

# On the nature of joint strength of paper – Effect of dry strength agents – Revisiting the Page equation

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**KEYWORDS:** Fibre-fibre bonding, Joint strength, Cationic starch, Carboxymethyl cellulose, Ionic groups, Microfibrillar cellulose, Nanofibrils, Nanofibrillar cellulose, Page equation, Interlaminar shear strength, Z-strength, BET surface area.

**SUMMARY:** This report deals with the effects of various chemical-treatments – carboxymethylcellulose-grafted (CMC) pulp in different ionic forms ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Al}^{3+}$ ), cationic starch, anionic polyacrylamide, and microfibrillated cellulose (MFC) as well as PFI-refining on the strength properties of never-dried bleached softwood kraft pulp. The general in-plane strength properties were measured together with z-strength and interlaminar shear strength. The sheet density was varied by pressing the wet sheets to various dry solids content. The relative bonded area of the sheets was determined by the BET surface area of the sheets using krypton adsorption.

Interlaminar shear strength is introduced as a measure for fibre-fibre bond strength and validates its use in the Page equation from first principles and it was shown to hold over a large range of tensile strengths. Only at very high tensile index values the calculated tensile index deviated from measured tensile index. This was most likely due to a shift from adhesive to cohesive failure of the joint. The various strength reinforcement methods used were all based on carbohydrate based additives and for those additives the specific joint strength was found to be independent of the specific additive, so the strength reinforcement is only related to the increased relative bonded area upon the addition of the strength adjuvant, although the additives consolidate the sheet on various structural levels.

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Throughout the papermaking history, papermakers have used dry strength additives in papermaking in order to reinforce paper/board materials, enhance printability etc. The mechanisms by which dry strength resins reinforce paper have been discussed in several classical contributions (Swanson 1956; 1961; Reynolds 1980; Robinson 1980; Eklund, Lindström 1991; Marton 1991) as well as in more recent accounts (Lindström et al. 2005). These investigations have discussed the effects of these additives on fibre-fibre bond strength and other fibre-structural features such as sheet formation etc.

Paper materials are random networks composed of ligno-cellulosic fibres with an appreciable strength. The basic factors affecting the strength of paper materials are (Lindström et al. 2005; Mäkelä 2009):

- Fibre tensile strength and length of fibres
- The specific bond strength (SBS) between fibres
- The relative bonded area (RBA)
- The structural features such as paper formation, fibre kinks, material distribution in the z-direction etc.
- Residual stresses on different levels: i.e. z-direction gradients, micro compressions etc.
- The straining/restraint during drying

Dry strength additives are expected to affect the specific bond strength (SBS) and the relative bonded area (RBA) in the sheet, but very little information is known about the relative importance of dry strength resin on SBS and RBA and other factors, although there have been some historical attempts to quantify these effects (Leech 1954).

Obviously, some mathematical modelling of paper strength is needed in order to sort out these effects, and it was not until the development of the Page equation (Page 1969) a useful concept was created.

One central problem when elucidating the effects of dry strength resins on paper strength is that the effects of these agents are comparatively small and that such additives also affect retention and formation of the paper sheet, which often obscure the effects of these additives.

New powerful chemical adjuvants such as fibre-surface modification of cellulose by the attachment of carboxyl-methylcellulose (CMC) and polyelectrolyte multilayering (also referred to as layer-by-layer assembly, LbL) (Lindström et al. 2005), as well as the emergence of various nanotechnologies based on nanocellulosic materials (Klemm et al. 2011), have now facilitated the evaluation of the effectiveness of chemical additives as their relative effects have previously been small, often within the experimental error of the experiments.

Dry strength treatments are not expected to affect the flexibility of fibres, but are expected to affect the SBS and the RBA as well as the sheet consolidation process. Many dry strength agents may be classified as gelatinous mucilages, from which it is hypothesized that they may stabilize the water meniscus during drying, by delaying the breakage, because of the higher viscosity of the meniscus, until a higher dry content is achieved. This concept goes back to the classical consolidation experiments by Lyne and Gallay (1954).

Hypothetically, a dry strength agent could be a pure consolidation agent, and hence the dry strengthening effect should be similar to that of wet pressing, albeit the fact that consolidation during wet pressing may take place on different structural levels compared to consolidation through chemical additives.

It has also been shown that certain adjuvants may decrease the build-up of stress concentrations during drying (Lindström et al. 1985; Gimåker et al. 2011). Hence, there are now at least three separate mechanisms by which dry strength agents may work, separately or in combinations (Lindström et al. 2005):

- By enhancing the consolidation of the sheet by affecting the Campbell forces on various structural levels during sheet consolidation
- By increasing the specific bond strength
- By decreasing the stress concentrations in the sheet

When the effect of dry strength resins are being evaluated, care must be taken to control and minimize the variations of variables such as: Sheet formation, fines retention and fibre curl and kinks.

There is a reasonably good understanding of how fibre strength, fibre length, fibre curl, fibre kinks, and fibre distribution (sheet formation) affect paper strength, but very little is known about the nature of the specific bond strength and how the RBA and the SBS are affected by various chemical adjuvants, see e.g. (Robinson 1980a; Uesaka 1984; Stratton 1991b).

The concept of RBA goes back to fairly established procedures developed by Thode and Ingmansson during the late 1950s (Thode and Ingmansson 1959).

It is obvious that an equation describing the strength of paper, invoking the above mentioned variables, would be enormously complex.

A simplified approach, the Page equation (see Eq 1), which describes the relationships between fibre strength, fibre length, SBS and RBA has been formulated, assuming a random distribution of straight fibres in a sheet with good formation (Page 1969). Page indirectly validated his equation, using data from the current literature using the light scattering coefficient to determine the RBA and indirect measurements of the SBS.

The historical context of the Page equation has also been examined (El-Hosseiny and Abson 1983) and the shear-lag approach (Carlsson, Lindström 2005) is an alternative framework, but leads to the same basic structure as the original Page equation. The Page equation has over the years, been shown to be a useful tool for strength analysis/evaluation of bonding potential of kraft pulps see e.g. (Jones 1972; Seth 1990; Stratton 1991a; Dasgupta 1994; Paavilainen 1994).

Indeed, the Page equation has also been used as an evaluation tool for the investigation of the effects of dry strength resins, such as cationic starch (Gaspar 1982; Howard and Jowsey 1989). In one investigation, it was, for instance, claimed that the effects of cationic starch it is due to an increased SBS (Howard and Jowsey 1989). There have also been attempts to extend the Page formula to include the values for fibre coarseness, fibre cohesiveness, and wet compactability (Clark 1973). These efforts have, however, not been followed up in the literature.

The fibre length, used in the Page equation is actually the effective fibre length, i.e. the average length of the load bearing elements within the sheet. It is only equal to the actual length of fibres, which are free from curl, kinks

and crimps (Page et al. 1985). Indeed, most of the improvements, with refining of the tensile strength of sheets made from previously dried kraft pulps arise from straightening of fibres and the removal of kinks such that the effective length of fibres within the sheet increases (Page et al. 1985). There will also be problems using the Page equation (Batchelor et al. 1996; Seth and Page 1996) with previously dried pulps unless the effective fibre length can be determined with accuracy and therefore never-dried pulps were used in this investigation. For straight fibres it has been shown that the measured length-weighted fibre length is a good indicator of the strength of the sheet (Pavilainen 1990), because the averaging process reduces the influence of the fines, which do not act as load bearing elements within the sheet but rather as a means of consolidating the sheet. It has become common practice to use the length-weighted fibre length in Page equation calculations.

The RBA is usually determined by the light scattering coefficient. Haselton (1955) early found that there was an excellent correlation between the RBA determined from the light scattering coefficient and data from BET-area determinations for different fibre populations. It was, however, found that when light scattering coefficient data, collected from CMC-grafted fibre populations (Duker and Lindström 2008) were compared with BET-area determinations on the same sheets there was no correlation between these data sets, because, sheet consolidation took place on the molecular level induced by CMC-grafting, which could only be traced in the BET-area determinations and not by the measurements of the light scattering coefficient.

There have also been successful efforts to avoid the determination of RBA data either from BET-area determinations or the scattering coefficient. Hence, Görres et al (Görres et al. 1989; Görres and Luner 1992; Görres et al. 1995) used the interactive multi-planar model (IMPM) (Kallmes et al. 1961) to derive a sheet structural parameter, which in concept is akin to the relative bonded area. Combining the IMPM-model with the Page equation allowed them to indirectly calculate the shear bond strength, which was well correlated with the measured bond strength.

The Page equation is given in Eq 1, using ISO nomenclature.

$$\frac{1}{\sigma_T^w} = \frac{9}{8 \cdot \sigma_{Zero}^w} + \frac{12 \cdot A \cdot \rho}{SBS \cdot P \cdot L \cdot RBA} \quad [1]$$

Where,

$\sigma_T^w$  = Tensile index, Nm/kg

$\sigma_{Zero}^w$  = Zero-span tensile index, Nm/kg

$A$  = Average fibre cross section, m<sup>2</sup>

$\rho$  = Density of the fibres, kg/m<sup>3</sup>

$SBS$  = Specific bonding strength, the shear bond strength per unit bonded area, Pa

$P$  = Perimeter of the fibre cross section, m

$L$  = Fibre length, m

$RBA$  = Relative bonded area in the sheet, %

The shear strength in this contribution was measured by two different methods as described in the methods section.

In this report, the SBS was calculated according to Eq 2 using the RBA, measured by BET-analysis.

$$\frac{\sigma_{Shear}}{RBA} = SBS \quad [2]$$

The Page equation then takes the following form:

$$\frac{1}{\sigma_T^w} = \frac{9}{8 \cdot \sigma_{Zero}^w} + \frac{12 \cdot A \cdot \rho}{\sigma_{Shear} \cdot P \cdot L} \quad [3]$$

This means that the Page equation can be used to calculate the tensile index, directly from first principles, if the interlaminar shear strength is determined.

If the same fibre material is used in the experiments and various dry strength additives are used, the inherent disadvantage of having various fibres with different fibre parameters is avoided.

The objective of this work was to investigate if the Page equation is useful for the analysis of how the SBS and sheet consolidation is affected by physiochemical grafting of fibres with CMC, starch additives, and MFC.

Firstly, this paper introduces interlaminar shear strength as a measure of for fibre-fibre bond strength and validates its use in the Page equation for the case when other parameters are kept constant. Secondly, it will be shown that the various carbohydrate additives merely function by consolidating the sheet, albeit at different structural levels.

## Materials and Methods

### Materials

In all experiments hand-sheet experiments using a never-dried (dry content around 40 wt-%) unrefined ECF-bleached softwood kraft pulp (Husum Kraft, Husum mills, M-real, Sweden) was used. Before use, the fines fraction was removed from the pulp using a Celleco-filter with a hole diameter of 100 µm.

For the physiochemical CMC grafting, a commercial CMC (Aquasorb A-500, Hercules, Sweden) was used. The CMC had a degree of substitution (DS) of approximately 0.4 and a molecular weight of approximately 700–1000 kDa (determined by HPLC by the supplier). Previous experiments have shown that this CMC has a very high surface selectivity  $(= (\text{Surface charge after grafting} - \text{Surface charge before grafting}) / (\text{Total charge after grafting} - \text{Total charge before grafting}))$  when grafted onto bleached softwood kraft pulps (surface selectivity: 75–100%).

The cationic starch (C-starch) used was Amylofax PW (DS = 0.035; Stalex, Sweden). The anionic polyacrylamide (A-PAM) was Percol 156 (charge density = 3.75 meq/g;  $M_w = 9 \times 10^6$ ; BASF, Germany) and the cationic polyacrylamide (C-PAM) was PL1520 (charge density = 1.73 meq/g;  $M_w = 7 \times 10^6$ ; Eka Chemicals, Sweden).

MFC was produced using a high hemicellulose sulphite pulp (Domsjö ECO Bright, Domsjö Fabriker AB, Sweden), the details of which has been described earlier (Pääkkö et al. 2007)

## Methods

### Pulp washing

The kraft pulp was first reslushed in deionised water in accordance to SCAN-C 18. Thereafter, the pulp was washed with deionised water on a Büchner funnel.

The pulp was washed to different counter-ion forms in different steps as follows:

**Hydrogen form ( $H^+$ ):** The pulp was immersed in 0.01 M HCl and the pH was adjusted to 2. The pulp was then soaked for 30 min and thereafter filtered and rinsed repeatedly with deionised water until the conductivity of the filtrate was below 5 µS/cm.

**Sodium form ( $Na^+$ ):** In order to wash the pulp to its sodium counter-ion form, the pulp was first washed to its hydrogen form and then transferred to its sodium form by soaking it in  $10^{-3}$  M  $NaHCO_3$ , at pH 9, for 30 min. Thereafter, the pulp was filtered and rinsed repeatedly with deionised water until the conductivity of the filtrate was below 5 µS/cm.

**Calcium form ( $Ca^{2+}$ ):** In order to wash the pulp to its calcium counter-ion form, the pulp was first washed to its sodium form and then to its calcium form by immersing the pulp in 0.05 M  $CaCl_2$  and left it to stand for 15 min. The pulp was then filtered and rinsed with deionised water until the conductivity of the filtrate was below 5 µS/cm.

**Aluminium form ( $Al^{3+}$ ):** In order to wash the pulp to its aluminium counter-ion form, the pulp was first washed to its sodium form and then to its aluminium form by immersing the pulp in 0.001 M  $AlCl_3$  at pH 5.0–5.5 for 30 min. The pulp was then filtered and rinsed with deionised water until the conductivity of the filtrate was below 5 µS/cm.

### Physiochemical grafting of CMC onto pulp

The CMC attachment, here termed physiochemical grafting, was performed on each pulp as described by Laine et al. (2000) and with conditions presented in Table 1.

In order to improve mixing between pulp and CMC, the CMC was dissolved in deionised water (5 g CMC/l) and the solution was stirred over night before use.

Before the grafting the pulp was set to its calcium form. The pulp was then mixed with the CMC solution and with  $CaCl_2$ . The pH was set to 8 using NaOH. The mixture was then inserted to an autoclave. The autoclave was heated up under constant agitation in a glycol bath which had a constant temperature of 120°C. After the two hours long grafting process, the pulp was washed with deionised water on a Büchner funnel until the conductivity in the filtrate was below 5 µS/cm.

The results from the grafting are shown in Table 2. The total amount of grafted CMC was calculated from the total charge density increase to be 20.6 mg/g ( $\pm 1$  mg/g), that is, the grafting efficiency can be considered as quantitative. The surface selectivity of the grafting was found to be 88%, i.e. most of the CMC was being attached onto the surface of the fibres. As reference, an untreated pulp washed to its  $Ca^{2+}$  form was used.

Table 1 - CMC physiochemical grafting conditions.

Water type	Deionised water
Pulp concentration	25 g/l
Electrolyte concentration (CaCl <sub>2</sub> )	0.05 M
CMC addition	20 mg CMC/g fibre
pH	8
Grafting temperature	120°C
Grafting time	120 min

### Sheet-forming

Before sheet forming the CMC grafted pulp was transferred to its Na<sup>+</sup>, Ca<sup>2+</sup> and Al<sup>3+</sup>-form, respectively, as described above and the reference pulp to its Ca<sup>2+</sup> form. Isotropic 80 g/m<sup>2</sup> hand sheets were formed, using deionised water (SCAN-C 26:76). Different structural densities were achieved by pressing each sheet for 5 min at different pressing levels (50, 100, 200, 400, 600, and 800 kPa; the reference was not pressed with 50 kPa).

In another series of experiments pulps were first refined in a PFI-refiner (ISO 5264-2) with 0, 500, and 2000 rev.. In this series of experiments, 2 and 5 wt-% C-starch was added to the stock before sheet-making. A-PAM was added (0.1 wt-% addition) as a co-adjuvant in order to secure quantitative retention of the cationic starch. Different structural densities were obtained by pressing each sheet for 5 min at different pressing levels (100, 200, 400, 600, and 800 kPa).

In a third series of experiments, MFC was added in quantities of 2, 5, 10, and 20 wt-%. As a retention aid, 0.04 wt-% C-PAM was used. In this series of experiments the sheets were pressed for 5 min at different pressing levels (200, 400, and 800 kPa; the 5 and 10 wt-%-MFC-sheets were only pressed with 400 kPa).

All pressed sheets were then dried under restraint at 23°C and 50% RH.

### Conductometric titration

The total amount of anionic groups (e.g. carboxyl acid groups) in the pulps was determined by conductometric titrations. Prior to the titration, the pulp was washed to different counter-ion form as described above. The pulp was first washed to its hydrogen form, then to its sodium form and finally to its hydrogen form again. The total charge densities of the pulps were then determined using conductometric titration according to the procedure described by (Katz et al. 1984).

By comparing the result from the conductometric titration of the CMC pulps with the result from the conductometric titration of the reference pulp, the amount of attached CMC could be determined (Eq 4).

$$\text{Attached CMC} = 100 \cdot \frac{q_{\text{CMC}} - q_{\text{Ref}}}{q_{\text{CMC-molecule}}} \quad [4]$$

Where,

$q_{\text{CMC}}$  = Total charge density of the CMC-pulp sample

$q_{\text{Ref}}$  = Total charge density of the reference pulp

$q_{\text{CMC-molecule}}$  = Charge density of the CMC molecule used.

### Polyelectrolyte titration

The surface charge density of the fibres was determined by the polyelectrolyte titration procedure optimised by (Horvath et al. 2006) from a method originally described by (Wågberg et al. 1985).

Table 2 - Total and surface charge of reference pulp and CMC-grafted (20 mg/g) pulp.

Pulp	Total charge (eq/g)	Surface charge (eq/g)	Charge ratio (surface/total)	Surface selectivity (%)
Reference	39.5	1.6	0.04	-
CMC pulp	83.6	37.2	0.44	88

### Retention of starch and microfibrillated cellulose

The retention of starch and microfibrillated cellulose measured by determining the sugar content in the white water using a standard colorimetric method (Dubois et al. 1956).

### Paper property evaluation

The paper properties were analysed by the following methods:

- Grammage: ISO 536:1995
- Structural density: SCAN-P 88:01
- Tensile properties: ISO 1924-3:2005
- Z-strength: According to Girlanda and Fellers (2007).
- Shear strength: two methods were used, depending on the sheet strength. For weak sheets the strip shear test (SST) was used (Nygårds et al. 2009). For stronger papers, the rigid block shear test (RST) was used (Fellers 1977; Nygårds et al. 2009).

### Determination of RBA

To evaluate the BET area of the sheets, BET-analysis was performed using the Micromeritics ASAP 2020 Surface Area and Porosity Analyser equipment (Micromeritics Instrument Corporation, USA). The paper samples to be analyzed were cut into pieces, typically weighing 4 g. Before the actual measurements, the sample strips were degassed in two steps. In the first step, the samples were placed in a vacuum oven at 117°C for at least 18 h. Then the samples were further degassed in the degas station in the BET-equipment at 117°C for 3 h. Finally, the samples were transferred to a 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 ( $p/p_0 = 0.05-0.02$ ), 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 can then be calculated according to Eq 5, (Ingmansson and Thode 1959; Thode and Ingmansson 1959).

$$RBA_{\text{BET}} = \frac{BET_0 - BET}{BET_0} \quad [5]$$

Where,

$RBA_{\text{BET}}$  = Relative bonded area measured with BET.

$BET_0$  = BET area for a sheet with tensile strength zero. The value is obtained by extrapolating the trend line for the BET area versus tensile index to zero tensile index.

$BET$  = BET area for the investigated paper.

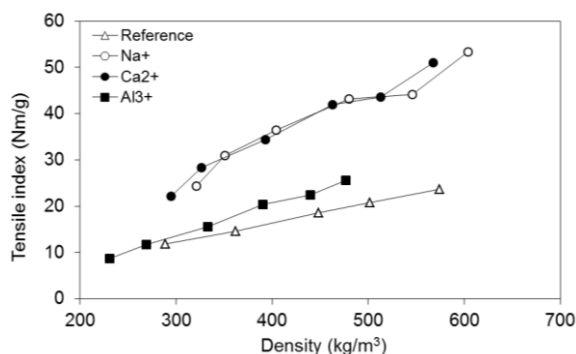


Fig 1 - Tensile index versus structural density for the investigated pulps. Bleached kraft pulp grafted with 2 wt-% CMC in different ionic forms ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ) and pressed to different densities.

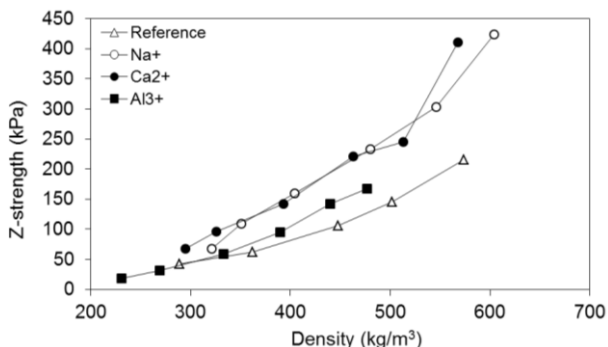


Fig 3 - Z-strength versus structural density for the investigated pulps. Bleached kraft pulp grafted with 2 wt-% CMC in different ionic forms ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ) and pressed to different densities.

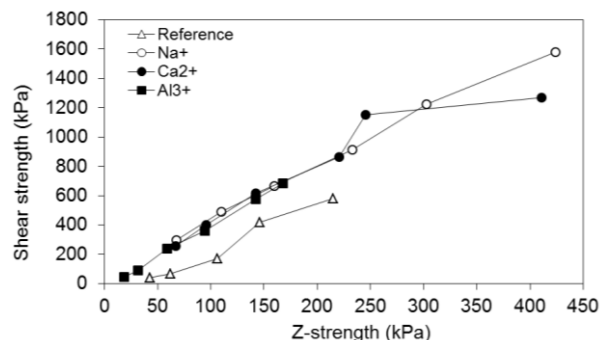


Fig 5 - Interlaminar shear strength versus z-strength for the investigated pulps. Bleached kraft pulp grafted with 2 wt-% CMC in different ionic forms ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ) and pressed to different densities.

It should be noted, however, that this classical definition of the RBA does not take into account that the lumen surface area should be conceived as non-bonding and should theoretically be withdrawn in the calculation of the RBA-values. This correction has been ignored, because it is very difficult to measure the lumen surface area independently.

Likewise, it can be noted that the Ingmansson and Thode definition to  $BET_0$  has been discussed and questioned by He et al. (2007).

The BET gas adsorption method has also been questioned (Hirn et al. 2013) recently, but not shown to be wrong, so the authors think it is fair to use classical models.

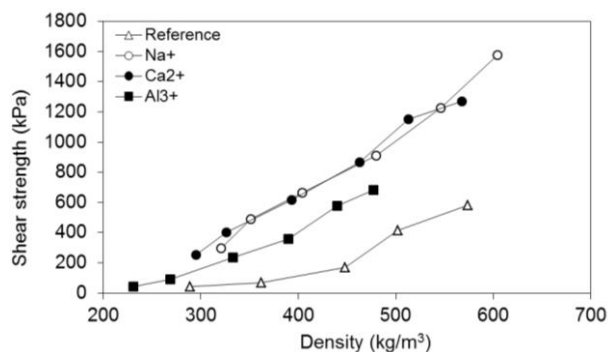


Fig 2 - Interlaminar shear strength versus structural density for the investigated pulps. Bleached kraft pulp grafted with 2 wt-% CMC in different ionic forms ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ) and pressed to different densities.

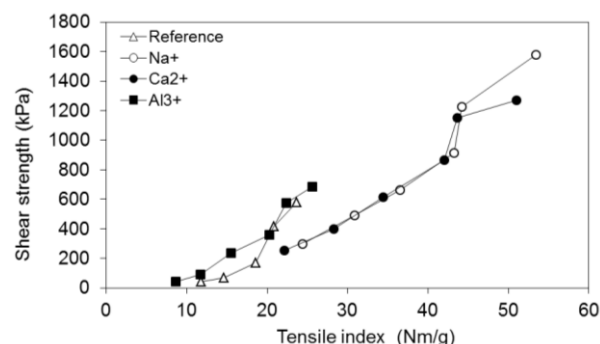


Fig 4 - Interlaminar shear strength versus tensile index for the investigated pulps. Bleached kraft pulp grafted with 2 wt-% CMC in different ionic forms ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ) and pressed to different densities.

## Results

The results from the experiments using the three series of experiments are reported as follows: The first series with physiochemical grafting of CMC in different ionic forms, the second series of experiments with PFI-refining and additions of cationic starch (and A-PAM) and a third series with addition of MFC. They will here be reported in separate sections below.

### The effects of physiochemical grafting of CMC in different ionic forms on paper strength properties

A first series of experiments were conducted using a never-dried bleached kraft pulp, from which the fines fraction had been removed and grafted with CMC, and transferred to different ionic forms ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ), formed into lab-sheets, pressed at a range of different pressing levels and dried under restraint.

Fig 1 shows how the tensile index of sheets made from a bleached kraft pulp grafted with 2 wt-% CMC ( $DS = 0.4$ ) is affected by the ionic form of the pulp. Several observations can be made. The strongest sheets were those in their  $\text{Na}^+$ -form or  $\text{Ca}^{2+}$ -form, whereas, the pulps in their  $\text{Al}^{3+}$ -form formed the weakest sheets.

The sheet density is slightly increased for the pulps in their  $\text{Na}^+$ -form, whereas the density of the pulps in their  $\text{Ca}^{2+}$ -form are not affected by the grafting. Interestingly, the sheets in their  $\text{Al}^{3+}$ -form show a considerably lower extent of sheet consolidation.

In Fig 2–3 the shear strength and z-strength are plotted versus the sheet density. Comparing all four strength data

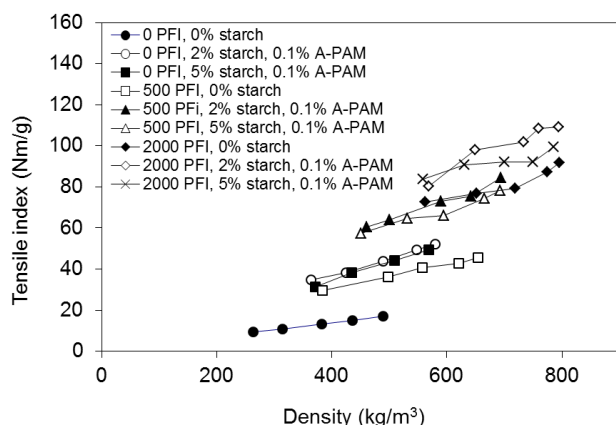


Fig 6 - Tensile index versus structural density for pulps beaten to different degrees in a PFI-refiner, after which the pulps were treated with C-starch and an A-PAM as a co-adjutant. The sheets were then pressed to different densities

( $\text{Na}^+$ ;  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ , and reference) a consistent picture emerges and that is that the strength decreases in the following order:  $\text{Ca}^{2+} \approx \text{Na}^+ > \text{Al}^{3+} > \text{reference}$  sheets. Finally, the interlaminar shear strength and z-strength is given vs the tensile index in Fig 4–5.

### The effects of refining and C-starch additions on strength properties of paper

A second series of experiments were conducted in a similar way, using the never-dried bleached kraft pulp, from which the fines fraction had been removed and refined to different levels (0, 500, and 2000 PFI-ref.).

To these pulps, various amounts of cationic starch (0, 2, and 5 wt-% C-starch) were added and sheets formed and pressed to various densities. In order to retain fines and C-starch, a retention adjuvant was used (0.1 wt-% A-PAM) in order to get an almost quantitative (>90 wt-%) retention of both C-starch and fines. The sheets were then dried under restraint and tested for their mechanical properties.

The tensile strength, shear strength, and z-strength versus sheet density are plotted in Fig 6–8. As expected the strength properties increase with refining, wet pressing, and increasing amount of strength adjuvant in the paper sheets. In Fig 9 and 10, interlaminar shear strength is displayed against tensile index and z-strength, respectively.

### The effects of adding MFC on strength properties of paper

A third series of experiments were conducted in a similar way, using the never-dried bleached kraft pulp, from which the fines fraction had been removed, and using different addition levels of MFC.

To these pulps, various amounts of MFC (0, 2, 5, 10, and 20 wt-%) were added and sheets formed and pressed to various densities (see the experimental section, for pressing levels in this series). In order to retain the MFC, a retention adjuvant was used (0.04 wt-% C-PAM) in order to get an almost quantitative (>90 %) retention of MFC. The sheets were then dried under restraint and tested for their mechanical properties. The effect of different additions of MFC on tensile index, interlaminar shear strength and z-strength are plotted in Fig 11–13.

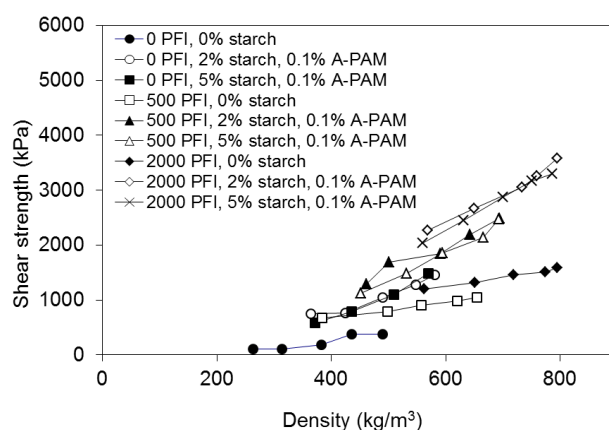


Fig 7 - Interlaminar shear strength versus structural density for pulps beaten to different degrees in a PFI-refiner, after which the pulps were treated with C-starch and an A-PAM as a co-adjutant. The sheets were then pressed to different densities.

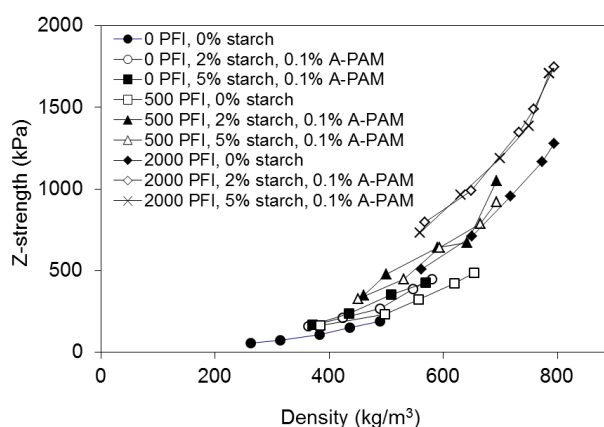


Fig 8 - Z-strength versus structural density for pulps refined to different degrees in a PFI-refiner, after which the pulps were treated with C-starch and an A-PAM as a co-adjutant. The sheets were then pressed to different densities.

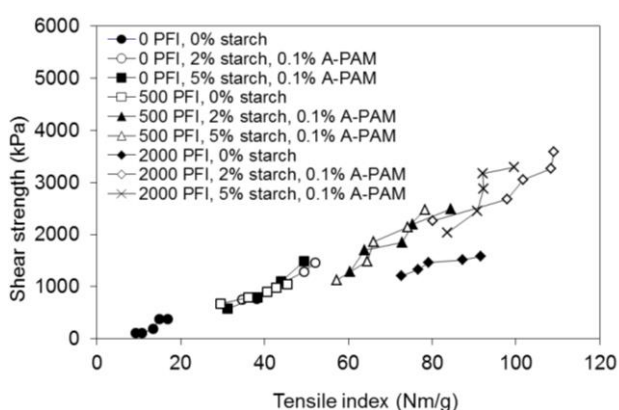


Fig 9 - Interlaminar shear strength versus tensile index for pulps beaten to different degrees in a PFI-refiner, after which the pulps were treated with C-starch and an A-PAM as a co-adjutant. The sheets were then pressed to different densities.

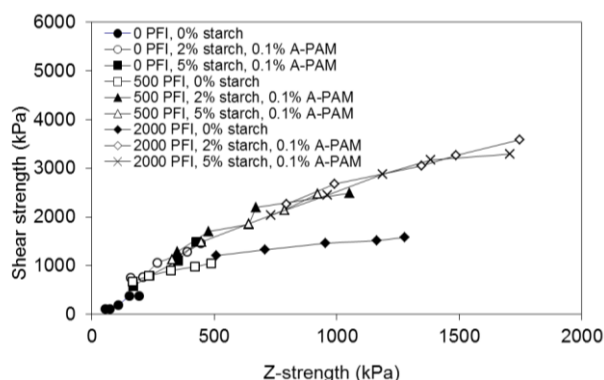


Fig 10 - Interlaminar shear strength versus z-strength for pulps beaten to different degrees in a PFI-refiner, after which the pulps were treated with C-starch and an A-PAM as a co-adjutant. The sheets were then pressed to different densities.

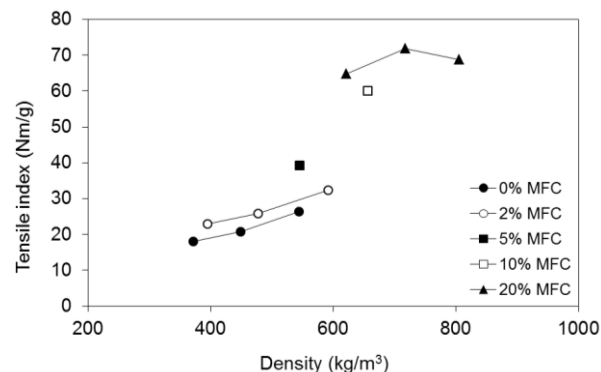


Fig 11 - Tensile index versus structural density for papers made with different additions of MFC. The sheets were also pressed to different densities.

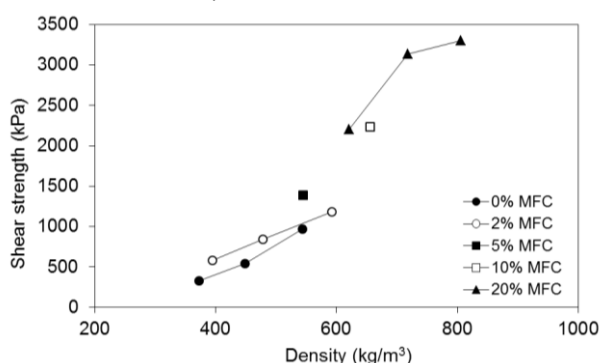


Fig 12 - Interlaminar shear strength versus structural density for papers made with different additions of MFC. The sheets were also pressed to different densities.

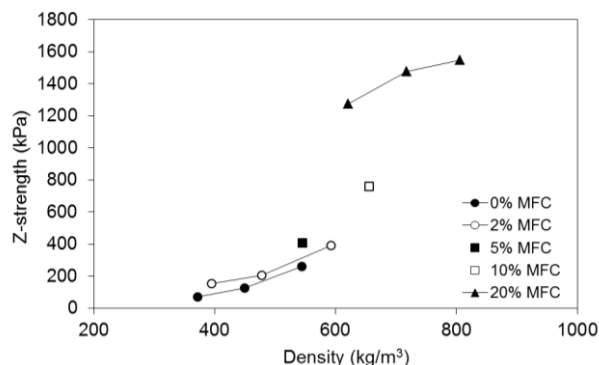


Fig 13 - Z-strength versus structural density for papers made with different additions of MFC. The sheets were also pressed to different densities.

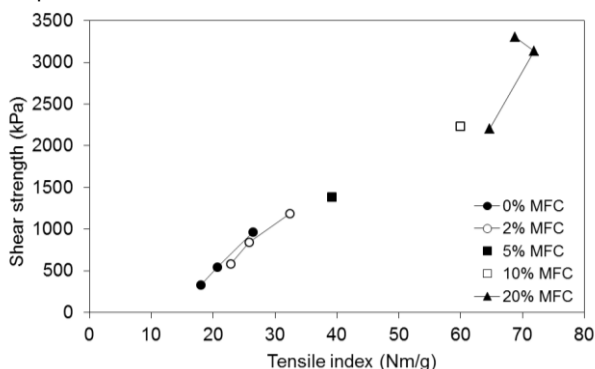


Fig 14 - Interlaminar shear strength versus tensile index for papers made with different additions of MFC. The sheets were also pressed to different densities.

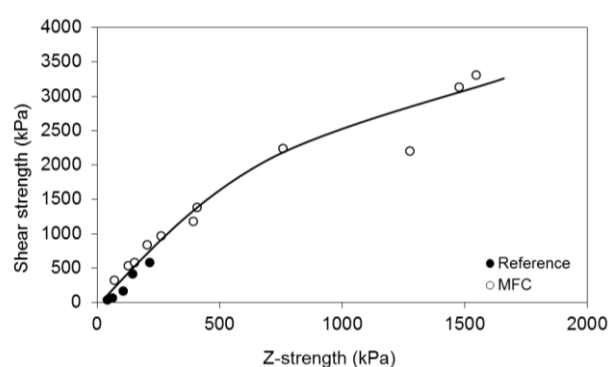


Fig 15 - Interlaminar shear strength versus z-strength for papers made with different additions of MFC. The sheets were also pressed to different densities.

Finally, the shear strength versus tensile index and shear strength versus z-strength are plotted in Fig 14–15.

## Discussion

The Page equation can be analysed by inserting relevant data for the parameters as well as the shear-strength, see Eq 3. The inherent advantage is that the same fibre parameters can be used for the bleached softwood kraft pulp. It is important to note that in the series with refining and C-starch additions, the same parameters were used for the refined pulps, which in itself is not entirely correct, but it does not affect the conclusions to be drawn.

For a bleached kraft pulp, the following values of the parameters were taken from a previous investigation from this laboratory (Duker and Lindström 2008) (the same, fines free, never-dried, unbeaten bleached kraft pulp was used in this investigation):

$$A \text{ (cross-sectional area of fibres)} = 2.4 \times 10^{-6} \text{ cm}^2$$

$$\rho = 1.56 \text{ g/cm}^3$$

$$g = 981 \text{ cm/s}^2$$

$$P \text{ (perimeter)} = 9 \times 10^{-3} \text{ cm}$$

$$\lambda \text{ (mean fibre length)} = 0.26 \text{ cm}$$

$$Z_0 = 1.5 \times 10^6 \text{ cm}$$



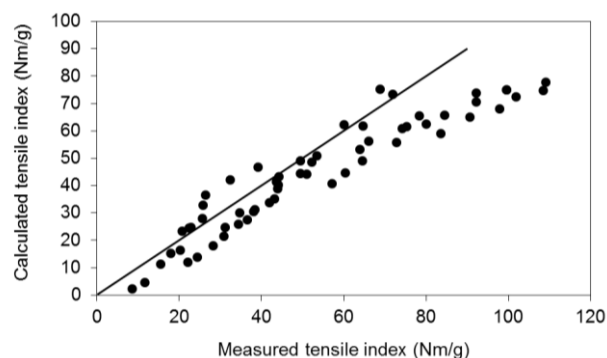


Fig 16 - Calculated versus measured tensile index from the Page equation for the investigated pulps.

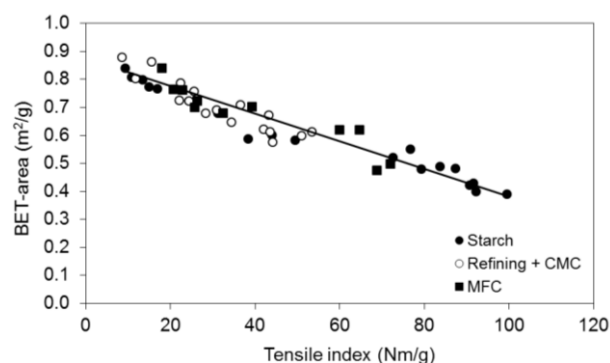


Fig 18 - BET-areas versus tensile index versus selected papers from the three series of data.

Using these values and the shear-strength values a prediction was made for the tensile index. As shown in *Fig 16* the prediction of the tensile strength properties of paper is surprisingly good. There is a deviation for the prediction of the strength at high tensile strength, but this deviation is most likely due to the cohesive nature of the joint at high tensile strengths. The Page equation was derived for adhesive failure and not for cohesive failure. The switch from adhesive failure to a cohesive failure in paper materials has among other authors been discussed in some detail by Nanko and Ohsawa (1989).

The performed type of attempt to validate the Page theory from first principles, using the shear strength and for the specific bond strength determination is novel, and cannot be found elsewhere in the literature. Regarding the importance of the shear strength for the tensile index, von Byrd (1989) reports a linear relationship between these properties for Southern Pine, but did not attempt to fit the data to the Page equation from first principles. To illustrate the linear relationship of the data in the current report the data from the different trial series (*Fig 4*, *9*, and *14*) has been plotted together in *Fig 17*.

It was also found that the BET-areas are linearly correlated with the tensile strength, see *Fig 18*. This implies that tensile index is only determined by the relative bonded area and not the specific bond strength. At the first moment, this may appear somewhat surprising, but it should be considered that the strength adjuvants used in all three series of experiments were carbohydrates, so there may be only smaller differences between the SBS for these additives, even though they

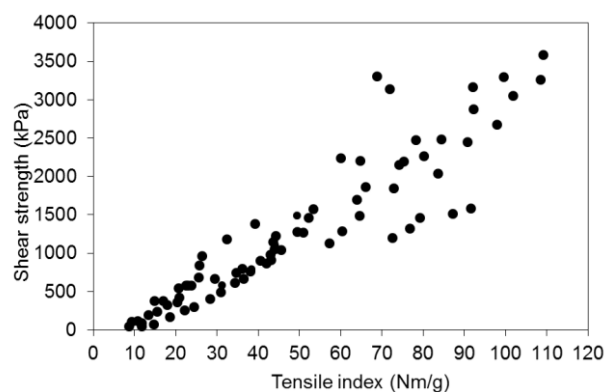


Fig 17 - Interlaminar shear strength versus tensile index for all data points plotted in *Fig. 4*, *9*, and *14*.

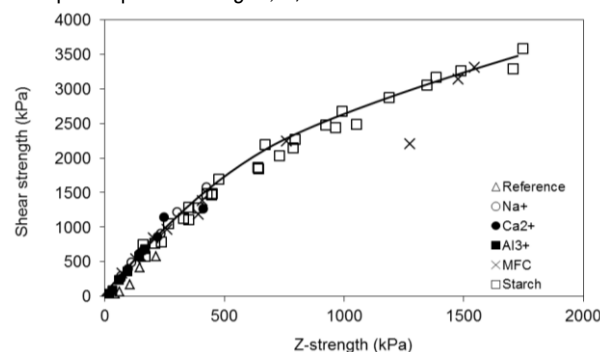


Fig 19 - Interlaminar shear strength versus z-strength for all investigated data-sets: CMC-grafted fibres in different ionic forms, C-starch additions and additions of MFC. The sheets were pressed to different densities.

have different charge. Experiments with different strength adjuvants, such as synthetic additives may show a different picture and may be of interest to explore in future studies.

The strength improvements by adding C-starch and A-PAM or MFC were all associated with an increased sheet density. It is likely that additives having a larger interactive entity, like MFC or C-starch/A-PAM complexes will bridge larger spaces in the wet sheet so that the capillary forces during consolidation will consolidate the sheet on a larger structural level, also associated with a density increase, whereas grafted molecules will predominantly consolidate the sheet on a molecular level associated with an increase in the RBA but not with an increase in the sheet density (compare also Duker and Lindström (2008)).

Finally, in *Fig 19* it can be noticed that if the interlaminar shear strength is plotted versus the z-strength, there is a direct correlation for all data-sets, apart from the PFI-refining curves, which showed a slight deviation from this curve (compare *Fig 1*). Currently, it is not understood why there is such a good correlation, but from an engineering point of view, it's an important and interesting relationship.

## Conclusions

- This communication introduces interlaminar shear strength as a measure for fibre-fibre bond strength and validates its use in the Page equation for the case that other parameters are kept constant. There is a deviation from the equation for high strength materials, but this



behaviour can be understood from the cohesive nature of fibre joints in strong sheets and the fact that the Page equation was derived for adhesive joints and not for cohesive joints.

- The various strength reinforcement methods used were all based on carbohydrate based additives (CMC, C-starch, and MFC) and for those additives the specific joint strength was found to be independent of the specific additive, so the strength reinforcement is only related to the increased RBA upon the addition of the strength adjuvant.
- Depending on the nature of the strength adjuvant, consolidation takes place on different structural levels. For CMC-grafted fibres, the consolidation (increased RBA), takes place on the molecular scale, whereas with starch complexes and MFC a significant consolidation takes place on the microscale. Consolidation on the molecular level does not increase sheet structural density, but consolidation on the microscale results in a significant increase in the sheet structural density.
- For the investigated data sets, the z-strength was intimately correlated with interlaminar shear strength, apart from the PFI-refining curves.

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