

# On the mechanisms behind the ability of CMC to enhance paper strength

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**KEYWORDS:** Surface carboxymethylation, CMC, BET-analysis, Light-scattering coefficient, Page's equation, RBA, Shear bond strength

**SUMMARY:** The attachment of CMC to pulp is known to have a strong impact on the tensile strength properties. The mechanisms behind the strength-enhancing ability of the CMC have been investigated by studying the effect of surface carboxymethylation on some basic fibre and sheet properties. Standard methods were used for the strength evaluation, and the relative bonded area was determined from both light-scattering measurements and BET-analysis. The effect of CMC on the shear bond strength was calculated using Page's equation. The attachment of CMC was shown to increase the shape factor and reduce the number of kinks per fibre, which is beneficial for the tensile strength. Surface carboxymethylation also increased the relative bonded area, but on a small-scale structural level detectable only using BET-analysis and not by the scattering coefficient. The sheet density was not affected by the treatment. CMC attachment also increased the shear bond strength. In order to use Page's equation for this evaluation, the relative bonded area had to be determined by BET-analysis. The positive effect of CMC on sheet formation also contributed to an increase in tensile strength.

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The use of carboxymethyl cellulose (CMC) as a strength-enhancing additive has been extensively studied in this laboratory for almost a decade (Laine et al. 2000; Laine et al. 2002a; Laine et al. 2002b; Laine et al. 2003a; Laine et al. 2003b; Duker et al. 2007). Its main advantage over other strength additives is its ability to increase the paper strength without affecting the sheet density (Laine et al. 2002a). In the present study an attempt was made to investigate the mechanisms behind the strength-enhancing ability of the CMC. The parameters taken into account are all included in the well-known Page equation, which relates the tensile strength of a paper to a number of fibre and sheet properties (1969):

$$\frac{1}{T} = \frac{9}{8Z} + \frac{12A\rho g}{bP\lambda RBA} \quad [1]$$

where  $T$  and  $Z$  are respectively the tensile strength of the sheet, expressed as breaking length, and the zero-span tensile strength (cm);  $A$  is the cross-sectional fibre area (cm<sup>2</sup>);  $\rho$  is the fibre density (g/cm<sup>3</sup>);  $g$  is the acceleration due to gravity (cm/s<sup>2</sup>);  $b$  is the shear bond strength per unit area (dynes/cm<sup>2</sup> = 0.1 Pa);  $P$  is the fibre perimeter (cm);  $\lambda$  is the mean fibre length (cm) and  $RBA$  is the relative bonded area.

The first term on the right-hand side of Eq 1 represents the contribution of fibre strength to the tensile strength of a paper sheet. The strength of the individual fibre is impaired by a number of factors including the removal of hemicelluloses (Leopold and McIntosh 1961; McIntosh 1963; Spiegelberg 1966; Sjöholm et al. 2000), large fibril angles (Page et al. 1972) and fibre defects (Page and El-Hosseiny 1976; Ljungqvist et al. 2003). A high  $\alpha$ -cellulose content, on the other hand, increases the fibre strength (Page et al. 1985a).

The determination of the zero-span index is the most common way to evaluate the fibre strength. The method was first developed by Hoffmann Jacobsen (1925) and its validity as a measure of individual fibre strength has been subjected to numerous studies and controversies over the years (see e.g. a review by Bronkhorst and Bennett 2002). The strength of the individual fibre can alternatively be determined by the tensile testing of individual fibres (e.g. Duncker and Nordman 1965; Page et al. 1972; Hardacker and Brezinski 1973; Mott et al. 2002) and by Single Fibre Fragmentation tests (Thuvander et al. 2001).

The second term on the right-hand side of Eq 1 gives the contribution of the joint strength to the tensile strength. It consists of two variables; the shear bond strength per unit area and the relative bonded area. The shear bond strength is dependent on the chemical composition of the fibres. The presence of lignin on the fibre surfaces is known to reduce the shear bond strength (Hartler and Mohlin 1975), presumably because lignin interferes with the formation of hydrogen bonds. The same authors also showed that an increase in the hemicellulose content, on the other hand, increases the shear bond strength. Morphological fibre properties, e.g. the degree of fibrillation, also influence the shear bond strength. Fibrils protruding from the surfaces of two approaching fibres will act as bonding agents and facilitate the development of mechanical and chemical interactions (Van den Akker 1959; Clark 1969; Nanko and Ohsawa 1989). The second variable, the relative bonded area, is dependent on the surface area of the fibres. A decrease in cell wall thickness increases the surface area and hence also the relative bonded area (Paavilainen 1994). Another parameter affecting the surface area is the surface roughness of the fibres. A smooth surface increases the relative bonded area (Davison 1972; Paavilainen 1994).

The joint strength is also influenced by the paper-making process itself. Beating is known to increase the relative bonded area, since the formation of fines and external fibrillation creates more surface area available for bonding (Clark 1969; Grén and Ljungqvist 1983; Paavilainen 1994). In addition, beating increases the fibre

flexibility (Frölander and Hartler 1970; Tam Doo and Kerekes 1989; Curto et al. 2003), and this also has a positive effect on the relative bonded area. Flexible fibres respond better to Campbell's forces during sheet consolidation (Ingmanson and Thode 1959; Paavilainen 1993). The addition of chemical strength agents leads to stronger joints. These may affect both the shear bond strength and/or the relative bonded area (see e.g. the review by Lindström et al. 2005).

Several authors have used single fibre measurements to evaluate the joint strength (see e.g. Schniwind et al. 1964; Mohlin 1974; Thorpe et al. 1976; Stratton and Colson 1993; Torgnysdotter and Wågberg 2003). These measurements are, however, time-consuming and, in order to obtain a reliable figure, a large number of measurements have to be performed. To estimate the contribution of the shear bond strength to the strength of a joint, the Page equation can be used (Page 1969; Paavilainen 1994; Gurnagul et al. 2001). The contribution of the relative bonded area can, in contrast, be evaluated directly. The method most commonly used to evaluate the relative bonded area is based on light-scattering (Ingmanson and Thode 1959). Alternatively, the nitrogen adsorption technique (BET analysis), established by Brunauer, Emmett and Teller (1938) and further developed for paper materials by Haselton (1955), or X-ray scattering (Caulfield 1973) can be used. A more recent method, for the determination of the relative bonded area is the contact zone analysis method developed by Torgnysdotter (2006).

The objective of the present study was to investigate the effect of surface carboxymethylation on the basic fibre and paper properties discussed above and thus to seek to establish the mechanisms behind the strength-enhancing ability of CMC. Earlier results, stating that the attachment of CMC increases the shear bond strength while RBA remains unaffected (Laine et al. 2002a), were re-examined. Moreover, Page's equation does not take into account the effects of fibre curl and sheet formation. These parameters are now known to have a significant impact on the tensile strength and they were therefore also considered. The zero-span tensile strength was taken as a measure of the fibre strength. RBA was evaluated both from light-scattering measurements and from BET-analysis, and the Page equation was used to calculate changes in shear bond strength.

## Materials and Methods

### Pulp and carboxymethyl cellulose

The pulp used in the experiment was produced from spruce logs. Both chipping and screening were performed at STFI-Packforsk. In the surface carboxymethylation process, a commercial CMC (Hercules, Sweden) with a degree of substitution of 0.4 and a molecular weight of 700-1000 kDa was used. These data were provided by the manufacturer.

### Kraft cooking

Screened chips were placed in steel autoclaves together with the cooking liquor. The conditions used during cooking are given in *Table 1*. The kappa number of the unbleached pulp was 25, determined by the standard procedure SCAN-C 1:00.

Table 1. Conditions in the kraft cook.

Process parameter	
Effective alkali	19%
Sulfidity	35%
Liquor-to-wood ratio	4:1
Temperature	165 °C
Cooking time	6 h
H-factor	1900

After the cooking, the pulp was bleached to ISO brightness 90%, using a DEDED sequence. The bleaching conditions are shown in *Table 2*. In the D1 and D2-stages, an acetate buffer was used. After bleaching, the pulp had a viscosity of 1126 ml/g, determined in accordance with ISO 5351:2004.

Table 2. Conditions in bleaching.

	D <sub>0</sub>	E <sub>1</sub>	D <sub>1</sub>	E <sub>2</sub>	D <sub>2</sub>
ClO <sub>2</sub> charge, % a Cl	5.00%	-	2.75%	-	1.50%
NaOH	0.65%	1.04%	-	0.30%	-
Temperature	50 °C	60 °C	70 °C	70 °C	70 °C
Time	60 min	60 min	120 min	60 min	240 min
Final pH	2.5	11.7	4.3	11.6	4.5

### Pulp pre-treatment

Prior to surface carboxymethylation, the pulp was washed in several stages. In the first washing stage, 0.01 M HCl was added to the pulp suspension in order to remove metal ions. The pH was adjusted to 2 using HCl and the pulp was kept at this pH for 30 minutes. The pulp was then repeatedly washed with deionized water until the conductivity of the filtrate was below 5 µS/cm. In a second washing stage, the pulp was transferred to its Na<sup>+</sup>-form with 1 mM NaHCO<sub>3</sub>. The pH was adjusted to 9 using NaOH and kept at pH 9 for 30 minutes. Subsequently, the pulp was washed with deionized water to a conductivity below 5 µS/cm, in order to remove water-soluble substances, e.g. lignin and hemicelluloses, from the pulp. In the final washing stage, the pulp was transferred to its Ca<sup>2+</sup>-form and the CaCl<sub>2</sub>-concentration in the aqueous phase was adjusted to 0.05 M. The pulp was left to stand for 15 minutes and then washed with deionized water until the conductivity of the filtrate was below 5 µS/cm.

### CMC attachment

In order to improve mixing between pulp and CMC during surface carboxymethylation, 0.76 g CMC was dissolved in 500 ml deionized water and the solution was continuously stirred overnight. Surface carboxymethylation was carried out in accordance with the method developed by Laine et al. (2000). The pre-washed pulp (37.5 g) and the CMC-solution were placed in contact in

a two-litre autoclave. To the suspension, 1 M CaCl<sub>2</sub> was added and the pH was adjusted. The conditions used during surface carboxymethylation are shown in *Table 3*. The autoclave was placed in a pre-heated glycolbath to stabilise the temperature and ensure a certain amount of stirring. After being in contact with the CMC solution, the pulp was repeatedly washed with cold deionized water to a conductivity of less than 5 µS/cm. A reference sample was treated under the same conditions, but without the addition of CMC.

Table 3. Conditions during surface carboxymethylation.

Process parameter	
CMC addition	20 mg CMC/g fibres
Pulp consistency	1.9%
Temperature	120 °C
Exposure time	2 h
pH	8
Electrolyte concentration (CaCl <sub>2</sub> )	0.05 M

## Analyses

The total charge of the fibres was analysed using conductometric titration (Katz et al. 1984), while the surface charge density was determined by the polyelectrolyte titration procedure optimised by Horvath et al. (2006) from a method originally described by Wågberg et al. (1985).

The water retention values (WRV) of the CMC pulp and of the reference pulp were determined according to SCAN-C 62:00. The WRV can be taken as a measure of pulp swelling (Scallan 1983) and the determination was made in deionized water and with the pulp in its Ca<sup>2+</sup>-form.

The fibre dimensions and the fibre curl were determined using the STFI FiberMaster (Karlsson and Fransson 1994). The FiberMaster measurement was based on 20 000 fibres.

Handsheets were prepared in accordance with SCAN-C 26:76, but with some modifications. All the sheets were made in deionized water, with the pulp in its Ca<sup>2+</sup>-form. The grammage of the handsheets to be used in the zero-span tensile testing was 45 g/m<sup>2</sup>, while the handsheets to be used in Z-strength testing had a grammage of 120 g/m<sup>2</sup> and, in order to vary the sheet density, they were subjected to different degree of wet-pressing. Half of them were wet-pressed once, using 400 kPa and a pressing time of 5 minutes. The other half were wet-pressed three times, using 400 kPa and a pressing time of 5 minutes. Subsequent to the wet-pressing, all the handsheets were dried under restraint in a conditioned room (50% RH and 23°C).

To investigate the effect of CMC on the relative bonded area (RBA), an additional set of handsheets was prepared. Their grammage was 80 g/m<sup>2</sup> and, by varying the wet-pressing pressure from 50 kPa to 800 kPa, sheets with different levels of bonding were obtained. The tensile strength and the light-scattering coefficient of these sheets were determined in accordance with ISO 9416:1998 using Kubelka-Munk theory. The RBA of each sheet was then calculated using the equation below

(Ingmanson and Thode 1959):

$$RBA_s = \frac{S_0 - S}{S_0} \quad [2]$$

where  $S$  is the scattering coefficient of the sheet and  $S_0$  is the scattering coefficient of a sheet consisting of unbonded fibres.  $S_0$  was determined by plotting the light-scattering coefficient versus tensile index and extrapolating the light-scattering coefficient to zero tensile strength. The relative bonded area of the sheets was also determined by measurement of their specific surface area, based on BET-analysis using an ASAP 2010 (Accelerated Surface Area and Porosimetry Analyzer) from Micromeritics. The paper samples to be analysed were cut into pieces, a sample typically weighing 4 g, and treated in vacuum at 100°C overnight. Thereafter, the samples were placed in the ASAP 2010 sample container to determine the krypton adsorption at -196°C, using different krypton pressures. From the initial part of the adsorption isotherm obtained, i.e. at low relative vapour pressures ( $p/p_0 = 0.05-0.20$ ), the monolayer coverage of krypton was determined. Knowing the size of a krypton molecule, the specific surface area of each paper sample was calculated. The specific surface area determined is thus a measure of the unbonded area in the sheet, and the RBA of each sheet was then calculated according to:

$$RBA_{BET} = \frac{(BET-area_0) - (BET-area)}{BET-area_0} \quad [3]$$

where  $BET-area$  is the specific surface area of the sheet and  $BET-area_0$  is the specific surface area of an unbonded sheet.

The physical properties of all sheets were tested according to the following standards: grammage ISO 536:1995, structure thickness and sheet density SCAN-P 88:01, tensile strength SCAN-P 67:93, zero-span tensile strength ISO 15361:2000, Z-strength SCAN-P 80:98 and light-scattering coefficient ISO 9416:1998. The primary data were treated in accordance with SCAN-G 2:63, using a 95% confidence interval. Sheet formation was measured using the STFI-formation method with  $\beta$ -radiography (Johansson and Norman 1996).

The shear bond strength per unit area was determined by the direct application of the Page equation (*Eq 1*). The inverted tensile strength ( $1/T$ ) was plotted against the inverted relative bonded area ( $1/RBA$ ) using data obtained from the second set of handsheets wet-pressed to different levels of bonding. The specific bond strengths were then calculated from the slopes of these plots using the fibre lengths obtained from the STFI FiberMaster evaluation and  $A = 2.4 \cdot 10^{-6} \text{ cm}^2$ ;  $P = 9.0 \cdot 10^{-3} \text{ cm}$ ;  $\rho = 1.56 \text{ g/cm}^3$  (Page 1969).

## Results

### Fibre modification using CMC

Attachment of CMC to the fibres resulted in an increase in the charge density. As can be seen in *Table 4*, both the

total charge and the surface charge were increased. The magnitude of the surface selectivity, defined as the number of charges introduced onto the fibre surface by surface carboxymethylation divided by the total number of charges introduced, implies that the fibre modification was surface selective. Some penetration into the fibre wall is, however, likely to occur due to the molecular weight distribution of the CMC. The amount of CMC attached was calculated from the total charge measurements, i.e. conductometric titration. During surface carboxymethylation, 20 mg CMC/g fibre material was attached to the fibres. Hence, the attachment level was 100%. The WRV increased by approximately 30%.

Table 4. Pulp characterization.

	Reference pulp	CMC pulp
Total charge	46.0 $\mu\text{ekv/g}$	87.2 $\mu\text{ekv/g}$
Surface charge	1.9 $\mu\text{ekv/g}$	35.2 $\mu\text{ekv/g}$
Surface selectivity	-	81%
WRV	1.48 g/g	1.88 g/g
Fibre length	2.6 mm	2.6 mm
Fibre width	29.5 $\mu\text{m}$	29.8 $\mu\text{m}$
Shape factor	86.0%	86.5%
No. of kinks per fibre	0.90	0.82
Dry zero-span index	174 $\pm 4$ Nm/g	189 $\pm 3$ Nm/g
Rewetted zero-span index	164 $\pm 2$ Nm/g	181 $\pm 4$ Nm/g

Fibre dimensions and the shape factor were evaluated using the STFI FiberMaster. These results are also shown in Table 4. Neither the fibre length nor the fibre width was affected by CMC attachment, whereas the shape factor was slightly increased. Attachment of CMC significantly reduced the number of kinks per fibre. Both the dry and rewetted zero-span index increased as a result of surface carboxymethylation.

Fig 1 shows the effect of CMC attachment on the paper sheet tensile strength. The sheet density was varied by wet-pressing, and at a given sheet density, paper sheets produced from the CMC pulp had a considerably higher tensile strength. Furthermore, the CMC-treated pulp exhibited a more powerful strength development during wet-pressing.

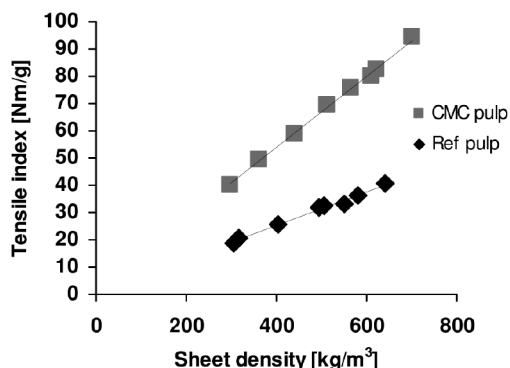


Fig 1. The effect of CMC attachment (20 mg/g) on tensile index, when added to a bleached and never-dried laboratory-produced pulp. Sheet density was varied by wet-pressing (50-800 kPa).

### Effect of CMC on relative bonded area

The relative bonded area was determined both by light-scattering measurements and by BET-analysis. The effects of wet-pressing and CMC on the light-scattering coefficient and on the specific surface area determined by BET, are shown in Fig 2. Both wet-pressing and surface carboxymethylation resulted in a decrease in the light-scattering coefficient and in the specific surface area. The effect of CMC was more pronounced in the case of the specific surface area. At a given wet-pressing level, the light-scattering coefficient, corresponding to unbonded areas scattering light, fell below the specific surface area determined by BET-analysis.

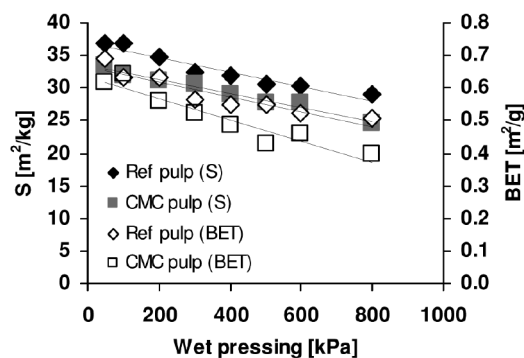


Fig 2. The effect of CMC attachment (20 mg/g) on the light-scattering coefficient and on the specific surface area determined by BET-analysis. CMC was added to a bleached and never-dried laboratory-produced pulp.

When BET-analysis was employed to determine the relative bonded area, both nitrogen gas and krypton gas were evaluated as adsorbing media. The RBA results shown here are, however, based on the krypton adsorption data. In order to obtain a linear correlation between light-scattering coefficient and specific surface area, as previously demonstrated by Haselton (1955), krypton was a necessity. The use of BET-analysis to evaluate the effect of strength additives on RBA will be the subject of a separate investigation in this laboratory.

Fig 3 shows the effect of CMC on relative bonded area with an increasing degree of wet-pressing. Both RBA determined by light-scattering measurements ( $RBA_S$ ) and RBA determined by BET-analysis ( $RBA_{BET}$ ) increased with increasing wet-pressing level. When light-scattering measurements were used to determine RBA, no effect of CMC on bonded area was detected. On the other hand, when BET-analysis was used, a significant increase in RBA was seen for the CMC pulp. This difference in bonding between the two pulp types increased with increasing wet-pressing level.

In Fig 4 the effect of wet-pressing on sheet density is shown instead. The sheet density also increased with increasing wet-pressing level, but the effect of CMC attachment on the sheet density was insignificant. As can be seen in Fig 5, the difference in  $RBA_{BET}$  between the reference pulp and the CMC pulp remained at any given sheet density level, and the  $RBA_S$  for the CMC pulp fell below  $RBA_S$  for the reference pulp over the whole density range investigated.

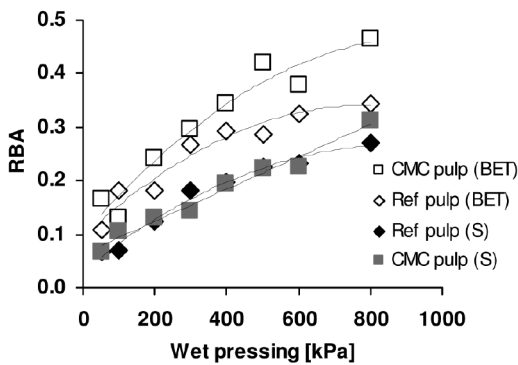


Fig 3. The effect of CMC attachment (20 mg/g) on relative bonded area, when added to a bleached and never-dried laboratory-produced pulp. RBA was determined both from light-scattering measurements (S) and from BET-analysis (BET).

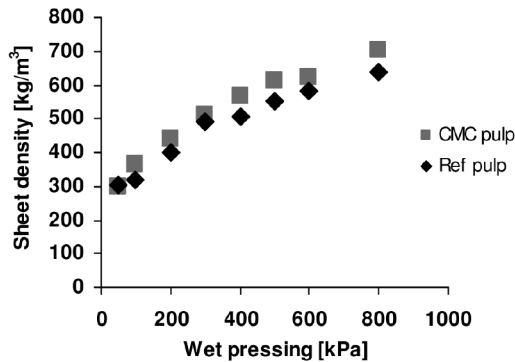


Fig 4. The effect of CMC attachment (20 mg/g) on sheet density, when added to a bleached and never-dried laboratory-produced pulp.

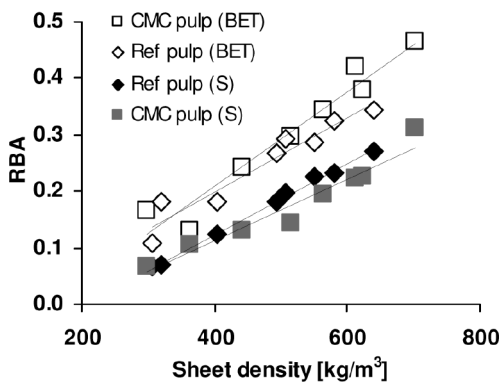


Fig 5. The effect of CMC attachment (20 mg/g) on the relationship between relative bonded area and sheet density, when added to a bleached and never-dried laboratory-produced pulp. RBA was varied by wet-pressing (50-800 kPa) and determined both from light-scattering measurements (S) and from BET-analysis (BET).

### Effect of CMC on shear bond strength

Fig 6a and Fig 6b show how Page's relationship between tensile strength and relative bonded area was affected by surface carboxymethylation. The relation is shown both for  $RBA_S$  and for  $RBA_{BET}$ . The slope of the curve is the specific bond strength and the intersection with the y-axis corresponds to the fibre strength. When light-scattering measurements were used to determine RBA, CMC appeared to have increased the specific bond strength by 67% and the corresponding increase for the fibre strength was 200%. When instead BET-analysis was used for determination of RBA, the specific bond strength appeared to have increased by 200%, while the fibre strength was unaffected.

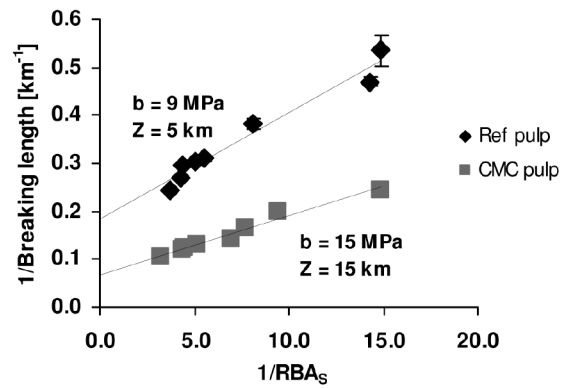


Fig 6a. The effect of CMC attachment (20 mg/g) on the shear bond strength per unit area as calculated from the Page equation. CMC was added to a bleached and never-dried laboratory-produced pulp. RBA was determined from light-scattering measurements.

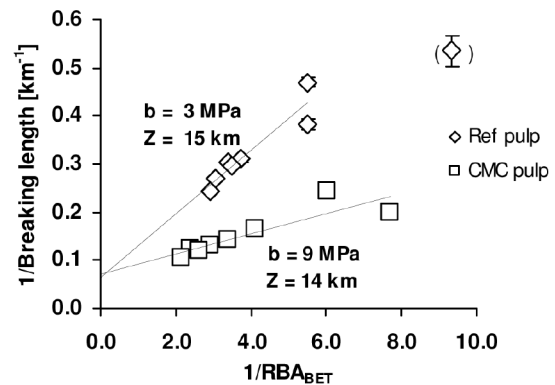


Fig 6b. The effect of CMC attachment (20 mg/g) on the shear bond strength per unit area as calculated from the Page equation. CMC was added to a bleached and never-dried laboratory-produced pulp. RBA was determined from BET-analysis.

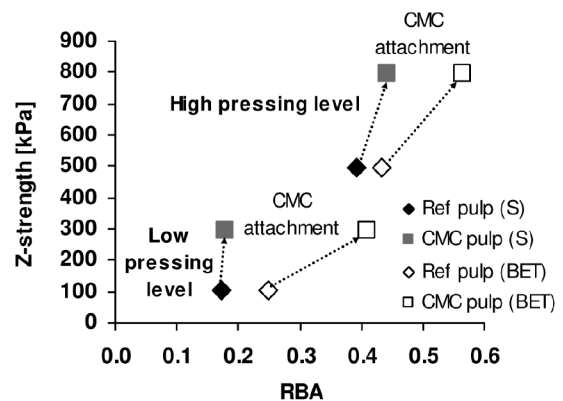


Fig 7. The effect of CMC attachment (20 mg/g) on the relationship between Z-strength and RBA, for two different pressing levels. RBA was determined both from light-scattering measurements (S) and from BET-analysis (BET), and the arrows indicate the effect of CMC attachment (20 mg/g) to a bleached and never-dried laboratory-produced pulp.

### Effect of CMC on sheet properties

The effect of CMC attachment on the relationship between Z-strength and RBA is shown in Fig 7, for two different pressing levels. Clearly, surface carboxymethylation resulted in an increase in Z-strength at both pressing levels. At the lower pressing level, however, CMC attachment had no effect at all on the RBA determined by light-scattering measurements. When instead BET-analysis was used to evaluate the RBA, a dramatic increase in the bonded area was seen. At the higher pressing level, an increase in bonded area as

result of CMC attachment was detected with both the RBA-methods. This increase was, however, more pronounced when BET-analysis was used.

The STFI-formation method with  $\beta$ -radiography was used to investigate the effect of CMC attachment on sheet formation. The results are presented in *Table 5*. At both the small-scale variation level and the large-scale variation level, the formation number of the CMC sheet was lower than the formation number of the reference sheet, indicating that CMC had a positive effect on formation.

Table 5. Effect of CMC on the formation number.

	Reference pulp	CMC pulp
$F_1$ [ $\lambda$ : 0.3-3.0 mm]	10.9	10.3
$F_2$ [ $\lambda$ : 3.0-30 mm]	5.6	5.0
$F_{tot}$ [ $\lambda$ : 0.3-30 mm]	12.2	11.4

## Discussion

This paper demonstrates the effects of CMC attachment on the fibre and on the sheet properties which determine the tensile strength. The surface carboxymethylation process gave an attachment level of 100%. The attachment was surface selective and resulted in a significant increase in the WRV (*Table 4*). The CMC molecule is thought to attach to the fibre surface in a bulky conformation containing loops and tails which thus retain water. The effect of CMC on the WRV has previously been discussed by Laine et al. (2002a; 2003a). In the papermaking process, retained surface water is more easily removed than water retained in the swollen cell-wall and the attachment of CMC does not affect the dry solids content after wet-pressing (Mesic 2002).

*Table 4* shows that CMC has a significant impact on the shape factor and on the number of kinks per fibre. This fibre-straightening effect of CMC, probably due to carboxyl group repulsion on the fibre surface, is in agreement with previous results (Duker et al. 2007). Straight fibres improve the effective stress distribution in a paper sheet, and this is in turn beneficial for the tensile strength (Page et al. 1985b; Mohlin et al. 1996).

Surface carboxymethylation increased both the dry and the rewetted zero-span tensile index (*Table 4*). The dry zero-span is often considered to be a measure of the fibre strength. The small increase in dry zero-span strength seen in *Table 4* is, however, best understood in terms of a network effect. Wink and van Eperen (1962) found the zero-span measurement to be dependent on inter-fibre bonding, and the same conclusion was later drawn by Cowan (1988). Surface carboxymethylation is, in the present work, shown to increase RBA and this enhancement in bonding is probably seen also as an increase in the dry zero-span index. The increase in rewetted zero-span index is best understood in terms of the increase in shape factor and fewer kinks per fibre. Several investigations have shown a strong correlation between the number of fibre deformations and the rewetted zero-span index (Mohlin et al. 1996; Mohlin et al. 2003; Duker et al. 2007).

In previous studies, the large impact of CMC on tensile strength (*Fig 1*) has been ascribed only to an increase in the shear bond strength per unit area, i.e. a higher specific bond strength (Laine et al. 2002a). The results presented in *Fig 3*, *Fig 5* and *Fig 7* show that this conclusion needs to be re-evaluated. *Fig 3* shows the effect of wet-pressing on the RBA for both the CMC pulp and the reference pulp. When BET-analysis was used to determine the RBA, an additional increase in RBA was seen in the case of the surface carboxymethylated pulp. This CMC effect was not recognized in earlier investigations. In the earlier studies, however, the change in RBA was determined by light-scattering measurements, and as can be seen in *Fig 3*, the change in bonding caused by CMC is only detectable with the BET-analysis. Optical methods are thought to be sensitive to a fibre-fibre separation of approximately 200 nm (half the wavelength of visible light), whereas the separation of two fibres in molecular contact may be as little as a few angstroms. The changes in bonded area, as a result of surface carboxymethylation, occur on a small-scale structural level not detectable with visible light. Nor do these changes affect sheet density, *Fig 4*. The small increase in sheet density seen between the two pulp types is not significant enough to explain the difference in relative bonded area detected with BET-analysis. The data shown in *Fig 5* support this conclusion. Similar results, regarding the difference between light-scattering measurements and BET-analysis for RBA determination, were found by Eriksson (2006), who used polyelectrolyte multilayers instead of CMC to improve paper strength properties.

The results presented in *Fig 6a* and *Fig 6b* differ considerably from each other. It becomes clear that Page's equation can be used for the evaluation of CMC's effect on the shear bond strength only if RBA is determined by BET-analysis. If light-scattering measurement is used instead, the relative bonded area is overestimated and it appears that the attachment of CMC increases the fibre strength by 200% (*Fig 6a*). That surface carboxymethylation would modify the individual fibre strength to that extent is inconceivable, nor can any indications of such an effect be found in the literature. Moreover, the rather constant dry zero-span index supports the conclusion that the fibre strength was unaffected by the CMC treatment. *Fig 5* provides further evidence that light-scattering measurement is unsuitable as a method to estimate RBA. In this figure, attachment of CMC appears to have decreased the relative bonded area. The use of Page's equation to calculate the effect of various strength additives on the shear bond strength has been utilized by several other authors (Gaspar 1982; Howard and Jowsey 1989; Dasgupta 1994). In all these studies, light-scattering measurements were used to determine RBA. The conclusions regarding the impact on the fibre strength of the additive used were, however, contradictory. From *Fig 6b* it can be concluded that surface carboxymethylation does increase the shear bond strength. The magnitude of the effect is large, approximately 200%. The cause of this increase is not known, but a probable explanation is that new bonds are formed within already existing

fibre joints. Similar findings have been reported in the literature. Leech (1954) used locust bean gum as a strength additive and demonstrated a dramatic increase in the bond strength at a given RBA. It was suggested that the strength increase was brought about by the formation of new, flexible bonds involving gum molecules. Moreover, locust bean gum was shown to have no effect on the fibre strength.

Fig 7 shows the effect of CMC on Z-strength. At the lower pressing level, the difference between light-scattering measurements and BET-analysis for determination of RBA was once more apparent. At the higher pressing level, an increase in RBA as a result of surface carboxymethylation was shown by both methods. CMC acts in the fibre-fibre joints and, at the higher pressing level, the increased degree of bonding was sufficiently for the CMC effect to be detectable also with light-scattering measurements. Z-strength has been used by several authors to investigate the effect of pulp type and various treatments on the bond strength (Retulainen and Ebling 1993; Koubaa and Koran 1995). Despite the fact that Z-strength testing involves a loading mode different from shear, it is notable that the relative increase in Z-strength seen at RBA 0.17, determined by light-scattering measurements, corresponds to the increase in shear bond strength calculated using Page's equation.

The positive effect of CMC attachment on the formation also contributes to an increase in paper strength. The decrease in the formation number seen in Table 5 is significant and the CMC formation spectrum (not shown here) was below the reference spectrum over the whole wavelength range investigated. This result is in total agreement with the findings presented by Yan et al. (2006), who showed that the tendency of fibres to flocculate is reduced by CMC attachment. Surface carboxymethylation increases the surface charge density of the fibres. This in turn results in a greater fibre-fibre repulsion, low friction between fibres (Horvath and Lindstöm 2007) and hence, improved formation.

CMC is shown to straighten the fibres, to increase the RBA and shear bond strength and to improve the formation. All these factors contribute to the positive effect of CMC on tensile strength. Their relative importances are not, however, known. Already in 1954, Leech tried to quantify the importance of these parameters for the tensile strength enhancement achieved with locust bean gum. The strength increase was ascribed to stronger bonds (60%), improved formation (25%) and a larger number of bonds (15%). Even though Leech's assessment was based on very simplified assumptions, it can be assumed that the contribution of shear bond strength is also the most important factor in the present investigation.

## Conclusions

The effect of CMC attachment on some basic fibre and sheet properties was examined in order to clarify the mechanisms behind the strength-enhancing ability of CMC. It was concluded that several factors contribute to the positive effect of CMC on tensile strength. Surface

carboxymethylation was shown to increase the relative bonded area, but on a small-scale structural level detectable only by BET-analysis and not by light-scattering measurements. The sheet density remains unaffected by the CMC treatment. The shear bond strength per unit area, calculated from Page's equation, was shown to significantly increase as a result of surface carboxymethylation. In order to use Page's equation to evaluate the effect of CMC on the shear bond strength, the RBA must be determined by BET-analysis. The positive effect of surface carboxymethylation on the fibre shape and on the formation also contributes to the increase in tensile strength

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