

The use of cationic starch and microfibrillated cellulose to improve strength properties of CTMP-based paperboard

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ABSTRACT

There is growing interest in using microfibrillated cellulose (MFC) as an alternative paper strength additive in papermaking, and in using chemi-thermomechanical pulp (CTMP) with high freeness in producing CTMP-based paperboard with high bulk properties. To achieve greater strength improvement results, particularly for packaging paperboards, different proportions of cationic starch (CS) or MFC can be used to significantly improve the z -strength, with only a slight increase in sheet density. Research in this area is exploring CS or MFC as potential strength additives in CTMP-based paperboard, which is interesting from an industrial perspective. The mean grammage of the CTMP handsheets produced was approximately 150 g m^{-2} , and it was found that blending CTMP with CS or MFC yielded handsheets with significantly improved z -strength, tensile index, and other strength properties at similar sheet densities. Blending CTMP with 5% TEMPO-based MFC increased the z -strength from 412 to 531 kN m^{-2} (a 29% improvement) at a sheet density of 522 kg m^{-3} and the tensile index from 38 to 43 kNm kg^{-1} . Blending CTMP with 20 and 10 kg t^{-1} of CS improved the z -strength to 605 kN m^{-2} (a 47% improvement) at a sheet density of 548 kg m^{-3} and to 527 kN m^{-2} (a 28% improvement) at a sheet density of 523 kg m^{-3} , respectively, and the tensile index to 60 and 51 kNm kg^{-1} , respectively. The z -strength also improved in 80% CTMP mixed with 20% sulphate pulp from 412 to 503 kN m^{-2} (a 91-unit increase) at a sheet density of 544 kg m^{-3} , for an improvement of approximately 22%. It is worth noting that though 100% sulphate pulp sheets had the highest z -strength (718 kN m^{-2}) and a high tensile index (59.5 kNm kg^{-1}), the sheet density was also the highest at 678 kg m^{-3} .

Keywords: *microfibrillated cellulose, cationic starch, chemi-thermomechanical pulp, strength additive, paperboard*

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1. Introduction

The art of papermaking has over two millennia of history, and the fibrous network of paper can be used in various applications such as paperboard, packaging, printing, writing, and hygiene paper products. Many researchers have demonstrated that microfibrillated cellulose (MFC) can be used in papermaking applications as a strength additive, to enhance barrier/coating properties, to improve paper gloss, and to reduce paper grammage. Turbak et al. (1983) and Herrick et al. (1983) were the first to research pulp fibre-derived MFC. MFC has been one of the hottest research fields of the past 10 years and has incredible properties such as high inherent strength and stiffness, a high aspect ratio, and a high specific surface area while being bio-based, biodegradable, sustainable, and lightweight. MFC is a family of nanocellulose materials that has been reviewed by various researchers (Hubbe et al., 2008; Siró and Plackett, 2010; Klemm et al., 2011; Abdul Khalil et al., 2012).

The demand for paperboard and other packaging materials are steadily increasing, as it is a more sustainable and eco-friendly material than the fossil based plastic materials. Paperboard packaging products provide crucial protection for various products. As paper strength properties are critical when paperboard must withstand high loads, there is research interest in seeking alternative methods for

improving the strength properties of paperboard materials. Regarding paper or paperboard strength development, it is well known that traditional methods such as refining or fibre beating improve flexibility and enhance the swelling ability, thereby improving the bondability and thus the strength properties of paper during formation. The main drawback of excess refining is that it could lead to paper densification, which could negatively affect the bending stiffness of paperboard.

It is well known that chemical additives such as starch can significantly enhance paper strength. Regarding cationic starch (CS) as a paper strength additive, [Howard and Jowsey \(1989\)](#) reported that 1–5% additions of CS were 75–85% retained and improved the bond strength per unit of the optically bonded area of the paper sheet, but with very little increase in the relative bonded area. [Howard and Jowsey \(1989\)](#) added 0–5% CS, blending it with pulp fibre suspension. Their results indicated that 1–2% CS was as good as 5% CS, noting very little variation between these amounts in terms of the sheet's apparent density, scattering coefficient, contact ratio, and breaking length. They also noted that the further addition of CS level from 4–5% CS did not greatly improve the strength properties, the optimal CS dosage being approximately 2%. They claimed that this optimal dosage was not determined by CS retention but rather by the diminishing effect of CS relative to its bonding ability, i.e., the bond strength per unit area.

[Wågberg and Björklund \(1993\)](#) used cellulosic fines to adsorb CS in bleached kraft pulps. They reported that never-dried fines could adsorb 120–150 mg CS g⁻¹ fines with a degree of substitution (DS) of approximately 0.015–0.03 g⁻¹ fines, while fines from dried pulp fibre could adsorb 200–250 mg CS g⁻¹ fines. Their main message was that CS adsorption is significantly controlled by the charge levels of the fines and fibres. They also reported that CS molecules must be adsorbed onto the fibres, fines, and MFC to be effective, so interaction is governed mainly by electrostatic forces between the negatively charged fibre material and the positively charged CS.

Comparative studies of the papermaking properties achieved by blending different grades of MFCs with pulp suspensions were reported by [Taipale et al. \(2010\)](#). They examined drainage behaviour as a function of the salt concentration, fixative type, pH, and type of MFC. They noted that mixing MFC with the pulp furnish significantly affected the drainage properties during papermaking. However, when investigating the influence of using cationic polyelectrolytes together with MFC, they noted that the drainage properties could be managed by using a certain dosage and combination of MFC and polyelectrolyte. They found that adding MFC reduced the drainage rate of the pulp suspension while significantly improving the mechanical strength of the resulting paper. [Taipale et al. \(2010\)](#) also reported that adding MFC to the pulp furnish improved the bonding property of the sheet because MFC has very thin fibrils and a high surface area. This means that the strength of the fibre network is improved by increasing the number of fibre–fibre bonds. They reported that CS with a DS of 0.035 is highly branched and, despite its high molecular weight, has a rather small radius of gyration that enables it to adsorb in a thin layer to the fibre surface.

The possibility of adding MFC to chemi-thermomechanical pulp (CTMP) fibre resources could add value in the mechanical pulping sector. The MFC used here was processed using a catalytic amount of the TEMPO/NaBr/NaClO system, and the resulting oxidised sulphite pulp fibres were subjected to high-shearing forces to produce sulphite pulp-derived MFC. Very few studies have examined the use of CS or MFC as strength additives in CTMP sheet-forming processes. Research into this problem area is exploring CS and MFC as potential strength additives in CTMP-based paperboard. In addition, for comparison purposes, we have considered the use of 100% sulphate pulp as well as a blend of 80% CTMP and 20% sulphate pulp to compare the improved strength properties of the CTMP-based paperboard relative to sheet densification. For simplicity, we generally use the abbreviation CS to refer to cationic starch and MFC to refer to TEMPO-based sulphite pulp-derived MFC.

2. Experimental

2.1. Pulp

The CTMP used here had a Canadian Standard Freeness value of approximately 400 mL and a Schopper-Riegler (SR) number of approximately 28; it was a softwood spruce CTMP from the SCA Östrand Pulp Mill (Sundsvall, Sweden). The sulphate pulp used was a flash-dried sulphate pulp, also from the SCA Östrand Pulp Mill. The sulphate pulp was pre-refined using an Escher-Wyss refiner at approximately 2% consistency, and the fibres were refined with a degree of beating of approximately 25 SR for all samples. The total charge measurements were made using conductometric titration according to the method described by [Katz et al. \(1984\)](#). The MFC was produced from a commercial sulphite softwood dissolving pulp (Domsjö Fabriker AB, Örnsköldsvik, Sweden) with very low hemicellulose (<5%) and lignin (<1%) contents.

Table 1 Total charge characteristics of the CTMP, sulphate pulp, and TEMPO-based MFC

Material	Total Charge ($\mu\text{mol g}^{-1}$)
CTMP	145
Sulphate pulp	90
TEMPO-based MFC	732

2.2. Cationic starch cooking

The trade name of the CS used here (DS, 0.065) was Solbond PC 65 (SOLAM GmbH, Emlichheim, Germany). In this work, 10 g of CS was added to 1 L of distilled water. While being stirred with a magnetic stirrer, the CS solution was heated to 95°C, being cooked for 30 min after the cooking temperature reached 88°C. Al foil was used to cover the beaker during cooking to retain heat in the beaker. The CS solution was then slowly cooled under ambient conditions. This procedure is as described by [Pettersson et al. \(2006a\)](#). Fresh CS solutions were prepared for every experimental trial to avoid the influence of CS degradation.

2.3. MFC processing

TEMPO-mediated oxidation was conducted using never-dried sulphite pulp according to the method described by [Saito et al. \(2006\)](#). The chemical oxidations were conducted using NaClO (Sigma-Aldrich, Stockholm, Sweden), NaBr (Sigma-Aldrich), and TEMPO (Sigma-Aldrich) catalysts. The dosage of NaClO used in these trials was 5 mmol NaClO g⁻¹ of cellulose. The pH was kept at 9–10 by adjustment with NaOH or HCl and the reaction time for the chemical oxidation was approximately 2 h. After the TEMPO-mediated oxidation, the pulp suspensions were thoroughly washed with distilled water and mechanically treated using the T-25 Ultra-Turrax high-speed homogeniser (IKA, Wilmington, NC, USA) to produce MFC. The homogenising equipment was set at 15,000 rpm for 60 min.

2.4. Sheet preparation and paper testing

The various laboratory handsheets were made according to the ISO 5269-2 method using a Rapid-Köthen sheet former (Paper Testing Instruments (PTI), Pettenbach, Austria). During the handsheet-making procedure, MFC was added to the CTMP fibre suspension and, after about 15 min of mixing, handsheets were formed. The same procedure was used for additions of CS to CTMP and of sulphate pulp to CTMP. The sheets were dried at 95°C at an applied pressure of 96 kPa for 10 min; paper testing was performed in the standard testing climate described in ISO 187, i.e., 23°C and 50% relative humidity. The CTMP was hot disintegrated. In this investigation, z-strength, tensile index, burst index, E-modulus, tensile energy absorption, strain at break, and sheet density were used to follow changes in strength properties, using standard methods. The final pulp concentration of the furnish was

approximately 6.0 g L⁻¹ and the mean grammage of the handsheets was 150 g m⁻². The aim of this work was to determine whether blending CTMP with sulphate pulp, CS, or MFC would significantly improve the paper strength properties of the resulting handsheets. The reference sheet in this work was 100% CTMP, while the dosage levels were as follows: 10 and 20 kg t⁻¹ of CS, 20% sulphate pulp, and 5% MFC. We finally prepared a 100% sulphate pulp sample to illustrate how the densities of chemical pulp sheets are higher than those of CTMP blended samples.

The handsheet properties were tested using standard procedures, as follows:

- grammage: ISO 5270
- thickness: ISO 5270
- tensile strength: ISO 1924-3
- bursting strength: ISO 5270
- z-strength: 15754

Table 2 Experimental conditions

Fibre furnish information	Amount/quality and properties
Primary pulp	CTMP
Cationic starch	10 and 20 kg t ⁻¹
MFC	5%
Sulphate pulp	20% and 100%
Handsheet grammage	150 g m ⁻²
Sheet densities	Approximately 450–700 kg m ⁻³
Paper strength properties	Z-strength, tensile index, burst index, E-modulus, tensile energy absorption, strain at break, and sheet density

3. Results and discussion

Apart from pulp fibre refining or beating, chemical additives (such as CS) have been used to improve mechanical strength properties during papermaking (Taipale et al., 2010). Tensile strength is measured as the relative bonded area (RBA) in the fibre network, and Page (1969) reported that the tensile strength of paper is dependent on the fibre length, fibre density, fibre strength, ratio of cross-sectional area to perimeter, fibre–fibre interaction, and RBA. Another way of improving paper strength is by blending pulp fibres with MFC, which has been recognised as a promising application area in the pulp and paper industry. The following researchers have explored the use of MFC as a strength additive in papermaking: (Eriksen et al. 2008; Taipale et al. 2010; Sehaqui et al. 2011; Hii et al. 2012; Gonzalez et al. 2013). Page (1969) stressed that the RBA of fibres is very important as it contributes significantly to the basic structural properties of paper. An equation for tensile strength development has been formulated (Page, 1969; Duker and Lindstrom, 2008). Hirn and Schennach (2015) have recently introduced a new method of quantifying bonding energies between pulp fibres during the papermaking process. In their work, they consider the following parameters: mechanical interlocking, capillary bridges, interdiffusion, hydrogen bonding, Van der Waals forces, and coulomb forces on the bonding energy.

In this study, the z -strength, tensile index, burst index, E-modulus, strain at break, and tensile energy absorption (TEA) results, all plotted against sheet density, are presented in Figures 1–6. It was noticed that blending CTMP fibres with sulphate pulp (20%), CS (20 and 10 kg t⁻¹), or MFC (5%) significantly enhanced the z -strength and tensile index with only a slight increase in the sheet density. It is well known that the z -strength is crucial when it comes to paperboard packaging products, and that there is a need to optimise the sheet densities at a given z -strength. In this work, we use cationic potato starch and anionically highly charged MFC (approximately 700 $\mu\text{mol g}^{-1}$). The idea of using CS and anionically charged CTMP fibres is that cations from the CS would have greater affinity to be attracted to and bind to the fibre surfaces; the TEMPO-based MFC, which is gel-like in texture, would help improve the bonding between the CTMP fibres.

The z -strength and tensile index results (Figures 1 and 2) for handsheets of CTMP blended with 5% TEMPO-based MFC indicate that the z -strength increased from 412 to 531 kN m⁻² (a 29% improvement) at a sheet density of 522 kg m⁻³, while the tensile index increased from 38 to 43 kNm kg⁻¹ (a 13% improvement). In sheets of CTMP blended with 20 and 10 kg t⁻¹ of CS, the z -strength increased to 605 (a 47% improvement) at a sheet density of 548 kg m⁻³ and to 527 kN m⁻² (a 28% improvement) at a sheet density of 523 kg m⁻³, respectively, while the tensile index improved to 60 and 51 kNm kg⁻¹, respectively. In sheets of 80% CTMP mixed with 20% sulphate pulp, the z -strength (Figure 1) increased from 412 to 503 kN m⁻² (a 91-unit or 22% improvement) at a sheet density of 544 kg m⁻³. In the 100% sulphate pulp sample, the z -strength was 718 kN m⁻², compared with 412 kN m⁻² in the reference 100% CTMP sample for a 306-unit or 74% improvement; the drawback, however, was the high sheet density of 678 kg m⁻³.

The z -strength results of using 5% MFC and of using 10 kg t⁻¹ of CS were approximately equal to that of using 80% CTMP blended with 20% sulphate pulp, except that the CTMP–sulphate pulp blend produced sheets with a rather high density. In comparison, the 100% sulphate pulp sample displayed much greater improvements in both the z -strength (718 kN m⁻²) and tensile index (59.5 kNm kg⁻¹), but at the cost of high sheet density, which is one reason we are trying to develop CTMP-based paperboard with high bulk properties. Regarding tensile strength (see Figure 2), it was observed that mixing 80% CTMP with 20% sulphate pulp enhanced the tensile index from 38 to 47 kNm kg⁻¹ (a 24% improvement); this can be compared with the results of blending CTMP with 10 kg t⁻¹ of CS (a tensile index of 51 kNm kg⁻¹) and with 5% TEMPO-based MFC (a tensile index of 43 kNm kg⁻¹).

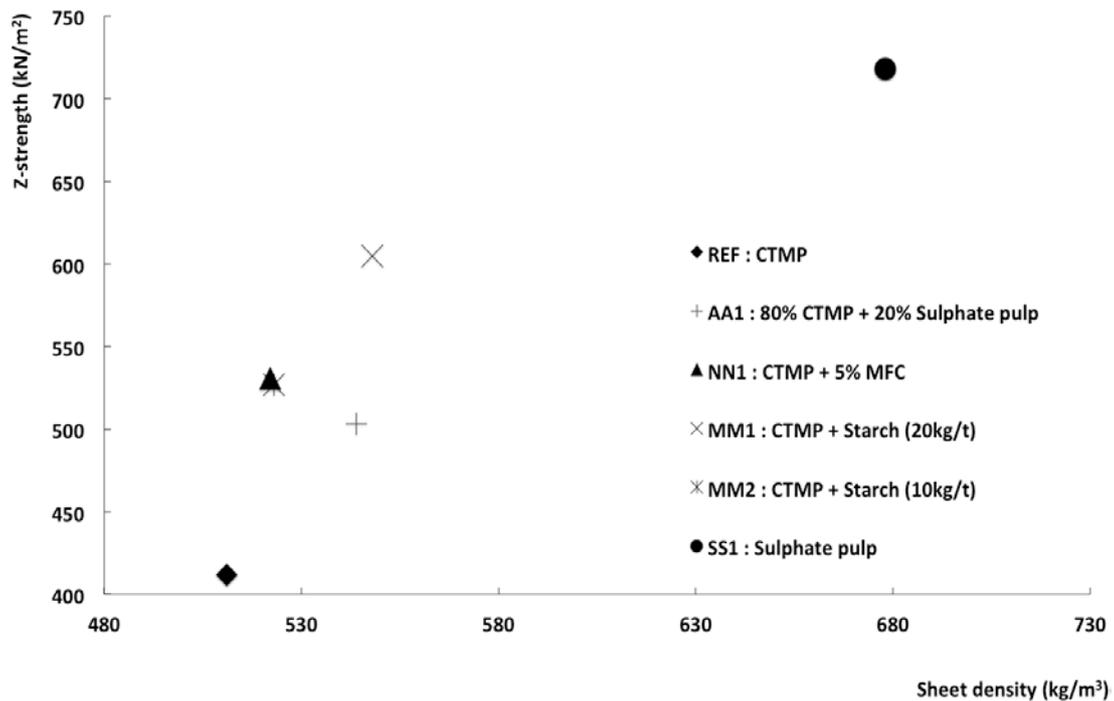


Figure 1. Z-strength as a function of sheet density

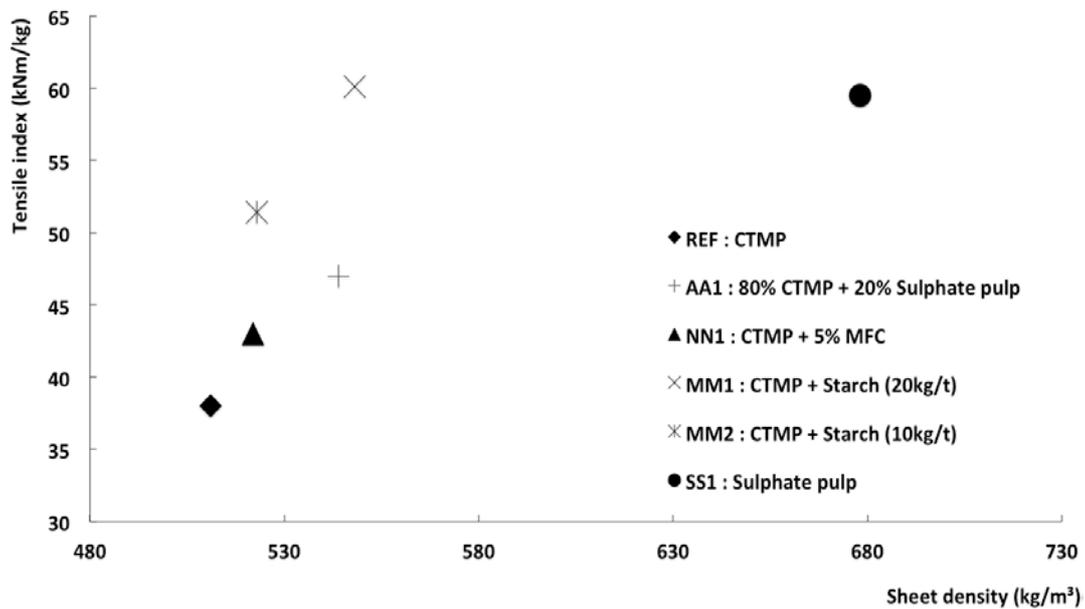


Figure 2. Tensile index as a function of sheet density

Pettersson et al. (2006a, 2006b) used CS and anionic carboxymethylcellulose (CMC) to improve the strength properties of CTMP-based paperboard. We learned from them that the progressive addition of sulphate pulp fibres to CTMP furnish resulted in more pronounced sheet densification, which led us to consider 20% sulphate pulp the optimal proportion of chemical pulp added to the CTMP fibre furnish. Our CS addition results are similar to theirs, though Pettersson et al.'s (2006a, 2006b) strategy was to use cationic potato starch and anionically charged CMC as means of significantly improving the Scott bond and tensile index values, with only a slight increase in sheet density (i.e., less densification), with the same suitability for paperboard applications. They used CMC because the chemical is commonly

used in tissue paper processing due to its high charge property, can retain high amounts of cationic wet strength resin in the sheet, and can significantly improve paper strength when used together with cationic polymers such as polyamidoamine-epichlorohydrin (PAE). Wågberg and Björklund (1993) previously noticed that 10 to 20 kg t⁻¹ (1–2%) of CS with a DS of 0.03–0.06 can be adsorbed onto bleached chemical pulp fibres before the fibre charges are consumed.

Figure 3 shows that there was an increase in strain at break with only a slight increase in sheet density in the handsheets of CTMP blended with 20 and 10 kg t⁻¹ of CS; the same applies for the handsheets of CTMP blended with 5% TEMPO-based MFC. The strain at break of the 100% sulphate-pulp handsheets was 3.45% compared with 1.58% for the reference sheet, for an improvement of approximately 118%. This is a greater improvement than the 2.35% achieved in the 20 kg t⁻¹ CS blended sample; however, it is worth noting that adding CS strengthens the paper with only a slight increase in sheet density (i.e., less densification), with the same suitability for paperboard applications. Regarding tensile energy absorption (TEA; see Figure 4), blending CTMP with 5% TEMPO-based MFC increased the TEA from 413 to 517 J kg⁻¹ (a 25% improvement) at a sheet density of 522 kg m⁻³. Blending CTMP with 20 and 10 kg t⁻¹ of CS increased the TEA to 964 J kg⁻¹ (a 133% improvement) at a sheet density of 548 kg m⁻³ and to 750 J kg⁻¹ (an 82% improvement) at a sheet density 523 kg m⁻³, respectively. The TEA also increased in 80% CTMP mixed with 20% sulphate pulp, from 413 to 700 J kg⁻¹ (a 287-unit or approximately 69% increase) at a sheet density of 544 kg m⁻³. In the 100% sulphate pulp sample, TEA increased by 1092 units relative to that of the reference, from 413 to 1505 J kg⁻¹, but with the drawback of high sheet density.

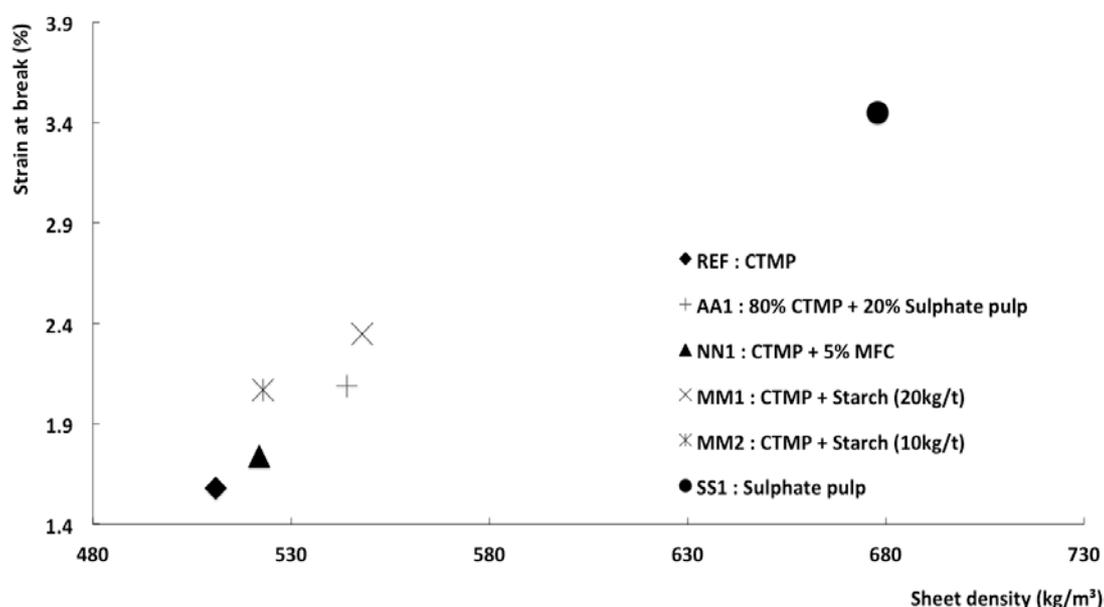


Figure 3. Strain at break as a function of sheet density

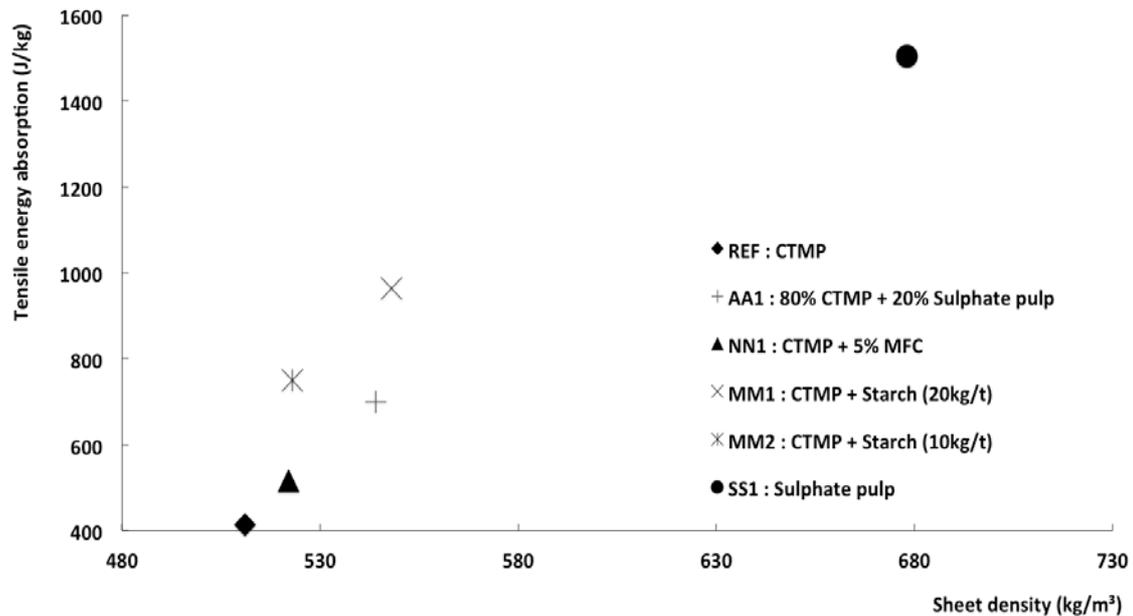


Figure 4. Tensile energy absorption as a function of sheet density

Ankerfors et al. (2014) used MFC as a strength additive in highly filled paper, conducting the work at pilot scale. Their results indicated that adding 2.5–5 wt% of MFC improved the strength of highly filled fine paper with a filler content of approximately 30%, z -strength being one of the most significantly improved parameters. They also explored the use of MFC and CS, which could further enhance the paper strength properties. By adding 5 wt% MFC and 5 wt% MFC + 2 wt% CS, Ankerfors et al. (2014) improved the tensile strength index to approximately 25 and 28 kNm kg⁻¹, respectively, at a filler content of 35%. This was an interesting result, because adding the 2% CS increased the tensile index by just 3 units at a 35% filler content. In the present work significant improvement was achieved by adding CS alone, which enhanced the strength largely due to the attraction between the cations of CS and the anions of CTMP fibres, and it appeared that a strength improvement plateau was reached at the 20 kg t⁻¹ level of CS addition. Regarding the z -strength, at a 35% filler content, Ankerfors et al. (2014) improved the z -strength to approximately 600 kPa by adding 5% MFC + 2% CS, while by adding 5% MFC alone, they still attained a z -strength of approximately 500 kPa. However, it is important to consider these strength levels relative to the respective sheet densities, which is one reason why we embarked on the present study. Ankerfors et al. (2014) did not emphasise the sheet densities, and the 5% MFC blended pulp sheet had a density of 800 kg m⁻³ while the 5% MFC + 2% CS blended pulp sheet had a density of 780 kg m⁻³. Given these two sheet densities, one would expect at least the much higher strengthening effect of the 5% MFC, as compared with that of the 5% MFC + 2% CS.

Paper strength development as a result of fibre beating was reported by Duker et al. (2007). Laine et al. (2002) stated that CMC, gums, and starches could be used as strength additives in the papermaking process. Mohlin and Alfredsson (1990) reported the effect of pulp fibre deformation on paper properties. The chemical properties affecting fibres during papermaking using both chemically and mechanically processed pulp fibres were reviewed by Lindström (1992). There is a growing trend towards using nanocellulose as an alternative paper strength additive in biomass-derived cellulose fibres. Paper strength development is influenced by several factors, including fibre length, specific bond strength, and fibre–fibre bonded area. Saito and Isogai (2007) used TEMPO-oxidised pulps together with cationic polymers such as polyacrylamide and polyvinylamine to enhance the wet strength of paper sheets. They claimed that the wet strength improvement was due to chemical interaction between the aldehyde groups present in the TEMPO-oxidised fibre and the cationic polymers in the sheets.

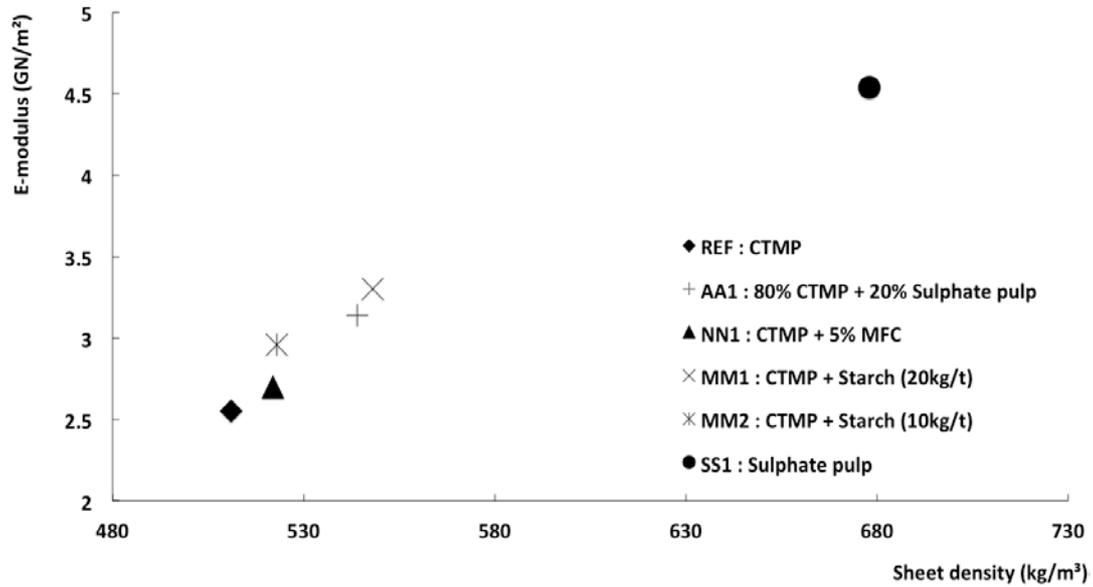


Figure 5. E-modulus as a function of sheet density

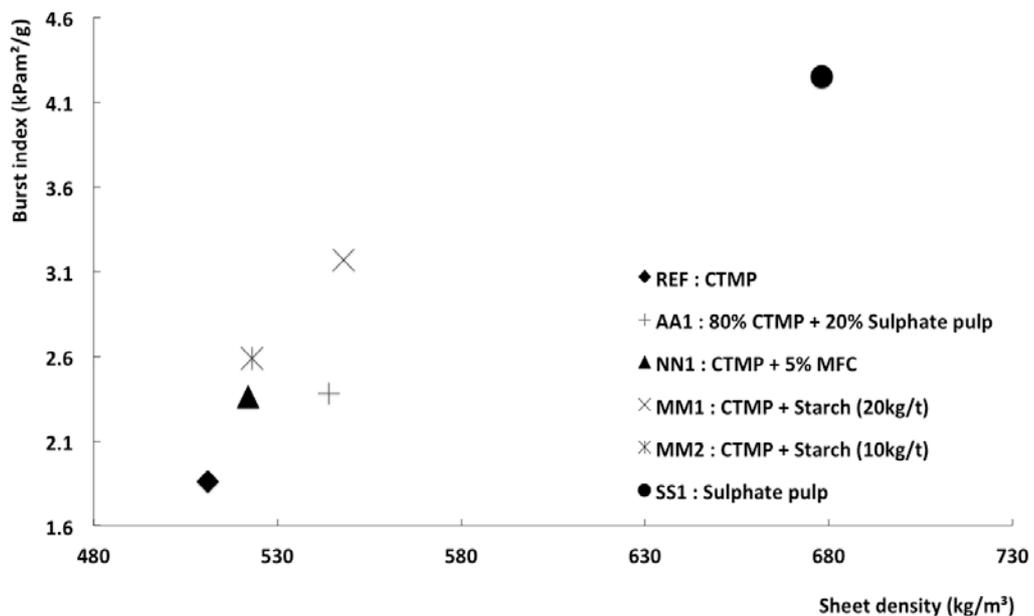


Figure 6. Burst index as a function of sheet density

Hii et al. (2012) studied the effect of MFC on paper strength and drainage properties using a combination of MFC, thermomechanical pulp (TMP), and ground calcium carbonate. They observed improvements in strength properties and barrier properties but worsened drainage behaviour. However, the press dewatering properties of microfibrillated cellulose added during sheet formation could be optimised without affecting the entire papermaking process. It is well known that the properties of chemical pulp fibres of, for example, dissolving or bleached kraft pulps differ from those of mechanical pulp fibres of, for example, TMP or CTMP. Su et al. (2013) reported that the drainage behaviour during papermaking is influenced by factors such as ionic strength, type of polyelectrolyte, pH, and fibre dimensions. The more nano-sized the fibre particle, the longer it will take for the fibre mat to form during drainage, indicating poor drainage properties.

The use of MFC as a strength additive has also been reported in our previous work (Osong et al., 2014). We decided to explore strength improvement properties in greater depth to determine whether TEMPO-oxidised MFC would have a better strengthening effect than CTMP-based MFC, and our results indicate that a lower dosage (5%) of sulphite pulp TEMPO-derived MFC had a better strengthening effect than that reported in our previous work (Osong et al., 2014). It has also been demonstrated that chemical pulp-based nanocellulose acts as strength enhancer in handsheets (Eriksen et al., 2008). Our main concern, however, was to investigate whether using CS or MFC on its own would better strengthen CTMP-based paperboard while having only a slight effect on the sheet density. These results could easily enable us to select the right CS and MFC levels depending on the final paper strength properties desired.

4. Conclusions

The results presented here indicate significant strength improvement in the resulting handsheets with the addition of different proportions of CS (i.e., 20 and 10 kg t⁻¹) and 5% TEMPO-based MFC to CTMP. We noticed that the strengthening impact of 5% TEMPO-based MFC was approximately equal to that of 10 kg t⁻¹ of CS. It is therefore possible to use CS or MFC to improve the strength properties of paperboard products. The 100% sulphate pulp handsheets exhibit both high z-strength and high tensile index values, but their sheet density was considerably higher than that of the other sheets. Comparing the z-strength of CTMP-based handsheets with that of sulphate pulp handsheets reveals that the sulphate pulp produced stronger sheets than did CTMP, but that the CTMP sheets have a considerably lower sheet density. As high bulk at a given strength is crucial in packaging applications, it is important to develop high z-strength at relatively low sheet densities. The results presented here give a clear indication that we can continually improve the strength properties of CTMP-based paperboard by manipulating the addition levels of either CS or MFC, while only slightly affecting the density of the resulting sheets.

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