

INFLUENCE OF ADSORBED AND DISSOLVED CARBOXYMETHYL CELLULOSE ON FIBRE SUSPENSION DISPERSING, DEWATERABILITY, AND FINES RETENTION

Henrikki Liimatainen,^{a*} Sanna Haavisto,^b Antti Haapala,^a and Jouko Niinimäki^a

The effect of adsorbed and soluble carboxymethyl cellulose (CMC) on dispersing, dewaterability, and fines retention of pulp fibre suspensions was investigated. CMC was added to a suspension in the presence of electrolytes, causing its adsorption to the fibre surfaces, or to a suspension without electrolytes, so that it stayed in the liquid phase. Both the CMC adsorbed on fibre surfaces and that in the liquid phase were able to disperse the fibre suspension due to the ability of CMC to reduce fibre-to-fibre friction in both phases. Adsorbed CMC promoted the formation of a water-rich microfibrillar gel on the fibre surfaces through the spreading out of microfibrils, leading to a decrease in friction at the fibre-fibre contact points and to the increased dispersion of fibres. CMC in the liquid phase of the suspension was in turn thought to prevent fibre-to-fibre contacts due to the large physical size of the CMC molecules. CMC in both phases had detrimental effects on dewatering of the pulp suspension, but adsorbed CMC caused more plugging of the filter cake, and this was attributed to its ability to disperse fibre fines, in particular. Thus, adsorbed CMC also reduced fines retention considerably more than did CMC in the liquid phase of a suspension.

Keywords: Carboxymethyl cellulose; Fibre; Dispersing; Deflocculation; Flocculation; Adsorption; Pulp

Contact information: a: Fibre and Particle Engineering Laboratory, Department of Process and Environmental Engineering, P.O. Box 4300, 90014 University of Oulu, Finland; b: VTT, P.O. 1603, 40101 Jyväskylä, Finland; *Corresponding author: henrikki.liimatainen@oulu.fi

INTRODUCTION

Carboxymethyl cellulose (CMC) is an anionic derivative of cellulose that is widely used in the food, textile, pharmaceutical, cosmetic, and paper industries as a thickener, binder, and stabilizer. In papermaking CMC is used as a wet-end additive to improve paper sheet dry strength and uniformity, i.e. formation, by virtue of its ability to disperse fibres and reduce their flocculation. One disadvantage of using CMC for this purpose is its detrimental effect on the dewatering properties of the fibre suspension. It reduces free water removal from the pulp and increases the amount of bound water attached to the fibre surfaces (Joutjärvi 2004). More detailed knowledge of the dispersing mechanism of CMC would be of particular interest in order to minimize its harmful effects on dewatering efficiency during the filtration of fibres.

The dispersing mechanisms of synthetic and natural polymers in fibre suspensions have been studied by several authors (Lee and Lindström 1989; Wasser 1978; Yan et al. 2006; Zhao and Kerekes 1993). Most of the polymeric dispersing agents have been

shown to affect either the surface properties of fibres, resulting in lower frictional forces between them (Yan et al. 2006; Zauscher and Klingenberg 2001), or fluid properties, by modifying shear viscosity (Beghelli 1998; Zhao and Kerekes 1993) and other rheological suspension properties (Lee and Lindström 1989). The mechanism of action of adsorbing, i.e. surface modifying, polymeric dispersants is attributed to the formation of a hydrated layer or electrosteric barrier on the fibre surfaces that reduces friction at their contact points (Yan et al. 2006), while the activity of non-adsorbing dispersing agents is based on the alteration of fluid properties. An increase in shear viscosity reduces the relative motion of the fibres and lowers the fibre crowding that would otherwise result in flocculation (Zhao and Kerekes 1993). Since the dosages of dispersing agents are often too low to effectively reduce the shear viscosity of a suspension, it has also been proposed that polymeric dispersants increase the elongational viscosity that occurs when polymers are forced to stretch out from the gap between two approaching fibres (Lee and Lindström 1989; Yan et al. 2006). This results in lower fibre crowding and reduces flocculation.

Several studies have also been published dealing with the dispersing mechanism of CMC (Beghelli and Lindström 1998; de Roos 1958; Giri et al. 2000; Horvath and Lindström 2007; Rantanen et al. 2006; Yan et al. 2006), but the results have been inconsistent, suggesting that its action may be related either to its adsorption to fibres (Beghelli and Lindström 1998; de Roos 1958; Giri et al. 2000; Horvath and Lindström 2007; Yan et al. 2006) or its effects on the liquid phase of the suspension (Rantanen et al. 2006; Paul et al. 2001). Yan et al. (2006) stated recently that the dispersing action is limited entirely to adsorbed CMC, whereas Rantanen et al. (2006) concluded that the CMC molecules located between fibres in the liquid phase prevents fibre flocculation by means of electrostatic repulsion, although they did not analyse the amount of adsorbed CMC. Since existing results regarding dispersing mechanisms involved in the action of CMC are ambiguous, and the various mechanisms have not been compared in the same frame of reference, it is unclear whether CMC is active when adsorbed to the surfaces of fibres or when in the liquid phase, nor is it known how these mechanisms affect dewatering and fines retention in pulp suspensions. Further knowledge of the dispersing mechanisms of CMC could be used to optimize CMC use as a dispersing agent in wet-end stock preparation, since the adsorption of CMC can be controlled by adjusting the chemical conditions (Watanabe et al. 2004)

The aim of this paper was to compare how CMC affects fibre dispersing when adsorbed to fibres and when it is in the liquid phase of the suspension and to clarify how these mechanisms affect dewatering and fines retention in the fibre suspension in filtration-based processes. The dispersive activity of CMC was characterized by measuring the strength of fibre network formed within suspensions of defined consistency. Fines retention and dewaterability of fibre suspension, analysed in terms of average filtration resistances (SFRs), were measured with a vacuum filtration apparatus and with a gravity-driven filtration system equipped with a pulsed ultrasound-Doppler (PUD) anemometer.

EXPERIMENTAL

Bleached pine (*Pinus sylvestris*) chemical pulp obtained in dry lab form was disintegrated in deionized water and beaten in a PFI mill (3000 revs) according to the EN ISO 5264-2:2002 standard. The Canadian Standard Freeness (CSF) value of pulp was 571 ml. The fines content, i.e. the proportion of the pulp fragments passing through a 200-mesh (76 μm) screen, was 4.5% w/w, measured with a Bauer McNett classifier. The total charge as obtained from methylene blue sorption (Fardim et al. 2002) and the zeta potential measured with a Müttek SZP-06 device, based on detection of the streaming potential of the sample, were -55 $\mu\text{mol/g}$ and -79 mV, respectively.

The pulp was treated with acid (0.01 M HCl) before the CMC additions in order to remove metal ions and then converted to sodium form by treatment with NaHCO_3 (0.001 M) at pH 9.5 (pH adjusted with a 0.1 M NaOH solution). It was then washed with deionized water until its conductivity was less than 5 $\mu\text{S/cm}$ (Wågberg and Björklund 1993). The filter papers used in these washing stages were: Schleicher & Schuell no. 604 and Macherey Nagel no. 617.

Four commercial sodium carboxymethyl cellulose (CMC) grades with different molecular weights and degrees of substitution were obtained from CP Kelco. Relative viscosity values measured at constant background salt concentration as given by the manufacturer were used to indicate the relative molecular weights of the CMCs. The molecular weight has been shown by Griebel et al. (1992) to increase with the viscosity of the CMC solution. All the grades were water-soluble, having a degree of substitution of 0.5 or higher. CMC samples I and IV were technical grades containing about 40% sodium chloride (NaCl) and sodium glycolate ($\text{HOCH}_2\text{COONa}$) as impurities, while samples II and III were purified grades containing about 2% impurities. The CMCs were supplied as dry powders, from which solutions with a CMC content of 1.0% were prepared by mixing the polymer granules into deionized water while stirring at 200 rpm for 90 min at room temperature. The properties of the CMC grades are summarized in Table 1. All the other chemicals used were of p.a. grade.

Table 1. Properties of CMC Grades

<i>Grade</i>	<i>Relative viscosity</i>	<i>DS</i>
CMC I	1.3	0.5
CMC II	1.7	0.7
CMC III	1.0	0.6
CMC IV	5.3	0.6

Fibre Treatment and Measurement of CMC Adsorption

The pulp fibres were treated with CMC in either of two manners: 1) CMC was adsorbed to the fibre surfaces in the presence of electrolytes in order to prepare a sample in which it was located only on the fibre surfaces and was absent from the liquid phase, and 2) CMC was added directly to the washed pulp suspension without electrolytes in order to produce a sample in which CMC remained in the liquid phase. The resulting pulp samples are referred to here as “adsorbed CMC” and “liquid phase CMC”, respectively.

The method used for the irreversible adsorption of CMC to fibre surfaces was modified from the procedure reported by Laine et al. (2000) in which the repulsion between the anionic fibres and negatively charged CMC that prevents the natural adsorption of CMC to fibres (Hensley and Inks 1959; Watanabe et al. 2004) is reduced by means of electrolytes. The adsorption was conducted by adding a CaCl_2 electrolyte solution (0.05 M) to a pulp suspension buffered to pH 8 with 0.01 M NaHCO_3 , followed by addition of the CMC. The suspension was then filtered after 60 minutes of adsorption, washed with deionized water and resuspended in order to separate out the CMC-covered fibres and remove any CMC that was left in the liquid phase. The samples containing CMC in the liquid phase were prepared by adding CMC directly to an electrolyte-free pulp suspension. The CMC treatments were conducted at a pulp consistency of 25 g/dm^3 (2.5% w/w) at room temperature. A reference was obtained for the analyses by treating a similar pulp by the same methods but without any CMC additions.

The amount of adsorbed CMC was determined at constant electrolyte concentration by colloid titration (Watanabe et al. 2004) using poly(dimethyldiallyl-ammonium) chloride (PolyDADMAC, $M_w \sim 150\,000$, Ciba Specialty Chemicals Ltd) as a cationic polymer. A sample from the liquid phase of the pulp suspension was filtered with a Büchner funnel (filter papers: Schleicher & Schuell no. 604 and Macherey Nagel no. 617), centrifuged and titrated using the Müttek Particle Charge Detector, PCD 03 pH. Calibration lines for PolyDADMAC consumption versus CMC concentration (correlation constants $R^2 > 0.97$) were used to determine the amount of CMC in the solutions. CMC concentration was also determined from the pulp washing water in order to confirm that CMC was irreversibly adsorbed on fibre surfaces. No significant amounts of CMC were found to detach under the chemical conditions used.

Measurement of Fibre Network Strength

The characterization of the fibre network strength was based on torque measurements performed on suspensions at a pulp consistency of 0.6%. A similar method has previously been used by Andersson et al. (1999), Jokinen et al. (2006), and Wikström and Rasmuson (1998). In the present case a Brookfield rotary viscometer DV-1+ with modified blade spindle was used, as described by Karjalainen (2004), and a shear diagram was constructed by measuring ten replicates for suspension torque on the blade at four rotational velocities (0.3 - 1.5 rpm), from which the apparent yield stress was obtained by extrapolating the linear portion of the diagram to a zero shear rate. A detailed description of the fibre network strength measurement method and apparatus is given by Karjalainen (2004).

Filtration Experiments

The effect of the CMC treatments on dewatering of the fibre suspension, in terms of average specific filtration resistances (SFRs), was characterized with a vacuum filtration apparatus and a gravity-driven filtration system equipped with a pulsed ultrasound-Doppler (PUD) anemometer. The vacuum filtrations were carried out by filtering the pulp suspensions through a wire (open area 16%; 0.20 mm monofilament) under a constant pressure difference of 18 kPa at room temperature. The fluid was drained without fibre mat formation at the beginning of the experiment, but a filter cake

started to form on the wire in the course of time, and the thickening of the fibre network evolved into cake filtration. The total filtration time was 120 seconds. The fibre consistency and total volume of suspension were 1.2% and 2500 cm³, respectively. The experimental set-up of the filtration apparatus was similar to that described previously (Liimatainen et al. 2006).

Average specific resistances after 13 seconds of filtration were calculated based on Eq. (1),

$$\frac{1}{A} \frac{dV}{dt} = \frac{\Delta p}{\eta \left(\alpha_{av} \frac{W}{A} + R \right)} \quad (1)$$

where dV/dt is the volumetric flow rate of the filtrate, A is the filtration area, Δp is the pressure difference across the fibrous mat and wire, η is the viscosity of the filtrate, α_{av} is the average specific filtration resistance of the filter cake, W is the mass of solids retained, and R is the filtration resistance of the wire. A detailed method for determining the SFR was presented by Wakeman and Tarleton (1999), for instance. The effect of particle retention was taken into account in the values presented here. The relative standard deviation (RSD) of the SFR measurement was below 5.5%. Fines retention was monitored in the filtration by measuring the turbidity of the filtrates with a Hach Ratio/XR turbidimeter after a constant cumulative amount of filtrate (1000 ml) had been obtained. The bound water content of the fibres, i.e. the removal of attached water, was evaluated by measuring the water content of the filter cakes after vacuum filtration and determining water retention values after the free water had been flowing from the cakes for a constant filtration time.

The gravity-driven filtration system measures the local time-dependent velocity field of the fibre phase during vertical filtration simultaneously with the instantaneous velocity of the free surface of the fibre suspension and fluid pressure on the filtration, enabling other relevant flow quantities such as fluid velocity, pressure, consistency, flow resistance and the structural stress of the fibre network to be calculated from these data using two-phase flow equations. The system thus provides detailed information on the dynamics of filtration and the material properties of the consolidating fibre suspension. The device and the measurement method have been explained in detail by Kataja and Hirsilä (2001).

The initial consistency of the fibre suspensions in the gravity-driven filtration experiments was 0.2% in a total volume of 8000 cm³, and the total filtration times varied from 50 to 70 seconds. The flow resistance taken here to characterise the effect of CMC treatments on dewatering was calculated as the ratio between the measured instantaneous total flux and the pressure loss in the fibre suspension during filtration. Flow resistances were compared after 30 seconds of filtration.

In addition, to the SFRs, a generally used drainage indicator, the Canadian standard freeness (CSF) value, was measured for the pulps according to TAPPI Method 227 om-99. This method differs significantly from the SFR methods, however, e.g. in that it measures drainage at the very beginning of filtration.

RESULTS

Adsorption of CMC

The adsorption of the different CMC grades to fibres in the absence and presence of electrolytes is shown in Fig. 1. The impurity content of the CMC (40% in samples I and IV, and 2% in samples II and III) is taken into account in the doses by presenting the results as a function of the amount of pure CMC.

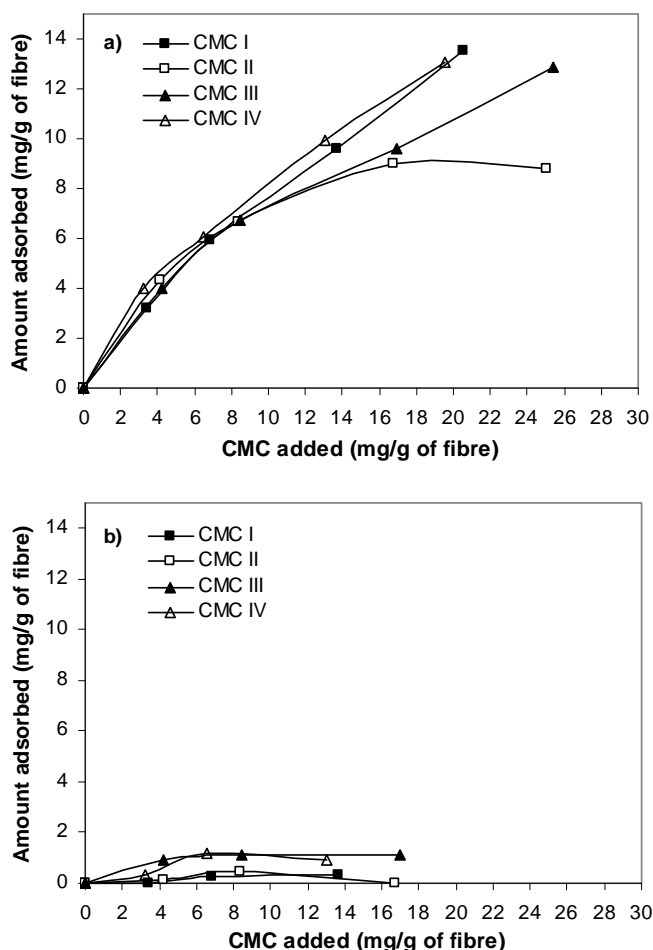


Fig. 1. Adsorption of CMC on fibres: (a) in the presence of electrolytes (0.05 M CaCl₂ and 0.01 M NaHCO₃), and (b) in the absence of electrolytes.

The difference between the CMC treatments, i.e. between adsorption in the presence and absence of electrolytes, is clearly seen in the amounts of adsorbed CMC. As expected, CMC, all grades of which were water-soluble and had a moderately high degree of substitution (0.5 or higher), showed only slight adsorption onto the anionic pulp fibres in the absence of electrolytes, due to repulsion between similar charges. This is also supported by the published results of Mitikka-Eklund et al. (1999) and Watanabe et al. (2004). The amount of adsorbed CMC as a function of dosage was almost constant for all CMC grades, the average being 0.4 mg/g pulp, showing that the amount of CMC in the liquid phase of the fibre suspension was over 80% of the total dosage, i.e. the

maximum adsorbed amount was about 20% of the total dosage. Although the impurity content of the CMC increased electrolyte concentration in the suspensions, the increase was defined too small to affect its adsorption, being about 0.005 M.

The presence of electrolytes screened the repulsion between the anionic charges, leading to increased adsorption of CMC to the fibres. The adsorption has been attributed to hydrogen bonding between the hydroxyl groups of CMC and cellulose (Laine et al. 2002; Watanabe et al. 2004). The molecular weight of CMC was not found to affect the amount adsorbed, but the increase in the degree of substitution seemed to reduce the maximum amount adsorbed, since the amount adsorbed was lower with CMC III than with other grades. Laine et al. (2000) and Watanabe et al. (2004) have also found that the adsorption of CMC increases as the degree of substitution decreases, while the increase in molecular weight leads to increase in adsorption. Since the plateau levels of adsorption were not reached with the CMC dosages used, and since CMC has been reported to follow a monolayer adsorption (Giri et al. 2000), the results suggest that the fibre surfaces were only partly covered by CMC. The maximum adsorption of CMC to bleached kraft softwood pulps has been observed to be 15 - 30 mg/g, depending on its molecular weight (Giri et al. 2000). This suggests that the surface coverages achieved here were about 45 to 90%.

Effect of CMC on Fibre Network Strength

The dispersive activity of the CMCs was characterized in terms of fibre network strength by measuring the apparent yield stresses of the CMC-treated pulps. Yield stress implies the stress below which the substance is an elastic solid. As the yield stress is exceeded, the fibre network breaks down to flocs and the fluid starts to flow (Wikström and Rasmuson 1998). Floc size in turn correlates with network strength, i.e. the state of dispersion can be related to network strength (Beghello and Lindström 1998).

The yield stresses, presented relative to the values for reference pulps treated under same conditions, are shown in Fig. 2. Both adsorbed CMC and liquid-phase CMC significantly reduced the fibre network strength, implying that CMC affected fibre dispersing both when located on the surface of the fibres and when contained in the liquid phase of the suspension. The CMCs adsorbed to the fibres reduced the network strength by 70 - 80% at the highest CMC dosage, however, whereas 40 - 60% reductions were obtained when the CMCs were in the liquid phase. Dispersive activity was not observed to alter systematically with either the molecular weight or the degree of substitution of the CMC.

Effect of CMC on Dewatering of the Fibre Suspension

The effect of CMC treatments on dewatering, i.e. removal of free water from the pulps, was analysed by measuring the average specific filtration resistance with a vacuum filtration apparatus and with a gravity-driven filtration system equipped with a pulsed ultrasound-Doppler (PUD) anemometer. The vacuum filtration method differed from the PUD measurements in that it involved a higher pressure difference across the fibrous cake and a higher fibre consistency in the filtered pulp suspension, so that the fluid velocity through the filter cake was higher and a thicker cake was formed. The SFRs, presented relative to the values for the reference pulps, are shown in Fig. 3 and 4. CMC

significantly increased the filtration resistance of the pulp, i.e. it reduced free water removal, both when the CMC was located on the surfaces of the fibres and when it was contained in the liquid phase of the suspension. The adsorbed CMCs caused a higher increase in SFR than that in the liquid phase in vacuum filtration, whereas the SFR increased in a similar manner as in the PUD method.

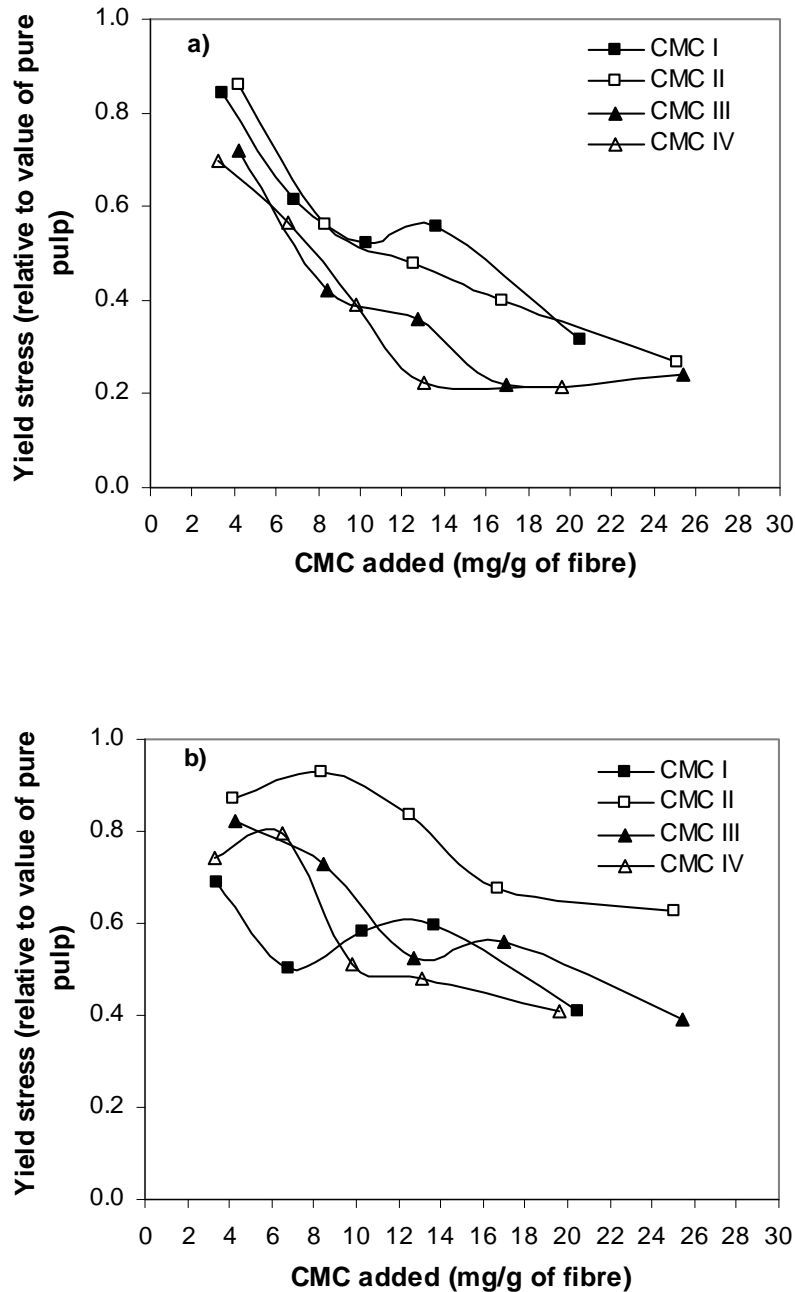


Fig. 2. Fibre network strength: (a) CMC adsorbed on fibres, and (b) CMC in the liquid phase.

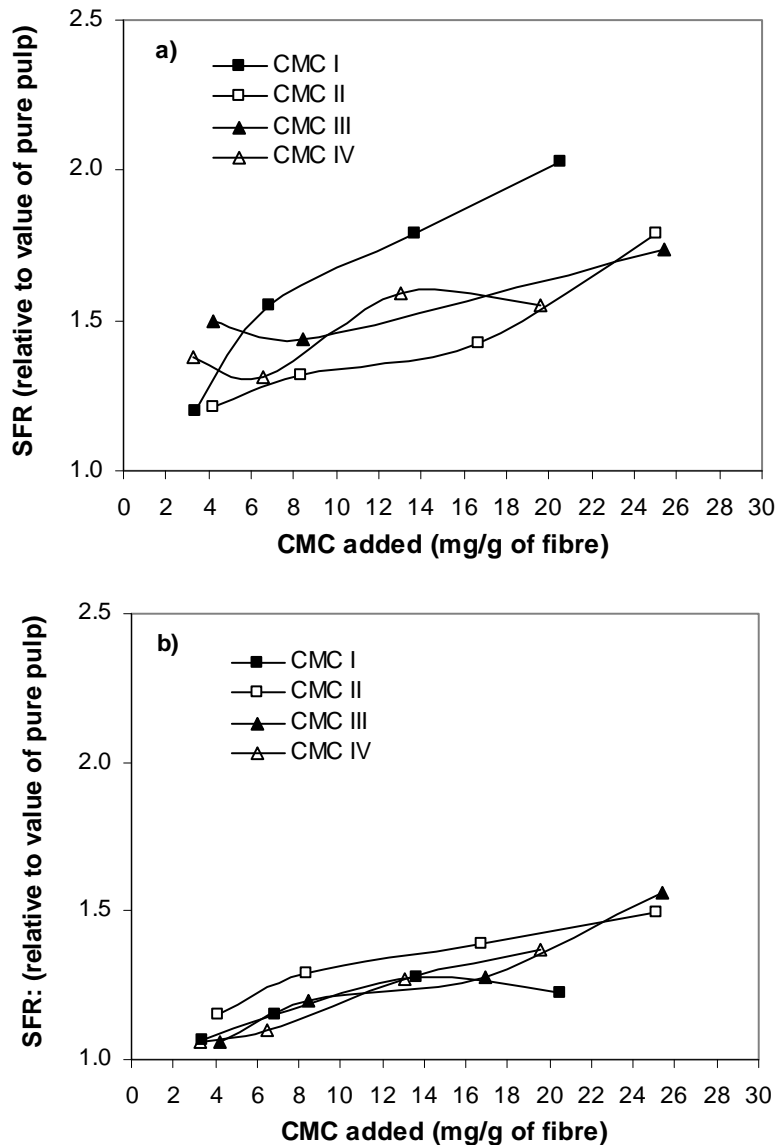


Fig. 3. SFR of the fibre suspension measured by vacuum filtration: (a) CMC adsorbed on fibres, and (b) CMC in the liquid phase.

Free water removal was also measured by the Canadian standard freeness (CSF) method. Where the SFR measurements characterized the average water removal after a longer period, CSF measured dewatering at the beginning of the water removal process. The CSF values for the CMC-treated pulps, shown in Fig. 5, display the same trend as was observed with the SFRs in that all the CMC grades reduced water removal from the pulp, the decrease being higher when CMC was adsorbed onto the fibres.

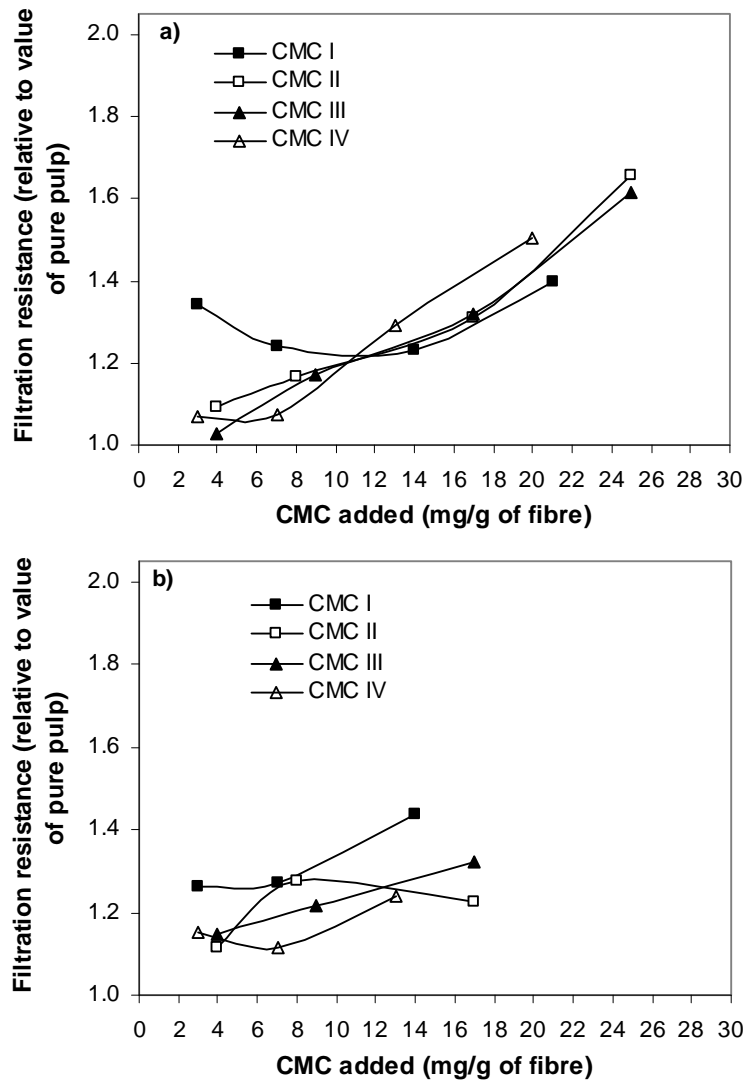


Fig. 4. Filtration resistance of the fibre suspension measured with a gravity driven-filtration system: (a) CMC adsorbed on fibres, and (b) CMC in the liquid phase.

The influence of the CMC treatments on the bound water content of the fibres, i.e. the removal of attached water, was evaluated by measuring the water content of the filter cakes after vacuum filtration and determining water retention values after the free water had been flowing from the cakes for a constant filtration time. The results presented relative to the values for the reference pulps are shown in Fig. 6. CMC was found to have a significantly smaller effect on the amount of bound water than on free water removal, since both adsorbed CMC and liquid phase CMC caused about a 1-4% increase in water retention. In contrast, Laine et al. (2002) have reported that adsorbed CMC increase significantly water retention. The reason for this may be that our method differed significantly from the SCAN method that Laine et al. (2002) used. CMC II and CMC IV were observed to have higher water retention values already at low doses, which may be associated to their high molecular weights.

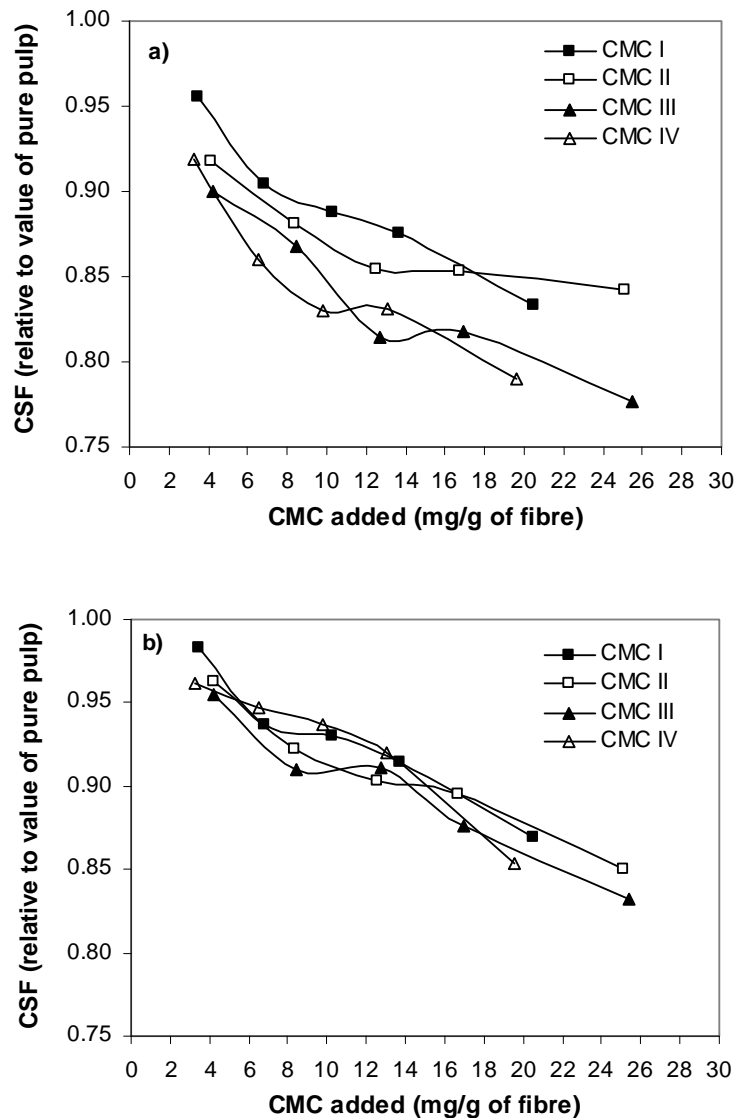


Fig. 5. CSF of the fibre suspension: (a) CMC adsorbed on fibres, and (b) CMC in the liquid phase.

Effect of CMC on Fines Retention

Fines retention during vacuum filtration, i.e. the attachment of fine particles of pulps to the filter cake, was characterized by measuring the turbidity of the filtrates after a constant cumulative amount of filtrate. Turbidity correlates with the total solid content of the filtrate but is not affected by CMC. The resulting turbidities, presented relative to the values for the reference pulps, are shown in Fig. 7. As also reported by Laine et al. (2002) adsorbed CMC was found to affect fines retention to a considerable extent, leading to four to five times higher turbidity values than for reference pulps with the highest CMC dosage, whereas liquid-phase CMC caused only 20 - 25% increases in turbidity.

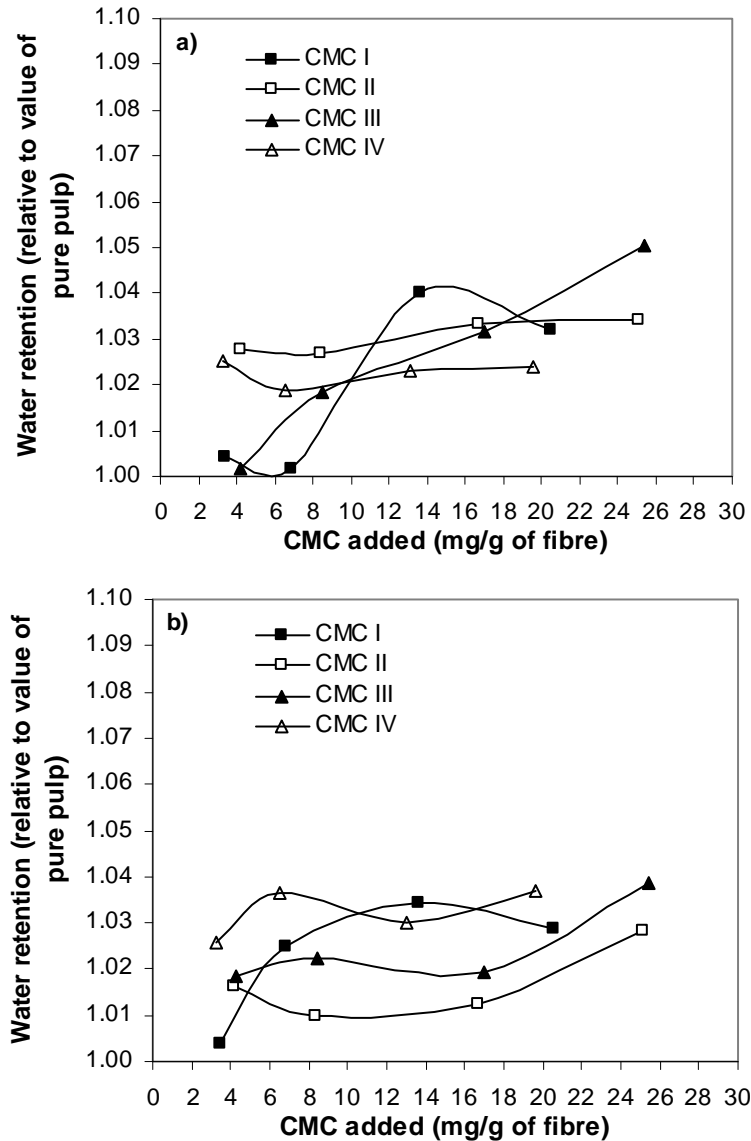


Fig. 6. Water retention in the filter cake: (a) CMC adsorbed on fibres, and (b) CMC in the liquid phase.

DISCUSSION

Dispersive Mechanisms of CMC

The dispersion of fibre suspensions, characterized in terms of yield stress values, was found to be affected by both adsorbed CMC and liquid-phase CMC, showing that CMC is effective in both phases for fibre dispersing. The yield stress of a pulp suspension, τ_y , has previously been related to the properties of the suspension by invoking classical beam theory, yielding the following equation (Bennington et al. 1990; Kerekes et al. 1985; Wahren and Thalen 1964),

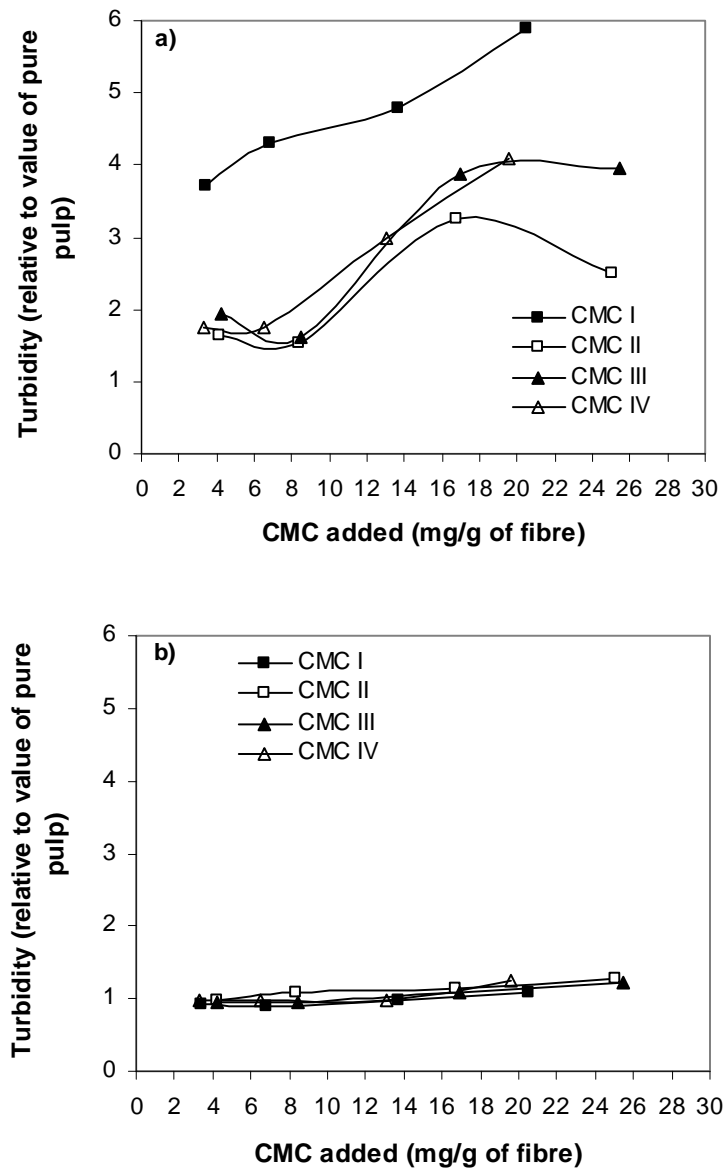


Fig. 7. Turbidity of the filtrate (a) CMC adsorbed on fibres, and (b) CMC in the liquid phase.

$$\tau_y = k\mu Ea^2 C_v^3 \quad (2)$$

where k is a constant characteristic of the suspension, μ is the coefficient of friction, E is the Young's modulus of the fibre cell wall, a is the fibre aspect ratio, and C_v is the volumetric concentration of fibres. Eq. (2), together with previously published network models (Farnood et al. 1994), show that a decrease in yield stress will be related mainly to a decrease in fibre-to-fibre friction, since the alteration in Young's modulus and volumetric consistency attributable to the fibre swelling caused by CMC is thought to be

small (Beghelli and Lindström 1998). Thus, the results suggest that the fibre dispersing achieved by CMC may be attributed to decreased fibre to fibre friction, both when the CMC is adsorbed to the surfaces of the fibres and when it is in the liquid phase of the suspension.

Mechanism based on adsorbed CMC

Although several authors have demonstrated that adsorbed CMC reduces inter-fibre friction (Giri et al. 2000; Horvath and Lindström 2007; Jokinen et al. 2006; Yan et al. 2006, Zauscher and Klingenberg 2001), it is still partly unclear how it affects the surface properties of fibres and what is the mechanism behind the decreased coefficient of friction of fibres. de Roos (1958) proposed in the late 1950's that CMC forms a hydrated layer on fibre surfaces that reduces inter-fibre adhesion and promotes pulp dispersing, while Yan et al. (2006) later explained that the dispersing activity of adsorbed CMC should rather be attributed to repulsion between CMC-covered fibres than to any decrease in adhesion by virtue of a hydrated CMC layer. They assumed that charged groups of adsorbed CMC molecules protruded out into the solution from fibre surfaces to cause steric and electrostatic repulsion between colliding fibres (Yan et al. 2006). Laine et al. (2002) in turn concluded, like de Roos, that these protruding CMC chains form a water-rich, friction-reducing layer, since the conformation of CMC molecules on fibre surface was found to affect the bound water content of the fibres. An increase in temperature or in the valency of the counter-ions in the anionic groups of CMC was observed to reduce the amount of bound water, because the expanded CMC molecules were compressed closer to the fibre surfaces. The mechanism suggested by Zauscher and Klingenberg (2001) was based on the assumption that CMC masks fibre surface roughnesses, resulting in a decrease in friction between sliding fibre surfaces. This mechanism is basically similar to the boundary lubrication of solid surfaces, where two rubbing surfaces are separated by a lubricant film of a few molecules in thickness (Bowden and Tabor 1967). Zauscher and Klingenberg (2001) concluded that the decrease in friction was related to thickness of this lubricating CMC layer, which was in turn associated with the conformation, molecular weight, and the amount of adsorbed CMC.

However, the above-mentioned mechanisms do not take into account the fibrillar nature of fibre surfaces. The fibre cell wall consists of strands called microfibrils (Hakkila 2000), which are some 5-6 nm thick and are thought to have significant effect on the chemical and physical properties of wet fibre surfaces (Laine 2007). Blomstedt (2007) and Mitikka-Eklund et al. (1999) reported that the adsorption of CMC to fibre surfaces stabilizes the external bundles of these microfibrils by means of electrostatic interactions, resulting in fanning out (i.e. delamination within groups of fibrils, while remaining attached to a fiber at one end) of the microfibrils and the formation of a water-rich microfibrillar gel. We conclude that the observed decrease in the coefficient of friction and the associated fibre dispersing achieved by adsorbed CMC may also be attributed to its disintegration effect on microfibrils. The distance of repulsion between fibres is presumably attributed to the thickness of water-rich microfibrillar gel. Previous results showing that fibre dispersing is related to the conformation of CMC, and the strength of the electrostatic repulsion promoted by it can presumably also be attributed to the effect of CMC on the properties of external microfibrils. The extended conformation

and high charge density of CMC promote disintegration of the microfibrils and lead to an increased bound water content and to fibre dispersing. It is interesting, however, that no direct correlation between the dispersive activity of CMC and its molecular weight or degree of substitution was found in our studies. The reason for this may be the low variability in the degree of substitution in our samples and the low sensitivity and reproducibility of the yield stress measurements.

Mechanism based on liquid phase CMC

The dispersive mechanism of certain non-adsorbing polymeric dispersing agents has been attributed to their ability to increase the shear viscosity of a suspension, which will in turn promote fibre dispersing in at least in two ways: by reducing the relative motion of fibres leading to crowding, and by suppressing turbulence in the suspension (Zhao and Kerekes 1993). The suppression of turbulence will reduce fibre flocculation, because fibres that are disturbed in the presence of turbulence tend to relax and crowd together effectively once the fluid velocity has decreased (Yan et al. 2006). However, since the CMC doses used in the present experiments had a negligible effect on the shear viscosity of the suspension (Beghelli 1998), the dispersive effect of CMC was more likely to have been related to factors other than shear viscosity. The yield stress measurements suggested that CMC in the liquid phase altered the coefficient of friction between the fibres, as was also the case with adsorbed CMC.

Contrary to adsorbed CMC, however, the liquid phase CMC presumably did not interact and mix with the microfibrils on the fibre surfaces, on account of the repulsion effect operating between the anionic CMC and the negatively charged microfibrils. Thus one explanation for the dispersive mechanism is that CMC molecules close of the fibre surfaces formed a non-adsorbed layer that prevented fibre contacts. This mechanism resembles the above-mentioned boundary lubrication, except that the lubrication layer is not bound to the rubbing surfaces. It is likely that the CMC layer reduces the contact area between sliding fibre surfaces by masking the surface asperities and thereby reduces the intensity of the inter-fibre contacts. The detailed mechanism behind the reduction in the coefficient of friction is still unclear, however. It has been proposed earlier that the friction between sliding fibres may be reduced by either expanded conformations of CMC molecules or electrostatic repulsion created by CMC (Rantanen et al. 2006), while Wasser (1978) has suggested that the high viscosity prevents removal of the lubricant layer from the fibre-to fibre contact points and promotes a decrease in inter-fibre friction. The fact that CMC has a stretched helical structure in water (Wang and Somasundaran 2005) and that its total stretched length could be several micrometers (Laine 2002) suggests that the large size of the CMC molecules could physically prevent fibre to fibre contacts.

Effect of CMC on Dewatering and Fines Retention

The CSF method and the SFR measurements performed with the vacuum filtration apparatus and the gravity-driven filtration system showed that both adsorbed CMC and liquid-phase CMC reduced the removal of free water from the pulp. This is not surprising, since CMC in both phases was observed to disperse fibres. Fibre dispersing and floc breakage will in turn have increased the hydrodynamic specific surface area of

the pulp. The Kozeny-Carman equation relates the physical properties of a suspension, including its specific surface area, to the permeability of filter cake, K , which is inversely proportional to the specific filtration resistance, α (Kozeny 1927; Carman 1937),

$$K = \varepsilon^3 / k_0 S_0^2 (1 - \varepsilon)^2 \quad (3)$$

where k_0 is the Kozeny constant, which characterizes the shape and orientation of the material, ε is the porosity, and S_0 is the specific surface area of fibres. Equation (3) shows that the increase in specific surface area of a pulp achieved by the dispersive action of CMC leads to a decrease in permeability, i.e. an increase in filtration resistance. In addition, this effect is more pronounced with adsorbed CMC, since it is more able to disperse fibres, as shown in the yield stress values (Fig. 2.). The permeability and SFR of a suspension will also be very strong function of the porosity of the filter cake, which has in turn been attributed to the packing structure of the fibres. We have observed previously (Liimatainen et al. 2008) that adsorbed CMC reduces the packing density of the pulp layer, i.e. increases its porosity, which, as stated in the Kozeny-Carman equation, should reduce the filtration resistance. The reason for the contradictory findings obtained here may lie in the fact that floc breakage by CMC leads to the formation of a more uniform cake that has smaller pores than a flocculated cake, which can easily be plugged by dispersed fine material of the pulp.

The specific permeability constants given by the Kozeny-Carman permeability equation,

$$K = k_S (1 - \phi_S) / \phi_S^2 \quad (4)$$

where the permeability of the fibre network is given as a function of the solid volume fraction Φ_S , instead of porosity (Kataja and Hirsilä 2001), were determined for each CMC treatment using the filtration analysis data including the measured fibre velocity field. Since the specific permeability constant k_S includes the specific pore surface area and the Kozeny constant, any change in it will reflect the behavior of pore size in the fibre network in the course of filtration. The results (Fig 8.) show decreasing permeability constants for both adsorbed and liquid-phase CMC, indicating at the same time a decrease in the void volume of the fibre network.

It has been suggested that polymeric dispersing agents also increase the flow resistance of fluids due to their ability to increase elongational viscosity (Lee and Lindström 1989), on the assumption that these dispersing agents adsorb energy from the fluid by becoming elongated in the direction of flow during drainage, which causes an increase in viscosity.

The fact that adsorbed CMC caused a higher increase in the SFRs than liquid-phase CMC when measured by vacuum filtration, whereas CMC treatments increased the SFRs to the same degree when assessed by the PUD method is probably related to the dispersal of fines, which was particularly promoted by adsorbed CMC. Since the filter cake was significantly thicker in vacuum filtration than in the PUD method, the former was more sensitive to the dispersive action of adsorbed CMC, as this action released fines from the fiber surfaces such that they plugged the thick filter cake.

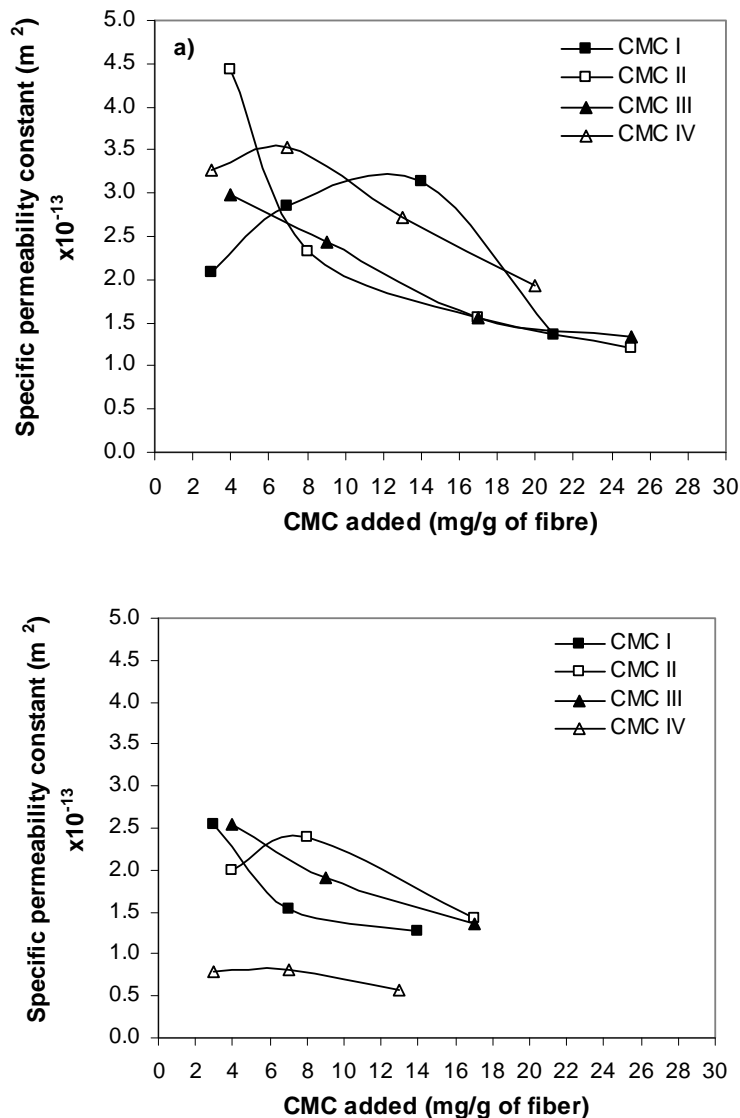


Fig. 8. Specific permeability constants: (a) CMC adsorbed on fibres, and (b) CMC in the liquid phase.

Adsorbed and liquid-phase CMC differed most significantly in their effects on fines retention, characterised in terms of turbidity, where adsorbed CMC caused four to five times higher turbidity values than in the reference pulps at the highest CMC dosage, whereas liquid-phase CMC resulted in only a 20 - 25% increase in turbidity. The reason for this is unclear, but one explanation may be that the disintegration of microfibrils caused by the adsorbed CMC released fibrillar fragments from fibre surfaces into the suspension and that these were then poorly retained before filter cake formation. It is also possible that adsorbed CMC was able to release individual fines from fines entanglements or from inside fibre flocs. These fines could act similar to ball bearings between fibres, reducing also the interfibre friction and the fibre network strength.

CONCLUSIONS

1. Both CMC adsorbed to fibre surfaces and CMC in the liquid phase are able to disperse a fibre suspension due to the ability of CMC in both phases to reduce fibre-to-fibre friction.
2. CMC in both phases has detrimental effects on the dewatering of a pulp suspension, but adsorbed CMC causes more plugging of the filter cake because it disperses the fines in particular. This means that adsorbed CMC also reduces fines retention considerably more than does CMC in the liquid phase of the suspension.
3. Adsorbed CMC promotes the formation of a water-rich microfibrillar gel on the fibre surfaces through the disintegration of microfibrils, which leads to a decrease in friction at the fibre-fibre contact points and to fibre dispersing. CMC in the liquid phase of the suspension is in turn thought to prevent fibre-to-fibre contacts due to the large physical size of the CMC molecules.

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