

## Weak Flocculation of Aqueous Kaolin Suspensions Initiating by NaCMC with Different Molecular Weights

Y. Li,<sup>1</sup> É.S. Nagy,<sup>2</sup> M.N. Esmail,<sup>1\*</sup> Z. Hórvölgyi<sup>2\*</sup>

<sup>1</sup>Department of Mechanical and Industrial Engineering, Concordia University, de Maisonneuve Blvd. W., H549 Montreal, Quebec H3G 1M8, Canada

E-mail: esmail@encs.concordia.ca

<sup>2</sup>Department of Physical Chemistry, Budapest University of Technology and Economics, H-1521 Budapest, Hungary

E-mail: horvolgyi.fkt@chem.bme.hu

**Summary:** The present work is an investigation of the effect of NaCMC with different viscosities (molecular weights) on the stability of aqueous kaolin suspensions at pH 5–6. The stabilizing effect of polymers was characterized by measuring the sedimentation volumes (for 2.5% kaolin suspensions) and some important rheological parameters (for 40% and 50% kaolin suspensions). In certain cases the stability of suspensions was also studied in the presence of 0.5–1.0% NaCl. The additives were incorporated into the suspensions separately and simultaneously, as well. In certain cases the effect of mixing order of NaCMCs was also studied. The lower viscosity NaCMC was found to be a better stabilizing agent than its medium viscosity counterpart at the studied polymer concentrations (0.005–1.0%). This was manifested in smaller sedimentation volumes and lower rheological parameters (viscosity, yield stress, degree of thixotropy and elasticity). The lower and the medium viscosity polymer were simultaneously and consecutively added in a mass ratio of 50:1 and 10:1. The resulted observation of low viscosity and yield stress, and more importantly thixotropy and elasticity, can be interpreted in terms of a “site-blocking” type flocculation.

**Keywords:** anionic polyelectrolyte; kaolin suspension; rheological properties; sedimentation volume; site-blocking flocculation

### 1 Introduction

The aqueous clay suspensions are of great importance in many fields of industrial applications/e.g. ceramics production, drilling fluids, paper coating.<sup>[1,2]</sup>

Neutral polymers or polyelectrolytes are frequently used as dispersant or flocculant agents. The combination of different polymers can cause synergetic effects. Due to the practical and theoretical importance, the competitive adsorption of neutral<sup>[3–5]</sup> and ionic<sup>[6–8]</sup> macromolecules was intensively studied in the past decades. Macromolecules can cause bridging flocculation if the molecular weight is great enough and the adsorption layer is not saturated. The efficacy of

flocculation can be improved, adding simultaneously a lower and a higher molecular weight polymer<sup>[6-8]</sup> in the suspension. In most cases cationic<sup>[6-8]</sup> or oppositely charged<sup>[9]</sup> polyelectrolytes are used for initiating flocculation resulting in strong floc structure. In the first case, the lower molecular weight polymer enhances the possibility of bridging formation of its higher molecular weight counterpart, blocking the active adsorption sites. Strong floc structure is required e.g. in papermaking<sup>[10]</sup> due to the high speed paperboard processing. The usage of the mixtures of cationic polymers has been suggested for this purpose.<sup>[6-8]</sup>

In paper coating liquids, including kaolin, the NaCMC is a commonly used additive.<sup>[11-15]</sup> There are many conflicting requirements for the coating color. High solid content, e.g., but low shear viscosity and certain degree of thixotropy and elasticity are required. It means that strong flocculation of the pigments should be avoided in the coating colors. That is why the site-blocking based flocculation, concerning the coating colors, is not studied, yet. On the other hand, there is a strong requirement to reach a weak flocculated state of pigments because it can result in advantageous optical properties of the coating layer.<sup>[14]</sup>

The main purpose of this work is to show that the above mentioned rheological properties are feasible in the aqueous kaolin suspensions using the mixture of a lower and a higher molecular weight NaCMC and certain cases inorganic electrolyte, NaCl. Due to the positively charged edges of kaolinite particles, the anionic polyelectrolytes can cause a weak flocculation based on the site-blocking mechanism. The rheological properties are examined by cone-plate viscometry. In order to get a better understanding of the rheological results, we compare them to the results of sedimentation volume investigations.

## 2 Experimental

### 2.1 Materials

Low and medium viscosity (lv and mv) NaCMC (carboxymethylcellulose sodium salt, Sigma), NaCl (sodium chloride, BDH, analytical reagent), kaolin (hydrated aluminium silicate, Sigma K-7375) and distilled water were used in preparation of samples. Every reagent was used as received. The particle size of kaolin was in the range of 0.1–4.0  $\mu\text{m}$ ; 90% of particles were smaller than 2  $\mu\text{m}$ . According to the manufacturer, the degree of substitution was 0.7 for the NaCMC. The molecular weight of polymers was determined by using capillary viscometry. Measuring the relative viscosity of aqueous solutions of NaCMCs in the presence of a strong

electrolyte (0.1 M NaCl), the intrinsic viscosity,  $[\eta]$ , was determined from which the average molecular weight of polymers was calculated. Molecular weights of 50000 Dalton ( $\pm 10\%$ ) and 151000 Dalton ( $\pm 10\%$ ) were found for the low and medium viscosity polymers, respectively.

## 2.2 Methods

### 2.2.1 Sample Preparation for the Rheological Investigations

The samples were prepared from suitable amounts of the stock solutions (of NaCMC and NaCl), kaolin powder and distilled water. The components were introduced simultaneously, and after completion, stirred using an overhead stirrer at around 800 rpm for five minutes. Samples with 50% kaolin content (and certain cases with 40% kaolin content) were prepared and investigated. In some cases we investigated the effect of mixing order of different molecular weight polymers on the rheological properties of 50% kaolin suspensions. The compositions are shown in Table 1.

Table 1. The compositions of samples prepared for the rheological investigations.  
lv: low viscosity; mv: medium viscosity.

Samples	Kaolin (%)	lv NaCMC (%)	mv NaCMC (%)	NaCl (%)
Re0(40)	40	-	-	-
Re1(40)*	40	-	1.0	-
Re2(40)*	40	-	-	1.0
Re3(40)*	40	-	1.0	1.0
Re0(50)	50	-	-	-
Re1(50)	50	0.1	-	-
Re2(50)	50	0.5	-	-
Re3(50)	50	-	0.5	-
Re4(50)	50	0.1	0.002	-
Re5(50)	50	0.25	0.25	-
Re6(50)**	50	0.5	0.01	-
Re7(50)	50	-	-	1.0
Re8(50)	50	0.5	-	1.0
Re9(50)	50	0.1	0.002	0.5
Re10(50)***	50	0.5	0.01	-
Re11(50)****	50	0.5	0.01	-
Re12(50)***	50	0.5	0.05	-
Re13(50)****	50	0.5	0.05	-

\* These samples were prepared from powders. \*\* The polymers were added at the same time. \*\*\* The low viscosity NaCMC was added first. \*\*\*\* The medium viscosity NaCMC was added first.

### 2.2.2 Rheologica Investigations

The rheological properties were measured at ambient temperature ( $23 \pm 1$  °C) using a cone-and-plate Haake-viscometer (RS100). The apparent and plastic viscosities, the Bingham yield stress and thixotropy were examined analysing the steady-state flow curves and hysteresis loops' "area". In the latter case, according to the Green method,<sup>[16]</sup> the up curves were always determined under steady-state conditions and the down curves were determined as quickly as possible. The elastic behaviour was investigated in certain cases by determining the storage ( $G'$ ) and loss ( $G''$ ) moduli of the samples from the results of oscillation tests.

Table 2. The compositions of samples prepared for the sedimentation volume investigations. lv: low viscosity; mv: medium viscosity.

Samples	Kaolin (%)	lv NaCMC (%)	mv NaCMC (%)	NaCl (%)
Sv0	2.5	-	-	-
Sv1	2.5	0.01	-	-
Sv2	2.5	0.02	-	-
Sv3	2.5	0.04	-	-
Sv4	2.5	-	0.005	-
Sv5	2.5	-	0.01	-
Sv6	2.5	-	0.02	-
Sv7	2.5	-	0.04	-
Sv8	2.5	-	-	0.2
Sv9	2.5	-	-	0.4
Sv10	2.5	-	-	0.6
Sv11	2.5	-	-	0.8
Sv12	2.5	-	-	1.0
Sv13	2.5	0.01	0.01	-
Sv14	2.5	0.02	0.02	-
Sv15	2.5	0.01	-	1.0
Sv16	2.5	0.02	-	1.0
Sv17	2.5	0.04	-	1.0
Sv18	2.5	-	0.01	1.0
Sv19	2.5	-	0.02	1.0
Sv20	2.5	-	0.04	1.0

### 2.2.3 Sample Preparation for the Sedimentation Volume Investigations

The samples were prepared from suitable amounts of the stock solutions (NaCMC and NaCl) and of kaolin suspension adding the necessary quantity of distilled water in scaled tubes, and

homogenized, shaking the tubes thoroughly. For practical reasons, we prepared more diluted (2.5%) kaolin suspensions for the sedimentation volume investigations. The compositions are shown in Table 2.

#### **2.2.4 Sedimentation Volume Measurements**

The sedimentation volumes were measured at ambient temperature ( $23 \pm 1$  °C). After homogenisation and waiting at least 24 hours, the equilibrated values were determined and used for the characterization of particle-particle interaction (adhesion). As well known, the higher sedimentation volumes correspond to stronger particle-particle adhesion.

### **3 Results and Discussion**

First, in this section, we give the results of the sedimentation volume examinations and provide some explanations. Second, we show the results of the rheological investigations for the 40% and 50% kaolin suspensions, and compare them with one another and with the results of the sedimentation volume studies. The pH of the kaolin samples was found to be between 5 and 6 (assessed by an indicator paper).

#### **3.1 Sedimentation Volumes ( $V_s$ )**

First, the effect of NaCl on the sedimentation volumes of aqueous kaolin suspensions was studied. By means of this investigation we can get indirect information about the state of surface charges of kaolinite particles. The results are shown in Figure 1. As can be seen the  $V_s$  values are decreasing with increasing concentration of the NaCl up to 0.6 M, then remaining at a constant value. It means that the particle-particle adhesion becomes weaker with adding NaCl in kaolin suspension. This can be explained in terms of screening the face-edge electric attractions conforming indirectly our assumption that the particle's edges are positively and the faces are negatively charged at the pH of present investigations.

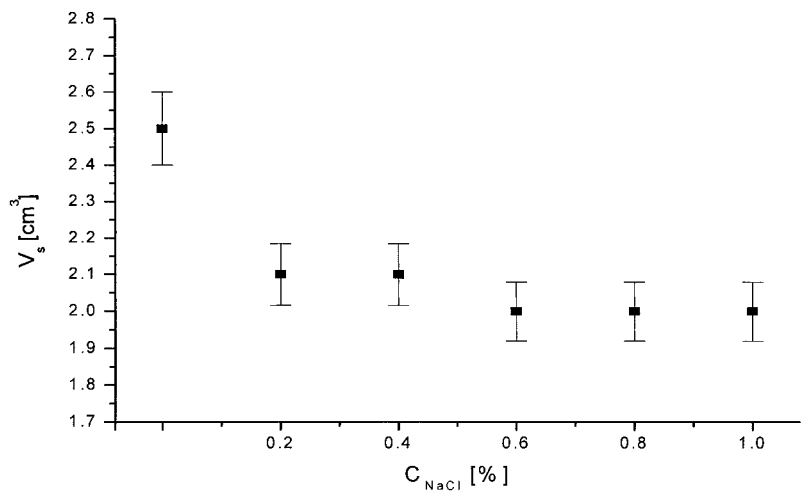


Fig. 1. Sedimentation volumes ( $V_s$ ) of 2.5% kaolin suspensions as a function of NaCl concentration ( $C_{\text{NaCl}}$ ).

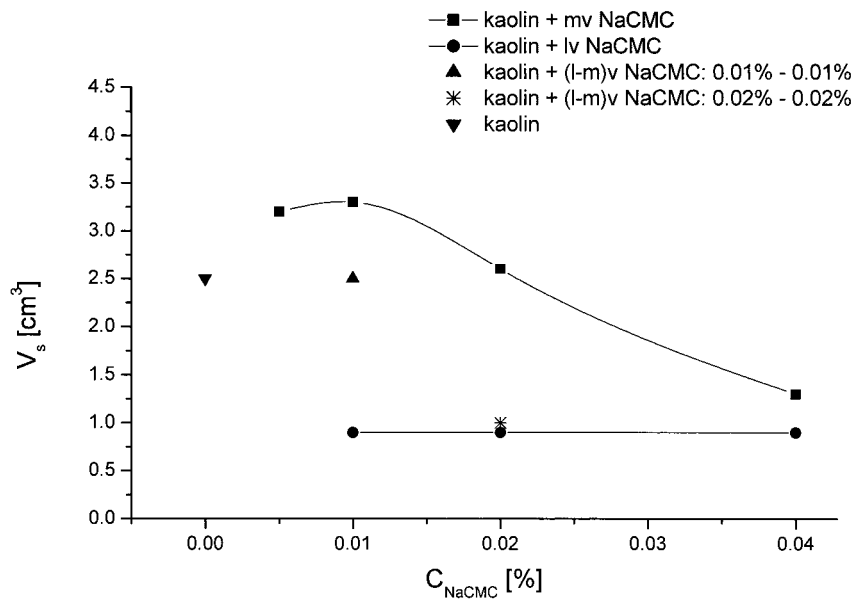


Fig. 2. Sedimentation volumes ( $V_s$ ) of 2.5% kaolin suspensions as a function of NaCMC concentration ( $C_{\text{NaCMC}}$ ). lv: low viscosity; mv: medium viscosity.

The sedimentation volumes, obtained for the low and medium viscosity NaCMC, are given in Figure 2. The low viscosity NaCMC shows a stabilizing effect in the whole concentration range, that is the  $V_s$  values significantly decrease with increasing concentration of polymer. In the case of the mv NaCMC, however, a maximum of  $V_s$  appears at the lowest polymer concentrations due to bridging flocculation. It means that the mv polymer can form bridges between the positively charged edges of different particles. The simultaneous addition of the low and medium viscosity polymers in the suspension leads to intermediate sedimentation volumes, indicating that beside the adsorption of lv NaCMC the “bridge forming adsorption” of mv NaCMC also occurs.

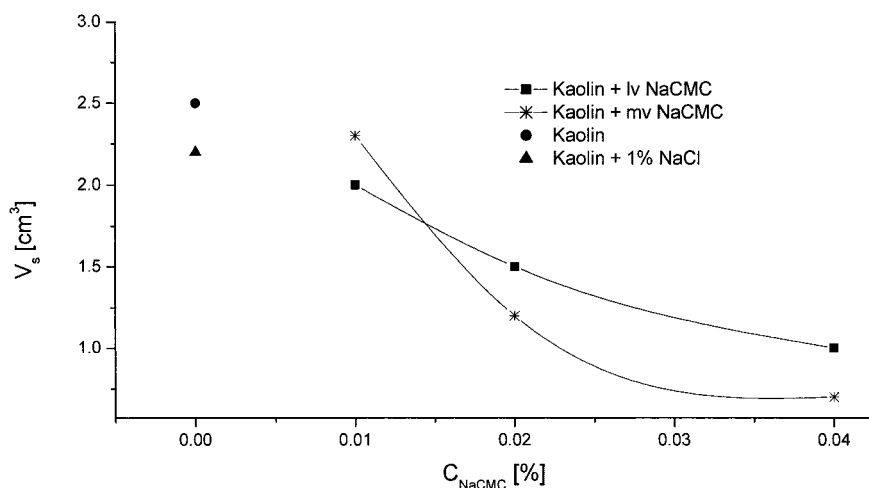


Fig. 3. Sedimentation volumes ( $V_s$ ) of 2.5% kaolin suspensions as a function of NaCMC concentration ( $C_{\text{NaCMC}}$ ) in the presence of 1% NaCl. lv: low viscosity; mv: medium viscosity.

The simultaneous addition of NaCl and NaCMC in the kaolin suspensions resulted in interesting observations. As can be seen in Figure 3, the NaCl diminishes the stabilizing capability of lv NaCMC, especially at the lower concentrations of the lv polymer (also see Figure 2). This effect can be attributed to the screening the electrostatic forces by the sodium chloride. On the one hand, the NaCl can decrease the adsorption capability of the negatively charged polymers on the positively charged edges. On the other hand, the sodium-ions also screen the electrostatic repulsion between the polymer-covered (negatively charged) particles. An opposite effect is observed for the mv NaCMC. The NaCl improves the stabilizing capacity

of the polymer, supposedly due to the hindered “bridge forming adsorption”. In the presence of NaCl the mv polymer molecules have a more coiled conformation due to the electrostatic screening between the polymer chains that is not favourable for the bridging formation.<sup>[11]</sup>

It should be noted that a serious time dependence of the “equilibrated” sedimentation volumes was observed in the presence of polymers. After a repeated homogenisation of the suspensions a significant decrease in the “equilibrated” sedimentation volumes was observed, especially for the higher viscosity polymer, indicating the lack of real equilibrium.

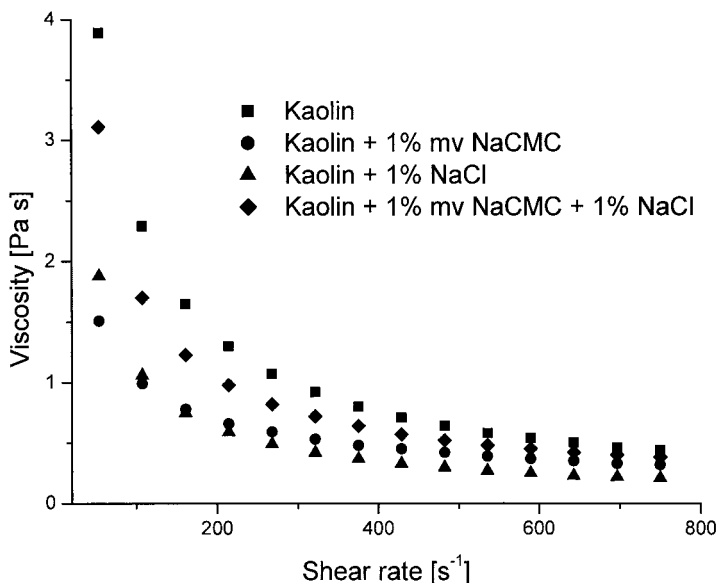


Fig. 4. Apparent viscosities as a function of shear rates obtained for the 40% kaolin composites.

### 3.2 Rheological Investigations

Every investigated sample showed non-Newtonian, mostly plastic behaviour. The viscosity curves for the 40% kaolin samples can be seen in Figure 4 /samples Re0(40)-Re3(40)/. The determined rheological parameters (the range of apparent viscosities, plastic viscosity, Bingham yield stress, “area” of the hysteresis loop) for both the 40% and 50% kaolin suspensions are given in Table 3 /samples Re0(40)-Re3(40)/ and in Table 4 /samples Re0(50)-Re9(50)/, respectively. Some characteristic results of thixotropy measurements for the 40% and 50% kaolin suspensions appear in Figures 5 and 6. The results concerning the effect of mixing order



of different molecular weight polymers can be seen in Table 5 and in Figure 7 /samples Re10(50)-Re13(50)/. The apparent viscosities at some values of shear rate, the Bingham yield values and loop areas concerning the thixotropic behaviour are shown in Table 5. The storage and loss moduli obtained from the oscillation test are depicted in Figure 7.

Table 3. The calculated rheological properties for the 40% kaolin samples.

Samples	Apparent viscosity range (Pa s)	Plastic viscosity (Pa s)	Bingham yield stress (Pa)	Thixotropy ("area" of the loop) (Pa/s)
Re0(40)	3.89-0.44	0.12	240	1810
Re1(40)	1.51-0.32	0.12	150	$3.1 \times 10^4$
Re2(40)	1.88-0.21	0.05	125	4180
Re3(40)	3.11-0.38	0.06	212	$4.7 \times 10^4$

The apparent viscosities are appeared at  $54 \text{ s}^{-1}$  and  $750 \text{ s}^{-1}$ , respectively. The standard deviation of the averaged values was found to be  $\pm 5\%$  in most cases.

Table 4. The calculated rheological properties for the 50% kaolin samples.

Samples	Apparent viscosity range (Pa s)	Plastic viscosity (Pa s)	Bingham yield stress (Pa)	Thixotropy ("area" of the loop) (Pa/s)
Re0(50)	8.20-0.55	0.10	330	$4.20 \times 10^4$
Re1(50)	7.26-0.47	0.18	225	-9960
Re2(50)	0.09-0.03	0.03	2.4	750
Re3(50)	3.00-0.30	0.16	116	$1.40 \times 10^4$
Re4(50)	4.90-0.32	0.13	151	-4630
Re5(50)	0.40-0.08	0.06	16	3040
Re6(50)	0.30-0.08	0.06	15	2590
Re7(50)	10.60-0.60	0.096	390	$3.2 \times 10^4$
Re8(50)	4.82-0.24	0.07	122	3460
Re9(50)	11.30-0.65	0.11	419	$7.44 \times 10^4$

The apparent viscosities are appeared at  $26 \text{ s}^{-1}$  and  $750 \text{ s}^{-1}$ , respectively. The standard deviation of averaged values of viscosities and yield stresses were found to be  $\pm 10\%$  in most cases. The standard deviation of averaged loop "areas" were  $\pm 15\%$ .

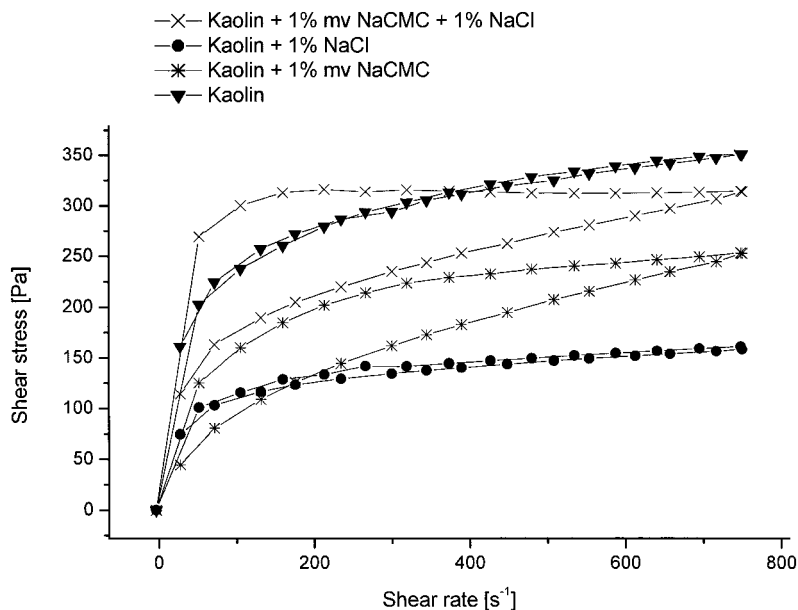
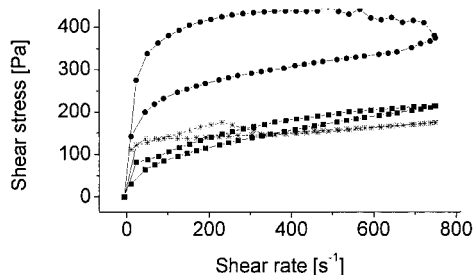


Fig. 5. Thixotropy curves for the 40% kaolin composites. The “down curves” always run under the “up curves”.

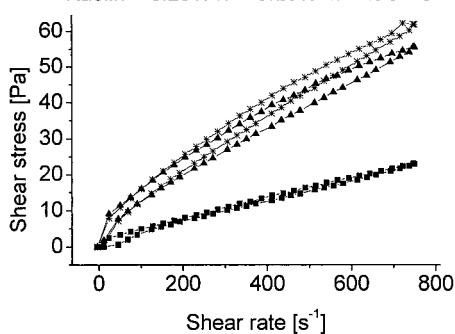
The section is organized as follows. First, we discuss the results for the kaolin suspensions without additives. Secondly, we deal with the outcome for the kaolin suspensions with individually added NaCl and NaCMCs. Then we interpret the results obtained for the kaolin suspensions with simultaneously and consecutively added lv and mv NaCMCs. And finally, the effects obtained for the kaolin suspensions with simultaneously added (l-m)v NaCMCs and NaCl are interpreted and discussed.

- Kaolin + 0.5% mv NaCMC
- Kaolin + 0.1% lv and 0.002% mv NaCMC + 0.5% NaCl
- \*— Kaolin + 0.5% lv NaCMC + 1% NaCl



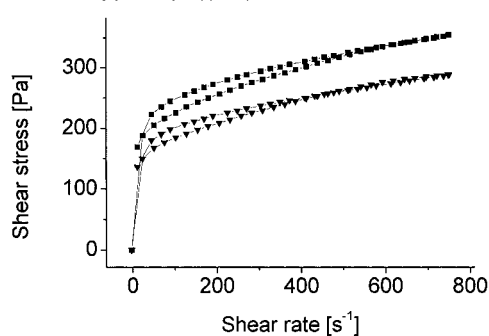
a)

- Kaolin + 0.5% lv NaCMC
- \*— Kaolin + 0.5% lv + 0.01% mv NaCMC
- ▲— Kaolin + 0.25% lv + 0.25% mv NaCMC



b)

- Kaolin + 0.1% lv NaCMC
- ▼— Kaolin + 0.1% lv and 0.002% mv NaCMC



c)

Fig. 6. Some characteristic thixotropy (a. b.) and antithixotropy (c.) curves for the 50% kaolin composites. The “down curves” run above the “up curves” for the case of antithixotropy.

Table 5. The rheological properties for the 50% kaolin suspensions prepared by sequential addition of polymers. For comparison the properties of 50% kaolin suspension is also shown.

	Kaolin	Re10(50)	Re11(50)	Re12(50)	Re13(50)
Shear rate [1/s]	Apparent viscosity [Pa s]				
0.27	9.59	0.18	0.22	1.93	0.27
103.80	6.63	0.14	0.17	1.15	0.20
152.00	5.04	0.12	0.15	0.86	0.17
200.20	4.09	0.11	0.13	0.71	0.16
	Bingham yield value [Pa]				
	850	18	25	125	25
	Loop area [Pa s]				
	-	2614	3732	12550	5301

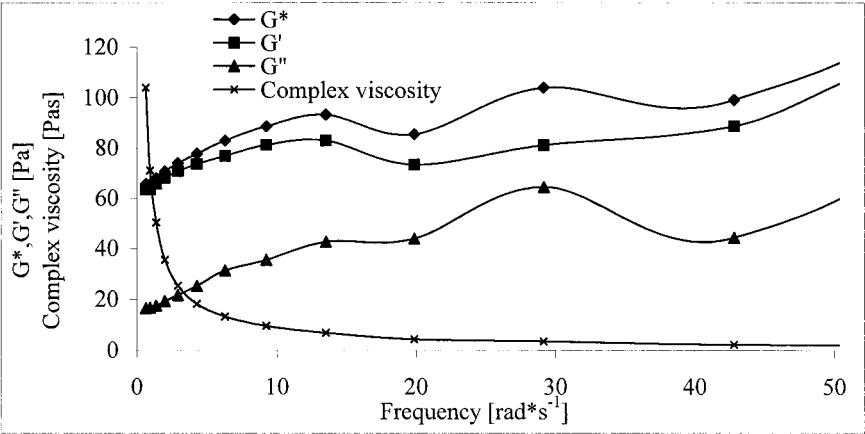


Fig. 7. Frequency sweep oscillation test of the 50% kaolin suspension containing the medium and low viscosity NaCMCs in a 1:10 mass ratio /sample Re12(50)/. The low viscosity NaCMC was added first. (G\*:complex modulus of torsional shear, G': storage modulus, G'': loss modulus).

### 3.2.1 Kaolin Suspensions without Additives/Samples: Re0(40) and Re0(50)/

The kaolin suspensions show relatively high viscosity and yield stress values, as expected (see Tables 3 and 4). A modest thixotropy was observed for the sample with the lower kaolin concentration (Table 3 and Fig 5), indicating the presence of a weak aggregated structure due to the face-edge attraction of particles (card-house structure). The “area” of hysteresis loop was significantly higher for the case of the more concentrated kaolin suspension (Table 4).

### 3.2.2 Kaolin Suspensions with Individually added NaCl and NaCMCs /samples: Re1(40), Re1(50), Re2(50), Re3(50), Re2(40) and Re7(50)/

The NaCl decreases the viscosity and the yield stress of the 40% kaolin suspension (Table 3/Re2(40)/ and Figure 4) showing an increase in the stability of suspension. This is in good agreement with the results of the sedimentation volume investigation (Figure 1). Significant effect, however, is not observed for the case of the denser suspension (Table 4/Re7(50)/). In this case the majority amount of water might be bounded in the liosphere around the particles, and the incorporated inorganic electrolyte can act as a “salting-out” agent causing destabilization of the suspension. Therefore, the observed behaviour can be attributed to two opposite effects: screening of the face-edge attraction and salting-out. The more significant thixotropy obtained for the 40% kaolin suspensions in the presence of NaCl, are presumably also due to the salting-out effect (Table 3). The salting-out effect can be related to the diminished hydration repulsion<sup>[17]</sup> between the particles.

The separately added polymers, independently of their molecular weights, always acted as stabilizing agents causing lower viscosity and yield stress parameters in comparison with the results of the kaolin suspensions without additives (Figure 4, Tables 3 and 4). There was an important difference, however, between the effect of lv and mv polymers (Table 4). The low viscosity NaCMC was found to be a better thinning (and stabilizing) agent than the mv NaCMC. This observation correlates well to the results of the sedimentation volume investigation and indicates “bridge-forming adsorption” of the higher viscosity polymer. In line with the above finding, it was established that the mv NaCMC in the 40% kaolin dispersion significantly increased the thixotropy (see the loop “area” column in Table 3). This can be interpreted in terms of a flocculation initiating by the mv NaCMC. It means that some amount of mv polymer takes part in bridge formation. A slight “viscosity shock” was also found earlier

after adding NaCMC in kaolin based coating colors.<sup>[14]</sup> But the reason for this effect (and for the presumable bridge formation) is not understood well. Maybe, the solid-liquid adsorption layer is unsaturated in the initial stage of polymer incorporation into the kaolin suspension and as a consequence of the irreversible nature of polymer adsorption<sup>[18]</sup> the polymer bridges cannot be eliminated easily during the mixing. *Vide supra* the time dependent “equilibrated” sedimentation volumes. When the samples were prepared from NaCMC solutions (50% kaolin suspensions), time dependence of viscosities was not found. However, when NaCMC powder was directly added in kaolin (40% kaolin suspensions), a continuous decrease in viscosity was found. It means that the polymer bridges were gradually breaking during the storage. (In this case, the measurements were carried out after a two-week storage.).

An increase in thixotropy was not observed in the case of the 50% kaolin suspension in the presence of the mv polymer (Table 4 /sample Re3(50/). The significantly greater loop “area” value ( $1.4 \times 10^4$  Pa/s), however, in relation to that of the suspension prepared from the lv polymer, also indicates a weak flocculated state. The creep recovery curve (not shown here) also confirms the above statement.<sup>[19]</sup> It shows real elasticity for the 50% kaolin suspension in the presence of 0.5% mv NaCMC but it reveals liquid-like behaviour even at lower stress in the presence of 0.5% lv polymer.<sup>[19]</sup> Interestingly, the lv NaCMC caused anti-thixotropy (Table 4 and Figure 6c) at a concentration of 0.1%.

### **3.2.3 Kaolin Suspensions with Simultaneously Added lv and mv NaCMCs/Samples: Re4(50), Re5(50) and Re6(50)/**

The mixture of the different viscosity polymers also increased the stability of kaolin suspensions leading to lower viscosity and yield stress values (Table 4). A small amount (0.01%) of mv NaCMC in the mixture (Re6(50)), however, increased the value of every rheological parameter in comparison with suspension of 0.5% lv NaCMC, presumably due to the bridge flocculation. Although, the apparent viscosities for this sample *ca.* were three times greater than the viscosities of the sample with 0.5% lv NaCMC (sample Re2(50)), these values are low enough, especially at higher shear stress, and do not affect significantly the runnability. On the other hand, the improved thixotropy can be advantageous after the coating. This effect can be attributed to the site-blocking bridging mechanism. Interestingly, the rheological

behaviour of the suspension does not change significantly if we alter the mass ratio of the lower and medium viscosity polymers drastically (from 50:1 to 1:1; sample Re5(50)).

### **3.2.4 The Effect of Mixing Order of Different Molecular Weight Polymers (Samples: Re10(50)-Re13(50))**

We studied the effect of mixing order of different molecular weight polymers on the rheological behaviour of 50% kaolin dispersions in order to get more information about the site-blocking flocculation in the present systems. The most important results concerning the rotational viscometry are collected in Table 5. Complete oscillation test was accomplished for sample Re12(50). The linear viscoelasticity range could only be found for this case (0–50 Pa), hence, the elastic and visous properties could be investigated at 25 Pa (Figure 7). As can be seen, the values of storage modulus ( $G'$ ) significantly exceed the loss modulus values in the investigated frequency range (0–50  $\text{rad.s}^{-1}$ ). The visual observations also revealed distinct differences among the samples. Sample Re12(50) showed a gelatinous (gel-like), colloiddally homogeneous structure for more than one month but the other samples separated into two phases within 1–2 days after the preparation. Summarizing the results in Table 5 and Figure 7 from practical viewpoint: the increased amount of mv NaCMC in the sample, provided the lv NaCMC was added first into the suspension, resulted in advantageous rheological properties, i.e. relatively low viscosity at higher shear rate, significant thixotropy and elasticity, as well. The improved rheological properties can be attributed to the site-blocking aggregation mechanism that takes place more effectively if we add the lv polymer first into the suspension and increase the mass ratio of mv NaCMC (sample Re12(50)).

### **3.2.5 Kaolin Suspensions with Simultaneously Added (l-m)v NaCMCs and NaCl/Samples: Re3(40), Re8(50), Re9(50)/**

When NaCl is added in the samples in the presence of polymer molecules, a drastic increase is observed in the rheological parameter values (Tables 3 and 4) even for the 40% kaolin suspension (sample Re3(40)) in the presence of 1% mv NaCMC. The observations are in good agreement with the results of the sedimentation volume investigations except for the latter case. It seems that the NaCl cannot suppress the “bridge forming adsorption” of the mv polymer in the dense suspensions presumably due to the increased number of particle-particle and particle-

macromolecule collisions. The incorporation of NaCl into the dense kaolin suspensions in the presence of polymers always increases the particle-particle adhesion resulting in higher viscosity and yield values (Tables 3-4) and in an increased degree of thixotropy (Tables 3-4 and Figures 5-6). Interestingly, the anti-thixotropy found for the kaolin suspension in the presence of 0.1% lv and 0.002% mv NaCMCs (sample Re4(50), Fig. 6c), was entirely eliminated by adding NaCl in the composite (Figure 6a).

It seems, however, that the NaCl at these relatively high concentrations (0.5% and 1%) cannot control gently the weak, site-blocking flocculation in the present systems. It always increases the viscosity drastically because of the strong electrostatic screening of particle-particle repulsion. However, additional study concerning the effect of inorganic electrolytes on this phenomenon is required.

## 4 Conclusion

Weak flocculation of the aqueous kaolin suspension (pH 5-6) was initiated by addition of NaCMCs with different molecular weights. The rheological and sedimentation volume investigations revealed that the lower molecular weight polymer alone increases the stability of the kaolin suspensions and decreases the viscosity but neither thixotropy nor elasticity was observed. However, the stabilizing ability of the higher molecular weight polymer was found to be weaker and consequently the suspension viscosity was higher, though thixotropy and elasticity was observed due to the bridging flocculation. However, when the lower and higher molecular weight polymers were simultaneously and consecutively added in the kaolin suspension (in a weight ratio of 50:1 and 10:1), the viscosity was lowered significantly, especially at higher shear rates, and the sample showed thixotropy and in certain cases elasticity, as well. The reason for this behaviour can be the bridge forming adsorption of the higher molecular weight NaCMC initiating by the lower molecular weight NaCMC by a site-blocking mechanism. Moreover, the adsorbed lower molecular weight polymers assure a significant repulsion between the particles resulting in a weak and very specific flocculated state of such composite, i.e. there is a not too deep secondary energy minimum in the total pair-potential energy curve.

The effect of an inorganic electrolyte, NaCl, was also studied on the stability of the aqueous kaolin suspensions (pH 5-6). We came to the conclusion that the bridge-forming adsorption of



the higher molecular weight polymer was hindered in the presence of NaCl in the case of dilute suspensions (2.5% kaolin content). This effect was not observed, however, for denser kaolin suspensions (40 and 50% kaolin content) presumably due to the more frequent particle-particle collisions. The NaCl was not found to be a suitable agent for the gentle control of aggregation at the applied concentrations (0.5% and 1%), since it caused strong destabilization of the denser kaolin suspensions.

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- [1] K. M. Beazly, in: *"Rheometry: Industrial Applications (Materials Science Research Studies Series, C.R. Tottle, Ed.)"*, K. Walter, Ed., Research Studies Press (Division of John Wiley & Sons LTD), Chichester, **1980**, 339.
- [2] J. C. Husband, in: *"Proc. Tappi Coating Conf., 1996, Nashville, TN, United States"*, Tappi Press, Atlanta, **1996**, 99.
- [3] F. Csempesz, S. Rohrsetzer, *Colloids Surfaces*, **1984**, 11, 173.
- [4] F. Csempesz, S. Rohrsetzer, P. Kovács, *Colloids Surfaces*, **1987**, 24, 101.
- [5] F. Csempesz, K. F-Csáki, *Langmuir*, **2000**, 16, 5917.
- [6] A. Swerin, G. Glad-Nordmark, L. Ödberg, *J. Pulp Paper Sci.*, **1997**, 23(8), J389.
- [7] A. Swerin, L. Ödberg, L. Wågberg, *Colloids Surfaces A: Physicochem. Eng. Asp.*, **1996**, 113, 25.
- [8] H. Tanaka, A. Swerin, L. Ödberg, S. B. Park, *J. Pulp Paper Sci.*, **1997**, 823, J359.
- [9] R. Aksberg, L. Ödberg, *Nordic Pulp Paper Res. J.*, **1990**, 4, 168.
- [10] S. Main, P. Simonson, *Tappi J.*, **1999**, 82(4), 78.
- [11] L. Jarnström, G. Ström, P. Stenius, *Tappi J.*, **1987**, 70(9), 101.
- [12] H. El-Saied, A. H. Basta, S. Y. El-Sayed, F. Morsy, *Pigment and Resin Technology*, **1996**, 25(4), 15.
- [13] M. Mäkinen, D. Eklund, in: *"Proc. Tappi Coating Conf. 1996, Nashville, TN, United States"*, Tappi Press, Atlanta, **1996**, 61.
- [14] T. Persson, L. Jarnström, M. Rigdahl, *Tappi J.*, **1997**, 80(2), 117.
- [15] X. Q. Wang, J. Grön, D. Eklund, in: *"Proc. Tappi Coating Conf. 1996, Nashville, TN, United States"*, Tappi Press, Atlanta, **1996**, 79.
- [16] H. Green, *"Industrial Rheology and Rheological Structures"*, John Wiley and Sons Inc, New York, 1949.
- [17] B. V. Derjaguin, N. V. Churaev, *Colloids Surfaces*, **1989**, 41, 223.
- [18] E. Dickinson, L. Eriksson, *Adv. Colloid Interface Sci.*, **1991**, 34, 1.
- [19] Y. Li, MSc Thesis, Department of Mechanical and Industrial Engineering, Concordia University, Montreal, Quebec, Canada 2001.