here are much closer to the conditions encountered in a papermill. These consistency and temperature conditions would allow for the CMC to be added as an integral step in the papermaking process, for instance, after the beating or refining (*44*).

MATERIALS AND METHODS

Pulp

The experiments were carried out with an industrial ECF-bleached spruce (*Picea abies*) kraft pulp. The pulp was obtained from a mill in the form of dry pulp sheets. The pulps were soaked in water and disintegrated prior to use (ISO 5263-1). The pulp was refined at 1000, 2000, 4000 or 7000 revolutions with a PFI mill (ISO 5264-2).

Carboxymethyl cellulose

A commercial CMC sample, Nymcel ZSB-10 (DS 0.2, DPV 750), was obtained from Noviant. Increased DS samples were produced with the following treatment (*15*): CMC (20 g) was mixed with 2-propanol (520 mL) in a beaker. After 15 minutes, 40% sodium hydroxide (45 mL) was added. The mixture was mixed for 30 minutes and then chloroacetic acid (2.2 or 5.4 g) was added during another 15 minutes. The beaker was covered and kept at 55°C for 4 h. After 4 h, the mixture was filtered in a Büchner funnel (filter paper Whatman no.1) and 70% methanol (150 mL) was added. The mixture was mixed and filtered. After cooling the filter cake, 90% acetic acid (about 10 mL) was added (pH neutral). The mixture was filtered and washed with 70% methanol (150 mL) and 90% methanol (250 mL). The CMC sample was subsequently dried at room temperature.

A portion of the modified CMC (3 g) was mixed with 65% nitric acid in methanol (73 mL). After 3 h mixing, the mixture was filtered in a Büchner funnel and washed with 70% methanol (~ 1000 mL) until pH was neutral. The sample was dried at room temperature. A sample of the CMC (500 mg) was weighed in a beaker and mixed with 70% methanol (4 mL). After a few minutes, deionised water (50 mL) and 0.5 M sodium hydroxide (12.5 mL) were added. The mixture was mixed for 2 h. The residual hydroxide was titrated with 0.1 M hydrochloric acid using a phenolphthalein indicator. The consumption of sodium hydroxide corresponded to a DS of 0.31 and 0.43 for the two modified CMC samples produced.

Sorption of CMC on pulps

Since the three types of CMC (having DS < 0.5) were insoluble in water, a stock CMC solution (< 10 g/L) was prepared in 2.5 M sodium hydroxide. Disintegrated or refined pulp was mixed with water and stock CMC solution to obtain a final pulp consistency of 5% (50 g/L) and an initial CMC concentration of 0.5 g/L (1% on pulp) (*15*). The pH of the mixture was 12.5. In some cases the pH was adjusted to 11 or 10 with hydrochloric acid. The sorptions were carried out in glass beakers (DS 0.31 and 0.43) or in an 8 L rotating autoclave (DS 0.2). The temperature was raised to 60°C over 10 minutes. After 60 minutes, the pulp suspensions were cooled, filtered and washed with deionised water.

Samples of the liquid phase were withdrawn (50 mL) after the sorption, filtered with 0.2 mm membranes and then analysed for dissolved carbohydrates by the phenol-sulphuric acid test (*45*). The reference pulps were treated under similar conditions but without CMC. Thus, the results of the phenol-sulphuric acid test were corrected for polysaccharides other than CMC.

Water retention value

Water retention values (WRV) of pulps were measured in accordance with standard SCAN-C 62:00 with a Jouan GR 4 22 centrifuge. WRVs were also determined for pulps immersed in aqueous solutions of sodium chloride (2.5-10 mM NaCl).

Papermaking properties

The laboratory handsheets were prepared by standard method ISO 5269-1 except for wet pressing at 490 kPa and drying in a drum at 60°C for 2 h. Handsheets were prepared in water and in dilute solution of sodium chloride (0.05 M NaCl). Laboratory sheets (Table 3) were prepared with a laboratory handsheet mold equipped with a white water circulating system. Grammage of the sheets was determined according to ISO 536, thickness and density according to ISO 534. The light scattering coefficient was measured with an Elrepho reflectometer by the standard method ISO 5631.

The tensile strength of the laboratory sheets was determined with a tensile testing machine (MTS 400M) using SCAN-P 38:80. The bonding ability (internal strength) was measured according to Tappi 833 pm-94. The tearing resistance (out-of-plane tear, Elmendorf) was determined according to the standard method ISO 1974.

Environmental scanning electron microscopy

Environmental scanning electron microscopy (ESEM) images of the paper sheets were taken with an ElectroScan ESEM 2020 instrument (*46*). The images were taken in the ESEM mode with GSED (gaseous secondary electron detector) at a temperature of about 23°C. Low-

acceleration voltage (4.9 to 5.1 kV) was used to prevent degradation of cellulose (*47*). The pressure in the chamber was 6 torr, the condenser lens setting 40% and magnification 500x.

RESULTS AND DISCUSSION

Sorption of CMC on pulp

The amount of CMC attached on pulp was evaluated by estimating the content of CMC in the sorption liquid by phenol-sulphuric acid test. Unbeaten pulps sorbed 52% of high-molecular-weight CMC (DP_v 750, DS 0.2) whereas beating of the pulp led to almost quantitative sorption at 1% addition of CMC (Fig. 1). These results are comparable with results achieved by other workers but the previous results were conducted with CMC (DS 0.5) at high temperature (120°C) and with the addition of an electrolyte ($CaCl_2$) (*39*) whereas our conditions are much closer to practical papermaking conditions. Previous studies by ESCA (labelling with Ca^{2+} ions) and polyelectrolyte titrations (zero ionic strength) have shown that the CMC is located mainly on the external fibre surface (*15*). The same study showed that the porosity of the cell wall clearly controlled the sorption of CMC. The CMC was bound strongly on the pulp and the sorption was irreversible, unaffected by washing or extensive beating afterwards (Fig. 1).

The amount of sorbed CMC depended strongly on the DS of the CMC (Table 1), decreasing when the DS of the CMC was increased. Earlier studies had shown that higher retention is obtained with moderately substituted CMC (*37*). Similar trends have been reported by Laine et al. (*39*), although the attachment of CMC (DS > 0.4) was only possible by adding relatively large amounts of calcium and no attachment took place under electrolyte-free conditions (*39*). In the present study we have managed to attach high amounts of CMC (DS 0.2 to 0.43) on the fibre surface without adding calcium. Moreover, we found the sorption of alkali soluble CMCs could be enhanced to some extent by lowering the pH (12.5 to 10) which is in contrast to Laine et al. who observed a decrease in the attached amount of CMC when the pH was decreased in the same range (pH 13 to 11) (*39*).

At this point it should be emphasized that the sorption mechanisms here and in the alternative study (*39*) are completely different because of the substantial elec-
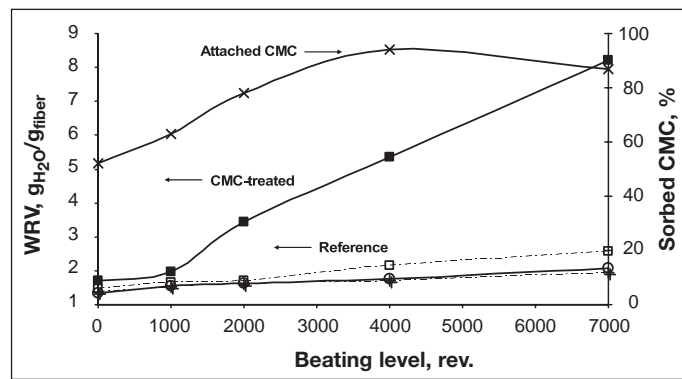
Fig. 1 Effect of beating on the attachment of CMC (Nymcel ZSB-10, DS 0.2, DP_V 750, pH 12.5) and the WRV of the pulp. Addition of CMC 1% on pulp. The solid line represents the WRV of the pulps in water and the dashed lines the WRV-values in 0.01 M NaCl. Key: filled square (■) CMC-treated, open square (□) CMC-treated+0.01 M NaCl, open circle (○) Reference, plus (+) Reference+0.01 M NaCl.

trolyte addition applied by Laine et al. to attach the CMC. Therefore, it is difficult to directly compare these two CMC modification methods (*15,39*). The results also imply that two different sorption mechanisms may exist. One suggestion is that CMC may adopt a similar chain conformation to crystalline cellulose, and the sorption of CMC with low DS is probably enabled by this conformational change, as in the case of wood xylans (*16,17*). It is this similarity in the chain conformations which enables association with cellulose microfibrils (CMFs). However, further fundamental studies are needed to fully understand the mechanism behind the CMC sorption.

Fibre properties of pulp treated with CMC

WRV is generally used to determine the swelling capacity of pulps. An increase in swelling by introducing more charged groups generally results in a higher WRV (*48,49*). From our results, the sorption of CMC on beaten pulps leads to a dramatic increase in their water retention values

(Fig. 1). Although the amounts of CMC in the beaten pulps were comparable, a more extensive beating led to a considerable further increase in WRV. However, WRV did not correlate with the amount of sorbed CMC and the increase of WRV could not be accounted for solely by the increase in the total charge of fibres. At the same degree of beating, the highest WRV was obtained with the CMC with DS 0.43 and pH 12.4 even though the degree of sorption was relatively low with this CMC grade (Table 1).

WRVs of the pulps were quite sensitive to the ionic strength (Fig. 1 and Table 1). The difference in the WRV values of pulps in water and in NaCl solution illustrates how much the water retention is based on osmotic pressure which in turn is affected by counter ions dissociating from the fibre (*49*). Ionic strength had less effect on those pulps that were treated with more extensively substituted CMC grades. Swelling was reduced to about half in the presence of an electrolyte and therefore decreased to the same level as the reference pulp (Fig. 1). Collapse of

Table 1
The effect of DS of CMC (Nymcel ZSB-10) on the amount of sorbed CMC on a beaten (4000 rev.) kraft pulp and the WRV of the pulp. Addition of CMC was 1% and pH of the mixture 12.5, 12.4, 11 and 10.

pH	DS	Sorbed CMC (% on pulp)	WRV (g/g) Water	WRV (g/g) 2.5 mM NaCl	WRV (g/g) 10mM NaCl
pH=12.5	0.2	94	3.43	1.99	1.69
pH=12.4	0.31	69	3.84	2.48	1.91
pH=12.4	0.43	38	4.16	3.13	2.09
pH=11.0	0.31	78	4.62	3.84	2.39
pH=11.0	0.43	48	4.47	3.91	2.33
pH=10.0	0.31	81	4.98	3.91	2.46
pH=10.0	0.43	50	4.84	3.88	2.57

the hydrated structure by electrolytes indicates that the CMF-water phase is stabilised by electrostatic interactions (*15*).

In the study by Mitikka-Eklund et al., fibres treated with CMC were examined with the aid of confocal laser scanning microscopy (CLSM) (*15*). It was shown that the main effect of CMC was to disintegrate external bundles of cellulose microfibrils (CMFs) and stabilise these in a water suspension. The huge amount of water in the CMC-treated fibres is bound into this external CMF-water gel. It is remarkable that the attachment of a small amount (< 1%) of water-insoluble CMC (DS 0.2) may increase the water retention by almost one thousand times its weight (Fig. 1). Comparable studies have shown that the water held by the CMC is present at the fibre surface and can therefore easily be removed by pressing (*5*). It is only the water in the cell wall that is difficult to remove during pressing. Another important observation is that the treatment with CMC increases the total anionic charge of the fibres only by approximately 20% (*15*). This change is significant for WRV however, because it reflects changes in the bulk anionic sites located mainly in the secondary cell wall.

Similar WRV results have been reported by Laine et al. (*40*) who reported a marked increase in WRV when the carboxyl groups on the CMC modified fibre surface were in their Na-form (washed with 0.001 M $NaHCO_3$). It was also shown that the WRV-values were highly dependent on the CMC attachment temperature - higher temperatures leading to more firmly attached CMC indicated by lower WRV of the pulp. Fundamental research on CMC sorption, preferably with a quartz crystal microbalance performed on cellulose model surfaces, would considerably enhance our understanding of this phenomenon.

Handsheet properties of pulp treated with CMC

A decrease in the carboxyl groups results reportedly in a reduction in WRV and further a decrease in the tensile strength (*48,49*). An increase in swelling brings about an improvement of the plasticity and flexibility of the fibres and increases their ability to bond extensively during sheet formation. Thus, the high water retention of the CMC-treated pulps led to high tensile and internal strengths, also when the comparison was made at a con-

Table 2
Sheet properties of beaten and unbeaten softwood pulp with and without sorbed CMC (DS 0.2) . REF=no CMC added, CMC= 1% CMC added.

| Sample/ Beating level rev.	Grammage g/m²	Thickness µm	Density kg/m³	Light scattering coefficient m²/kg	Tear index mNm²/g	Tensile index Nm/g	Internal strength J/m²
REF							
0	60.8	126	483	32.7	21.5	31.7	79.2
1000	65.2	117	559	27.4	23.2	44.2	156
2000	65.1	107	606	23.6	20.2	61.0	239
4000	62.6	96.6	648	20.6	17.3	73.5	411
7000	60.7	87.6	693	17.5	13.7	86.7	554
CMC							
0	66.8	125	533	29.0	23.3	38.4	157
1000	67.3	110	611	24.2	16.3	72.7	339
2000	64.7	101	639	20.9	11.3	89.1	510
4000	64.8	98.6	657	18.2	11.0	94.2	704
7000	65.4	94.3	694	15.6	8.6	105.1	965

Table 3
Sheet properties of beaten (2000 rev.) softwood pulp with and without sorbed CMC (DS 0.2, 0.31, 0.43) and the effect of electrolyte (0.05 M NaCl) added. REF=no CMC added, CMC= 1% CMC added, salt=preparing the sheets in 0.05 M NaCl.

Sample	Grammage g/m²	Thickness µm	Density kg/m³	Light scattering coefficient m²/kg	Tear index mNm²/g	Tensile index Nm/g	Internal strength J/m²
REF	64.8	111	582	24.0	20.0	65.7	254
REF+salt	64.9	104	624	22.9	18.8	67.8	344
DS =0.2							
CMC	66.3	103	642	21.3	12.9	84.2	499
CMC+salt	66.3	127	521	26.4	17.5	71.7	310
DS =0.31							
CMC	68.0	121	563	24.1	-	59.0	255
CMC+salt	67.1	116	579	23.9	-	64.9	314
DS =0.43							
CMC	66.6	110	605	22.6	-	65.8	271
CMC+salt	66.5	112	593	23.3	-	72.8	352

stant sheet density (Table 2). During beating the tensile and internal strengths of the CMC-treated pulps developed faster than those of the untreated (reference) pulps.

A trend in papermaking is towards increased recycling of process waters, and hence there is growing interest in knowing what effects the higher electrolyte concen-
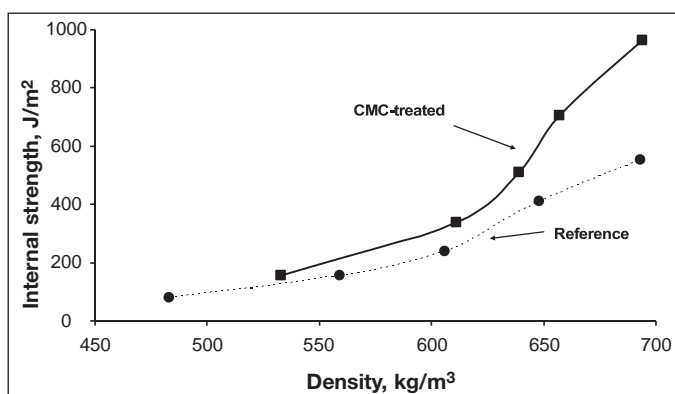
Fig. 2 The effect of CMC treatment (1% ZSB-10 addition, DS 0.2, DP$_v$ 750, pH 12.5) of the unbeaten and beaten kraft pulps on internal strengths of paper sheets relative to their density. The solid and dashed lines denote changes caused by beating (0, 1000, 2000, 4000 and 7000 revolutions).
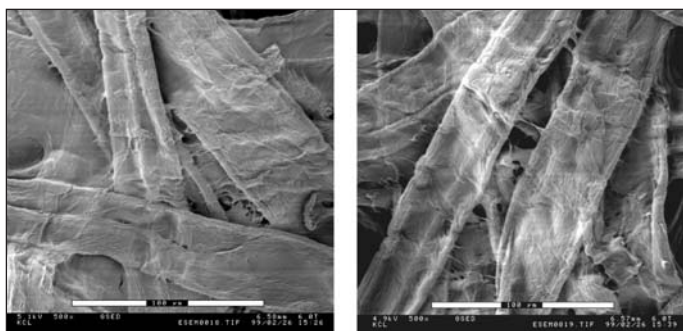
Fig. 3 ESEM images of sheets of a beaten (2000 revolutions) and CMC-treated (78% Nymcel ZSB-10 on pulp, pH 12.5, DS 0.2) pulp in water. Microcompressions are visible in both images, the left picture also shows ruptures in the bonded areas during drying.
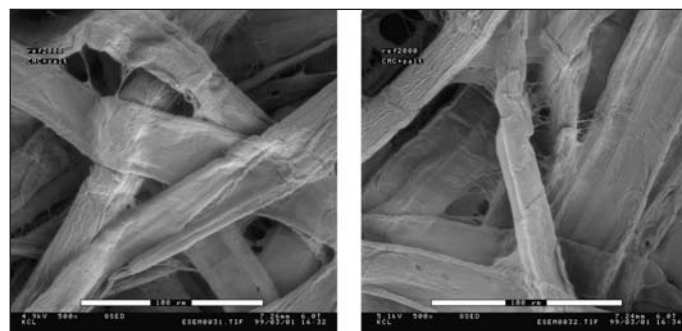
Fig. 4 ESEM images of sheets prepared from a beaten (2000 revolutions) and CMC-treated (78% Nymcel ZSB-10 on pulp, pH 12.5, DS 0.2) pulp in 0.05 M sodium chloride. Typical of the sheets is the low number of microcompressions, large intact bonded areas and smaller bridges between fibres.

trations have on paper properties. The effect of an electrolyte on the sheet properties was investigated by preparing the laboratory sheets in both water and in dilute solutions of sodium chloride (0.05 M NaCl).

In the sheets prepared in water, the sorption of CMC on cellulosic fibres clearly increased the density, internal and tensile strength, compared to the properties of the reference pulp at identical beating levels (Fig. 2, Table 2). Laine et al. also reported that CMC-treated pulps increased the tensile index of fibres markedly, whereas density and light scattering coefficient were unaffected by the CMC-modification (40). Thus, similar trends were reported in both investigations, but the direct comparison of these two studies is difficult because of the different DS of the CMC grades. One difference was that in our study we obtained a slight increase in density. An explanation of this could be that the CMC-treatment disintegrates external bundles of CMF on the fibre surface and therefore the CMC might be able to penetrate between the microfibrils leading to a denser sheet .

The laboratory sheets prepared in sodium chloride (0.05 M) led to exceptionally low density of the sheets (Table 3). In spite of that, the bonding (indicated by internal and tensile strength) remained at a high level.

In summary, the selective modification of the fibre surface with CMC greatly increased the interfibre bonding in paper sheets, due to microfibrillation of the external fibre surface (15). Meanwhile, the charged groups on the surface of fibres have an important role to enhance the development of the bond and paper strengths (5,6). However, the CMC-water interactions are more important for bonding of fibres than any specific chemical

structure on the external surfaces.

To further explore the superior bonding properties induced by the CMC addition, the handsheets were investigated with environmental scanning electron microscopy (ESEM). The sheets prepared from CMC-treated pulp showed an extensive formation of micro-compressions and some ruptures of bonded areas during drying (Fig. 3). No ruptures and only few microcompressions were visible in the ESEM images of sheets prepared from a CMC-treated pulp in 0.05 M sodium chloride (Fig. 4). The microfibrils on the fibre surface formed large bonded areas in the crossings and narrow bridges between fibres. However, the amount of bridges formed depended on the sheet forming medium and drying conditions in the sample chamber. The surface of the fibres seems to be smoother and cleaner when the CMC modified pulps were treated with electrolyte before sheet forming (Fig. 4).

These findings indicated that a decreased shrinkage of the partially destabilised CMF gel on the fibre surfaces was a major reason for the decrease in deformations when sheets were formed in the electrolyte solution. The low amount of deformations also led to improved out-of-plane and in-plane tear indices (data not shown).

To summarise, the ESEM images clearly showed that different chemicals created different types of bonds between fibres. The addition of CMC created a smooth (chemical) "membrane" on top of the fibres, forming a net of long bridges between fibres.

CONCLUSIONS

We have developed a method to attach CMC on the surface of kraft pulp fibres in a simple fashion resulting in a stronger

fibre network. The advantage of the method is in the simplified preparation conditions: no high temperatures or high electrolyte additions are necessary to obtain an irreversible sorption of CMC. Low degree of substitution (0.2) in the CMC enables the attachment in 60°C and 5% pulp consistency. These conditions potentially allow for an easy integration of the CMC treatment in a paper mill, for instance, after the refining stage.

The CMC treatment significantly increased the WRV of the pulp and, consequently, the internal bond strength of the handsheets prepared from the CMC modified pulp. In other words, the strength properties improved remarkably: the increase in tensile index of the handsheets was between 20 to 60% of the reference pulp. The formation of ideal interfibre bonds appears to require shrinkage of the CMC-water structure before sheet formation because the preshrinkage prevents deformations during drying.

The introduced surface modification method is potentially beneficial for many applications in paper mills but its usage is not confined merely to the field of pulp and paper; for example, textiles would undoubtedly benefit from a stronger fibre network. Further research is suggested before the actual industrial applications if only because the behaviour of CMC-treated fibre with other wet end chemicals in a paper machine has to be scrutinised. Fundamental research is warranted to further elucidate the sorption mechanism that is still subject to debate.

ACKNOWLEDGEMENTS

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