

# Electrosteric stabilization of concentrated cement suspensions imparted by a strong anionic polyelectrolyte and a non-ionic polymer

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## Abstract

Strong polyelectrolytes, known as superplasticizers, improve the initial fluidity of concentrated cement suspensions through electrostatic stabilization. These polyelectrolytes do not maintain the initial fluidity, however, primarily due to an increase in the ionic strength of the cementitious suspension. Consequently, non-ionic polymers are often used in conjunction with polyelectrolytes to provide steric stabilization and hence to sustain the desired fluidity over a longer time, and this has led to the development of copolymers with both electrostatic and steric (electrosteric) functionalities. To design such polymers, it is necessary to optimize the balance between electrostatic and steric stabilization to maximize suspension fluidity. We have quantified the effects of a strong anionic polyelectrolyte, melamine formaldehyde sulfonate (MFS), and a non-ionic polymer, hydroxypropylmethylcellulose (HPMC), on the zeta potential of cement particles and the steady shear and low-amplitude rheological properties of concentrated cement suspensions. While the adsorption of MFS onto the cement particle surfaces leads to a sign inversion in the zeta potential, the adsorption of the non-ionic HPMC has no significant effect on the potential. The addition of HPMC to the suspensions substantially reduces the steady shear viscosity and the storage modulus at constant MFS concentration; in addition, there exists an intermediate HPMC concentration that minimizes fluidity. The resulting suspension fluidity is also maintained over a longer time than in the absence of HPMC. This improvement in the stability and fluidity of cement suspensions is attributed to “complementary electrosteric dispersion/stabilization”, and provides insight to the design of polymers with electrosteric functionality.

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## 1. Introduction

In a previous paper, we described our studies on the stabilization of concentrated cement suspensions using superplasticizers, which are strong anionic polyelectrolytes [1]. These polymers adsorb onto the cement particle surfaces through electrostatic attraction, and as a result provide electrostatic stabilization of the particles. This allows for greater particle loading and improved workability of the suspension [2]. Such qualities are critical for self-compacting engineered cementitious composites (SC-ECCs), for example.

These composites are designed to flow into a complex building structure without any extreme compaction, similar to self-compacting concrete [3], and to exhibit extremely ductile pseudo strain-hardening performance in the hardened state, similar to engineered cementitious composites (ECCs) [4,5]. This ductile performance is achieved by the micromechanical criteria to optimize the matrix, fiber, and interfacial properties [6].

However, these strong polyelectrolytes do not maintain the initial fluidity of a fresh cementitious suspension [7], which is necessary to achieve self-compactability [3]. In the previous paper, we showed that while addition of the superplasticizer melamine formaldehyde sulfonate (MFS) initially reduces the suspension viscosity and storage modulus, these rheological properties increase rapidly after a short time. This fast fluidity

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loss is primarily due to the increase in the ionic strength of the cementitious suspension, which leads to re-flocculation driven by van der Waals attraction. Since the strong polyelectrolytes do not provide significant steric repulsion to prevent this re-flocculation, copolymers such as weak or grafted polyelectrolytes have been developed to provide both electrostatic and steric—“electrosteric”—stabilization in a single molecular species [8–11]. The design of these copolymers must optimize the balance between electrostatic and steric stabilization to achieve a desired fluidity of the suspension. This design has been primarily based on trial and error modification of polymer structures, such as altering the length of the steric chains and the number of ionic groups on the backbone. For example, Yamada et al. [10] suggested that polymers with longer grafted chains, shorter backbones, and a greater proportion of ionic groups will improve the fluidity of cementitious suspensions. Increasing the length of the grafted chain or the proportion of ionic groups too much, however, may hinder the adsorption of other molecules and reduce the dispersion of the particles.

It is necessary to first understand the individual roles of electrostatic stabilization and steric stabilization on fluidity prior to designing a copolymer that will provide the appropriate balance of both. In the work reported here, we have quantified the effect of both a superplasticizer (MFS) and a non-ionic polymer (hydroxymethylcellulose, HPMC) on the zeta potential of cement particles and the rheological properties of concentrated cement suspensions. HPMC has been used as a viscosity agent to prevent segregation in a cementitious suspension [12,13], and has also been widely used as a steric stabilizer to reduce strong flocculation in silica suspensions [14]. By using two polymers—one to achieve electrostatic stabilization and one to achieve steric stabilization—we are able to separately quantify the effect of each type of stabilization on the resulting fluidity of the suspension.

Previous studies have used rheological measurements to quantify the effect of polymeric admixtures on the fluidity of concentrated cement suspensions. For example, several studies have related the effects of strong polyelectrolytes on the zeta potential, the interparticle interactions, the suspension fluidity, and the hydration process using the plastic viscosity, yield stress, and deformability (see, for example, Refs. [14–25]). While some studies have focused on the effect of superplasticizer addition on the low-amplitude oscillatory shear (LAOS) behavior of cement pastes [26–31], no study has systematically addressed the effect of both an electrostatic stabilizer and a steric stabilizer on the microstructure and subsequent LASO behavior, however.

In this work, the amount of MFS and HPMC adsorbed onto Type I Portland cement particles is quantified and related to the measured zeta potential of the particles. Then, both steady-shear and LAOS properties of suspensions are measured as a function of polymer concentration. The steady-shear properties were measured to characterize the response of the suspension microstructure to steady shear (irreversible) deformation, while the LAOS properties were measured to quantify changes in the suspension microstructure with polymer and particle concentrations. The results of this work will provide guidelines

to aid in the design of copolymers to function as both an electrostatic dispersant and a steric stabilizer.

## 2. Experimental section

### 2.1. Materials

Type I ordinary Portland cement (LaFarge Cement Co., France) was used as received. The cement was stored in a dry environment to avoid hydration prior to use. The superplasticizer, melamine formaldehyde sulfonate [MFS, molecular weight (MW)=20,000–30,000], was used as received in an aqueous solution of 33 wt.% (W. R. Grace Chemical Co., Boston, MA). The non-ionic polymer, hydroxypropylmethylcellulose (HPMC, MW=150,000; Dow Chemical Co., Midland, MI) was dissolved in water before addition to the cement suspension. De-ionized (DI) water was used in all suspensions.

Using a vibrating mixer, the cement particles were first mixed with water for 30 s to form a paste. Next, a HPMC solution at a known concentration was added to the cement paste and the paste was further mixed for 30 s. Then, a known amount of the aqueous MFS solution was added to the cement paste, and the paste was mixed for another 2 min. The sequential addition of the polymer solutions was adopted to promote the adsorption of HPMC molecules onto the particles, since the MFS chains are preferentially adsorbed due to strong electrostatic attraction. The cement particle volume fraction was varied from 0.46 [weight of water/weight of cement (W/C)=0.40] to 0.56 (W/C=0.25). The compositions of the cement suspensions are detailed in Table 1. Note that the concentration of MFS necessary to disperse the particles increases with the cement particle volume fraction.

### 2.2. Adsorption isotherms

The adsorption isotherm for MFS was measured using ultraviolet spectroscopy as described in a previous paper [1].

Table 1  
Effect of MFS and HPMC concentrations on the storage moduli growth rates

Cement volume fraction	$W_{\text{MFS}}/W_{\text{Cement}}$ (%)	$W_{\text{HPMC}}/W_{\text{Cement}}$ (%)	$\alpha$ (MPa/min)	$\beta$ (MPa/min)
0.51	1.00	0	0.4	3.9
		0.013	0.1	1.4
		0.050	0.1	0.6
		0.100	0.1	0.3
0.53	1.00	0	0.4	2.6
		0.013	0.3	1.4
		0.050	0.3	1.0
		0.100	0.2	2.5
0.53	1.67	0	1.1	7.9
		0.013	0.5	4.1
		0.050	0.8	1.0
		0.100	1.4	0.9
0.56	1.67	0	22	–
		0.013	15	–
		0.050	9.0	–
		0.100	4.2	–

The adsorption isotherm for HPMC was quantified by viscometry. Dilute cement suspensions were prepared with a constant particle concentration and varying HPMC concentration following the mixing procedure detailed above. Then, the cement particles bearing adsorbed HPMC were removed by centrifugation, and the viscosity of the resulting supernatant was measured with a Cannon-Fenske capillary viscometer. The concentration of HPMC in the supernatant was calculated using measured viscosities of solutions with known HPMC concentrations.

To quantify the competitive adsorption between HPMC and MFS, the amount of MFS adsorbed onto the cement particles in the presence of 0.05% (w/w) HPMC was measured by ultraviolet spectroscopy (Varian Australia Ltd., Melbourne, Australia). The mixing procedure to prepare the dilute suspensions was the same as described in Section 2.1. Then, the cement particles bearing adsorbed MFS were removed by centrifugation and the supernatant collected for UV analysis. The changes in the UV absorbency at 490 nm to mark the non-adsorbed MFS in the supernatants were compared.

### 2.3. Zeta potential measurements

To investigate the effects of both HPMC and the binary mixture of HPMC and MFS on the surface potential of the cement particles, the zeta potential of the particles was measured by electrophoresis (Zeta-Meter Inc., Staunton, VA). Cement suspensions with a constant particle concentration and varying polymer concentration were prepared. For the binary mixtures, the HPMC concentration was kept constant at 0.05% (w/w) and the MFS concentration was varied. Following the adsorption of the polymer(s), the suspensions were diluted with DI water. The velocity of the particles under an applied voltage was measured, from which the electrophoretic mobility (velocity/electric field) was calculated. The mobilities were converted to zeta potentials, using the Helmholtz-Smoluchowski equation:

$$\zeta = \frac{\eta u}{\varepsilon} \quad (1)$$

where  $\zeta$  is the zeta potential,  $\eta$  is the fluid viscosity, and  $\varepsilon$  is the dielectric permittivity. Eq. (1) is valid for  $\kappa a > 100$ , where  $\kappa^{-1}$  is the Debye length of the particles and  $a$  is the particle radius.

### 2.4. Rheological measurements

The steady-shear and low-amplitude oscillatory shear (LAOS) properties of the suspensions were measured using a controlled-strain rheometer (VOR, Bohlin Instruments, Gloucestershire, England). A concentric cylinder geometry with a gap spacing of 1.4 mm was used; the sample temperature was fixed at  $25 \pm 1^\circ\text{C}$ . To eliminate the dependence of the microstructure on shear history, a pre-shear was applied to the samples prior to the rheological measurements. This pre-shear consisted of subjecting the samples to a shear rate of  $150 \text{ s}^{-1}$  for 30 s, followed by a rest time of 3 min for the steady-shear

measurements and between 10 and 60 min for the LAOS measurements.

During the steady-shear measurements, the shear stress was measured as a function of shear rate ranging from  $0.00146$  to  $146 \text{ s}^{-1}$ , from which the suspension viscosity was calculated. The relative viscosity was calculated by dividing the suspension viscosity by the medium viscosity, measured using a capillary viscometer.

During the LAOS measurements, the storage modulus ( $G'$ ) and the loss modulus ( $G''$ ) were measured as a function of frequency (from 0.01 to 0.1 Hz) and as a function of time (at 1 Hz) within the linear viscoelastic region (LVR). The critical strain marking end of the LVR tends to decrease with increasing particle concentration, so the maximum strain employed for all measurements was kept constant at 0.0002.

## 3. Results and discussion

### 3.1. Adsorption isotherm

The HPMC adsorption isotherm is shown in Fig. 1. The amount of HPMC adsorbed at complete surface coverage (approximately 0.06%) is much less than that of the strong polyelectrolyte [1], MFS, illustrating that the charged MFS has a greater affinity for the cement particle surface. Also shown in Fig. 1 is a straight line that corresponds to 100% adsorption of the HPMC molecules. There is a greater increase in the concentration of non-adsorbing HPMC molecules for concentrations greater than approximately 0.1%. This is found to lead to a significant increase in the suspension medium viscosity.

When both HPMC and MFS are present, there is competitive adsorption between the two polymers for the limited adsorption sites. Since MFS has a greater affinity for the particle surface, HPMC was first added to the suspensions to promote its adsorption [31], followed by the addition of MFS after a specified time had elapsed (from 0.5 to 10 min). Fig. 2 shows that increasing the HPMC concentration, at a constant MFS concentration of 1%, leads to a small increase in absorbance of the supernatant at a wavelength of 490 nm. This increase in absorbance corresponds to an increase in the concentration of non-adsorbing MFS chains, which is due to a decrease in the

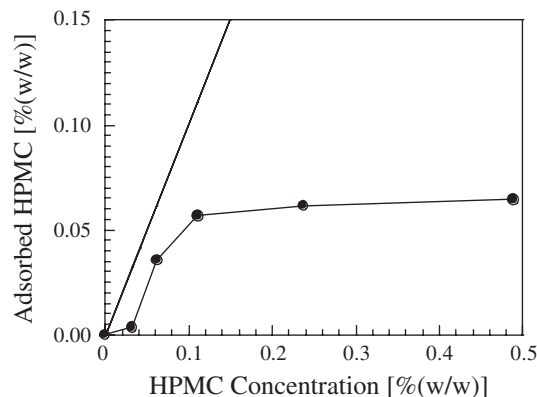


Fig. 1. Adsorption isotherm of HPMC,  $\bullet$ — Actual, — 100% adsorption of HPMC assumed.

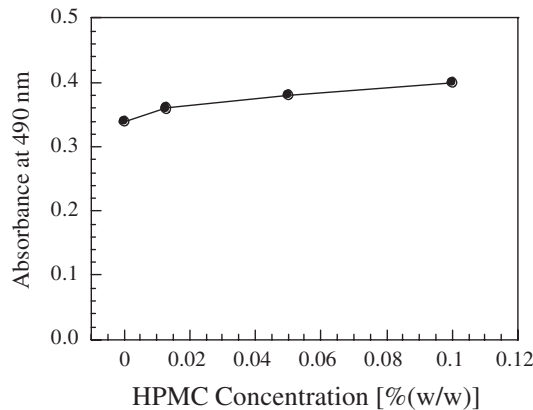


Fig. 2. Increase in the concentration of non-adsorbed MFS (overall MFS concentration of 1% (w/w)) in the suspending medium due to the addition of HPMC.

amount of MFS adsorbed onto the particles. Hence, the pre-adsorbed HPMC chains reduce the number of adsorption sites for MFS. It is not expected that the MFS chains displace the adsorbed HPMC chains due to the higher molecular weight of the non-ionic chains [32].

### 3.2. Zeta potential measurements

Cement particles are composed of interstitial phases with a positive potential ranging from 20 to 40 mV and of silicate phases with a negative potential of approximately  $-10$  mV [33]. Hence, the measured zeta potential represents a composite potential for the particle surface. We have shown that the adsorption of MFS leads to a sign reversal in the zeta potential of the cement particles, resulting in short-term electrostatic stabilization of the particles and subsequent changes in the flow properties including reductions in the viscosity and storage modulus [1]. The negatively charged MFS adsorbs predominately onto the interstitial phases [22,34] and not onto the silicate phases, which results in the sign reversal in the potential. For MFS concentrations of 1% and greater, the changes in the zeta potential becomes less significant, which mirrors the smaller increase in the amount of MFS adsorbed at these concentrations.

However, little change in the zeta potential is expected upon the addition of the non-ionic HPMC. This is supported by the data shown in Fig. 3(a). The small decrease in the zeta potential observed at the largest HPMC concentration is likely due to the increase in the effective volume of the particles owing to the formation of thicker adsorption layers.

The effect of the adsorption of MFS in the presence of HPMC on the zeta potential is shown in Fig. 3(b). The MFS concentration was varied from 0 to 1.75%, while the HPMC concentration was kept constant at 0.05%; the zeta potential data for 0% HPMC (i.e., MFS only) is shown for reference. As shown in Fig. 3(a), 0.05% HPMC alone has no significant effect on the zeta potential. In combination with MFS, the presence of adsorbed HPMC causes the sign reversal in the potential to occur at a larger MFS concentration. For example, the isoelectric point occurs at a MFS concentration of approximately 0.15% in the

absence of HPMC and at a concentration of approximately 0.33% in the presence of 0.05% HPMC. In addition, the magnitude of the potential is reduced at a given MFS concentration. These results are in correspondence with the reduction in the amount of adsorbed MFS when HPMC is present.

### 3.3. Effect of HPMC on the steady shear properties

The effect of HPMC (in the absence of MFS) on the steady-shear properties of the cement suspensions is shown in Fig. 4. Both the low-shear ( $0.06 \text{ s}^{-1}$ ) and high-shear ( $23.3 \text{ s}^{-1}$ ) viscosities are shown as a function of HPMC concentration for a particle concentration of 0.46. The concentration of HPMC was varied from 0 to 0.1% (w/w), since the adsorption isotherm showed that the concentration of non-adsorbing HPMC increases significantly for HPMC concentrations greater than approximately 0.1%. It is not possible to measure the rheological properties of the suspensions prepared without MFS for particle concentrations larger than 0.49 because of the extensive flocculation of the particles and subsequent large suspension viscosity.

As shown in Fig. 4, the low-shear viscosity gradually decreases up to a HPMC concentration of 0.05%, then increases at a HPMC concentration of 0.1%. The high-shear viscosity increases with increasing HPMC concentration. In contrast,

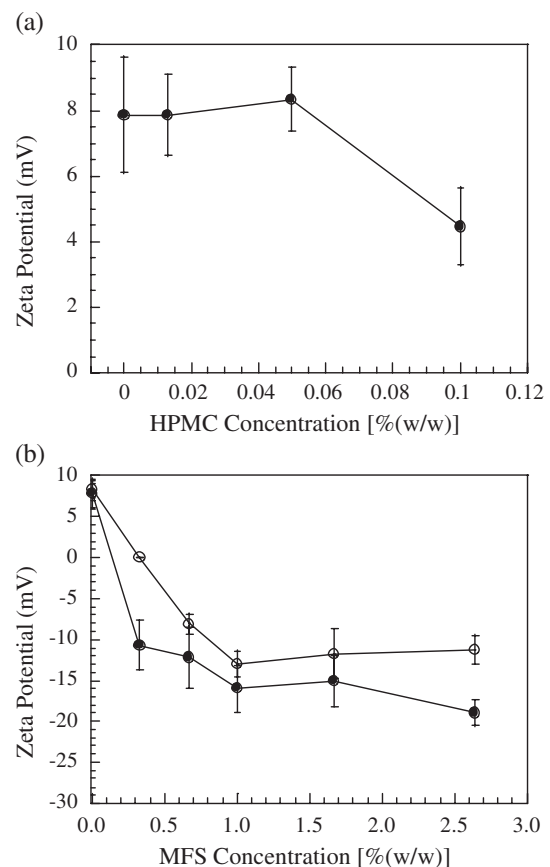


Fig. 3. Effect of the polymers on the zeta potential of the cement particles: (a) HPMC (no MFS); (b) MFS, -●- HPMC 0% (w/w), -○- HPMC 0.05% (w/w).



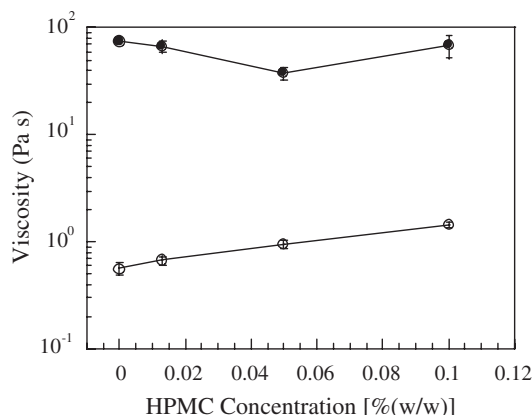


Fig. 4. Effect of HPMC on the viscosity of cement suspensions at  $\phi_{\text{cement}} = 0.46$ ; -●- shear rate of  $0.06 \text{ s}^{-1}$ , -○- shear rate of  $23.2 \text{ s}^{-1}$ .

both the low-shear and high-shear relative viscosities continuously decrease with increasing HPMC concentration (not shown here). Hence, the increases seen in the viscosities are due to the increase in the medium viscosity caused by non-adsorbing HPMC chains. These data show that the adsorbed HPMC molecules provide some stabilization to flocculation of the particles. As shown in Fig. 3(a), HPMC has a negligible effect on the zeta potential and hence the electrostatic interactions between the particles. The reduction in the particle interactions, as inferred through the reduction in the viscosities, is due solely to steric hindrance.

#### 3.4. Effect of HPMC and MFS on the steady shear properties

The effect of both MFS and HPMC on the steady-shear properties is shown in Fig. 5(a) and (b) for particle concentrations of 0.51 and 0.53, respectively. In Fig. 5(a), both the low-shear ( $0.06 \text{ s}^{-1}$ ) and high-shear ( $23.3 \text{ s}^{-1}$ ) viscosities are shown as a function of the admixture concentrations; in Fig. 5(b), only the low-shear viscosities are shown since little variation was noted in the high-shear viscosities. The concentration of HPMC was varied from 0 to 0.1% at constant MFS concentrations ranging from 0.33% to 1.67%.

As shown in these figures, increasing the MFS concentration reduces the dynamic viscosity, irrespective of the applied shear rate. As is expected, the reduction in the viscosity is larger at the lower shear rate. These viscosity reductions are attributed to the enhancement of electrostatic repulsion between the cement particles as the number of adsorbed MFS molecules increases [1]. These data also illustrate that, at a given MFS concentration, the suspension viscosity is minimized at an intermediate HPMC concentration. With the exception of the lower-shear data at a MFS concentration of 0.33% (Fig. 5(a)), this minimum occurs at a HPMC concentration of 0.013%. It is striking that the addition of HPMC at a concentration of 0.013% leads to a large decrease in the viscosity at intermediate MFS concentrations.

The observed increases in the viscosities seen in Fig. 5(a) and 5(b) can be attributed to increases in the suspending medium viscosity due to non-adsorbed HPMC. While not shown here, the relative viscosities decrease with increasing

HPMC concentration. Thus, the adsorbed HPMC molecules enhance suspension stability due to steric repulsion. Since the viscosity also decreases with increasing MFS concentration, the adsorbed MFS molecules enhance suspension stability through electrostatic repulsion.

#### 3.5. Effect of HPMC and MFS on the LAOS properties

Strongly flocculating cement suspensions generally exhibit viscoelastic flow behavior, for which the storage modulus increases with frequency followed by a plateau in the modulus above a critical frequency where the flocculated microstructure is less able to dissipate the energy and the suspensions responds like an elastic solid [1]. The storage modulus measured at such a high frequency is related to the strength of flocculation, especially when strong interparticle forces, such as van der Waals or electrostatic forces, are present in the suspension [35]. In addition, the loss modulus is less than the storage modulus and tends to be less dependent on the frequency. This flow behavior is characteristic of solid-like viscoelastic materials. What is of interest in this study is how the addition of both HPMC and MFS modulates the magnitude of the moduli and their dependence on the frequency, since the variations of these properties directly reflect the changes in the flocculated microstructure.

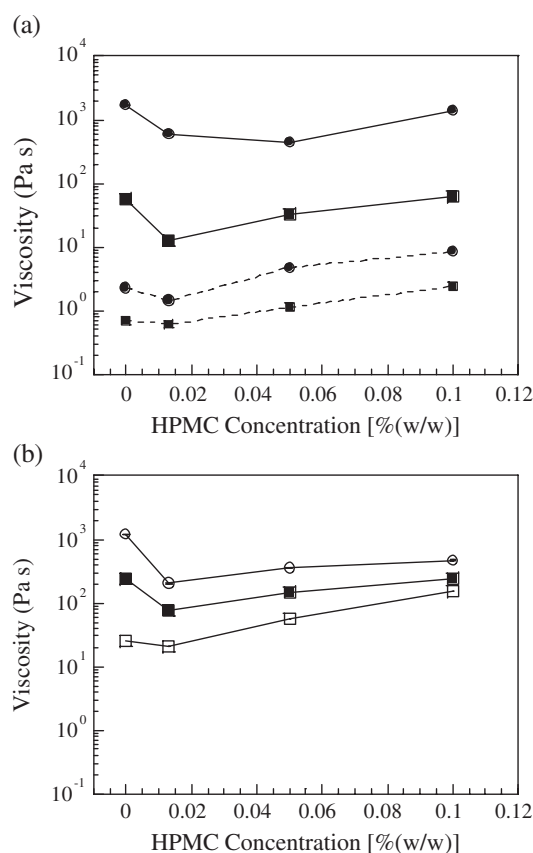


Fig. 5. Effect of both HPMC and MFS on the viscosity of cement suspensions at (a)  $\phi_{\text{cement}} = 0.51$  and (b)  $\phi_{\text{cement}} = 0.53$  measured at shear rates of  $0.06 \text{ s}^{-1}$  (—), and  $23.2 \text{ s}^{-1}$  (- - -); -●- MFS 0.33% (w/w), -○- MFS 0.67%, -■- MFS 1.00% (w/w), -□- MFS 1.67% (w/w).

Shown in Fig. 6 are representative LAOS data for a particle concentration of 0.51. At a given HPMC concentration, the storage modulus decreases with increasing MFS concentration. This trend was noted in our previous study for suspensions that were stabilized only by MFS [1]. At a given MFS concentration, the storage modulus displays a minimum with increasing HPMC concentration, paralleling the dependence of the viscosity on HPMC concentration. For both MFS concentrations, the minimum in the modulus is observed at a HPMC concentration of 0.013%. In addition, at the larger MFS concentration of 1.0%, a HPMC concentration of 0.1% leads to a storage modulus that is larger than that of a suspension that does not contain HPMC. This latter behavior is likely due non-adsorbed HPMC chains increasing the medium viscosity, which will be discussed below.

The dependence of the LAOS data on polymer admixture concentration for three different particle concentrations is shown in Fig. 7(a) and (b). The storage moduli measured at 0.1 Hz are plotted as a function of HPMC concentration in Fig. 7(a); for each data set, the MFS concentration is constant. Two key observations can be drawn from this data. First, the storage modulus increases with increasing particle concentration, which is expected [36]. Second, regardless of the particle concentration or MFS concentration, the storage modulus is a minimum at a HPMC concentration of 0.013%.

These moduli reflect not only the strength of the flocculated networks in the cement suspensions but also the viscosity of the suspending media; increasing the medium viscosity will lead to an increase in the measured storage modulus. At larger HPMC concentrations, the non-adsorbed polymer will increase the medium viscosity and in turn increase the measured modulus. To normalize the modulus data for the effect of the non-adsorbed polymer, the storage moduli were divided by the medium viscosity to obtain the reduced storage modulus, as shown in Fig. 7(b). At particle concentrations of 0.51 and 0.53, the moduli are minimized at a HPMC concentration of 0.013%. However, the moduli are largest when there is no HPMC in the suspension, in contrast to the data shown in Fig. 7(a). At a particle concentration of 0.56, the moduli either become

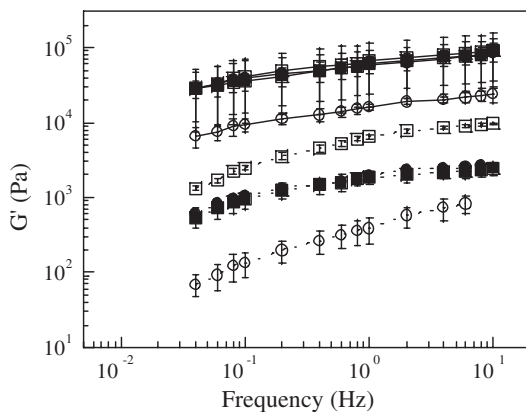


Fig. 6. Low-amplitude oscillatory shear properties of cement suspensions quantified with storage modulus ( $G'$ ) at  $\phi_{\text{cement}}=0.51$  and MFS 0.33% (w/w) (—) and 0.67% (w/w) (---): ●— HPMC 0% (w/w), ○— HPMC 0.013% (w/w), ■— HPMC 0.050% (w/w), □— HPMC 0.100% (w/w).

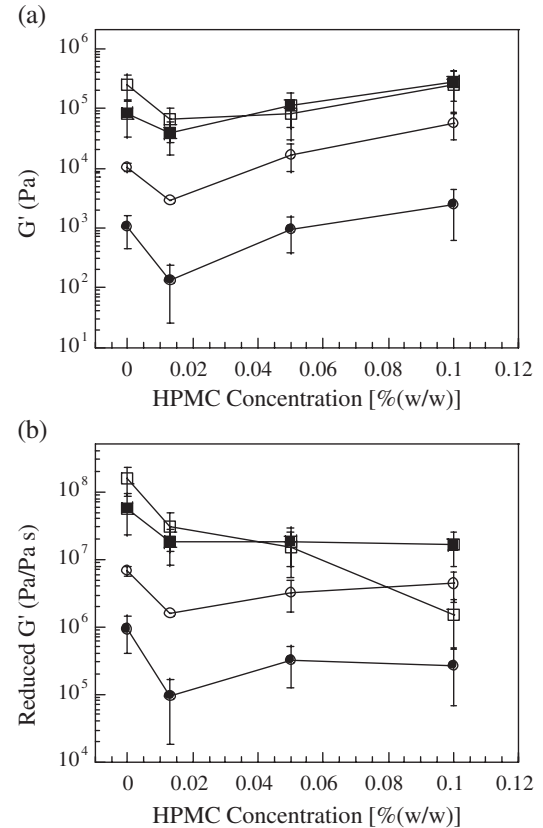


Fig. 7. Effect of the particle and polymer concentration on the low-amplitude oscillatory shear parameters of the cement suspensions. (a) Storage modulus ( $G'$ ) measured at 0.1 Hz. (b) Reduced storage modulus ( $G'$ ) measured at 0.1 Hz. ●—  $\phi_{\text{cement}}=0.51$ , MFS 1.00% (w/w), ○—  $\phi_{\text{cement}}=0.53$ , MFS 1.67% (w/w), ■—  $\phi_{\text{cement}}=0.56$ , MFS 1.33% (w/w), □—  $\phi_{\text{cement}}=0.56$ , MFS 1.67% (w/w).

constant or continuously decrease with increasing HPMC concentration. These data confirm that HPMC provides some steric repulsion when adsorbed onto the cement particles and improves the suspension stability.

The moduli were also measured as a function of time at a frequency of 1 Hz. This measurement provides information about how rapidly the flocculated structure forms in the suspensions following the breakdown of any existing structure by the pre-shear [37]. In general, the rate of increase in the storage modulus becomes greater after 30 min, irrespective of the polymer admixture concentrations. The dependence of the reduced storage moduli on time  $t$  can be expressed using the following:

$$\text{For } t \leq 30 \text{ min: } G'_{\text{red}}(t) = G'_{0,\text{red}} + \alpha t$$

$$\text{For } t > 30 \text{ min: } G'_{\text{red}}(t) = G'_{1,\text{red}} + \beta t \quad (2)$$

where  $G'_{0,\text{red}}$  is the reduced storage modulus at 0 min,  $G'_{1,\text{red}}$  is the reduced storage modulus at 30 min, and  $\alpha$  and  $\beta$  are the growth rates.

The values of  $\alpha$  and  $\beta$  as a function of particle and polymer concentration are given in Table 1. Note that it was not possible to measure the storage moduli after 30 min for a particle concentration of 0.56 because the torque exceeded the

limits of the rheometer. At all particle concentrations, increasing the HPMC concentration reduces the rate of growth of the modulus, with the exception of the value of  $\beta$  for a HPMC concentration of 0.1% at a particle concentration of 0.53. This analysis confirms that HPMC function as a steric stabilizer in the cement suspensions, as was also concluded from the other LAOS and viscosity data.

### 3.6. Contribution of MFS and HPMC to suspension stability

In our previous work, we demonstrated that the addition of MFS to cement suspensions improved suspension stability through electrostatic repulsion [1]. In addition, there exists an optimal MFS concentration at a given cement particle concentration that balances suspension fluidity and cohesiveness. However, while the adsorbed MFS chains initially disperse the electrostatically flocculated cement particles, the dissolution of ions from the particle surfaces increases the ionic strength of the suspension and weakens the electrostatic repulsion. This allows van der Waals attraction to dominate the interparticle interactions at later times.

In this work, we have shown that the adsorbed HPMC chains, which are insensitive to ionic strength changes in the suspending medium, enhance the suspension stability over that imparted by the adsorbed MFS chains. While the addition of HPMC leads to a small reduction in the amount of MFS adsorbed, there appears to be no significant reduction in the electrostatic dispersion provided by the adsorbed MFS. In addition, the stabilization provided by the adsorbed HPMC chains is enhanced by the presence of MFS, since the adsorption of MFS provides electrostatic dispersion to the particles that are initially flocculated because of electrostatic attractive forces. This is noted by the decrease in the viscosities (Fig. 5(a) and (b)) and storage moduli (Fig. 6) with increasing MFS concentration. These results emphasize the beneficial effects of *complementary and stepwise electrosteric dispersion/stabilization* imparted by the adsorbed HPMC and MFS chains on improving the stability of cement suspensions.

Note that retardation of the hydration process, which may be enhanced by the addition of HPMC, is regarded to be negligible in this study for two reasons. First, the HPMC concentrations employed in this study are very small compared to the dosage of polysaccharides used as a retarder to reduce the diffusion of calcium ions in the suspending medium [7,38,39]. Second, the desirable fluidity improvement is measured a few minutes after preparing the suspensions while the hydration process on the silicate phases is activated generally after 3 h.

In our earlier work, we observed an increase in the viscosity and storage modulus with increasing MFS concentration for a particle concentration of 0.56. The apparent loss in stability of the suspensions was attributed to depletion flocculation due to excess MFS chains in the solution. In this work, the presence of HPMC appears to suppress depletion flocculation at this particle concentration. For example, as shown in Fig. 7(a), increasing the HPMC concentration leads to approximately equivalent storage moduli at MFS concentrations of 1.33% and 1.67%. This suppression is likely due to the interpenetration of the adsorbed layer by the free (nonadsorbed) polymer molecules [40].

It is also of interest to note the similarities between the steady-shear and LAOS data. The reduction observed in the storage moduli upon adding 0.013% HPMC (at a constant MFS concentration) coincides with a reduction in the low-shear viscosities, especially at larger MFS concentrations. Since this HPMC concentration leads to a small decrease in the zeta potential, the observed increased in stability is due to steric repulsion imparted by the adsorbed HPMC molecules. A further increase in the HPMC concentration leads to an increase in the viscosities and the storage moduli; this is due to the increase in the non-adsorbed HPMC in solution.

Fig. 8 schematically describes the effect of both HPMC and MFS on the nature of the polymer adsorption layer. In the absence of HPMC, MFS preferentially adsorbs onto the aluminate phases because of electrostatic attraction [22,34]. In the absence of MFS, HPMC will adsorb onto both the aluminate and silicate phases; if MFS is added at a later time, it will adsorb onto open sites on the aluminate phases. The adsorbed MFS

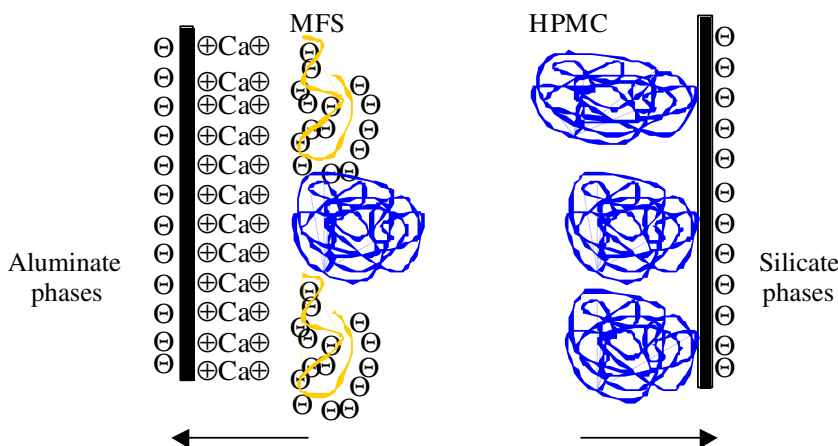


Fig. 8. Schematic description of the polymer adsorption layer resulting from the competitive adsorption of the ionic MFS and the nonionic HPMC. Electrosteric repulsion between aluminate phases bearing adsorbed MFS and HPMC and silicate phases bearing adsorbed HPMC.

chains not only neutralize the positively charged surface sites, but also lead to a net negative surface potential upon sufficient adsorption. This creates electrostatic repulsive forces between the cement particles and results in their dispersion. However, the high ionic strength of the suspending medium that arises over time leads to a compression of the electrical double layers, leading to the reduction in the electrical repulsive forces [19]. The adsorbed HPMC chains provide steric repulsion against van der Waals attraction that dominates at high ionic strengths and prevent particle re-flocculation. Such stepwise dispersion and stabilization imparted by MFS and HPMC lead to the observed reduction in the viscosity and shear modulus.

The adsorbed MFS chains tend to adopt a flatter conformation than the adsorbed HPMC chains. Since the HPMC concentrations are less than that required for complete surface coverage, the thickness of steric layers composed of the HPMC chains is assumed to be on the order of the radius of gyration, which is approximately 50–60 nm. The surface coverage of the particles becomes greater with increasing HPMC concentration and extending the mixing time following the addition of the HPMC solution, which is not shown here [41]. Overall, the total surface coverage by the adsorbing polymers is increased with the inclusion of HPMC.

At higher concentrations, the adsorbed HPMC chains lead to a thicker steric layer, and it is likely that the nonadsorbed polymer chains interpenetrate this thicker layer. This consequently reduces the osmotic pressure difference caused by excess non-adsorbed MFS chains. As a result, the addition of HPMC reduces the depletion flocculation noted at high MFS concentrations in the absence of HPMC.

The results of this work have been successfully implemented in the development of self-consolidating ECCs containing polyethylene [42] and poly(vinyl alcohol) fibers [43]. These fiber-filled composites show self-consolidating flow behavior in the fresh state and tensile-strain-hardening behavior in the hardened state. For example, the composite containing the poly(vinyl alcohol) fibers exhibited tensile strains of up to 5% before failure. The method of constitutive rheological control outlined in this paper has a potential to be extended to other materials in which the processing parameters are constrained by the mechanical requirements of the material. In addition, the results of this work provide insight to the design of polymers for material processing in which both electrostatic and steric functionalities are desired.

#### 4. Conclusions

Cement particles bearing only adsorbed MFS are electrostatically dispersed, but are rapidly re-flocculated, owing to the absence of the thick steric adsorption layers to prevent flocculation due to van der Waals attraction. In contrast, the adsorption of both MFS and HPMC provides an initial electrostatic barrier and a longer-term steric barrier to flocculation, respectively. We have shown that the rheological behavior of cement suspensions can be precisely controlled through the manipulation of the relative amounts of both

polymers. At a given particle and MFS concentration there exists an optimal HPMC concentration that leads to minima in the low-shear viscosity and storage modulus as well as in the growth rate of the modulus, which is indicative of the rate of structure growth in the suspension. The self-consolidating behavior of the cement suspension is optimized at this HPMC concentration. The results of this work have been successfully applied to the development of self-consolidating engineered cementitious composites containing polymer fibers. In addition, the results of this work provide insight to the design of polymers for material processing in which both electrostatic and steric functionalities are desired.

#### References

- [1] H.J. Kong, S.G. Bike, V.C. Li, Effects of a strong polyelectrolyte on the rheological properties of concentrated cementitious suspensions, *Cem. Concr. Res.* 36 (2006) 851–857.
- [2] F. Farouq, J. Szabowski, S. Wild, Influence of superplasticizers on workability of concrete, *J. Mater. Civ. Eng.* 11 (1999) 151–157.
- [3] H. Okamura, K. Ozawa, Mix-design for self-compacting concrete, *Concr. Lib. JSCE* 25 (1995) 107–120.
- [4] V.C. Li, in: M.W. Grutzeck, S.L. Sarkar (Eds.), *Proceedings of Engineering Foundation Conference on Advances in Cement Concrete*, American Society of Civil Engineers, New Hampshire, 1994, pp. 24–29.
- [5] V.C. Li, Fiber reinforced concrete: present and the future, in: B.A. Bentur, A. Mufti (Eds.), *Canadian Society of Civil Engineers*, 1998, p. 64.
- [6] T. Kanda, V.C. Li, Multiple cracking sequence and saturation in fiber reinforced cementitious composites, *Concr. Res. Technol., JCI* 9 (1998) 19–33.
- [7] G.H. Tattersall, G. Banfill, *The Rheology of Fresh Concrete*, Pitman Advanced Publishing Program, Boston, MA, 1989.
- [8] A. Ohta, T. Sugiyama, Y. Tanaka, *Proc. 5th CANMT/ACI International Conference*, Rome, Italy, 1997, pp. SP173–SP179.
- [9] K. Yoshioka, E. Sakai, M. Daimon, A. Kitahara, Role of steric hindrance in the performance of superplasticizers for concrete, *J. Am. Ceram. Soc.* 80 (1997) 2667–2671.
- [10] K. Yamada, T. Takahashi, S. Hanehara, M. Matsuura, Effects of the chemical structure on the properties of polycarboxylate-type superplasticizer, *Cem. Concr. Res.* 30 (2000) 197–207.
- [11] J.A. Lewis, H. Matsuyama, G. Kirby, S. Morissette, J.F. Young, Polyelectrolyte effects on the rheological properties of concentrated cement suspensions, *J. Am. Ceram. Soc.* 83 (2000) 1905–1913.
- [12] M. Yurugi, N. Sakata, G. Sakai, *International Conference on Concrete under Severe Conditions*, Sapporo, Japan, August, 1995.
- [13] K.H. Khayat, Z. Guizani, Use of viscosity-modifying admixture to enhance stability of fluid concrete, *ACI Mater. J.* (1997 (Jul.)) 332–340.
- [14] Y. Ryo, Y. Nakai, M. Kawaguchi, Viscoelastic measurements of silica suspensions in aqueous cellulose derivative solutions, *Langmuir* 8 (1992) 2413–2416.
- [15] H. Uchikawa, D. Sawaki, S. Hanehara, Influence of kind and added timing of organic admixture on the composition, structure, and property of fresh cement paste, *Cem. Concr. Res.* 25 (1995) 353–364.
- [16] M. Daimon, D.M. Roy, Rheological properties of cement mixes: II. Zeta potential and preliminary viscosity studies, *Cem. Concr. Res.* 9 (1979) 103–111.
- [17] C.M. Neubauer, M. Yang, H.M. Jennings, Interparticle potential and sedimentation behavior of cement suspensions: effects of admixtures, *Adv. Cem. Based Mater.* 8 (1998) 17–27.
- [18] M. Yousuf, A. Mollah, P. Palta, T.R. Hess, Chemical and physical effects of sodium lignosulfonate superplasticizer on the hydration of Portland cement and solidification/stabilization consequences, *Cem. Concr. Res.* 25 (1995) 671–682.



- [19] D. Bonen, S.L. Sakar, The superplasticizer adsorption capacity of cement pastes, pore solution composition, and parameters affecting slump loss, *Cem. Concr. Res.* 25 (1995) 1423–1434.
- [20] R. Shaughnessy, P.E. Clark, The rheological behavior of fresh cement pastes, *Cem. Concr. Res.* 18 (1988) 327–341.
- [21] L.J. Struble, G.K. Sun, Viscosity of Portland cement paste as a function of concentration, *Adv. Cem. Based Mater.* 2 (1995) 62–69.
- [22] H. Uchikawa, S. Hanehara, T. Shirasaka, D. Sawaki, Effects of admixtures on hydration of cement, adsorptive behavior of admixture, and fluidity and setting of fresh cement paste, *Cem. Concr. Res.* 22 (1992) 1115–1129.
- [23] S. Hanehara, K. Yamada, Interaction between cement and chemical admixture from the point of cement hydration, absorption behaviour of admixture, and paste rheology, *Cem. Concr. Res.* 29 (1998) 1159–1165.
- [24] M.Y.A. Mollah, W.J. Adams, R. Schennach, D.L. Cocke, A review of cement-superplasticizer interactions and their models, *Adv. Cem. Res.* 12 (2000) 153–161.
- [25] R.J. Flatt, Y.F. Houst, A simplified view on chemical effects perturbing the action of superplasticizers, *Cem. Concr. Res.* 31 (2001) 1169–1176.
- [26] M.A. Schultz, L.J. Struble, Use of oscillatory shear to study flow behavior of fresh cement, *Cem. Concr. Res.* 23 (1993) 272–282.
- [27] L.J. Struble, M.A. Schultz, Using creep and recovery to study flow behavior of fresh cement paste, *Cem. Concr. Res.* 23 (1993) 1369–1379.
- [28] C.F. Zukoski, L.J. Struble, Rheology of cementitious systems, *Mater. Res. Soc. Bull.* 18 (1993) 39–42.
- [29] W.-G. Lei, L.J. Struble, Microstructure and Flow Behavior of Fresh Cement Paste, *J. Am. Ceram. Soc.* 80 (1997) 2021–2028.
- [30] L. Struble, R. Szecsy, W.G. Lei, G.K. Sun, Rheology of cement paste and concrete, *Cem., Concr. Aggreg.* 20 (1998) 269–277.
- [31] M. Sjöberg, L. Bergström, A. Larsson, E. Sjöström, The effect of polymer and surfactant adsorption on the colloidal stability and rheology of kaolin dispersions, *Colloids Surf., A Physicochem. Eng. Asp.* 159 (1999) 197–208.
- [32] J. Fleer, M.A.C. CohenStuart, J.M.H.M. Scheutjens, T. Cosgrove, B. Vincent, *Polymers at Interfaces*, Chap. 4, Chapman & Hall, New York, NY, 1993.
- [33] H. Uchikawa, Conference in tribute to Reogurd, M.M., Importance of Recent Microstructure Development in Cement and Concrete, Sherbrooke, Canada, 1994, pp. 63–118.
- [34] B. Blank, D.R. Rossington, L.A. Weinland, Adsorption of admixtures on Portland cement, *J. Am. Ceram. Soc.* 46 (1963) 395–399.
- [35] R.G. Larson, *The Structure and Rheology of Complex Fluids*, Oxford University Press, New York, 1999.
- [36] T. Shikita, D.S. Pearson, Viscoelastic behavior of concentrated spherical suspensions, *J. Rheol.* 38 (1994) 601–616.
- [37] G.S. Grover, S.G. Bike, Monitoring flocculation in-situ sterically stabilized silica dispersions using rheological techniques, *Langmuir* 11 (1995) 1807–1812.
- [38] G. Mantegazza, E. Alberti, in: V.M. Malhotra (Ed.), 4th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, ACI International, Farmington Hills, MI, 1994, pp. 105–119.
- [39] T. Kawai, T. Okada, Proceedings 3rd International Conference, in: M. Malhotra (Ed.), ACI International, Detroit, MI, 1997, pp. SP119–SP130.
- [40] P. Jenkins, M. Snowden, Depletion flocculation in colloidal dispersions, *Adv. Colloid Interface Sci.* 68 (1996) 57–96.
- [41] H.J. Kong, PhD dissertation, The University of Michigan, 2001.
- [42] H.J. Kong, S.G. Bike, V.C. Li, Development of a self-consolidating engineering cementitious composite employing electrosteric dispersion/stabilization, *Cem. Concr. Compos.* 25 (2003) 301–309.
- [43] H.J. Kong, S.G. Bike, V.C. Li, Constitutive rheological control to develop a self-consolidating engineered cementitious composite reinforced with PVA fibers, *Cem. Concr. Compos.* 25 (2003) 333–341.