STRENGTH ENHANCEMENT OF A FIBER NETWORK BY CARBOXYMETHYL CELLULOSE DURING OXYGEN DELIGNIFICATION OF KRAFT PULP

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Sorption of carboxymethyl cellulose (CMC) on the fiber surface was applied during oxygen delignification to enhance the strength properties of softwood kraft pulp. Unlike many previous efforts, the focus was not set on the improvement of selectivity of oxygen delignification, i.e. retaining stable viscosity vs. decreasing kappa number. Instead, without an improved selectivity, handsheets from CMC-treated fibers exhibited a 15% improvement in tensile index and 25% improvement in tear index after a full bleaching sequence in comparison to the untreated reference pulp. Since it is demonstrated that the CMC addition can be incorporated as an integral step in the fiberline process, the method offers an effortless and viable option to produce pulp resulting in stronger paper products.

Keywords: Carboxymethyl cellulose, Oxygen delignification, Selectivity, Tear strength, Tensile strength

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INTRODUCTION

At present, it is common to include an additional step between cooking and bleaching of kraft pulp: oxygen delignification. An environmentally agreeable choice, oxygen delignification is used to remove ca. 50% of the residual lignin before its selectivity towards lignin is lost (McDonough 1996). The reasons for the limit of lignin removal during oxygen delignification are still under debate (Gellerstedt and Heuts 1997; Moe and Ragauskas 1999; Argyropoulos and Liu 2000; Yang et al. 2003; Rööst et al. 2003; Kontturi et al. 2005; Shin et al. 2006), but the most explicit evidence suggests that covalent bonds between lignin and carbohydrates hinder the selective removal of lignin after a certain point (Chirat and Lachenal 1997; Fu and Lucia 2003; Axelsson et al. 2004). The purpose of this paper is to present a method which leads to a stronger fiber network after oxygen delignification of kraft cooked fibers without a drastic improvement in the selectivity towards lignin.

The chemistry of oxygen delignification has been resolved to a relatively high degree with model compound studies (for reviews, see Gierer 1997 and Gavrilescu 2005). The hydroxyl radical has been pointed out as the detrimental species, cleaving the glycosidic bonds of cellulose by a substitution reaction at the anomeric carbon (Guay et al. 2002), thus reducing the degree of polymerization of cellulose and, consequently, the fiber strength (Yang et al. 2003). Since its commercial introduction in the 1970s, improving the selectivity of oxygen delignification has been subject to repeated endeavors (Suchy and Argyropoulos 2002; Chen and Lucia 2002; Van Heiningen and

Violette 2003; Argyropoulos et al. 2004; Gaspar et al. 2004; Ruuttunen and Vuorinen 2005). So far, the only widespread procedure adapted by the industry is the addition of magnesium sulfate to impede the formation of hydroxyl radicals in the reaction mixture (Lidén and Öhman 1997).

Independent of developing a more efficient result from oxygen delignification, there is a vast area of research which focuses on improving the strength properties of paper products during the papermaking process. These methods function mainly by the addition of various polyelectrolytes – labeled dry strength agents - in the wet end of paper machine (Pelton 2004; Hubbe 2006). Recently, more refined tools, such as polyelectrolyte multilayers, have been applied in laboratory scale to yield substantial strength gains for paper (Wågberg et al. 2002; Eriksson et al. 2006). An additional interesting development in the field of enhancing the strength of a fiber network is the sorption of carboxymethyl cellulose (CMC) on the fiber surface, resulting in remarkably strong paper after the treatment (Mitikka-Eklund et al. 1999; Blomstedt and Vuorinen 2006; Laine et al. 2002, 2003a, 2003b; Ekevåg et al. 2004; Watanabe et al. 2004). CMC sorption is not subordinate to conventional strength agents: the mechanism of strengthening is very different to those of ordinary strength agents, and CMC has to be attached to the fiber in a separate step in the papermaking process. The strength gains by this method are considerably higher than when CMC has been used as a conventional dry strength agent, i.e., added to the wet-end of the paper machine (Beghello et al. 1997). Thus, CMC addition as a separate step has been termed "bipolar activation technology" (Laine et al. 2002, 2003a, 2003b) or "fiber engineering" (Mitikka-Eklund et al. 1999; Blomstedt and Vuorinen 2006), depending on the group involved with the research and on the technique applied to attach the CMC. It is noteworthy that the former technique employs high electrolyte concentration to screen the repulsion between the anionic fibers and anionic CMC, whereas the latter method relies on the low degree of substitution (DS), i.e. low charge density of the CMC, to enable the adsorption on the fibers. This latter method will be exploited in this work, since the highly alkaline conditions of oxygen delignification are optimal for properly dissolving the CMC with a low DS.

This paper intends to demonstrate how the CMC addition may be included in the oxygen delignification as an integral part of the chemical pulping process. Regrettably often in papermaking research, the pulping process and the paper machine are treated as isolated entities. Optimization of pulping parameters focuses on the preparation of strong, lignin-free fibers without considering the end product: a network of fibers. Optimization in the paper machine, on the other hand, focuses on the preparation of as strong a fiber network as possible without taking into account the effect of the raw material (pulp). Therefore, to combine the approach of strong fibers with the aim for strong fiber networks, we have tried to investigate the effect of CMC addition during oxygen delignification on the strength properties of the whole fiber network in the form of laboratory handsheets. Furthermore, the CMC-treated, oxygen delignified pulp will be subjected to subsequent bleaching stages to explore the full benefit of the strength improvement.

EXPERIMENTAL

Materials

Kraft cooked, unbleached spruce pulp was provided by a pulp mill in Eastern Finland. The CMC used for the sorption was Nymcel ZSB-10, F1226 (sodium salt) with a degree of substitution (DS) 0.2. NaOH, $MgSO_4$, phenol were all p.a. grade from Aldrich. Sulfuric acid was obtained as a 98 % (p.a.) solution from VWR.

Methods

Oxygen delignification with CMC sorption

Oxygen delignification was performed in an air bath digester in 10 % pulp consistency. The oxygen pressure applied was 8 bar, alkali charge 2.5 % NaOH on pulp, temperature $100^{O}C$. 1 % $MgSO_4$ on pulp was added as a stabilizer. The initial concentration of CMC in the suspension was 1 % on pulp. Prior to its addition, CMC was dissolved in 2 M NaOH solution and the amount of NaOH in that solution was taken into account when calculating the total alkali charge of the mixture. The high alkali charge during the delignification guaranteed that the CMC with a low DS (0.2) was properly dissolved throughout the procedure. The delignification was carried out for 60 minutes. Reference delignification stages were performed without the CMC addition.

Determining the extent of CMC sorption

The amount of attached CMC was quantified by analysing the carbohydrate content from the filtrates by phenol-sulfuric acid assay (Chaplin 1986) and assuming that the rest of the carbohydrates had adsorbed on the fibers. Since there is some carbohydrate detachment from the fiber during oxygen delignification, the phenol-sulfuric acid assay was prepared for the reference pulps, too. The amount of CMC that was not attached was then determined from the subtraction.

Table 1. The Bleaching Conditions for the Post Oxygen Delignification Stages (D_1ED_2).

Bleaching stage	Temperature [°C]	Time [min]	Consistency [%]	ClO_2 [%, act. Cl_2]	NaOH [%]	Final pH
O$\mathbf{D_1}$	50	60	10	3.0	0.6	5.0
OD_1**E**	60	60	10	-	1.8	12.4
$OD_1E$$\mathbf{D_2}$	60	180	10	1.5	0.5	6.4

Subsequent bleaching stages

After the oxygen stage, both the CMC treated pulp and the reference pulp were bleached by using the sequence D_1ED_2 (D for chlorine dioxide stage, E for alkaline extraction stage). Each stage was performed in a polyethylene bag with the conditions listed in Table 1.

Testing of pulps

The viscosity was determined according to the standard method SCAN-CM 15:88. The kappa number was determined according to SCAN-C 1:77.

Testing of laboratory handsheets

Handsheets were prepared according to the standard method SCAN-C 26:76 except for the wet pressing (490 kPa was applied) and drying (2h at 60^{O}C in a drum drier was applied). Density was determined by ISO 534:1988. The strength properties were determined with the following standard procedures: tensile index (ISO 1924-2:1994), out-of-plane Elmendorf tear index (ISO 1974:1990), and bonding ability as Scott bond (TAPPI UM 403).

RESULTS AND DISCUSSION

Selectivity and Brightness

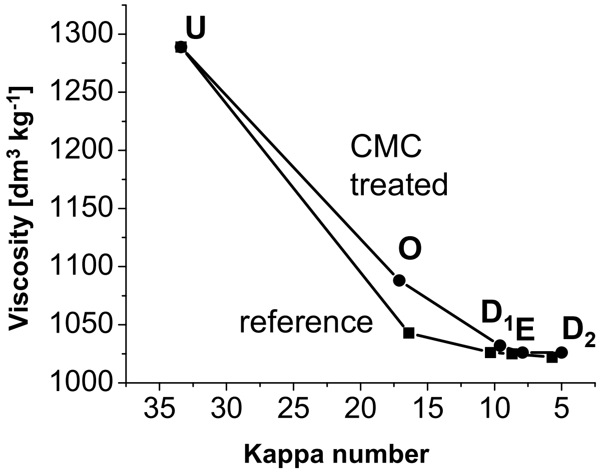

Fig. 1. Kappa number as a function of viscosity in the CMC-treated (•) and reference ( ) pulps unbleached (U), after oxygen delignification (O), after first chlorine dioxide bleaching stage (D$_1$), after alkaline extraction (A), and after second chlorine dioxide bleaching stage (D$_2$).

The filtrate analysis after oxygen delignification revealed that 85 % of the CMC had been attached to the fiber, which is on the same order of magnitude that has been achieved with the CMC sorption during the kraft cook (Ekevåg et al. 2004). The selectivity of oxygen delignification and the subsequent bleaching stages for the CMC-treated and the reference pulps is expressed in Figure 1. Viscosity represents a measure of the degree of polymerization (DP) of cellulose in the fiber and the reduction in kappa number is a sound quantification of the delignification for softwood pulps. Figure 1 indicates a small improvement of selectivity for the CMC-treated pulp after the oxygen delignification stage and negligible deviations after the subsequent D$_1$ED$_2$ stages. It is noteworthy that the CMC sorption during oxygen delignification does not affect the delignification at all since the kappa numbers of the CMC-treated pulp and the reference pulp are essentially similar. We can speculate that the larger viscosity of the CMC-treated fibers arises from the protective effect of the dissolved CMC which has not been adsorbed on the fibers: the detrimental hydroxyl radicals degrade the dissolved CMC rather than the cellulose within the fibers. Whatever the case, the small improvement in selectivity depicted in Fig. 1 has no industrial significance.

CMC sorption in the oxygen delignification stage does not affect the brightness development during oxygen delignification and the subsequent bleaching in any way (results not shown). This, together with the kappa number development, indirectly indicates that the removal of lignin and chromophoric structures is largely unaffected by the CMC addition. Moreover, the data suggest that additional consumption of bleaching chemicals by CMC is negligible.

Strength Properties

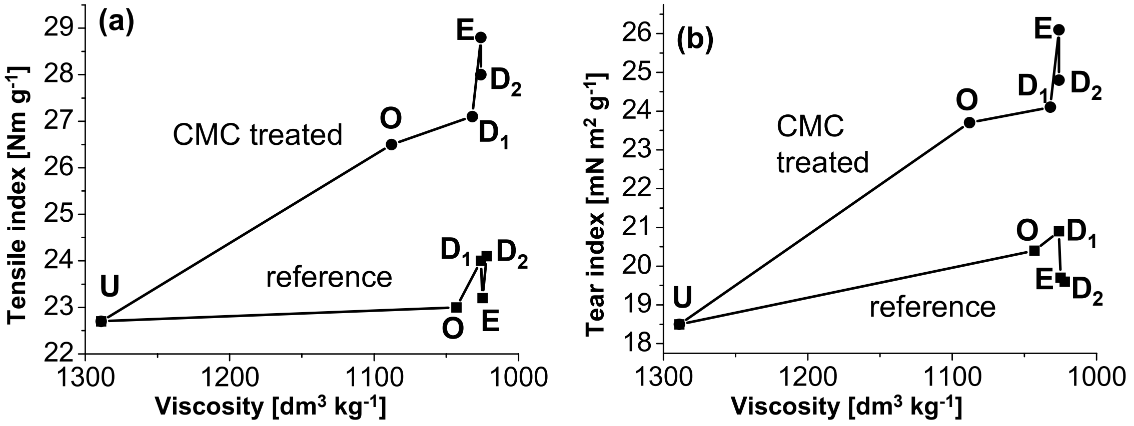

Fig. 2. (a) Tensile index as a function of viscosity, (b) tear index as a function of viscosity of the handsheets prepared from the CMC-treated (●) and reference (■) pulps unbleached (U), after oxygen delignification (O), after first chlorine dioxide bleaching stage (D_1), after alkaline extraction (A), and after second chlorine dioxide bleaching stage (D_2).

Figure 2a illustrates the development of the tensile index as a function of viscosity during oxygen delignification and the subsequent bleaching stages. The reference plot (without CMC sorption) indicates that although the viscosity drop during oxygen delignification was substantial, the tensile index stayed unaffected. This is a reported phenomenon, and sometimes the tensile index may even increase slightly after oxygen delignification (Yang et al. 2003). The same behavior was evident for tear index (Fig. 2b). In fact, the viscosity within the fiber needs to achieve a certain critical value before its decrease starts to affect the strength of the fiber network by decreasing tear and tensile indices (Rydholm 1965). Figures 2a and 2b, moreover, show that further bleaching by D_1ED_2 stages did not markedly influence the viscosity or the strength properties of the reference pulp.

However, when the pulp was subjected to CMC sorption during the oxygen delignification stage, both the tensile (Fig. 2a) and tear (Fig. 2b) indices increased considerably. After additional bleaching by D_1ED_2 stages, the strength improvement was maintained, but to a smaller degree. The effect of CMC is emphasized in Fig. 3 in the more traditional tear-tensile graph. The strength gains by CMC addition were significant after the full D_1ED_2 bleaching: 25 % increase in tensile index and 35 % increase in tear index with respect to the values of the unbleached pulp. The reference pulp without the CMC sorption demonstrated a mere 5 % increase in both tear and tensile indices after oxygen delignification followed by D_1ED_2 bleaching. In other words, in comparison with the reference pulp without the added CMC, the CMC treated pulp possessed a 15 % improvement in tensile index and 25 % improvement in tear index after the full D_1ED_2 bleaching.

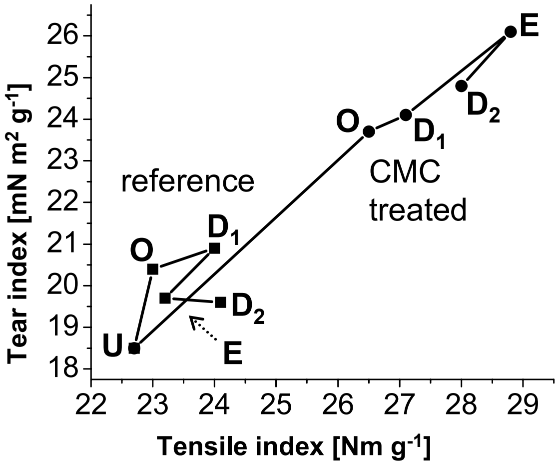

Fig. 3. Tear index as a function of tensile index of the handsheets prepared from the CMC-treated (•) and reference (■) pulps unbleached (U), after oxygen delignification (O), after first chlorine dioxide bleaching stage (D_1), after alkaline extraction (A), and after second chlorine dioxide bleaching stage (D_2).

In the previous research, CMC sorption to an already fully bleached softwood kraft pulp has resulted in up to 200 % increase in the tensile index (Laine et al. 2003b). The quoted method of addition, however, requires a separate step in the pulp preparation process and with its requirements of high temperature (120^{O}C) and high electrolyte concentration, it is somewhat cumbersome to insert into the fiberline. To overcome this, Ekevåg et al. (2004) made an effort to include the CMC addition in the kraft cook. In consequence, the authors managed to improve the tensile strength of unbleached softwood kraft pulp by 20 %. The work by Ekevåg et al. (2004) also features subsequent bleaching performed on the CMC treated pulp, which resulted in 10 % increase of tensile index compared with the reference stage. Therefore, the 15 % improvement in tensile index (Fig. 2a) is a competitive result. The tear index in the quoted study (Ekevåg et al. 2004), on the other hand, was decreased by 20 % upon CMC addition. This inverse tear-tensile relationship is common with softwood pulps after the tear strength has passed through a maximum (Page 1994) and, moreover, tear index is more susceptible to a decrease in viscosity than the tensile index (Rydholm 1965). Furthermore, the tear strength of softwood kraft pulp expresses a decline along an industrial bleaching sequence (MacLeod et al. 1995). A constant increase of tear index with a steady growth in tensile index has only been achieved before with oxygen delignification and subsequent bleaching of hardwood pulps (Hunt and Hatton 1987; Tran 2001), which express altogether a very different behavior with respect to the tear and tensile indices (Van den Akker 1958). Furthermore, the conventional dry-strength additives do not increase the tear strength but usually decrease it slightly (Davison 1980). The unimproved tear strength appears even when CMC is applied as a conventional dry-strength additive in the wet-end of the paper machine (Beghello et al. 1997). The increase in both tear and tensile indices (Figs. 2 and 3) is an unexpected and positive result.

Bonding and Bond Strength

As mentioned in the introduction, numerous methods to improve the selectivity of oxygen delignification have been presented (Suchy and Argyropoulos 2002; Chen and Lucia 2002; Van Heiningen and Violette 2003; Argyropoulos et al. 2004; Gaspar et al. 2004; Ruuttunen and Vuorinen 2005). The direct comparison of those results with this work, however, is complicated because they focus on the relationship between the kappa number and viscosity, i.e., the selectivity of oxygen delignification, not the direct enhancement of the strength properties of the subsequent paper. In fact, often the papermaking strength properties of the pulps have not been presented in the pertinent publications. Indeed, there are several factors that dictate the strength properties of a fiber network and the degree of polymerization (DP) of the cellulose in the fibers, represented by viscosity, is only one of them. As mentioned above, the cellulose DP affects the paper strength after it decreases past a certain threshold value (Rydholm 1965). This threshold, however, is not usually reached under industrial pulping conditions.

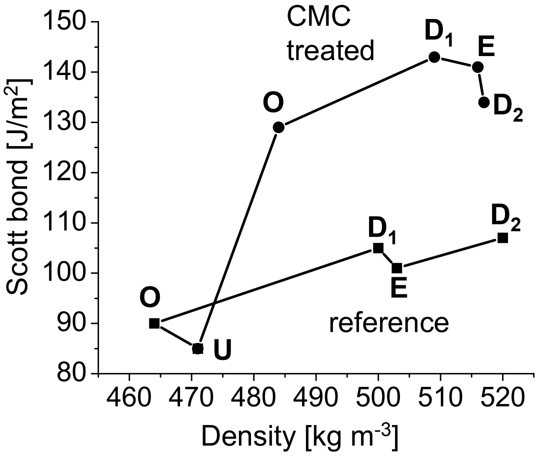

Fig. 4. Scott bond as a function of density of the handsheets prepared from the CMC-treated (•) and reference (■) pulps unbleached (U), after oxygen delignification (O), after first chlorine dioxide bleaching stage (D_1), after alkaline extraction (A), and after second chlorine dioxide bleaching stage (D_2).

The DP of cellulose affects the strength properties allegedly because it governs the strength of individual fibers to an extent (Gurnagul et al. 1992). Although the fiber strength is an important quality, the strength of a fiber network is also strongly influenced by the bonding between the fibers, namely by the extent of bonding and by the strength of the fiber-fiber bond. The extent of bonding and the internal bond strength of the fiber network after oxygen delignification and the bleaching stages was examined by plotting the Scott bond (z-directional bond strength) as a function of density (extent of bonding) in Fig. 4. The increased Scott bond values due to CMC addition are in line with the improved strength properties of Fig. 2 but, interestingly, the density of the handsheets after oxygen delignification was hardly affected by the CMC addition. Although the two previously published basic methods of CMC addition both improve the strength properties of paper, they differ markedly in their influence on density. The method introduced by Laine et al. (2003b) has a minute effect on density, which raises speculation that the strength improvement comes mainly from the increased surface charge, which strengthens the fiber-fiber bond. In contrast, the method of Mitikka-Eklund et al. (1999) has an incremental impact on the sheet density, which led the authors to hypothesize that, in addition to the increased surface charge, the flexibility of the fibers increases and the CMC addition also positively influences the number of fiber-fiber bonds. We propose that this fundamental difference implies that also the mechanism of CMC addition is very different between these methods. Therefore, the reduced growth of density in Fig. 4 is surprising, since the method of addition applied here is essentially the one introduced by Mitikka-Eklund et al. (1999). It is evident that the prevalent conditions in oxygen delignification affect the CMC adsorption. It is probable that the presence of magnesium sulfate, although small in concentration (ca. 8 mmol dm^{-3}), renders the sorption different. The high temperature and pressure ($100^{O}C$, 8 bar) also contribute to the speculation that the adsorption mechanism here may well be akin to the one presented by Laine et al. (2003b). Since this method allegedly functions mainly by adding more charge on the fiber surface to improve the strength of the fiber-fiber bond, an interesting experiment for future research would be to see whether any CMC with a higher degree of substitution can be attached in the conditions of oxygen delignification.

As mentioned in the previous, the surface charge of the fibers has been acknowledged as an important factor in the strength of the fiber-fiber bond (Barzyk et al. 1997), which is indeed a major contributor to the strength gains achieved by the highly charged CMC species (Laine et al. 2003a, 2003b) as well as polyelectrolyte multilayers (Wågberg et al. 2002; Eriksson et al. 2006). In a recent work, Zhang et al. (2005) made an attempt to optimize the amount of charged groups in the fiber by tuning the conditions of oxygen delignification. As a result, the authors presented a 20 % increase in tensile index when the charge of the fibers was increased by 60 % during oxygen delignification. Regrettably, no other strength properties were tested and the authors did not investigate how the tensile strength would behave as a function of further bleaching stages. Unfortunately, we do not possess data on the charge properties of our pulps, because they are outside the scope of this descriptive introductory paper. It would be interesting to investigate, for instance, how the CMC attachment presented in this paper affects the strength properties when the charge of the fibers has been optimized according to Zhang et al. (2005). However, when delignification is concerned, other factors affecting the fiber-fiber bond should also be considered, such as the amount of surface lignin (Shao and Li 2006) or the DP of cellulose on the fiber surface (Kontturi and Vuorinen 2006). In the industrial conditions, moreover, the strength losses to fibers and the fiber network by mechanical damage have to be taken into account. For instance, concerning oxygen delignification, Allison et al. have suggested that most of the strength losses are induced by mechanical changes, such as fiber deformations (Allison et al. 1998). This view has also been put forward as a generalization (MacLeod et al. 1987; Molin et al. 1996). More fundamental research on the origin of these different contributions to paper strength is required for better understanding the factors that affect the strength of a fiber network.

Impacts on the Fiberline Process

There is admittedly a drastic difference in the strength improvement of the fiber network depending on whether the CMC addition has been performed as a separate step or integrated in the process like in this work. We can speculate that probably the CMC is degraded to a lower molecular weight during oxygen delignification, thus enabling the penetration of CMC inside the fiber matrix. When the surface-specificity of the attached CMC is lost, the strength gains are also lost to a considerable degree (Laine et al. 2002). However, the method presented here offers a viable, realistic option with genuine strength improvements to include the CMC addition in the pulping and the subsequent papermaking process. The industrial applicability is something that still remains an unresolved problem with, for instance, polyelectrolyte multilayer deposition on fibers, in spite of the huge strength gains by that technique (Wågberg et al. 2002; Eriksson et al. 2006).

A further advantage is provided by the chemical nature of CMC. The inorganic catalysts designed to improve the selectivity of oxygen delignification (Suchy and Argyropoulos 2002) always raise questions about the toxicity, although the authors are sometimes prudent with the environmental implications (Gaspar et al. 2004). As a non-toxic cellulose derivative, CMC causes no environmental concerns.

It is clear that many factors affect the strength of a fiber network during the pulping process: the DP of cellulose in the fiber, the charge density on the fiber surface, the amount of lignin and extractives on the fiber surface, the flexibility of the fibers, etc. This introductory report does not intend to assess the contributions of these qualities. Rather, it serves as an example that simple treatments without the insertion of additional steps in the fiberline process have potential to positively influence the properties of the end product.

CONCLUSIONS

1. CMC sorption has been successfully included in the oxygen delignification of softwood kraft pulp with strength gains in both tear (+35%) and tensile (+25%) indices of the handsheets prepared from fully (D_1ED_2) bleached pulp. Formerly, CMC sorption has required a separate step of addition in the papermaking process.
2. Upon CMC sorption, the fiber-fiber bond was strengthened, as demonstrated by the increase in Scott bond, whereas the amount of bonds was largely unaffected, as witnessed by the relatively stable density of the handsheets.
3. The strength gains on the handsheets were achieved without an improvement in the selectivity of oxygen delignification.

ACKNOWLEDGMENTS

Sustainpack project is acknowledged for the financial support.

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Article submitted: May 25, 2007; Peer-review completed: Nov. 5, 2007; Revised version accepted: Nov. 16, 2007; Published: Dec. 2, 2007