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**Sustainpack**

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**D2.50 Report on the effects/strategy of CMC deposition on tensile stiffness/ tensile strength of top layers of board**

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Laboratory of Forest Products Chemistry  
Helsinki University of Technology

**The effects/strategy of CMC deposition on tensile stiffness / tensile strength of  
top layers of board**

PROJECT REPORT FOR SUSTAINPACK

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## Introduction

This deliverable was launched in order to explore the effect of carboxymethyl cellulose (CMC) treatment to tensile stiffness of hardwood pulps. We focussed on bleached hardwood kraft pulp because of its widespread use as the material in the top layers of packaging board. Likewise, the effect of CMC treatment on tensile stiffness was monitored systematically because of the pivotal role of the stiffness index in packaging materials.

Several studies exist on the CMC treatment of bleached kraft pulps (see e.g. Blomstedt and Vuorinen *Appita J.* **2006**, 59, 44 or Laine et al. *Nordic Pulp Paper Res. J.* **2003**, 18, 316). The strength gains achieved by this surface specific sorption of CMC on the pulp fibres are exceptionally high: up to 200% increases in tensile strength have been reported. The reported effect of CMC sorption on tensile stiffness index, however, has been indifferent. Therefore, in this deliverable we intend to demonstrate that CMC sorption can be successfully applied to bleached hardwood kraft with substantial concomitant increase in the tensile stiffness index.

The results are divided in two parts. In the first section, we will elaborate on the effects of CMC treatment to a single pulp species, namely bleached birch kraft pulp. The effect of different drying techniques with the handsheets is of special interest due to the importance of the drying method on tensile stiffness. CMC sorption was also performed to DDJ fractionated pulp to illuminate the influence of fines. The second section consists of a comparison of bleached eucalyptus kraft pulp with the birch kraft in the first section.

## Experimental

### Pulp and carboxymethyl cellulose

The birch pulp used in the studies was a mixture of ECF bleached birch (95%) and aspen (5%) kraft pulp. The pulp was refined in 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 eucalyptus pulp used in the studies was industrial ECF bleached eucalyptus kraft pulp. The pulp was refined in Voith Sulzer LR1 research refiner with disk fillings 2/3-1.46-40D, designed for short-fibre pulps. The refining consistency was 4.0% and specific edge load 0.3 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 ( $DP_v$ ) 700 for the CMC grade used.

### DDJ fractionation

Fines were removed from the birch pulp by using a Super Dynamic Drainage Jar-apparatus (DDJ) in KCL, Finland. 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

The commercial KajaaniFiberLab analyses were carried out according to TAPPI T271. 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.

### **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). The sorptions (reference pulp pH 5.5 and CMC pulp pH 11) were carried out in glass beakers. The temperature was raised to 60°C in 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 and acid methanolysis combined with gas chromatography (GC). 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.

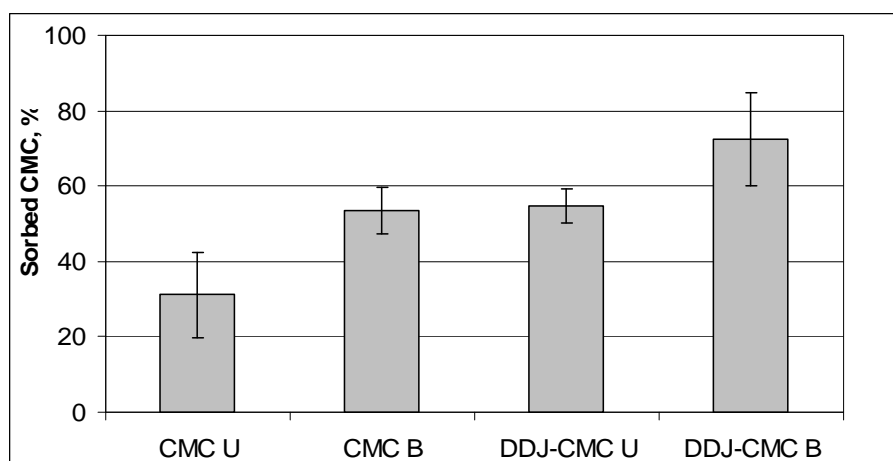
The laboratory sheets were prepared in deionised water by the standard method ISO 5269-1, with the exception of wet pressing at 490±20 kPa (4 min. 20 sec) and drying in a drum dryer at 60°C for 2 h. When drying plates were used the wet pressing was carried out in two steps. The first pressing was at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

The grammage of the sheets was determined by standard method ISO 536, density and thickness according to ISO 534. The light scattering coefficient was measured with an Elrepho reflectometer by standard method ISO 5631. The tensile strength and tensile stiffness of the laboratory sheets were determined with a tensile testing machine (MTS 400M) according to SCAN-P 38:80. Bonding ability (internal strength) was measured according to Tappi 833 pm-94.

## **Results Part I – Bleached Birch Kraft**

### **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*). Moreover, 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. Although the main trends of the attached amount of CMC are certainly detectable in *Fig 1*, there is considerable variation that was observed between the two analysis methods, which can be due to soluble hemicelluloses in the sorption filtrates.



**Figure 1.** The attached amount of CMC on unbeaten (U, 0 kWh/t) and beaten (B, 30 kWh/t) CMC-treated (CMC) unfractionated and fractionated (DDJ) hardwood pulp.

### Fibre properties of pulp treated with CMC

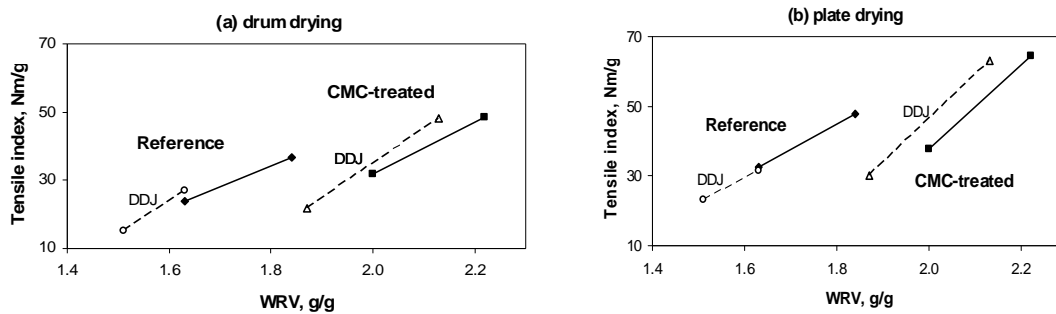
The fibre properties of the CMC-treated pulps are listed in *Table 1*. Concerning the curl values, it is clearly evident that the fractionated pulps have higher curl values compared to the nonfractionated hardwood pulp (*Table 1*). This happens probably because the DDJ fractionation process makes the fibres curlier. These higher curl value is 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 makes the fibres straighter. In addition, the cell wall thickness and fibre width is slightly higher for the fractionated pulp. The fines content is 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 have been fractionated the SR-number is equal and lower than the SR-numbers of the nonfractionated pulp. This could be explained by the fact that nearly all fines have been removed during the fractionation resulting in a pulp that has practically the same properties despite beating or not.

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

Sample/ Beating level (kWh/t)	Cell wall thickness ( $\mu\text{m}$ )	Fibre length (mm)	Fibre width ( $\mu\text{m}$ )	Curl value (%)	Coarseness (mg/m)	Fines content (%)	SR- number
<b>Non fractionated</b>							
0	5.7	0.99	20.7	15.9	0.094	1.38	23.2
30	5.8	0.98	20.7	14.8	0.090	1.66	16.2
<b>DDJ-fractionated</b>							
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 is generally used to determine the swelling capacity of pulps. Introduction of additional, charged groups by, for example, CMC generally results in a higher WRV. In consequence, sorption of 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 previous

work performed by our group (Mitikka-Eklund et al. *Fibre engineering*. 10th International Symposium on Wood and Pulping Chemistry. Book 1: Oral Presentations. Yokohama: 1999. p. 432). Beating of the pulp led to an increase in the 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, which is expected since fines swell more than fibres in general.



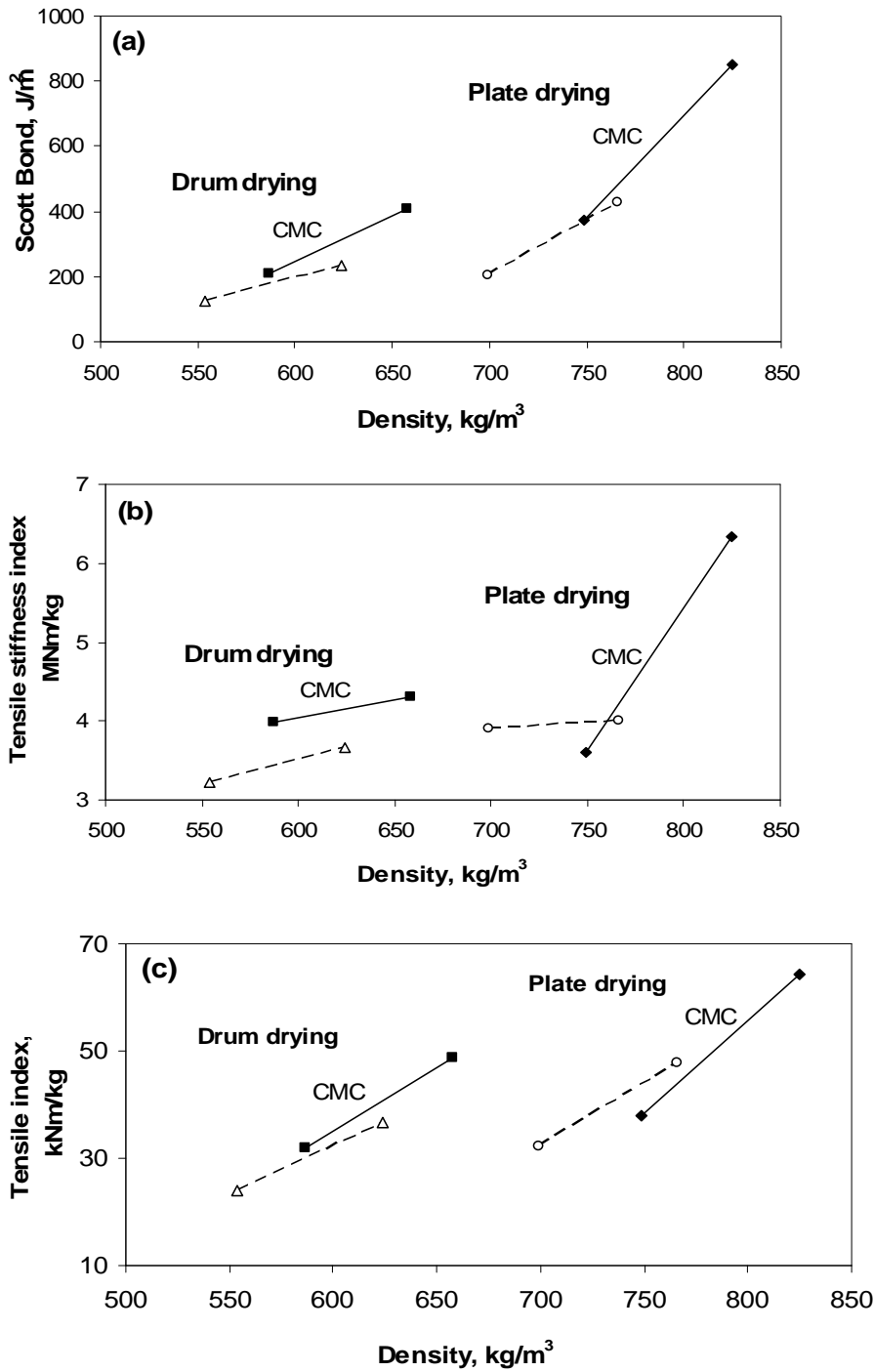
**Figure 2.** The effect of CMC addition and drying conditions ((a) drum and (b) plate dried sheets) on the tensile strength properties versus water retention values (WRV). The solid (nonfractionated) and dashed lines (DDJ-fractionated) denote changes caused by beating (0 and 30 kWh/t). Abbreviations: (◆) Reference, (■) CMC-treated, (○) DDJ-fractionated reference, (Δ) DDJ-fractionated CMC-treated pulp.

## 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 sheets are restrained. In *Fig. 3* it can be seen 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. Similar stiffness values have not been published before.

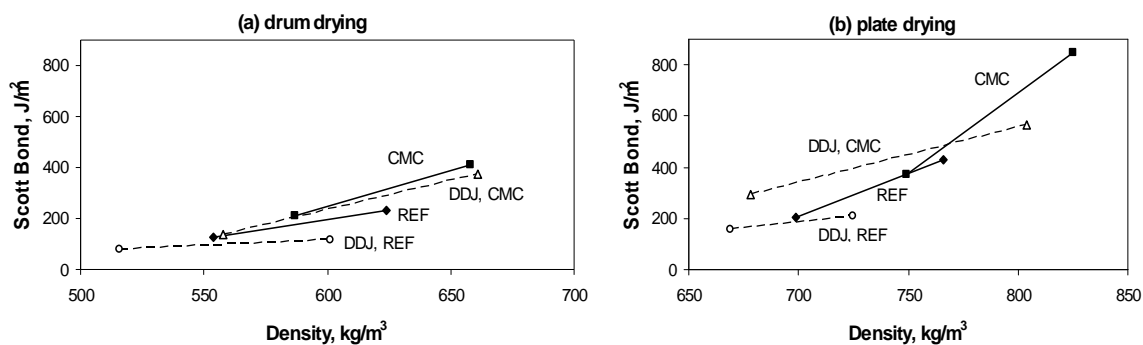
The drastic influence of the drying technique on the tensile stiffness index can be attributed to earlier results: drying under restraint has been found to greatly increase the tensile stiffness of paper (Wahlström and Fellers *Tappi* **2000**, 83, 42). The CMC sorption seems to have an incremental effect on this.



**Figure 3.** The effect of CMC addition and drying conditions (drum and plate dried sheets) on (a) tensile index, (b) tensile stiffness index and (c) Scott Bond (internal strength) versus density of the sheets. The solid (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.

### 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. *Fig. 4* shows that the same trends between reference and CMC-treated pulps were seen in both fractionated and nonfractionated pulp, although lower densities were reached when the sheets were fractionated. 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 in strength values was seen when the pulps were beaten. This dramatic increase in internal strength cannot merely be 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 to this can be that the nonfractionated beaten pulp contains more fines thus leading to higher internal strength values.



**Figure 4.** The effect of 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 (CMC-treated) and dashed lines (reference) denote changes caused by beating (0 and 30 kWh/t). Abbreviations: (◆) Reference, (■) CMC-treated, (○) DDJ-fractionated reference, (△) DDJ-fractionated CMC-treated pulp.

### Summary on the results from bleached birch kraft pulp

All strength properties of subsequent handsheets were improved upon CMC sorption on bleached birch kraft pulp. In particular, tensile stiffness index was greatly increased (75%) when the handsheets from CMC treated pulp were subjected to restrained drying between drying plates. Fines removal by fractionation led to lower strength levels due to increased curl and lower Scott bond.

## Results Part 2 – Bleached Eucalyptus Kraft

### Sorption of CMC on fibres

Unbeaten eucalyptus pulp sorbed about 30-40% of high-molecular weight CMC ( $DP_v$  700, DS 0.32) whereas beating of the pulp led to 60-80% sorption at 1% CMC addition. The results correlate well with the sorption degrees reported in the previous passage for birch kraft pulp (*Fig. 1*).

### Fibre properties

One reason why we wanted to look closer at the fibre morphology of eucalyptus pulp was because the strength properties were different from birch. Significant difference in strength values was detected especially in the tensile stiffness values within these two hardwood

species. It should be mentioned that considerable variations in morphological properties exist between different individuals of the same wood species, and even within the same tree. The fibre dimensions and cross-sectional dimensions of eucalyptus, reference and CMC-treated pulp are illustrated in Table 2. Furthermore, Table 2 shows that beating of the pulp makes the fibres straighter in other words the curl values decreases when the pulps are refined. In addition, longer beating produces more fines and fibrillation of the fibres. The decreasing curl and coarseness values and increasing fine content by beating eucalyptus pulp are in agreement with the fibre properties of birch (Table 1), although eucalyptus pulp has less fines when refined to the similar level as birch. A lower fines content for eucalyptus pulp would be expected to lead to better drainage and drying properties but lower strength properties.

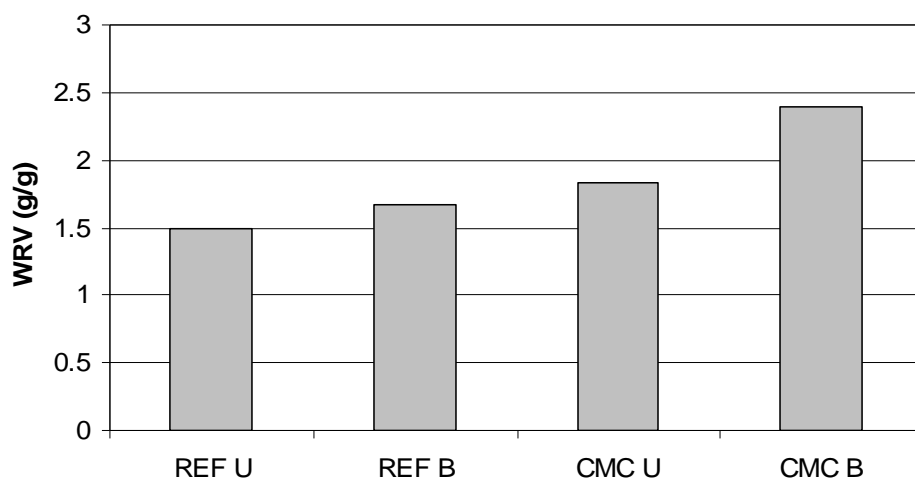
**Table 1.** Cell wall thickness, length-weighted fibre length, fibre width, fibre curl, fibre coarseness, fines, fibrillation, kink content and vessel cell content of original, reference (REF) and CMC-treated (CMC) eucalyptus pulp.

Sample/ Beating level (kWh/t)	Eucalyptus	Eucalyptus	REF	REF	CMC	CMC
	0	30	0	30	0	30
Cell wall thickness ( $\mu\text{m}$ )	4.4	4.4	4.3	4.3	4.4	4.4
Fibre length (mm)	0.86	0.87	0.83	0.84	0.83	0.86
Fibre width ( $\mu\text{m}$ )	15.9	15.8	16.0	15.9	15.9	15.8
Curl value (%)	21.0	18.1	23.1	21.7	21.9	19.3
Coarseness (mg/m)	0.067	0.067	0.068	0.066	0.068	0.064
Fines content (%)	1.34	1.37	1.29	1.44	1.13	1.20
Fibrillation (%)	0.72	0.79	0.76	0.92	0.62	0.77
Kink (1/m)	2454.2	1689.2	3121.1	2750.7	2495.8	1919.5
Vessel (1/m)	27.6	20.9	34.6	28.2	23.9	22.7

An interesting observation is that the vessel content decreases for the CMC-treated pulp compared to the corresponding reference pulp (Table 2). One explanation to this could be that the CMC layer on top of the surface of fibres helps the vessels to stay inside the fibre network, resulting in decreased vessel content. This means that CMC modified fibres would be an easy way to reduce the vessel picking problem (a phenomenon where some hardwood vessel elements on paper surface tend to be picked of by the ink-tackiness of printing press, creating white spots on the surface).

When birch and eucalyptus fibre properties are compared the following conclusions could be made. Eucalyptus pulps have smaller cell wall thickness, fibre length, fibre width and coarseness than birch pulp. These results are in accordance with the earlier reports (e.g. Patt et al. *Wood Sci. Technol.* **2006**, *40*, 39). Also the chemical composition of hardwood pulps has a strong influence on the final fibre and sheet properties. According to literature, eucalyptus contains more lignin and cellulose and less hemicellulose than birch and beech. High hemicellulose content improves beatability fibre flexibility and tensile strength but reduces pulp opacity.

As for the swelling capacity, both CMC sorption and beating of the pulp led to an increase in the WRV values as could be expected (Fig. 5). The increased WRV values in the eucalyptus pulps are similar to the ones in birch pulps (Fig. 1).



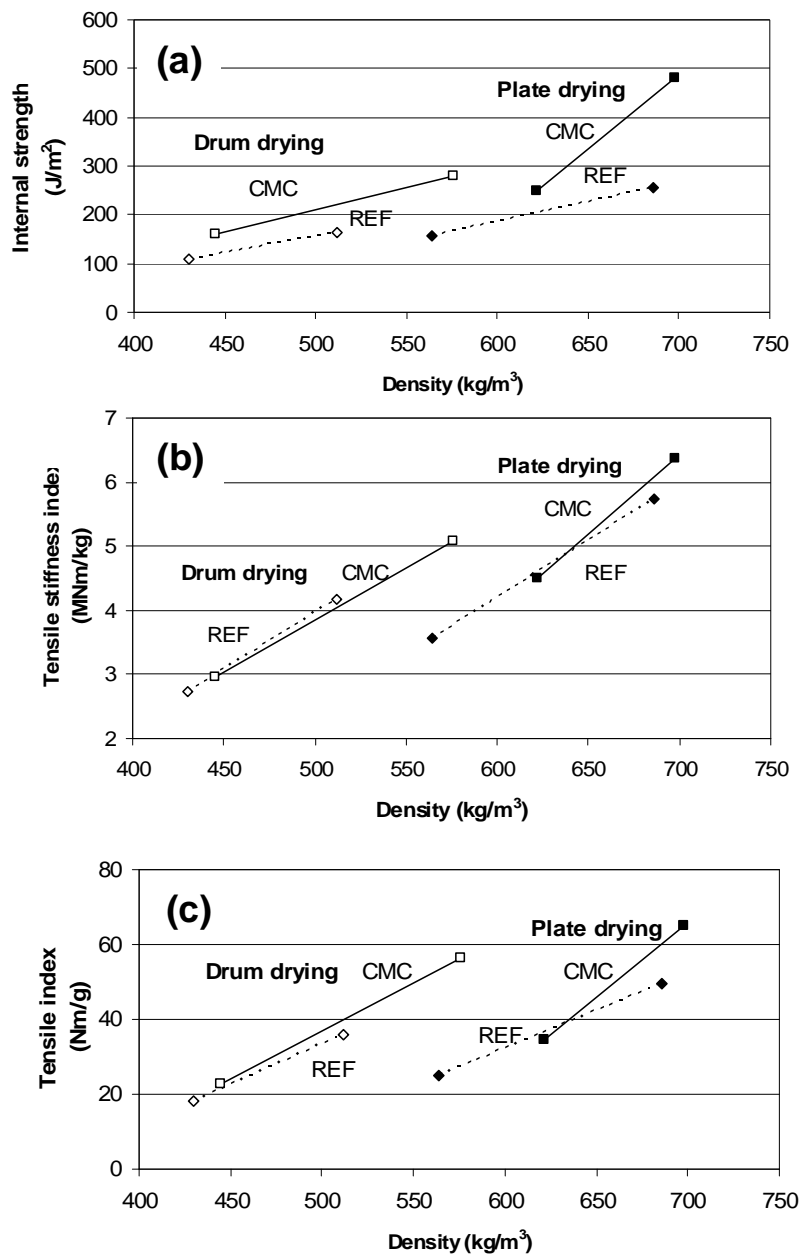
**Figure 5.** Water retention values of unbeaten (*U*) and beaten (*B*) reference (*REF*) and CMC-treated (*CMC*) eucalyptus pulp.

### Sheet properties of pulp treated with CMC

The effect of CMC treatment and different drying techniques on the strength properties of handsheets from eucalyptus pulp are highlighted in Figure 6. Similar to the birch pulps (Fig. 3 and Fig. 4), drying under strain results in greater internal strength (Fig. 6a), tensile stiffness (Fig. 6b), and tensile strength (Fig. 6c) on the handsheets from CMC treated fibres. However, the relative increases in tensile strength (Fig. 6c) and tensile stiffness (Fig. 6b) are far lower than those of birch pulp (Fig. 3). One major difference between eucalyptus and birch is that eucalyptus also gives high strength properties for the reference pulp.

### Summary on the results from bleached eucalyptus kraft pulp

The main conclusions are that CMC-treated eucalyptus pulp gave high strength properties. The strength properties were similar to that of birch, except that also the reference pulps gave high strength properties.



**Figure 6.** The effect of CMC addition and drying conditions (drum and plate dried sheets) on (a) internal strength, (b) tensile stiffness index and (c) tensile strength versus density of the sheets. The solid (CMC-treated) and dashed lines (reference) denote changes caused by beating (0 and 30 kWh/t). Abbreviations: ( $\diamond$ ) Reference drum dried, ( $\square$ ) CMC-treated drum dried, ( $\blacklozenge$ ) Reference plate dried, ( $\blacksquare$ ) CMC-treated plate dried.

## **Conclusions**

Contrary to earlier studies, we have found that the enhancement of tensile stiffness index is feasible by CMC sorption on bleached hardwood kraft fibres. The key to the optimisation of tensile stiffness lies in the selection of the correct drying technique. When handsheets from bleached birch fibres were dried under restraint with drying plates, a 75% increase in tensile stiffness was observed upon CMC treatment. Also the effect of fractionation on the CMC treatment was studied and a negative impact on the strength properties was found, probably induced by the increased fibre curl caused by DDJ fractionation.

The effect of CMC treatment on the tensile stiffness of bleached eucalyptus pulp was far less significant than in the case of birch pulp. However, the reference values for eucalyptus pulp were greater than those for birch pulp.