IV

Blomstedt, M., Kontturi, E. and Vuorinen, T. (2007) Optimising CMC sorption in order to improve tensile stiffness of hardwood pulp sheets. *Nord. Pulp Pap. Res. J.* ***22****(3): 336-342.*

Optimising CMC sorption in order to improve tensile stiffness of hardwood pulp sheets

Minna Blomstedt, Eero Kontturi and **Tapani Vuorinen**,Helsinki University of Technology, Finland

KEYWORDS: Hardwood pulp, Surface modification, Carboxymethyl cellulose (CMC), Sorption, DDJ-fractionation, Tensile stiffness, Sheet and Fibre properties

SUMMARY: An ECF-bleached hardwood pulp was treated with carboxymethyl cellulose (CMC) under specified conditions. This paper studies the combined effect of CMC modification, drying conditions and DDJ-fractionation of hardwood pulp on fibre and strength properties of paper. The drying effect was investigated by drying the sheets in a drum (free drying) or on a plate (restrained drying). The CMC-treatment increased markedly the tensile stiffness index of the handsheets dried under restraint. Moreover, all strength properties were significantly increased after the CMC modification. The effects of the fines were investigated in the second part by fractionating the pulp by a Super DDJ. Fines affected internal and tensile strength positively.

ADDRESSES OF THE AUTHORS: Minna Blomstedt (minna.blomstedt@tkk.fi), **Eero Kontturi** (eero.kontturi@tkk.fi) and **Tapani Vuorinen** (tapani.vuorinen@tkk.fi): Helsinki University of Technology, Laboratory of Forest Products Chemistry, P.O.Box 6300, FI-02015 TKK, Finland.
Corresponding author: Minna Blomstedt

In essence, tensile stiffness represents the elastic modulus of paper, measured as the slope of the primary part of the load-elongation curve during the tensile testing. It is an important mechanical property of paper and especially important for liner- and boxboards. Many factors affect the stiffness of paper, such as interfibre bonding degree, fibre strength, drying shrinkage and moisture content (Wahlström, Fellers 2000). In this work a novel method for improving the tensile stiffness will be introduced.

Mechanical treatments such as refining and handling of chemical pulp fibres introduce curl, kinks and micro-compressions to the fibres, which affect the stiffness of the final sheet. Several authors have studied the effects of fibre deformation (fibre kink, curl) on the pulp and sheet properties (Mohlin, Dahlbom 1996; Joutsimo, Wathen 2005; Seth 2006; Page, Seth 1979; Omholt 1999). Mohlin and co-workers (1996) showed that different levels of kink after refining were directly reflected in the tensile stiffness. When fibres are straight tensile stiffness is higher compared to deformed fibres, due to the higher fibre segment activation (Joutsimo, Wathen 2005). Fibre segment activation means the modification of originally kinky, curly or otherwise deformed fibre segments, unable to carry load, into active components of the network (Vainio, Paulapuro 2005). Activation requires both bonding and shrinkage of the fibres. When the segments are activated the modulus of elasticity (tensile strength) increase and both segments and bonded areas are capable of carrying load (Joutsimo, Wathen 2005; Page, Seth 1979; Omholt 1999; Vainio, Paulapuro 2005). Furthermore, the curly fibres tend to form a sheet that has higher stretch and tear indices than the sheets made of straight fibres, whereas the zero-span fibre strength is not dependent on fibre curl and kinks (Joutsimo, Wathen 2005; Page, Seth 1979). According to Seth (2006) deformation seems to have a much larger effect on the sheet tensile strength than on elastic modulus.

Refining changes the properties of fibres, fibres swell more, shrink more than unrefined pulp. Most of the fibre deformations, curl, kinks and dislocations vanish during beating of the pulp and bonding level is raised (Mohlin, Dahlbom 1996; Joutsimo, Wathen 2005; Seth 2006; Page, Seth 1985). Hence, refining causes the activation or straightening of fibres, resulting in higher tensile stiffness as well as higher tensile strength. It can be discussed if the changes in the sheet properties are due to straighter fibres or improved bonding.

Besides the properties of individual fibres, the properties of paper are dramatically affected when the shrinkage and stretching of the fibre web are varied during the drying process (Wahlström, Fellers 2000). Upon drying, the structure of the sheet is tightened by the shrinkage in the fibres (Page, Seth 1979). Crimps are partly removed and the elastic properties of the sheet increase. This happens only if the sheet is restrained from shrinkage so that the fibre segment dry under stress and the slackness is removed (Lobben 1975; Giertz, Lobben 1967). When shrinkage is allowed no such tightening of the structure occurs and the modulus or stiffness is low. Hence, the elastic modulus or tensile stiffness of sheets dried without restraint is considerably lower (Wahlström, Fellers 2000; Page, Seth 1979; Vainio, Paulapuro 2005). Furthermore, if the paper is stretched or the shrinkage is reduced, then the tensile stiffness index and tensile index increase, whereas the strain to break and bonding strength decreases (Vainio, Paulapuro 2005; Chance 1992). In other words, the final impact on paper strength is in fact a combination of drying stresses, the degree of shrinkage, the solid content at which shrinkage takes place and the drying strategy (Vainio, Paulapuro 2006). The paper strength properties are also affected by the type of raw material used, the extent of beating and the fibre orientation of the wet paper.

Previous studies in this laboratory showed that sorption of CMC of low degree of substitution (DS< 0.5) on cellulosic pulps greatly enhanced the strength properties of the handsheets (Mitikka-Eklund, Halttunen 1999; Blomstedt, Mitikka-Eklund 2007; Blomstedt, Vuorinen 2007; Blomstedt, Vuorinen 2006). The amount of CMC attached on pulp depended on several factors, including degree of polymerisation (DP), DS and charge of CMC, pH and ionic strength of the sorption medium and beating level of the pulp (Blomstedt, Mitikka-Eklund

2007). Similar studies were conducted by Laine et al. (2000, 2002). Moreover, Watanabe et al. (2004) developed an advanced wet-end system with CMC and Rantanen et al. (2006) studied the effect of CMC on pulp dispersing. However, tensile stiffness is a quality that the previous CMC treatments have failed to improve.

The present paper examines the combined effect of the CMC modification, drying conditions (plate/drum) of hardwood kraft pulp and their papermaking properties. In addition, the role of the fines was investigated by DDJ-fractionating the pulp. The CMC modification of pulp strongly increased the strength properties of the handsheets. Especially the tensile stiffness for the CMC modified pulp was increased significantly by drying the sheets under restraint, which is closer to the real papermaking conditions. These kinds of papers can be useful when high stiffness is required, for example in packaging materials.

Materials and Methods

Pulp and carboxymethyl cellulose

The experiments were carried out with a mixture of industrial ECF bleached birch (95%) and aspen (5%) kraft pulps. The pulp was refined in a Voith Sulzer LR1 research refiner. The pulp was refined with disk fillings 2/3-1.46-40D, designed for short-fibre pulps. The refining consistency was 4.0% and specific edge load 0.5 Ws/m. Specific refining energy (SRE) levels were 0 and 30 kWh/t.

The Schopper-Riegler (SR) numbers of the pulp samples were determined according to the standard method ISO 5267-1.

The commercial CMC sample, Nymcel ZSB-16, was obtained from Noviant. The degree of substitution was 0.32 and the degree of polymerisation (DPv) 700 for the CMC grade used.

DDJ fractionation

Fines were removed from the birch pulp by using a Super Dynamic Drainage Jar-apparatus (DDJ). Super DDJ is equipped with a wire tank with a 200-mesh wire and a mixer. The pulp concentration was about 0.5% (approximately 1kg dry pulp) when fed into the apparatus. Fines were removed from the pulp in 500g batches. The fibres were collected and had a pulp concentration of about 10% after the fractionation.

Fibre properties

Fibre dimensions and deformations were analysed with a commercial KajaaniFiberLab analyser (Richardson, Riddell 2003). Samples were prepared according to the equipment manufacturers' recommendations (KCL standard 225:89). The stock consistency used to calculate the coarseness values was determined by the standard method SCAN-C 17:64 and fibre length was determined according to TAPPI T271. More detailed information about the analyser can be found in the publication by Turunen et al. (2005).

Sorption of CMC on pulp

Because the CMC grades applied were partly insoluble in water, stock CMC solutions (< 10 g/L) were prepared in 2.5 M sodium hydroxide. The refined pulp was mixed with water and the stock CMC solution to obtain a final pulp consistency of 2.5% (25 g/L) and an initial CMC concentration of 0.25 g/L (1% on pulp) (Mitikka-Eklund, Halttunen 1999). Sorption (reference pulp pH 5.5 and CMC pulp pH 11) was carried out in glass beakers. The temperature was raised to 60°C for 30 minutes. After 60 minutes, the pulp samples were cooled, filtered and washed with deionised water.

Samples of the liquid phase were withdrawn (about 50 mL) after the sorption, centrifuged for 30 minutes and then analysed for dissolved carbohydrates by the phenol-sulphuric acid test (Dubois, Gilles 1956) and acid methanolysis combined with gas chromatography (GC) (Sundberg, Sundberg 1996). The reference pulps were treated under similar conditions but without CMC. Thus, the results of the phenol-sulphuric acid test were corrected for polysaccharides other than CMC.

Water retention value and papermaking properties

Water retention values (WRV) of the pulps were measured in accordance with standard SCAN-C 62:00 with a Jouan GR 4 22 centrifuge.

The laboratory sheets were prepared in deionised water by the standard method ISO 5269-1, with the exception of wet pressing at 490±20 kPa (for 4 min 20 s) and drying in a drum dryer at 60°C for 2 h. When drying plates were used the wet pressing was carried out in two steps. The first pressing was at 400±10 kPa (for 5 min 30 s) and then the blotters were removed and replaced before the second wet pressing at 400±10 kPa (for 2 min 20 s).

The density of the sheets was determined by standard method ISO 534. The tensile strength and tensile stiffness of the laboratory sheets were measured with a tensile testing machine (MTS 400M) by standard method SCAN-P 38:80. Bonding ability (Scott Bond or internal strength) was determined according to Tappi 833 pm-94.

Results and Discussion

Sorption of CMC on fibres

The degree of sorption of CMC was evaluated by estimating the content of CMC in the sorption liquid by phenol-sulphuric acid test and acid methanolysis combined with GC. Unbeaten pulp sorbed 25-40% of high-molecular weight CMC (DP_V 700, DS 0.32) whereas beating of the pulp led to 50-60% sorption at 1% CMC addition (*Fig 1*). Other comparable studies have shown that CMC sorption of similar magnitude requires high temperature and addition of an electrolyte ($CaCl_2$) (Laine, Lindström 2000). Because of the substantial electrolyte addition applied by Laine et al. (2000), the sorption mechanisms here and in the alternative study are different. Added electrolyte screens the electrostatic repulsion between anionic fibres and anionic CMC. In our case, however, the DS of CMC is substantially lower,

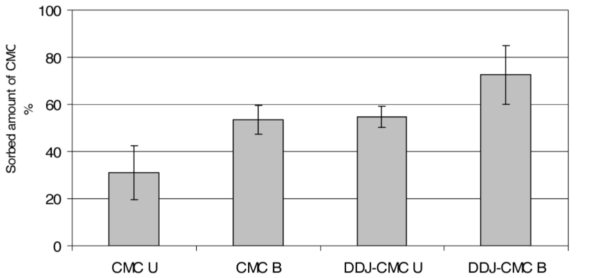

Fig 1. The attached amount of CMC on unbeaten (U, 0 kWh/t) and beaten (B, 30 kWh/t) CMC-treated (1% CMC addition, pH 11, 60ºC, 1h) nonfractionated and fractionated (DDJ) hardwood pulp.

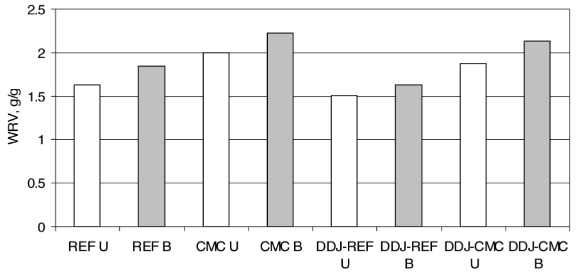

Fig 2. The effect of CMC addition on the water retention values (WRV). The *white columns* represent the unbeaten pulp (0 kWh/t, U) and the *grey columns* the beaten pulp (30 kWh/t, B). Standard deviation values varies from 0.001-0.008. *Abbreviations:* Reference (REF), CMC-treated (CMC), DDJ-fractionated reference (DDJ-REF), DDJ-fractionated CMC-treated pulp (DDJ-CMC).

meaning that the repulsion is smaller. Therefore, it may well be that the CMC sorption here is driven by the conformational similarity between CMC and cellulose in the microfibrils on the fibre surface (Mitikka-Eklund 1996). Without hard evidence, however we have to emphasize that this is mere speculation. Therefore, it is difficult to compare these CMC modification methods. The unbeaten and DDJ-fractionated pulp sorbed 50-60% of the CMC added and beating led to a sorption degree of 60-80% (*Fig 1*). It seems that more CMC was attached onto the fibres when the fibres were fractionated before the CMC-treatment. The considerable variation that was observed between the two analytical methods can be due to soluble hemicelluloses in the sorption filtrates. Although the variation is large, the main trends of the attached amount of CMC are certainly detectable (*Fig 1*). For obvious reasons, more CMC is attached on softwood pulp (Blomstedt, Mitikka-Eklund 2007). Also the effect of DS and pH on the sorption of CMC on softwood pulp has been investigated in a recent publication (Blomstedt, Mitikka-Eklund 2007). The attached amount of CMC decreased when the DS of the CMC was increased.

Fibre properties of pulp treated with CMC

The fibre properties of the fractionated and nonfractionated pulps are listed in *Table 1*. It is clearly evident that the fractionated pulp had a higher curl value compared to the nonfractionated hardwood pulp (*Table 1*). These higher curl values are expected to have a negative effect on the strength properties of the fractionated pulp sheets. Furthermore, *Table 1* shows that beating of the nonfractionated pulp made the fibres straighter. These results correlated well with the results presented earlier by Mohlin and Omholt (1996, 1999) who showed that PFI-mills efficiently reduces fibre curl. In addition, the cell wall thickness and fibre width was slightly higher for the fractionated pulp. The fines content was smaller and average fibre length higher in the fractionated pulps as could be expected when most of the fines have been removed during the fractionation. Longer beating of the fibres produces more fines. Moreover, when the fibres were fractionated the SR-numbers before and after beating were lower than the SR-numbers of the nonfractionated pulp.

The results shown in *Table 1* correlate well with the fibre properties published by Blomstedt et al. (2006). Other investigations have shown that microdeformations and microcompressions may affect large parts of the fibre length due to increased sheet shrinkage potential and extensibility (Omholt 1999). According to Paavilainen (1990) cell wall thickness of softwood pulp is an even more important factor for the papermaking potential of pulp than fibre length. Moreover, Lobben et al. (1975) presented that coarse and straight fibres need little refining to become active in the fibre network compared to slender and curved fibres. According to Seth (2006) it should be kept in mind that the curl and shape indices measured by the analysers are inadequate because they do not directly measure deformation, but only the response of the fibre deformations. Recent work has shown that zero-span tensile index can be used to quantify fibre deformation (Mohlin, Dahlbom 1996; Joutsimo, Wathen 2005). However, there is still no suitable technique for quantifying microcompressions. These considerations should be born in mind when assessing the effect of CMC modification on fibre and paper properties.

WRV is generally used to determine the swelling capacity of pulps. Introduction of additional charged groups generally results in a higher WRV (Wistara, Young 1999; Scallan 1983). Accordingly, sorption of anionic CMC on beaten and unbeaten pulp led to an increase in their water retention values compared to the untreated (reference) pulps (*Fig 2*). However, the WRV values of hardwood pulp did not increase as much as the WRV values of softwood pulp in the publication by Mitikka-Eklund et al. (1999, 2007), probably because the level of sorption is higher in softwoods than in hardwoods. Beating of the pulp led to an increase in the

Table 1. Cell wall thickness, length-weighted fibre length, fibre width, fibre curl, fibre coarseness, fines content and SR-number of nonfractionated and DDJ-fractionated hardwood pulp. (0= 0 kWh/t refining, 30= 30 kWh/t refining)

Sample/Beating level (kWh/t)	Cell wall thickness (µm)	Fibre length (mm)	Fibre width (µm)	Curl value (%)	Coarseness (mg/m)	Fines content (%)	SR-number
Nonfractionated							
0	5.7	0.99	20.7	15.9	0.094	1.38	16.2
30	5.8	0.98	20.7	14.8	0.090	1.66	23.2
DDJ-fractionated							
0	6.0	1.03	21.3	19.0	0.095	0.38	12.0
30	5.9	1.01	21.2	19.1	0.091	0.40	13.3

WRV values as could be expected. The same trends in the WRV values were seen for the fractionated and nonfractionated pulps, although the fractionated pulps had in general slightly lower WRVs. These results are in agreement with the results shown by Laivins and co-workers (1996) who showed that fines swell more than fibres and pulp.

Sheet properties of pulp treated with CMC

The effect of drying: The effect of drying was investigated by two different methods: (i) drum drying, where the dimensions of the sheet are allowed to develop freely, and (ii) plate drying, where the dimensions of the sheet are restrained. *Fig 3* demonstrates that the density values of the plate dried sheets were significantly higher than for the drum dried sheets, due to the more compact structure of the sheets when dried on a plate. Furthermore, the internal strength (Scott Bond), tensile stiffness and tensile strength values were higher for the plate dried CMC sheets, especially when the pulps were beaten. The same trends were seen in the internal strength and tensile stiffness values. A substantial increase (75%) in the tensile stiffness index was observed when the pulp was CMC-treated, beaten and dried under restraint. Such improvement in tensile stiffness is a unique and unprecedented feature in fibre modification with CMC. It suggests that CMC-treatment has true potential for tailoring various paper properties for different end products.

The stiffness largely originates from the different drying technique. The influence of the drying technique of tensile stiffness, apparent in *Fig 3*, was studied by Wahlström et al. (2000). Reduction of shrinkage or an imposed stretch leads to a large increase in tensile stiffness and a large decrease in strain to break. In other words, when the sheets are dried under restraint and neither shrinkage or stretch is allowed during the drying process the tensile stiffness is higher than when freely dried (Wahlström, Fellers 2000; Lobben 1975; Chance 1992). Furthermore, according to Wahlström (2000), when the naturally accruing shrinkage is restrained, a stress builds up in the paper leading to a higher stiffness of the fibres in their axial direction. The same increasing trend in tensile stiffness when drying under restraint was also clearly seen in our results illustrated in *Fig 3*.

Similar results to those shown in *Fig 3* were also reported by Zhang et al. (2004) who showed that sheets dried on a plate had higher density and tensile and internal strength and tensile stiffness than cylinder dried sheets. In addition, higher temperature in cylinder drying gave high tensile stiffness but low fracture energy. Zhang and co-workers (2004) showed that drying conditions influenced the tensile stiffness more than the tensile index, and fracture index more than internal strength. Recently Vainio et al. (2005) have studied how the interfibre bonding and fibre activation affect the strength properties of handsheets. In-plane properties of the sheets were improved by increasing drying stress due to the increasing activation in the fibre network (Vainio, Paulapuro 2005), whereas bond strength in most cases was decreased by increasing drying stress.

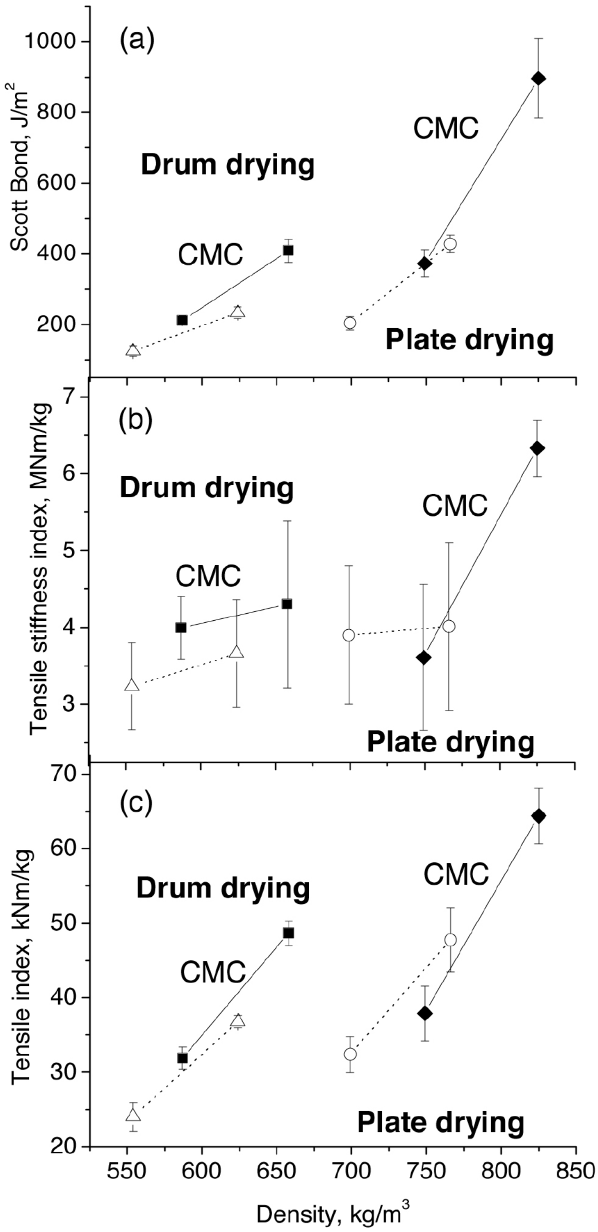

Fig 3. The effect of CMC addition and drying conditions (drum and plate dried sheets) on (a) Scott Bond (internal strength), (b) tensile stiffness index and (c) tensile index versus density of the sheets. The *solid lines* (CMC-treated) and *dashed lines* (reference) denote changes caused by beating (0 and 30 kWh/t). *Abbreviations:* (Δ) Reference drum dried, (■) CMC-treated drum dried, (❍) Reference plate dried, (◆) CMC-treated plate dried.

Previous studies in this laboratory have shown that modifying fibres with CMC resulted in superior sheet properties (when drying in the cylinder drum), but the elastic properties were less effected. Similar results were reported by Laine et al. (2002). However, the previous studies did not investigate the effect of the drying technique on tensile stiffness upon CMC modification. Recently, Vainio et al. (2006) investigated the effect of polyelectrolyte complexes of polyacrylamides and CMC on strength properties of paper. They showed that the polyelectrolyte addition did not affect the tensile stiffness, i.e. activation, whereas increasing drying stress increased activation significantly (Vainio, Paulapuro 2006). However, the z-directional and in-plane directional bond strength increased by adsorption of polyelectrolyte complexes.

Moreover, *Fig 3* illustrates that also the densities increased upon CMC-treatments. The light scattering values were also measured (data not shown) and the values correlated expectedly with the density values. In other words, density decreased when light scattering increased.

Also the fibre properties have an impact on tensile stiffness. Previous investigations have shown that deformed fibres (fibre curl, kink) form a fibre network where the load distribution is nonuniform compared to a situation with straight and undeformed fibres, thus leading to lower strength properties (Joutsimo, Wathen 2005; Page, Seth 1979). It has been shown that straight fibres have higher tensile stiffness compared to deformed fibres due to higher fibre segment activation (Joutsimo, Wathen 2005). Accordingly, *Table 1* shows that the beaten pulp has lower curl and coarseness values than unbeaten, thus leading to higher strength properties and tensile stiffness (*Fig 3*). Also Retulainen et al. (1993) showed that low coarseness fibres yield better strength and optical properties. According to Lobben (1975) two kinds of activation take place during beating. Firstly, beating increases the size and the number of bonds. The number of segments between bonds is increased and their length reduced. –Hence the greater densities as a function of beating (*Fig 3*). Secondly, drying under tension results in improved tensile strength and stiffness of the fibres or fibre segments (Lobben 1975). This can be seen in *Fig 3* where the strength properties are substantially increased when the sheets are dried under tension.

As discussed above, fibre deformation (curl) is a very important fibre property. Commonly an increase in strength is attributed either to increased bonding, through increased flexibility or fibrillation or to increased shrinkage stress. According to Page (1985) an even more important factor is that more than half of the improvement upon beating comes from straightening out, during beating, of the fibres that have been curled and kinked during pulping and bleaching. This should be kept in mind when laboratory results are interpreted and papermaking processes are planned.

In conclusion: when the sheets are dried under restraint and CMC-treated the strength properties (internal and tensile strength) are substantially increased, especially the tensile stiffness values.

The effect of fractionation: The pulps were fractionated in order to get more information about the role of the fines on the strength properties of the sheets. According to Retulainen et al. (1993) the main consequences of fines are increased density and improved activation of fibre segments and fibre wall material. Our results illustrated in *Figs 4-5* correlated well with the proposed increased densities and improved activation reported by Retulainen et al. (1993). Furthermore, *Fig 4* shows that the same trends between reference and CMC-treated pulps were seen in both fractionated and nonfractionated pulp.

When the fractionated and nonfractionated pulps were compared quite equal levels of internal strength values were seen for the unbeaten pulps but a dramatic increase

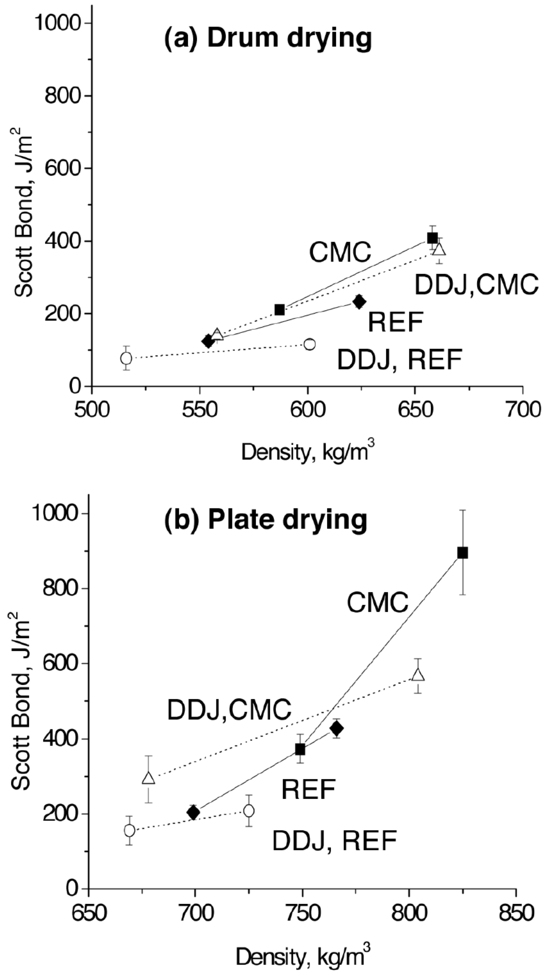

Fig 4. The effect of fractionation, CMC addition and drying conditions ((a) drum and (b) plate dried sheets) on the Scott Bond (internal strength) versus density of the sheets. The *solid lines* (nonfractionated) and *dashed lines* (DDJ-fractionated) denote changes caused by beating (0 and 30 kWh/t). *Abbreviations:* (◆) Reference, (■) CMC-treated, (○) DDJ-fractionated reference, (Δ) DDJ-fractionated CMC-treated pulp.

in strength values were seen when the pulps were beaten. This dramatic increase in internal strength cannot be merely explained by the slight increase in WRV after the CMC treatment (*Fig 2*). A marked increase (130%) in internal strength was observed especially when the pulps were CMC-treated, plate dried, nonfractionated and beaten. One explanation of this could be that the nonfractionated beaten pulp contains more fines thus leading to higher internal strength values. Similar results were published by Retulainen et al. (1996) who showed that interfibre bonds can be strengthened by the addition of dry strength chemicals and fines. Chemical pulp fines improved tensile strength, whereas mechanical pulp fines greatly improved light scattering and smoothness of the sheets. Moreover, fines have been shown to contribute to sheet consolidation, wet web strength and interfibre bonding (Retulainen, Moss 1993). Generally it can be said that fines affect density, tensile and internal strength, tensile stiffness, light scattering positively and tear strength negatively (Retulainen, Moss 1993). This is clearly seen in *Figs 4-5* as a decrease in density, internal strength and tensile stiffness when the pulps are fractionated. The same increasing trends are also seen for the CMC

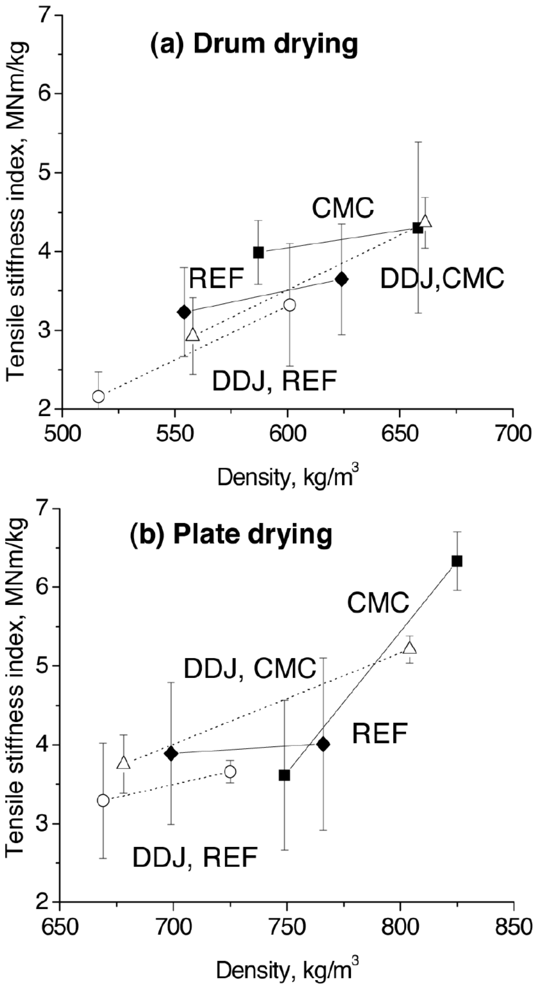

Fig 5. The effect of fractionation, CMC addition and drying conditions ((a) drum and (b) plate dried sheets) on the tensile stiffness index versus density of the sheets. The *solid lines* (nonfractionated) and *dashed lines* (DDJ-fractionated) denote changes caused by beating (0 and 30 kWh/t). *Abbreviations*: (◆) Reference, (■) CMC-treated, (○) DDJ-fractionated reference, (△) DDJ-fractionated CMC-treated pulp.

modified pulps. In addition, fines affect drainage rate negatively and fibre-fibre bonding negatively. It has been shown that smaller particles have better bonding ability but also the shape of the fines is an important factor (Retulainen, Luukko 2002). Paavilainen (1990) has proposed that the total surface area and bonding ability are the most important characteristics of the chemical pulp fines.

It should be mentioned that we also prepared sheets with circulating water. The results (data not shown) showed that the strength properties did not increase further. One explanation to this is that the added CMC maybe is able to bind the small fines in the fibre network so they do not end up in the circulating water resulting in equal strength properties.

Studies on fibre deformation and its effect on sheet properties may shed some light on the results in *Fig 5*. According to the current understanding of the mechanism of the stress-strain relationship of fibre, fibre curl will make the fibres less effective in carrying load (Omholt 1999). The network becomes less activated and the modulus of elasticity, as well as tensile strength, is reduced (Joutsimo, Wathen 2005). Stress transfer from one bond to the next is necessary in order to engage the whole sheets structure in carrying load, which is not possible when the fibre segment between the bonds are bent. *Table 1* and *Fig 2* shows that curl values were higher and WRV values lower for the fractionated pulps. Because the fractionated fibres were curlier than the non-fractionated a slightly lower stiffness was observed (*Fig 5*). Although more CMC was attached on the fractionated pulp fibres it did not result in better strength properties as would be expected. Earlier investigations have shown that fibre deformation seems to have a much larger effect on the sheet tensile strength than on elastic modulus (Seth 2006).

It can be concluded that the nonfractionated CMC-treated pulp sheets in general had higher internal strength and tensile stiffness than the DDJ-fractionated pulp (*Figs 4-5*).

Conclusions

Sorption of CMC on cellulosic fibres opens up new possibilities for the paper industry. The main advantages indicated by these experiments are good tensile and internal strength and especially tensile stiffness of paper. This previously unreported increase in tensile stiffness (75%) demonstrates that CMC modification can be very useful, for example, in packaging material applications.

The highest tensile stiffness values were obtained when the beaten hardwood pulp was CMC-treated and dried under tension. Hence, the paper strength properties are highly affected by the drying conditions. The fractionation experiments showed that fines affect the strength properties in a positive manner, also with CMC-treated pulp.

Acknowledgement

The authors wish to thank Emilia Vänskä for her excellent assistance in the laboratory work and Sari Panula-Ontto (KCL) and Myrtel Kåll for their help during the fractionation and KajaaniFiberLab analyses. The financial support from Sustainpack (6th Framework program of European Union) is gratefully acknowledged.

Literature

Blomstedt, M., Mitikka-Eklund, M. and Vuorinen, T. (2007): Simplified modification of bleached softwood pulp with carboxymethyl cellulose, Appita, 60(4), 309.

Blomstedt, M. and Vuorinen, T. (2007): Modification of a softwood kraft pulp with a carboxymethyl cellulose and cationic surfactants, J. Wood Sci. 53(3), 223.

Blomstedt, M. and Vuorinen, T. (2006): Fractionation of CMC-modified hardwood pulp, Appita, 59(1), 44.

Chance, J.L. (1992): Restrained drying: commercial experience, Appita, 45(2), 131.

Dubois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A. and Smith, F. (1956): Colorimetric method for determination of sugars and related substances, Anal. Chem. 28(3), 350.

Giertz, H.W. and Lobben, T. (1967): Recent developments in pulping processes, Pap. Technol. 8(3), 211.

Joutsimo, O., Wathen, R. and Tamminen, T. (2005): Effects of fiber deformations on pulp sheet properties and fiber strength, Paperi Puu, 87(6), 392.

Laine, J., Lindström, T., Glad-Nordmark, G. and Risinger, G. (2002): Studies on topochemical modification of cellulosic fibres. Part 2. The effect of carboxymethyl cellulose attachment on fibre swelling and paper strength, Nord. Pulp Paper Res. J. 17(1), 50.

Laine, J., Lindström, T., Glad-Nordmark, G. and Risinger, G. (2000): Studies on topochemical modification of cellulose fibres Part 1. Chemical conditions for the attachment of carboxymethyl cellulose onto fibres, Nord. Pulp Paper Res. J. 15(5), 520.

Laivins, G.V. and Scallan, A.M. (1996): The influence of drying and beating on the swelling of fines. J. Pulp Paper Sci. 22(5), J178.

Lobben, T.H. (1975): The tensile stiffness of paper. Part 1: a model based on activation, Norsk Skogindustri, 29(12), 311.

Mitikka-Eklund, M., Halttunen, M., Melander, M., Ruuttunen, K. and Vuorinen, T. (1999): Fibre engineering. 1, Oral presentations, 10th International Symposium on Wood and Pulping Chemistry, Yokohama, pp. 432-439.

Mitikka-Eklund, M. (1996): Sorption of xylans on cellulose fibres, Lic. Thesis, University of Jyväskylä, Jyväskylä, 76.

Mohlin, U., Dahlbom, J. and Hornatowska, J. (1996): Fiber deformation and sheet strength, Tappi J. 79(6), 105.

Omholt, I. (1999): The effects of curl and microcompresisons on the combination of sheet properties, Int. Paper Physics Conf., San Diego, USA, pp. 499-515.

Paavilainen, L. (1990): Importance of particle size – fibre length and fines – for the characterization of softwood kraft pulp, Paperi Puu, 72(5), 516.

Page, D.H., Seth, R.H., Jordan, B.D. and Barbe, M.C. (1985): Curl, crimps, kinks and microcompressions in pulp fibres – their origin, measurement and significance, Mechanical Engineering Publications Limited, Oxford, pp. 183-227.

Page, D.H., Seth, R.S. and De Grace, J.H. (1979): The elastic modulus of paper. I. The controlling mechanisms, Tappi, 62(9), 99.

Rantanen, M., Molarius, S., Pikkarainen, S., Knuutinen, J. and Pakarinen, P. (2006): Effect of carboxymethyl cellulose on pulp dispersing, Paperi Puu, 88(6), 346.

Retulainen, E., Luukko, K., Fagerholm, K., Pere, J., Laine, J. and Paulapuro, H. (2002): Papermaking quality of fines from different pulps: the effect of size, shape and chemical composition, Appita, 55(6), 457.

Retulainen, E., Moss, P. and Nieminen, K. (1993): Effect of fines on the properties of fibre networks. Vol. 2, Products of papermaking, Transactions of the 10th Fundamental Research Symposium, London, pp. 727-769.

Retulainen, E. and Nieminen, K. (1996): Fibre properties as control variables in papermaking? Part 2. Strengthening interfibre bonds and reducing grammage, Paperi Puu, 78(5), 305.

Richardson, J.D., Riddell, M. and Burrell, P. (2003): Experience with the FiberLab V3.0 analyser for measuring fibre cross-sectional dimensions. 57th APPITA Annual Conf., Melbourne, Australia, pp. 315-322.

Scallan, A.M. (1983): The effect of acidic groups on the swelling of pulps: a review, Tappi J. 66(11), 73.

Seth, R.S. (2006): The importance of fibre straightness for pulp strength, Pulp Paper Can. 107(1), 34.

Sundberg, A., Sundberg, K., Lillandt, C. and Holmbom, B. (1996): Determination of hemicelluloses and pectins in wood and pulp fibres by acid methanolysis and gas chromatography, Nord. Pulp Paper Res. J. 11(4), 216.

Turunen, M., le Ny, C., Tienvieri, T. and Niinimäki, J. (2005): Comparison of fibre morphology analysers, Appita, 58(1), 28.

Vainio, A. and Paulapuro, H. (2005): Observations on interfibre bonding and fibre segment activation based on the strength properties of laboratory sheets, Nord. Pulp Paper Res. J. 20(3), 340.

Vainio, A., Paulapuro, H., Koljonen, K. and Laine, J. (2006): The effect of drying stress and polyelectrolyte complexes on the strength properties of paper. J. Pulp Paper Sci. 32(1), 9.

Wahlström, T. (2000): Influence of shrinkage and stretch during drying on paper properties, Pap. Technol. 41(6), 39.

Wahlström, T. and Fellers, C. (2000): Biaxial straining of handsheets during drying – effect on in-plane mechanical properties, Tappi J. 83(8), 42.

Watanabe, M., Gondo, T. and Kitao, O. (2004): Advanced wet-end system with carboxymethyl-cellulose, Tappi J. 3(5), 15.

Wistara, N. and Young, R.A. (1999): Properties and treatments of pulps from recycled paper: Part 1. Physical and chemical properties of pulps, Cellulose, 6(4), 291.

Zhang, G., Keränen, J. and Niskanen, K. (2004): Effect of drying conditions on the mechanical properties of paper, Paperi Puu, 86(3), 164.

Manuscript received March 7, 2007
Accepted April 30, 2007