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# **Influence of hydroxypropylguars on rheological behaviour of cement-based mortars**

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## *ABSTRACT*

Hydroxypropylguars (HPGs) are used as water retention agents in modern factory-made mortars. Nevertheless, these molecules can also impact also the rheological behavior of cement-based materials. The influence of HPG and its dosage on mortars rheological properties was thus investigated thanks to a suitable measurement procedure. HPG allows keeping a positive yield stress value while the yield stress of hydroxypropyl methyl cellulose (HPMC) mortars was found to decrease with an increase in dosage. HPG increases the shear-thinning behavior and the consistency of mortars. The study of pore solution viscosity suggests that the entanglement of HPG coils beyond a threshold dosage is crucial to understand the rheological macroscopic behavior of HPG-admixed mortars. Nevertheless, the increase in mortar viscosity induced by HPG was lower than expected which reveals additional and specific repulsive forces induced by polysaccharides.

## *KEYWORDS:*

*polysaccharide (D), hydroxypropylguar (D), admixture (D), mortar (E), rheology (C)*

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## 1 Introduction

Characterization and understanding of rheological properties of cement-based materials are crucial since they affect the properties and thus durability of hardened materials. Roussel et al. [1] have established the physical parameters which govern the steady state flow of fresh cement paste. According to the authors, cement-based materials can be represented as biphasic system consisting of suspended particles in a continuous fluid phase. This composition results in complex interplay between colloidal interactions, Brownian forces, hydrodynamic forces and direct contact forces between particles.

The stability of a cement paste results therefore from the balance between attractive and repulsive interactions. Because of adsorbed ions at the surface of the cement particles, there are repulsive electrostatic forces [2]. Otherwise cement particles tend also to agglomerate because of Van der Waals attractive forces [3]. Nonat et al. [4–6] have highlighted these short-range attractive forces by means of optical microscopy observations and particle size measurements.

Natural polysaccharides or their derivatives are well-known to act as viscosity-enhancing admixtures (VEA) by modifying the rheological behavior of cementitious materials [7]. Concrete, mortar and cement grout with high fluidity (e.g. self-compacting concrete or self-leveling underlayment) have been developed in order to facilitate placement. However, the use of highly flowable mixtures may lead to segregation or excessive bleeding and subsequently, durability issues. The use of VEAs allows overcoming this problem by enhancing the sedimentation resistance while maintaining high fluidity [8–13]. The incorporation of VEA in shotcrete or render mortar is also very useful to ensure sagging resistance for thick application on vertical support, and allows sufficient fluidity for normal pumpability [10,14–17] by supplying shear thinning rheological behavior. Thus

polysaccharides provide high yield stress and apparent viscosity at low shear rate but low resistance to flow at high shear rate [7].

Recent studies show that it is more complicated since results from literature are contradictory. For instance, the evolution of yield stress with the dosage of polysaccharide depends strongly on the kind of binder and polysaccharide studied. Khayat and Yahia [11] and Sonebi [12] report a steady increase in yield stress of cement grout by increasing dosage of welan gum. Leemann and Winnefeld [10] obtained similar results with starch derivatives incorporated in self-compacting mortar. In contrast, Cappellari et al. [17] obtained a reduction in yield stress of mortar with increasing dosage of hydroxyethyl methyl cellulose. The results of Paiva et al. [15] and Bouras et al. [18] show an initial decrease followed by an increase in mortar yield stress when the dosage of hydroxypropyl methyl cellulose and starch ether, respectively, increases. In addition, these trends can be amplified or modified when several polysaccharidic admixtures are blended, due to synergic effect and formation of interpolymer complexes [19]. Among the polysaccharidic VEAs, microbial-source polysaccharides such as welan gum [11–13,20,21] and cellulose ethers [14–17,22] are the most widely used and studied. Nevertheless, the hydroxypropylguar (HPG) are now well-established in the construction industry as water retention agent for mortars [23].

Guar gum is a natural polysaccharide extracted from the seeds of *Cyamopsis tetragonolobus*. It consists of a  $\beta(1-4)$ -linked D-mannopyranose backbone with random branchpoints of galactose via an  $\alpha(1-6)$  linkage. Hydroxypropylguar is obtained from the native guar gum via an irreversible nucleophilic substitution, using propylene oxide in the presence of an alkaline catalyst. It is one of the most widely available derivatives of guar gum since it has application as thickener in many important industries, including hydraulic fracturing process, paper manufacturing, water treatment or textile printing [24–28].

The manufacture of HPG has the advantage of having a more reduced impact on the environment than cellulose derivatives. Indeed, guar gum exhibits a higher chemical reactivity and is soluble in cold water because of its branched-chain structure with a lot of hydroxyl groups. Thus, the chemical modification of the native guar gum requires normal reaction conditions of temperature and pressure, does not generate large quantity of by-products, and requires minimal purification procedure [23].

The efficiency of HPG as good water retention agent has been shown by several authors [17,29–31] but studies about their effect on rheological properties are very scarce. Izaguirre et al. [32] have worked with aerial lime-based mortars and Cappellari et al. [17] have characterized only one HPG. However, the formulation of modern factory-made mortars requires choosing a specific type and dosage of polysaccharide to obtain the desired water retention performance and rheological behavior suitable for the application. These requirements underscore the need to characterize and understand the influence of HPG on mortar rheological properties.

The aim of this paper is to characterize and understand the influence of HPG and its dosage on the rheological properties of cement-based mortars. This study will be divided into three parts. Firstly, the impact of HPG on mortar rheological behavior will be described using the parameters of the Herschel–Bulkley model. Then, the effect of HPG on pore solution viscosity will be presented. The pore solution was extracted from the mortar by means of centrifugation. Finally, the relationship between pore solution and mortar viscosities will be investigated.

## 2 Material and methods

### 2.1 Mineral and organic compounds

#### 2.1.1 Mineral products

Mineral products used in this study consist in ordinary Portland cement, siliceous sand (DU 0.1/0.35, Sibelco) and limestone filler (BL 200, Omya).

Chemical and phase compositions of the cement used are given in Table 1. It is an ordinary Portland cement (OPC), classified CEM I 52.5 R CE CP2 NF type cement according to EN 197-1 and French NF P 15-318 standards. Phase composition was determined by Rietveld refinement method (Siroquant V2.5 software) after XRD analysis (D5000, Siemens). Oxide composition was quantified by means of X-ray fluorescence spectroscopy (SRS3400, Bruker-AXS).

The median particle diameters by volume ( $D_{50\%}$ ), determined by means of laser diffractometry with dry powder disperser, (Mastersizer 2000 and Scirocco dispersing unit, Malvern), are about 310, 12 and 6  $\mu\text{m}$  for the sand, cement and filler respectively.

**Table 1:** Chemical and phase compositions of the investigated cement.

Chemical composition (% wt)				Phase composition (% wt)			
Oxides	XRF	Oxides	XRF	Phases	XRD (Rietveld)	Phases	XRD (Rietveld)
CaO	66.9 ± 0.8	MgO	1.16 ± 0.01	C <sub>3</sub> S	79.4 ± 0.5	Gypsum	1.3 ± 0.2
SiO <sub>2</sub>	20.9 ± 0.2	TiO <sub>2</sub>	0.32 ± 0.03	C <sub>2</sub> S	8.2 ± 0.4	Anhydrite	3.2 ± 0.2
Al <sub>2</sub> O <sub>3</sub>	4.7 ± 0.1	P <sub>2</sub> O <sub>5</sub>	0.14 ± 0.01	C <sub>3</sub> A	3.3 ± 0.2	Hemi-hydrate	0.8 ± 0.3
SO <sub>3</sub>	2.4 ± 0.2	MnO	0.04 ± 0.01	C <sub>4</sub> AF	4.1 ± 0.9	Free CaO	0.5 ± 0.2
Fe <sub>2</sub> O <sub>3</sub>	2.6 ± 0.1	K <sub>2</sub> O	0.10 ± 0.01				
LOI	2.1 ± 0.1						

### 2.1.2 Organic admixtures

Seven polysaccharidic water retention admixtures were investigated: five hydroxypropylguars (HPG 1, HPG 2, HPG 3, HPG 5 and HPG 6) and two hydroxypropyl methyl celluloses (HPMC1 and HPMC 2) as references for comparison since they are widely used in industry.

Fig. 1 shows the molecular structure of HPMC and HPG (substituent positions are arbitrary).

Table 2 provides a qualitative description of the admixtures. The qualitative substitution degrees are provided by the manufacturers.

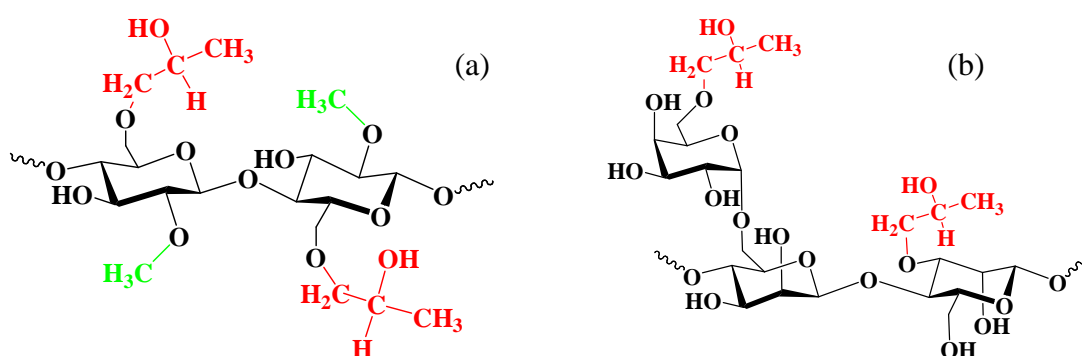


Fig. 1: Molecular structure of (a) HPMC and (b) HPG.

All the HPG samples, provided by *Lamberti S.p.A*, exhibit similar molecular weight, about  $2 \cdot 10^6 \text{ g} \cdot \text{mol}^{-1}$ . The molar substitution ratio ( $MS_{HP}$ ) represents the number of moles of hydroxypropyl groups per mole of anhydroglucose unit and is less than 3 for the investigated HPG samples. It appears from Table 2 that the only difference between HPG 1, 2 and 3 is the molar substitution ratio while HPG 5 and 6 exhibit additional substitution (short or long alkyl chains).

The degree of substitution ( $DS_M$ ) represents the amount of methoxyl groups per anhydroglucose unit and is about 1.8 for HPMC 1 and HPMC 2. The molecular weights are about  $0.25 \cdot 10^6$  and  $1 \cdot 10^6 \text{ g} \cdot \text{mol}^{-1}$  for HPMC 1 and HPMC 2 respectively, which constitute the only difference between these two samples.



**Table 2:** Qualitative description of the admixtures used.

Admixtures	MS <sub>HP</sub>	DS <sub>M</sub>	Additional substitution
HPMC 1	Very low	Very high	/
HPMC 2	Very low	Very high	/
HPG 1	Low	/	/
HPG 2	Medium	/	/
HPG 3	High	/	/
HPG 5	High	/	Short alkyl chain
HPG 6	High	/	Long alkyl chain

## 2.2 Preparation of mortars

Admixtures were dissolved in deionized water. Polymer dosages in mortars varied from 0.1 to 1.6% by weight of cement (bwoc) by preparing polymer solutions of concentrations varying from 1 to 16 g.L<sup>-1</sup>. Complete dissolution of all polymers was obtained by means of magnetic stirring for 24h.

Mortars were prepared according to the following mixture proportions: 30 wt.% of cement, 65 wt.% of siliceous sand and 5 wt.% of limestone filler. Dry mixture (*i.e.* cement, sand and filler) was homogenized in a shaker (Turbula, Wab) with low shear forces for 15 min.

Admixture solutions were then added in order to obtain a water to cement ratio W/C = 1. Dry mixture and admixture solution were mixed (MIx40, CAD Instruments) in accordance with EN 196-1 [33]. A control test was performed with a mortar without admixture.

Each mortar studied was divided into two parts after mixing. One part was used to study mortar rheological properties, while the other portion was centrifuged in order to determine pore solution viscosity.

It is worth noting that the mortar formulation with high W/C was adapted from the CEReM (European consortium for study and research on mortars) mixture design [34,35]. This work is part of a larger study that focuses on the influence of HPG on overall mortar properties at early age, including mortar water retention capacities. Regarding water retention, the high

W/C ratio corresponds to extreme conditions which allow highlighting the effectiveness of HPG as water retention agent.

### **2.3 Rheological measurements**

All the rheological measurements were obtained with Anton-Paar Rheometer MCR 302, thermostated at 20 °C because rheological properties are temperature-dependent.

#### *2.3.1 Mortars*

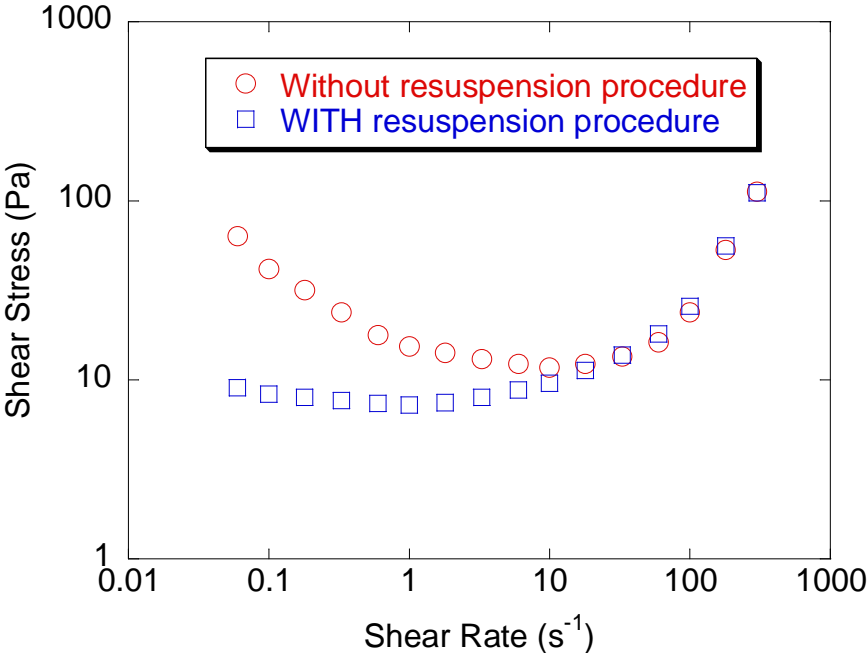
Fresh mortar rheological properties were investigated with vane-cylinder geometry.

According to many authors [17,18,36], this system is suitable for granular pastes like mortars. The gap thickness, distance between the periphery of the vane tool and the outer cylinder, was set at 8.5 mm, which is an order of magnitude higher than the maximum size of sand particles, in order to be less sensitive to the heterogeneity of the mortar [37]. Using a Couette analogy, the shear stress and shear rate were calculated from the torque and the applied rotational velocity respectively [38,39], after calibration with glycerol.

The mortar was introduced into the measurement system at the end of the mixing cycle, i.e. 4 min after the contact between cement and water. The suspension was then held at rest for 6 min. At 10 min, the mortar was pre-sheared for 30 s at  $100 \text{ s}^{-1}$  in order to re-homogenize the sample and to eliminate its shear history because of thixotropic character of cementitious materials [40,41]. After a period of rest of 4.5 min, the rheological measurements were started at 15 min. At this time, the hydration rate is very low which allows overcoming the irreversible effect of cement hydration on rheological behavior, especially at low shear rate [40].

Imposed shear rate was decreased by step from 300 to  $0.06 \text{ s}^{-1}$ . At each shear rate, the measuring time was adjusted in order to obtain a steady state whatever the formulation [42,43]. Nevertheless, because of high W/C ratio, many mortar mixtures with an insufficient

amount of VEA experienced sedimentation before reaching steady state, which distorts results from rheological measurements. The samples were therefore systematically submitted to high shear rate ( $100 \text{ s}^{-1}$ ) for 20 s before each imposed shear rate in order to resuspend particles of the mortar within the mortar mixtures. In a previous study, Patural et al. [35] validated this resuspension procedure in case of non-settling samples. Here, a comparison between the rheograms of mortars without admixture, which constitute the most critical case with regard to sedimentation, obtained with or without the resuspension procedure was made (Fig. 2). No effect was observed at shear rates higher than  $10 \text{ s}^{-1}$ . At lower shear rate, rheogram obtained with resuspension procedure exhibits expected behavior. In contrast, results obtained in standard steady state regime (i.e. without resuspension procedure) exhibit an increase in shear stress when the shear rate decreases. This may be attributed to the particle sedimentation which induces an artificial increase in shear stress. Therefore the resuspension procedure allows keeping particles in suspension even at low shear rate.



**Fig. 2:** Interest of resuspension procedure for a mortar without admixture, the most critical case with regards to sedimentation.

### 2.3.2 Pore solution

At 15 min (i.e. similar to mortar rheological measurements), a large representative sample of mortar was centrifuged (Thermo Scientific, Sorvall Legend XF) for 10 min at 4,500 rpm.

Then, the supernatant was collected and centrifuged again (Eppendorf, MiniSpin Plus) at higher speed (14,500 rpm) for 5 min which allows removing residual particles.

The steady shear flow of final supernatant, representing pore solution, has been investigated using decreasing logarithmic ramps in the  $10^3 - 1 \text{ s}^{-1}$  range with cone and plate geometry ( $2^\circ$  cone angle, 50 mm diameter). Flow curves,  $\eta = f(\dot{\gamma})$ , exhibited typical shear thinning behavior with a Newtonian region in the low shear rate range. Experimental data were well correlated with the Cross model [44]:

$$\eta(\dot{\gamma}) = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (\alpha\dot{\gamma})^n} \quad (1)$$

where  $\eta_0$  is the zero-shear rate viscosity,  $\eta_\infty$  the infinite rate viscosity,  $\alpha$  a relaxation time and  $n$  a non-dimensional exponent.

Among Cross parameters, the zero-shear rate viscosity represents the constant viscosity in the Newtonian plateau at low shear rate and was chosen to characterize pore solution viscosity.

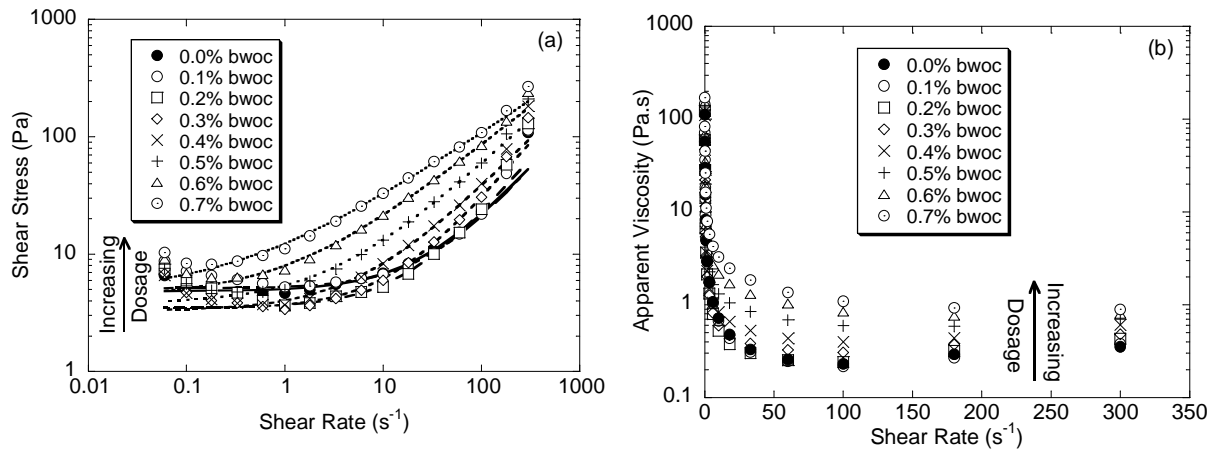
## 3 Results and discussions

### 3.1 Influence of HPG on mortar rheological properties

Rheological properties of admixed cement-based materials are decisive parameters according to the desired applications. Thus, the influence of HPG on rheological properties of admixed cement-based mortars was first characterized. The results can be expressed as shear stress  $\tau$  according to shear rate  $\dot{\gamma}$ . The Herschel-Bulkley (HB) model [45] is often used to describe mortar rheological behavior:

$$\tau = \tau_0 + K\dot{\gamma}^n \quad (2)$$

where  $\tau_0$  is the yield stress,  $K$  the consistency coefficient and  $n$  the fluidity index which characterizes shear-thinning behavior of mortar.



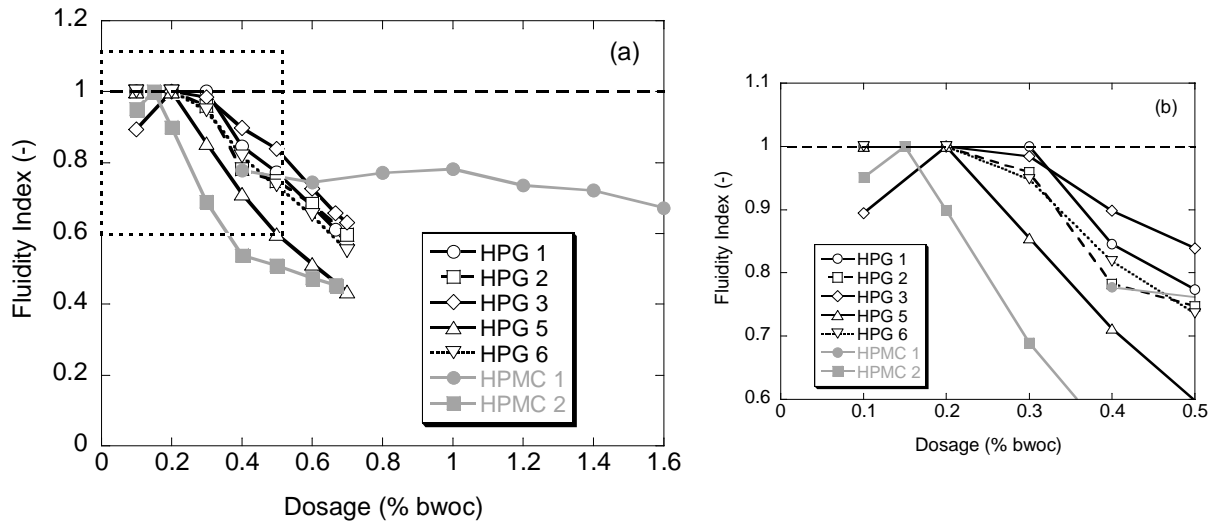
**Fig. 3:** (a) Shear stress and (b) apparent viscosity versus shear rate according to the dosage  
Example of HPG 1  
Markers represent experimental data and lines represent calculated values according to HB model (Eq 2).

Fig. 3a shows classical rheograms obtained according to the dosage of HPG 1. Experimental data were fitted well with the HB model independent of dosage. The same results were obtained for all the experimental data whatever the admixture. In the following, the three HB parameters were thus chosen to compare admixtures to each other.

It is worth mentioning that mortars were found to be slightly shear-thickening when the shear rate is higher than  $100 \text{ s}^{-1}$  (Fig. 3b). Indeed, an increase in the shear rate leads to an increase in the apparent viscosity ( $\tau/\dot{\gamma}$  ratio) at high shear rate, especially at low dosages. The same behavior was observed by many authors [1,16–18,40] and was attributed to the predominant effect of particle inertia at high shear rate. According to Phan et al. [40], this implies that the HB model is not valid at this range of shear rate. Therefore, these data points have not been fitted to the HB model.

### 3.1.1 Fluidity Index

Fig. 4a shows the evolution of the fluidity index  $n$  according to the admixture used and its dosage. For the control test and at low VEA dosage, fluidity index was found to be equal to 1 which means that the non-admixed mortars are Binghamian. When the dosage of HPG or HPMC increases, the fluidity index decreases. Indeed, whatever the polysaccharidic admixture tested, the fluidity index seems to start decreasing at a dosage ranging from 0.2 to 0.3% bwoc (Fig. 4b). This means that, above this dosage the mortars become shear-thinning and this rheological behavior gets more and more pronounced as the HPG dosage increases. This is in good agreement with the literature concerning welan gum [11], cellulose ethers and HPG [17]. Moreover, admixed mortars with HPG 5 exhibit a more shear-thinning behavior (lower fluidity index) than mortars admixed with other HPG, whatever the dosage.



**Fig. 4:** (a) Evolution of the fluidity index ( $n$ ) according to the dosage and the admixture studied (b) focus on the transition from Binghamian to shear-thinning behaviors.

As suggested by Khayat [7], polysaccharides enhance the shear thinning behavior of cementitious materials by making the pore solution (which is Newtonian in the absence of admixture) shear-thinning. Indeed, polymers exist in solution in coil form. Above a specific dosage, entanglement occurs between polymer coils, inducing a shear-thinning behavior to

the solution. At low shear rate, the entanglement of polymer coils leads to a higher pore solution viscosity and thus higher mortar viscosity. When the shear rate increases, the polysaccharide chains align in the direction of the flow resulting in less and less effect on mortar fluidity. The presence of additional alkyl chains enhances the entanglement and, thus, the shear-thinning behavior, which may explain why admixed mortar with HPG5 exhibits the highest shear-thinning behavior among HPG studied. These assumptions will be verified in section 3.2.

3.1.2 Yield stress

Fig. 5 shows the evolution of the yield stress calculated from Herschel-Bulkley model according to the dosage. The mortar without admixture exhibits a yield stress value of 5 Pa. In additions, the yield stress varies very slightly with the polymer dosage whatever the admixture considered. This unfortunate result may be due to the high W/C ratio used in this work resulting in a very low solid volume fraction and thus low values of yield stress since they are strongly linked [1,3,10]. Nevertheless, it is possible to identify trends.

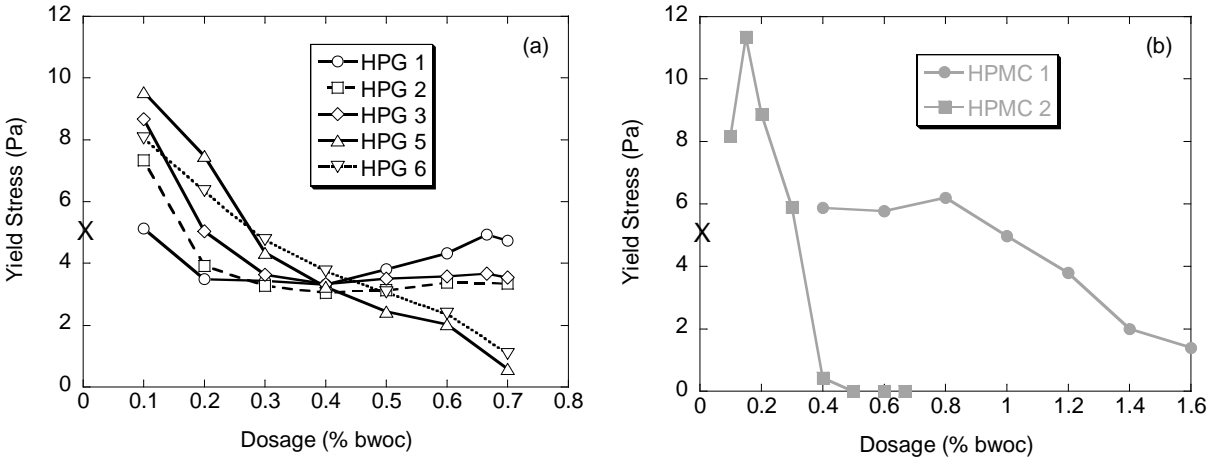


Fig. 5: Evolution of the yield stress ( $\tau_0$ ) according to the dosage and the admixture studied (a) HPG (b) HPMC.

Yield stress exhibited by mortars admixed with HPG and HPMC is of the same order of magnitude. However, for HPMC (Fig. 5b), yield stress decreases when the dosage increases. These results are not common since several papers reported that an increase in VEA dosage leads to a rise in the yield stress [10–12,21,46,47], but is in agreement with recent study [17]. In the case of HPG (Fig. 5a), an increase in polymer dosage leads also to a decrease in yield stress values of mortars admixed with HPG 5 and HPG 6. In contrast, when the dosage of HPGs 1-3 increases, yield stress decreases first and then remains stable.

The yield stress of neat cementitious materials is attributed to the existence of a network of attractive colloidal interactions [1]. The enhancement of yield stress by polysaccharide is often attributed to the entanglement of polymer coils making the pore solution and hence the admixed material shear-thinning. The sample thus exhibits higher viscosity at low shear rate and higher yield stress. Moreover, polysaccharides such as HPG and HPMC are able to adsorb on cement grains [29,48]. Since polysaccharides exhibit long chains, the same molecule can adsorb on separate cement particles and draw them together. This phenomenon is known as polymer bridging flocculation [49–51] and induces a rise in yield stress [7,13,16]. However, according to several authors, polysaccharides lead to an increase in the entrained air amount [15,17], highlighted by a rise in the total porosity from 15 to 50% and a drop of the mortar density [35,52–54], to steric hindrance induced by their adsorption on cement grains [16] and repulsive depletion forces induced by polymers dissolved in pore solution [16]. All these factors tend to decrease impact of Van der Waals attractive forces and thus yield stress. The overall competition between these opposing effects may lead to non-monotonic evolution of the yield stress with dosage [17].

Characterization of yield stress with mortar mix-design corresponding to an industrially-used standard mixture is of course required to confirm that HPG allows maintaining yield stress



while the yield stress decreases with an increase in dosage of HPMC and HPG with additional alkyl chains.

3.1.3 Consistency

According to many authors, incorporation of polysaccharide leads to an increase in apparent viscosity of cement-based materials because of an increase in the pore solution viscosity [7,10,12,13]. Fig. 6a shows the evolution of the consistency coefficient, which is a parameter of HB model, as a function of the dosage for the different admixtures studied. It appears effectively that an increase in polymer dosage leads to an increase in consistency.

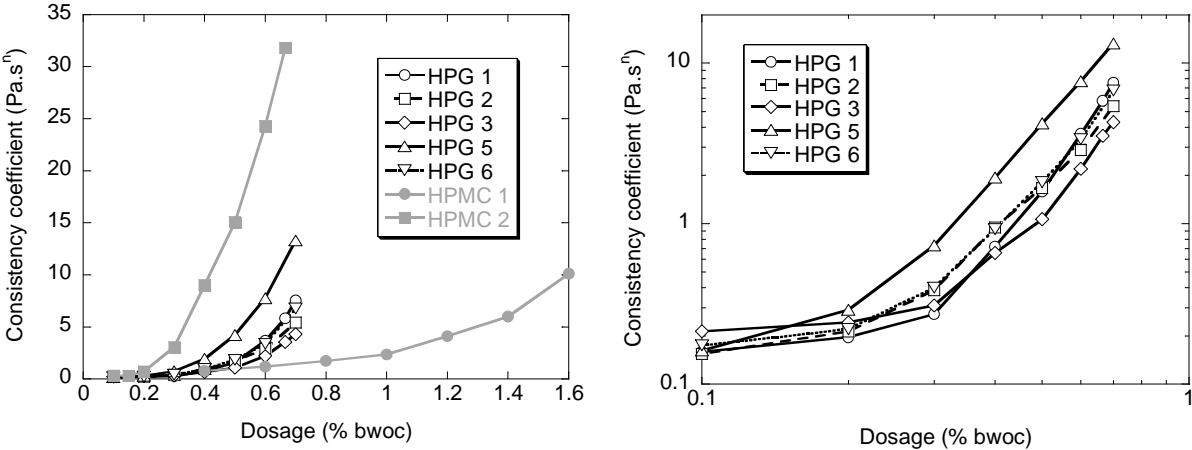


Fig. 6: Evolution of the consistency coefficient (K) according to the dosage and the admixture studied in linear scale (a), only for HPG in logarithmic scale (b).

Three trends emerge from these results: (i) HPMC 2 which is the best VEA, (ii) HPG with intermediate behavior, and (iii) mortars admixed with HPMC 1 which exhibit the lowest consistency whatever the dosage.

Fig. 6b represents the evolution of consistency coefficient of mortars admixed with HPG only, using logarithmic scale. It allows highlighting an evolution of consistency according to the dosage in two steps. The consistency increases slightly at first, until reaching a given dosage for which a sudden increase in consistency is observed. Similar results were reported

by Cappellari et al. [17] who have attributed the first regime to an increase in air content which results in dispersing effects that offset the increase in consistency.

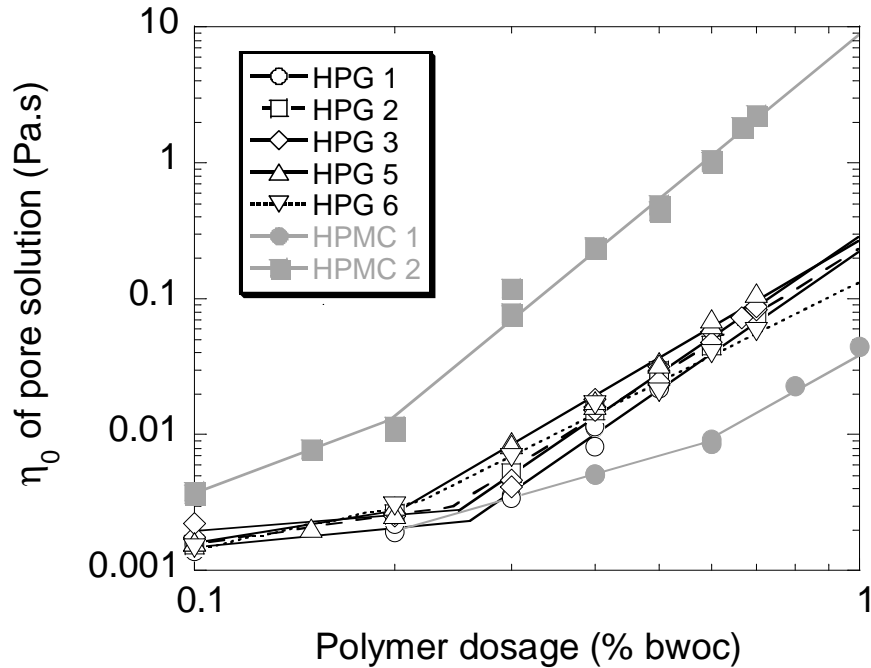
Nevertheless, another hypothesis may be assumed. Indeed, Fig. 6b is found to be quite similar to typical curve representing the evolution of polymer solution viscosity with polymer concentration (see section 3.2). It means that the consistency coefficient of admixed cement-based materials is strongly linked to the rheological behavior of the pore solution. In solution, the transition between diluted and semi-diluted solution is marked by an abrupt change in slope due to the overlapping of polymer coils which induces a dramatic change in flow behavior and viscosity of the solution. If this assumption is correct, the evolution of the pore solution viscosity of admixed cement-based materials, according to the polymer dosage, should exhibit similar trends. Moreover, the change of slope and thus the overlapping of coils should occur for polysaccharide dosages ranging from 0.2 to 0.3% bwoc, since the consistency coefficient strongly changes in this range of dosage.

### **3.2 Pore solution viscosity**

The influence of HPG on pore solution viscosity was characterized.

As discussed earlier, the flow curves of pore solutions  $\eta = f(\dot{\gamma})$  exhibit well-known shear-thinning behavior of polysaccharides solutions. This behavior gets more pronounced when the introduced amount of HPG in the mortar increases. This is highlighted by the double logarithmic plots of zero-shear viscosity versus the concentration (Fig. 7). Indeed, two well-defined linear concentration-dependences of zero-shear rate viscosity are observed. The dosage corresponding to the intersection of these two straight lines, called critical coil-overlap concentration  $C^*$  in literature, is essential to understand the rheological behavior of polymer solution. Below this threshold concentration, individual polymer molecules provide their individual contribution to the viscosity since they are present as isolated coils (diluted

regime). Thus the solution viscosity increases slightly with the concentration. Above this critical concentration, the polymer solution becomes semi-dilute. Thus, an entanglement of polymer coils and formation of polymer agglomerates are expected, leading to a sudden increase in the solution viscosity [55,56].



**Fig. 7:** Determination of polymer dosage corresponding to agglomerate formation.

From Fig. 7, it is possible to establish the critical polymer dosage corresponding to the formation of polymer agglomerates in the pore solution. Table 3 presents the dosage necessary for the formation of these polymer agglomerates in the mortar pore solution. Nevertheless, one should keep in mind that these dosages do not correspond to real concentrations of dissolved polymer present in the pore solution, but to the polymer dosage necessary to form agglomerates. Indeed, a certain amount of water is lost due to cement hydration and mortar drying. Moreover, a non-negligible amount of polymer may be trapped into the mortar paste during hydration [57] and/or irreversibly adsorbed onto cement phases [48]. Therefore it is impossible to estimate the real concentration of polymer in solution without its measurement.

**Table 3:** Polymer dosage corresponding to the formation of agglomerates into the admixed mortar pore solution.

	HPG1	HPG2	HPG3	HPG5	HPG6	HPMC1	HPMC2
Polymer dosage (% bwoc) corresponding to formation of agglomerates	0.26	0.25	0.25	0.20	0.22	0.58	0.20

In addition, Fig. 7 highlights that HPMC 2 exhibits the strongest viscosity-enhancing effect on pore water, far ahead of HPG, while HPMC 1 exhibits the weakest influence on viscosity. The difference between HPMC 1 and HPMC 2 is ascribed to difference in molecular mass. Among HPG, pore solution viscosities of mortars admixed with HPG 1, 2 and 3 are similar despite the increase in substitution degree. In literature, an increase in the DS conducts to a decrease in zero-shear rate viscosity. However, in the same time, polymer adsorption on cement phases is also reduced [29]. Consequently, the effect of substitution degree on viscosity is compensated by the effect of adsorption ability, leading to comparable viscosities. Therefore the formation of polymer aggregates occurs at similar polymer dosage of about 0.25% bwoc for HPG 1, 2 and 3 (Table 3). On the contrary, the formation of polymer aggregates is obtained at slightly lower polymer dosage (0.2% bwoc) in the presence of additional alkyl chains (HPG 5 and 6). The interconnection between alkyl chains creates intermolecular interactions through specific hydrophobic interactions which cause a decrease in the coil-overlapping concentration.

The polymer dosages corresponding to the start of the fluidity index decrease in Fig. 4b and to the change in slope in Fig. 6b are consistent with those inducing formation of HPG aggregates in pore solution (Table 3). The results seem to indicate a significant relationship between the effect of HPG on pore solution viscosity and on mortar rheological behavior.

### 3.3 Relationship between pore solution and mortar viscosities

Many empirical expressions have been proposed to describe the viscosity of highly concentrated granular suspensions. The most famous one is the Krieger-Dougherty equation:

$$\eta = \eta_0 \left(1 - \frac{\Phi}{\Phi_m}\right)^{-2.5\Phi_m} \quad (3)$$

where  $\eta$  is the viscosity of the paste,  $\eta_0$  the viscosity of the interstitial fluid,  $\Phi$  the solid volume fraction and  $\Phi_m$  the solid volume fraction corresponding to maximum packing.

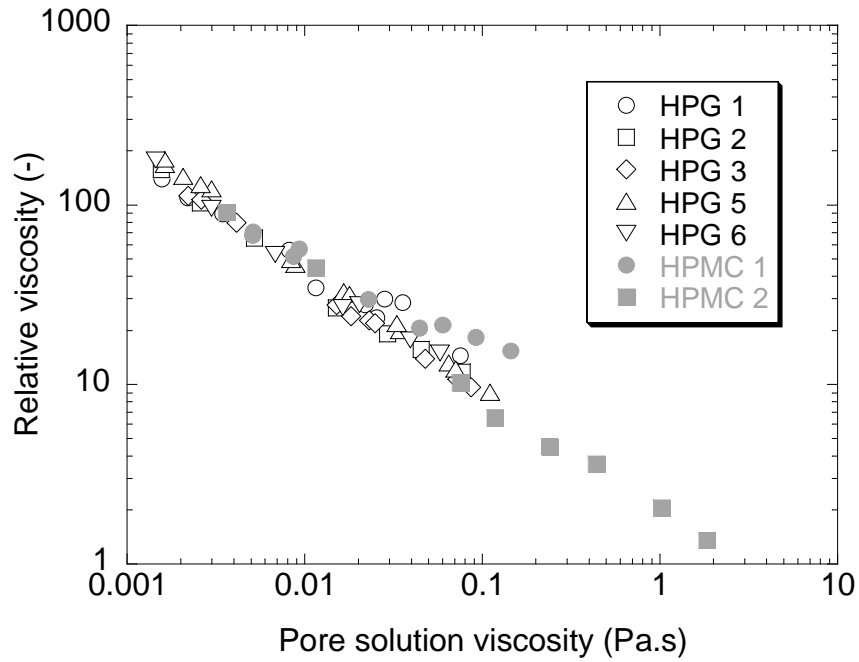
According to this equation, the viscosity of a suspension is directly proportional to the viscosity of the suspending fluid. When applied to our study, it appears that the viscosity of mortar is proportional to the pore solution viscosity as expected from previous results.

Nevertheless, some results may be contradictory as polysaccharidic VEA seems to preferentially increase the pore solution viscosity versus the effective viscosity of the mortar.

In order to check the proportionality between these two viscosities, the relative viscosity  $\eta_{rel}$  defined as the ratio between macroscopic mortar viscosity and interstitial fluid viscosity (Eq. 4) has been plotted as a function of pore solution viscosity (Fig. 8).

$$\eta_{rel} = \frac{\eta_{app (100s^{-1})}}{\eta_0} \quad (4)$$

where  $\eta_{app (100s^{-1})}$  is the mortar viscosity at  $100 \text{ s}^{-1}$  and  $\eta_0$  the pore solution viscosity directly extracted from the mortar by means of centrifugation.



**Fig. 8:** Evolution of relative viscosity (Eq. 4) according to pore solution viscosity.

It is worth mentioning that the models describing the viscosity of granular pastes, including the Krieger-Dougherty equation, have been developed for particles in suspension in a Newtonian fluid, which is not the case here since the pore solution exhibits a shear-thinning behavior. This is the reason for taking the mortar viscosity at  $100 \text{ s}^{-1}$  in Eq. 4. At this shear rate, the mortar viscosity is indeed pseudo-Newtonian and thus does not depend on shear rate (Fig. 3b).

According to Krieger-Dougherty equation, a horizontal line should be expected. A steady decrease in the relative viscosity is however observed when the pore solution viscosity increases (i.e. increase in polymer dosage) as shown in Fig. 8. This means that polysaccharides increase both pore solution viscosity and macroscopic mortar viscosity but the latter increase is lower than expected. Polysaccharides induce therefore additional and specific repulsive forces. This unexpected phenomenon has been previously observed by Lambois-Burger et al. [58] and Brumaud [16].

Lambois-Burger et al. [58] have studied the effect of non polysaccharidic VEA on the flow of suspensions of cement and silica particles. They highlighted the antagonistic effects of hydrodynamic lubrication forces which result, on the one hand, in a viscous dissipation that increases the suspension viscosity, but prevent on the other hand the direct contact between particles and the friction which promotes flow. The authors argue moreover that this reduction of overall energy dissipation is only due to the non-adsorbed polymer.

Brumaud [16] has tested this hypothesis by increasing pore solution viscosity of cement paste using glycerol. As proportionality between pore solution and macroscopic cement paste viscosities was obtained with glycerol, the author has dismissed the effect of hydrodynamic repulsive forces due to the high pore solution viscosity. The author then proposed that polymers in the gap between particles induce repulsive depletion forces.

The increase in air content induced by polysaccharide may also participate in the decrease in relative viscosity. Indeed the increase in air content should result in the decrease in solid volume fraction  $\Phi$  while the solid volume fraction corresponding to maximum packing  $\Phi_m$  remains constant. Therefore it can be assumed that the ratio  $\Phi/\Phi_m$  decreases which induces mathematically a decrease in relative viscosity  $\eta/\eta_0$  according to Eq. 3.

#### **4 Conclusions**

This paper focuses on the influence of HPG and its dosage on rheological behavior of cement-based mortars. The rheograms were obtained over a wide range of polymer dosage thanks to an efficient resuspension procedure which allows keeping particles in suspension even at low shear rate and low polymer dosage. Herschel-Bulkley model was used to fit the resulting rheograms. It appears that:

- (i) HPG has a strong impact on the shear-thinning behavior of admixed mortars: the higher the dosage, the more pronounced the shear-thinning behavior.
- (ii) HPG induces an increase in mortar yield stress compared to the un-admixed mortar. Then, in the case of HPMC and the HPG polysaccharide with additional alkyl chains, the yield stress was found to decrease with the increase in the polymer dosage. On the contrary, the yield stress of common HPG-admixed mortars remains stable in over the whole range of dosage studied.
- (iii) HPG increases the mortar consistency.

The effect of HPG on pore solution, i.e. the shear-thinning behavior and the entanglement of polymer coils which leads to a strong increase in pore solution viscosity, was investigated in order to explain the effect of HPG on mortar rheological behavior. It emerges that the dosage corresponding to the formation of polymer agglomerates in pore solution is crucial, as for water retention [30]. Below this threshold concentration, the mortar exhibits a Binghamian behavior and the increase in consistency is slight.

However, there is no direct proportionality between pore solution viscosity and mortar viscosity. Indeed, the increase in mortar viscosity due to polysaccharidic VEA was lower than expected which means that polysaccharides induce specific additional repulsive forces.



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