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## Influence of the polysaccharide addition method on the properties of fresh mortars

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**ABSTRACT:**

This study focused on comparison of polysaccharide addition methods, either in powder form, or as a solute in the mixing water. The influence of the methods was assessed by measuring water retention and rheological properties with one cellulose ether and two guar ethers.

Polysaccharides were more efficient to enhance water retention and rheological properties when they are pre-dissolved in the mixing water. This is related to differences in polymer concentration in the pore solution of mortar. These differences are not stemming from a difference in dissolution kinetics, but from a difference in adsorption on growing hydrates. Being immediately available when it is pre-dissolved, the admixture slows down the nucleation and growth of hydrates limiting in turn the surface area for further adsorption. Consequently, more molecules are left in the interstitial solution and a lower dosage is required to achieve the overlapping of polymer coils, responsible for the effectiveness of polysaccharides.

**KEYWORDS:**

*Polysaccharide (D), Admixture (D), Water retention (C), Rheology (C), Method of addition*

## 1 Introduction

Polysaccharides, natural or derivatives, are commonly used as admixtures in modern factory-made mortars. They are able to improve the water retention capacity of cement-based mortars at fresh state [1–6]. Limiting the absorption of mixing water by the substrate allows enhancing mechanical and adhesive properties of the mortar [7,8]. Due to their thickening properties, polysaccharides improve also the mortars rheological properties since their use results in a highly shear thinning material [9]. This particular rheological behavior induced by polysaccharides ensures a high apparent viscosity at low shear rate in order to ensure sagging and sedimentation resistance, while maintaining a high fluidity because of low viscosity at high shear rate [10–16]. The major drawback of the use of polysaccharide in cement-based materials is the induced delay of cement hydration [17–22].

Most studies are devoted to the influence of cellulose derivatives since they represent the most widely industrially used polysaccharidic admixtures. Nevertheless, the use of hydroxypropylguars (HPGs) is of interest since the HPG manufacturing is less pollutant than cellulose ethers [23]. HPG is now well-established in the construction industry as water retention agent for mortars [23]. In previous studies, the influence of HPG on water retention capacity [24] and rheological properties [25] of cement-based mortars was investigated. In agreement with other authors [1,4,5], the importance of polymer coil overlapping for the efficiency of HPG as admixture was highlighted.

The influence of HPG on the early age hydration of cement has been also investigated [26]. It was assumed that the mechanism responsible for the hydration delay is a decrease in the hydrates growth rate because of HPG adsorption on hydrated phases via polar interactions. The influence of the HPG pre-dissolution in the liquid phase has been studied too. A higher hydration delay was noticed after pre-dissolution, especially for HPG with low substitution degree.

Method of chemical admixtures addition, and in particular the delayed addition, has been often investigated by researchers in order to improve the knowledge about the working mechanism of these molecules in the cement-based materials. Delayed addition of retarders such as sucrose, EDTA, calcium ligno-sulphonate, oxalic acid or organic acid has been studied [27–29]. It was found for example that delayed addition of sucrose leads to a greater percentage of sugar remaining in solution because less retarder is consumed in the initial reaction [29]. Therefore, sucrose retards further hydration when its addition is delayed. It is also well known that the fluidity and the fluidity loss of fresh cement-based materials are

affected by the time of superplasticizers addition [30–33]. Flatt and Houst [34] have proposed a simplified view on the effects of superplasticizers in concrete. It appears that superplasticizers interact with the ongoing chemical reactions and hence these molecules can be consumed in an organo-mineral phase formed around cement particles. The delayed superplasticizer addition allowed confirming this hypothesis since the admixture is more effective to contribute to the dispersion because the polymer consumption is reduced.

The polysaccharide pre-dissolution in mixing water was useful to better understand the interaction between HPG and cement and its impact on cement hydration kinetics [26]. The aim of the current paper is to reuse this simple method of investigation in order to examine the key properties of freshly-mixed mortars induced by polysaccharides: water retention capacity and rheological behavior.

These two properties will thus be characterized on mortars prepared with two methods of addition: (i) “dry addition”, the common way where the polymer is added as dry powder and homogenized with all the solid phases before being put into contact with water and (ii) “pre-dissolved”, where the polymer is first dissolved in the mixing water before being mixed with the dry mixture composed of sand and cement. The characterizations of dissolution kinetics and adsorption ability of polysaccharides will be useful to interpret the experimental data. Finally, a schematic representation of the interaction between polysaccharide and cement will be presented and its impact on mortar macroscopic properties will be discussed.

## **2 Materials**

### ***2.1 Cement***

This study was conducted using a CEM I 52.5 R CE CP2 NF type cement according to the EN 197-1 and NF P 15-318 standards. Chemical and phase compositions of the cement used are presented in Table 1. Oxide composition was determined by X-ray fluorescence spectroscopy using a Bruker-AXS SRS3400 instrument. Phase composition was obtained by XRD using a Siemens D5000 instrument. Siroquant V2.5 software was employed to quantify the amounts of individual phases present in the cement by following Rietveld's method of refinement.

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

| Chemical composition (% wt)    |             |                               |             | Phase composition (% wt) |                   |              |                   |
|--------------------------------|-------------|-------------------------------|-------------|--------------------------|-------------------|--------------|-------------------|
| Oxides                         | XRF         | Oxides                        | XRF         | Phases                   | XRD<br>(Rietveld) | Phases       | XRD<br>(Rietveld) |
| CaO                            | 66.1 ± 1.2  | TiO <sub>2</sub>              | 0.24 ± 0.01 | C <sub>3</sub> S         | 73.0 ± 0.53       | Gypsum       | 1.7 ± 0.15        |
| SiO <sub>2</sub>               | 20.2 ± 0.4  | P <sub>2</sub> O <sub>5</sub> | 0.05 ± 0.01 | C <sub>2</sub> S         | 12.7 ± 0.50       | Anhydrite    | 2.3 ± 0.28        |
| Al <sub>2</sub> O <sub>3</sub> | 4.8 ± 0.1   | MnO                           | 0.04 ± 0.00 | C <sub>3</sub> A         | 4.2 ± 0.18        | Hemi-hydrate | 0.8 ± 0.30        |
| SO <sub>3</sub>                | 3.5 ± 0.2   | K <sub>2</sub> O              | 0.01 ± 0.01 | C <sub>4</sub> AF        | 6.1 ± 0.22        | Free CaO     | 0.5 ± 0.13        |
| Fe <sub>2</sub> O <sub>3</sub> | 2.9 ± 0.1   | LOI                           | 2.2 ± 0.2   |                          |                   |              |                   |
| MgO                            | 1.11 ± 0.02 |                               |             |                          |                   |              |                   |

## 2.2 Organic admixtures

The description and comparison of the cellulose and guar chemistry were detailed in [35]. Guar gum is a polysaccharide extracted from the seed endosperm of *Cyamopsis tetragonolobus*, a native plant from India. This is a galactomannan consisting of a (1–4)-linked  $\beta$ -D-mannopyranose backbone, with random branchpoints of galactose via an  $\alpha$ -(1–6) linkage. The ratio of mannose to galactose is about 1.8. HPG are obtained from the native guar gum via an irreversible nucleophilic substitution, using propylene oxide in the presence of an alkaline catalyst. Cellulose is a polysaccharide composed of individual anhydroglucose units linked through  $\beta$ -(1–4) glycosidic bonds. Because of strong intermolecular hydrogen bridging bonds, cellulose is not soluble in water. Thereby, cellulose ethers are obtained by pretreating cellulose with base (alkali cellulose) in order to break hydrogen bonds and to make accessible the active groups for etherifying agents. In the present work, two HPG and one HMPC were studied. Table 2 presents the qualitative substitution degrees (provided by the manufacturer), the weight-average molecular mass (determined by size-exclusion chromatography, analyses were carried out on a Water apparatus) and the parameters characterizing the concentration dependence of zero-shear viscosity of admixtures dissolved in 20 mM lime solution ( $b_1$  and  $b_2$ ) as explained in section 3.2.

The molar substitution ratio ( $MS_{HP}$ ) is defined as the number of hydroxypropyl groups per anhydroglucose units and is less than 3 for our molecules. The degree of substitution, noted  $DS_M$ , represents the amount of substituent methoxyl groups on the anhydroglucose units of cellulose and is about 1.8 for HPMC 2 according to the manufacturer. The weight-average molecular mass is noted as  $M_w$  and the critical overlap concentration of polymer coils is noted as  $C^*$ .

**Table 2:** Description of the admixtures used.

|        | MS <sub>HP</sub> | DS <sub>M</sub> | Mw (10 <sup>3</sup> g.mol <sup>-1</sup> ) | C*  | b <sub>1</sub> | b <sub>2</sub> |
|--------|------------------|-----------------|---|-----|----------------|----------------|
| HPG 1  | Low              | -               | 1700 ± 80                                 | 3.7 | 1.4            | 4.1            |
| HPG 3  | High             | -               | 1800 ± 50                                 | 3.2 | 1.2            | 4.0            |
| HPMC 2 | Very Low         | Very High       | 950 ± 50                                  | 2.3 | 1.5            | 3.9            |

These three polysaccharidic admixtures were chosen since they exhibit strong (HPG 1), medium (HPG 3) and slight (HPMC 2) pre-dissolution effect regarding cement hydration kinetics [26].

### 3 Methods

All tests were carried out at controlled temperature because fresh mortar properties and dissolution kinetics are temperature-dependent. All the rheological measurements were carried out with Anton-Paar Rheometer MCR 302.

#### 3.1 Freshly-mixed mortars properties

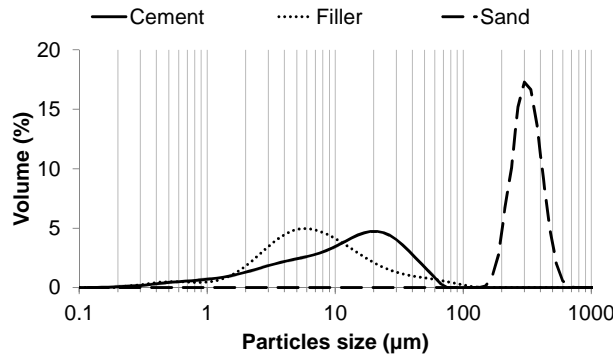
For a given formulation (i.e. kind and dosage of admixture), freshly-mixed mortars properties (i.e. water retention and rheological properties) and pore solution viscosity were determined on the same mortar which have been divided into three parts. Each test was repeated in order to ensure the reproducibility of the results. Moreover, the same procedure was performed with a mortar without admixture as a control test.

##### 3.1.1 Preparation of mortars

In the case of pre-dissolved addition, admixtures were previously dissolved in deionized water. Complete dissolution of all polymers was obtained after strong stirring for 24h by means of a magnetic stirrer. Polymer dosages in mortars varying from 0.1 to 0.66% by weight of cement (bwoc) by preparing polymer solutions of concentrations ranging from 1 to 6.66 g.L<sup>-1</sup>.

Mortars were then prepared according to the following mixture proportions: 30 wt.% of cement, 65 wt.% of siliceous sand (DU 0.1/0.35, Sibelco) and 5 wt.% of limestone filler (BL 200, Omya). Particle size distribution of the solid phases given in Fig. 1, was determined employing a laser-based particle size analyzer with dry powder disperser (Mastersizer 2000

equipped with Scirocco dispersing unit, Malvern). The median particle diameters by volume ( $D_{50}\%$ ) are about 310, 12 and 6  $\mu\text{m}$  for the sand, cement and filler respectively.



**Fig. 1:** Particle size distribution of the mineral phases.

Dry mixture (*i.e.* cement, sand, filler, and polymer in the case of dry addition) was homogenized in a shaker (Turbula, Wab) for 15 min. Deionized water or admixture solution, according to the method of polymer introduction, was then added to the dry mixture in order to obtain a water to cement ratio  $W/C = 1$ . Mortars were mixed (MIx40, CAD Instruments) in accordance with EN 196-1 [36].

It is worth mentioning that the mortar formulation with high  $W/C$  was adapted from the CEReM (European consortium for study and research on mortars) mixture design [2,3]. This work is indeed a part of a larger study that focuses on the influence of HPG on overall mortar properties at the fresh state. Moreover, regarding water retention, high  $W/C$  ratio corresponds to extreme conditions which are useful to highlight the effectiveness of HPG as water retention agent.

### 3.1.2 Water retention measurements

Different tests, based on a measurement of the removed water after suction or depression, allow measuring the water retention capacity of freshly-mixed mortar [3]. The test specified in the ASTM C1506-09 standard [37] was performed 15 min after mixing in order to measure the water loss of mortar under depression. The standardized apparatus was submitted to a vacuum of 50 mm of mercury for 15 min. Then, water retention capacity, noted  $WR$ , was calculated using the following equation:

$$WR (\%) = \frac{W_0 - W_1}{W_0} \times 100 \quad (1)$$



$W_0$  represents the initial mass of mixing water;  $W_1$  is the loss of water mass after aspiration.

### 3.1.3 *Mortars rheological properties*

The method used to investigate the fresh mortar rheological properties was well detailed in a previous study [25]. Briefly, a vane-cylinder geometry was employed with the gap thickness, distance between the periphery of the vane tool and the outer cylinder, of 8.5 mm. The calibration was performed with glycerol, following the Couette analogy [38,39].

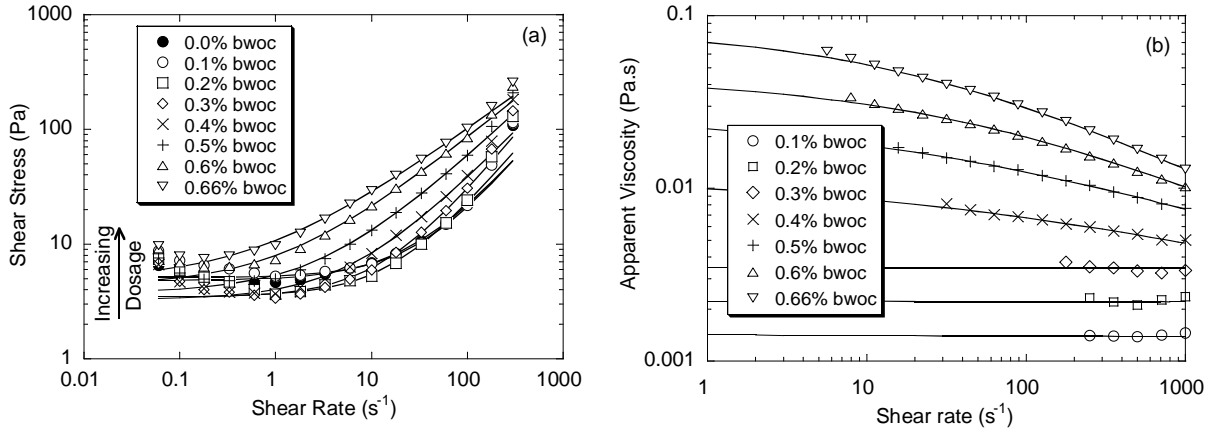
The mortar was introduced into the measurement system at the end of the mixing. The suspension was then held at rest for 6 min. Ten minutes after the contact between cement and water, the mortar was pre-sheared for 30 s at  $100 \text{ s}^{-1}$  in order to re-homogenize the sample and to clear its flow history. After a period of rest of 4.5 min, the rheological measurements were started, i.e. at the age of 15 min.

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 [40,41]. Nevertheless, because of sedimentation risk due to high  $W/C$  ratio, the samples were systematically sheared at  $100 \text{ s}^{-1}$  for 20 s before each imposed shear rate in order to put back in suspension particles of the mortar. This resuspension procedure was validated in [3] and [25]. Finally, the measurement procedure took about 17 min for 16 steps.

The results can be expressed as shear stress  $\tau$  according to shear rate  $\dot{\gamma}$ . Experimental data were fitted well with the Herschel-Bulkley (HB) model [42], which is often used to describe mortars rheological behavior (see Fig. 2a):

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

where  $\tau_0$  is the yield stress,  $K$  the consistency coefficient and  $n$  the fluidity index which characterizes how shear-thinning the mortar is. In the following, the three HB parameters were thus chosen to compare admixtures to each other.



**Fig. 2:** (a) Mortar shear stress and (b) pore solution viscosity versus shear rate according to the dosage – example of pre-dissolved HPG 1 – markers represent experimental data and lines represent calculated values according to (a) Herschel-Bulkley model (Eq 2) and (b) Cross model (Eq 3).

### 3.1.4 Pore solution viscosity

At 15 min (i.e. similar to water retention and mortars rheological measurements), a large volume of mortar, in order to have a representative sample, 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 [43,44]. Experimental data were well correlated with the Cross model [45] (see Fig. 2b):

$$\eta(\dot{\gamma}) = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (\alpha\dot{\gamma})^n} \quad (3)$$

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 region at low shear rate and was chosen to characterize pore solution viscosity.

### 3.2 Dissolution kinetics

The dissolution process was monitored by viscosity measurements. The procedure was the following, adapted from Wang et al. [46]: HPG was introduced (final concentration: 6.66 g.L<sup>-1</sup>) through a sieve in 1L of 20 mM lime solution. The dispersion through a sieve allows having a good dispersion of the sample into the vortex created by the mechanic stirrer and thus minimizing the aggregation of particles and producing a homogeneous polymer solution. The experiment was done in a sealed reactor, thermostated at 20°C, under continuous flow of nitrogen in order to avoid carbonation of lime.

At different times, an aliquot of approximately 5 mL was taken from the batch solution and centrifuged by means of a micro-centrifuge (Eppendorf MiniSpin Plus, 14500 rpm) for 5 min in order to remove undissolved particles. The supernatant was collected and homogenized by vortex-stirring. The viscosity measurements were then performed exactly in the same way than for the pore solution. Finally, the concentration at a given time was calculated from calibration curves.

The concentration dependence of zero-shear viscosity is well known and can be described by two power-law type correlations ( $\eta_0 = aC^b$ ) where the exponent  $b$  differs depending on the regime considered [43]. At low concentrations, the zero-shear viscosity increases slightly with the concentration (the exponent  $b_1$  ranges from 1 to 1.5). Above a threshold concentration, so-called critical coil-overlap concentration  $C^*$ , the polymer coils begin to bring into contact with one another. Therefore a dramatic change in flow behavior occurs which results in a sudden increase in the concentration-dependence of zero-shear rate viscosity (the exponent  $b_2$  varies from 3.5 to 5) [43,47,48]. The critical coil-overlap concentration can be established from a double logarithmic plot of  $\eta_0$  versus the concentration. It corresponds to the intersection of the two straight lines. For each admixture, the zero-shear viscosities of 20 solutions, with known concentrations from 0.5 to 20 g.L<sup>-1</sup> obtained after complete dissolution of polymers, were determined. It was thus possible to obtain the power-law correlations (characterized by  $C^*$ ,  $b_1$  and  $b_2$ ) which were used as calibration curves. The data are given in Table 2.

### 3.3 Adsorption measurements

A High TOC II apparatus (Elementar, Hanau, Germany) equipped with a CO<sub>2</sub> detector was used to quantify the amount of polymer adsorbed on cement. As to determine the pore solution viscosity, a large volume of mortar was centrifuged at 15 min. The alkaline pore

solution containing the non-adsorbed polymer was diluted with 0.1 M HCl at a ratio of 1:10 (vol/vol) in order to obtain a final pH of about 1.0 [4] and then tested with the TOC analyzer. The TOC analyzer was first calibrated with pore solution of a control mortar without admixture and with solutions of admixture of known concentration. Thus the adsorbed amount was calculated from the difference in concentrations of polymer present in pore solution and in solution without contact with cement, taking into account the amount of organic carbon in cement.

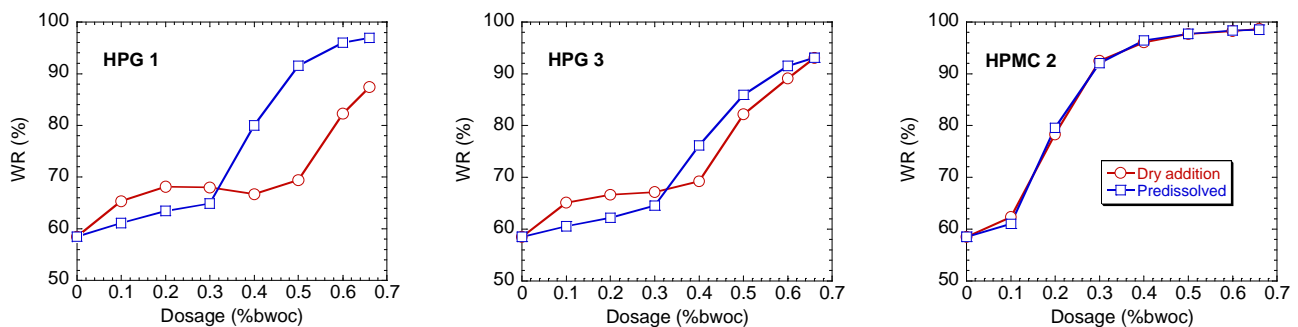
## 4 Results

### 4.1 Fresh state properties of mortar

#### 4.1.1 Water retention capacity

The effect of method of polysaccharide introduction on WR of admixed mortars according to the dosage is presented Fig. 3.

The control test performed with a mortar without admixture exhibits a low WR value of  $58.5 \pm 0.8$  %. Then, as expected, WR is dosage dependent. The WR is improved as a result of increased amount of admixture until reaching very high WR values. Nevertheless, whatever the polymer, the increase in WR is not linear. Below a threshold dosage, the increase in WR is slight. The increase in WR is much more important above this critical dosage.



**Fig. 3:** Impact of pre-dissolution on water retention (WR) capacities of fresh mortars according to the dosage and kind of admixture.

Regarding the impact of the method of introduction, the effectiveness of HPMC 2 as water retention agent seems not to be affected by the pre-dissolution.

On the contrary, the effectiveness of HPG, and especially HPG 1, as water retention agents is significantly influenced by the method of introduction. Indeed, the water retention capacity is

slightly better when the polymer is added dry at low dosage. As the dosage increases, the effectiveness of HPG as water retention becomes better when HPG is pre-dissolved in mixing water. It is strongly significant for HPG 1. At a dosage of 0.5% bwoc, the water retention capacity of mortar admixed with pre-dissolved HPG 1 is 24% higher than the mortar admixed with dry HPG 1. For HPG 3, a maximum difference of 10% is noticed for a dosage of 0.4% bwoc.

Nevertheless, the curves of water retention as a function of the dosage exhibit similar shape. The critical dosage above which the WR increases strongly with the dosage is just shifted towards higher dosage, when the admixture is added according to the dry way.

4.1.2 Rheological properties

The rheological properties of admixed mortars at fresh state were characterized with the parameters of the Herschel-Bulkley model used to fit the experimental data.

The evolution of mortar consistency according to the dosage and the method of introduction of the admixture is shown in Fig. 4. An increase in polymer dosage leads to an increase in the consistency coefficient.

Once again, no impact of HPMC 2 pre-dissolution is evidenced, while HPG 3 and especially HPG 1 is much more efficient to increase the consistency when they are previously dissolved in the mixing water, mostly at high dosage. For example, for a polymer dosage of 0.66% bwoc, the HPG 1 pre-dissolution leads to an increase in the consistency coefficient, from 1.8 to 5.8 Pa.s<sup>n</sup>.

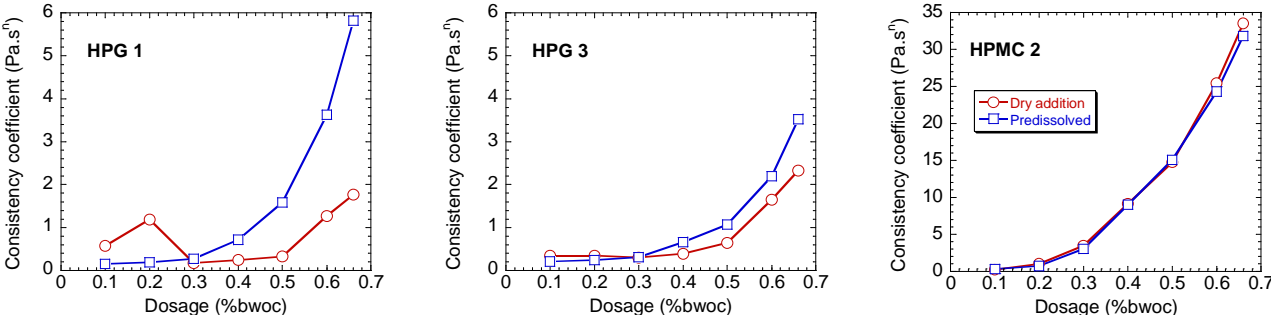
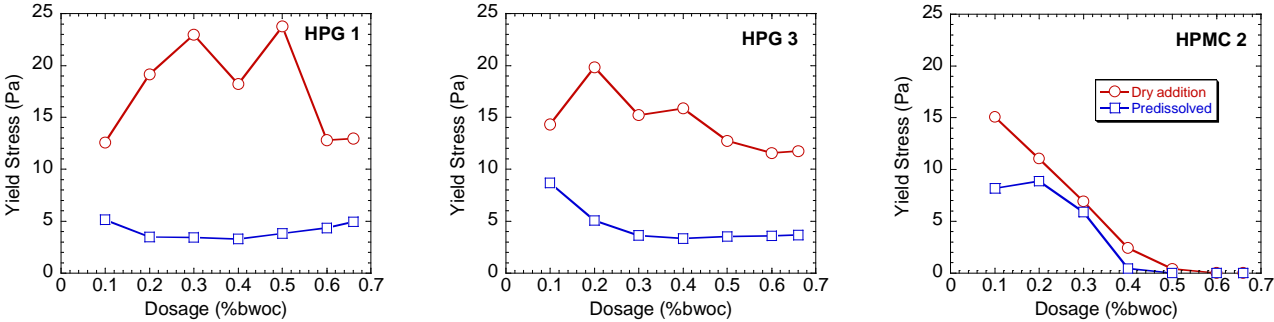


Fig. 4: Impact of pre-dissolution on consistency coefficient (K) of fresh mortars according to the dosage and kind of admixture.

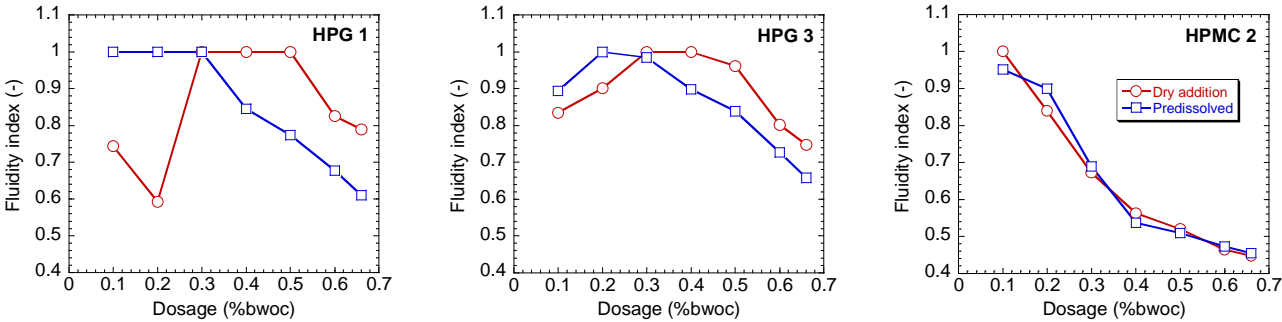
Regarding the yield stress, as expected [25]  $\tau_0$  was found to decrease with dosage in the case of HPMC 2, while it remains stable in case of HPG (Fig. 5). Nevertheless, a strong difference

according to the method of introduction is observed. Indeed, when the HPG is pre-dissolved, the yield stress value is about 5 Pa, and much higher than 10 Pa when the HPG is added dry.



**Fig. 5:** Impact of pre-dissolution on yield stress ( $\tau_0$ ) of fresh mortars according to the dosage and kind of admixture.

Fig. 6 gives the impact of pre-dissolution on fluidity index of fresh mortars. As described in previous study [25], the fluidity index remains almost stable around 1.0 until a threshold dosage. Above this dosage, the fluidity index decreases. This overall evolution of the fluidity index as a function of the polymer dosage is the same whatever the method of introduction. Nevertheless, as in the case of water retention (Fig. 3), the regime change occurs at higher dosage when the polymer is added dry. Moreover, it is worth noting that for the dry method of addition, the fluidity index is below than 1.0 at low dosage. The impact of pre-dissolution is not significant in the case of HPMC 2.



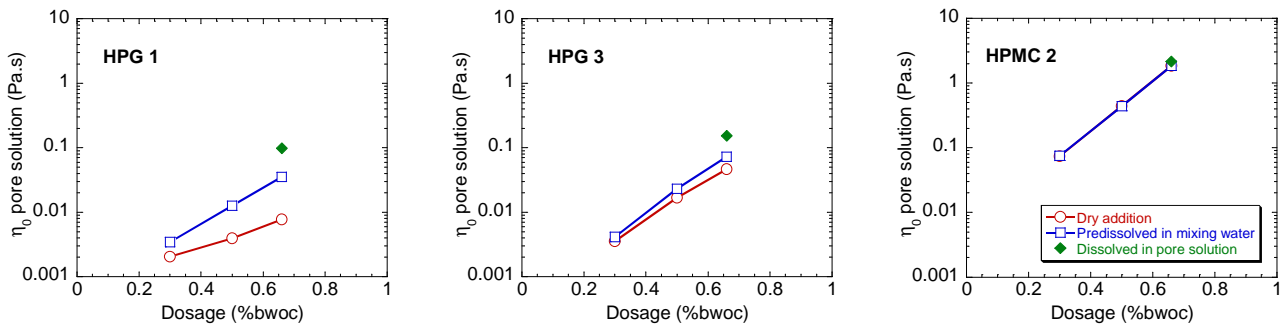
**Fig. 6:** Impact of pre-dissolution on fluidity index ( $n$ ) of fresh mortars according to the dosage and kind of admixture.

To sum up, a strong impact of pre-dissolution on macroscopic properties was found for HPG-admixed mortars. Indeed, when the polymer is pre-dissolved in mixing water, the water retention capacity and the consistency of the mortar is significantly higher, while the yield stress is lower. The differences are stronger in the case of HPG 1 than for HPG 3. On the

contrary, the method of admixture addition does not affect the macroscopic properties of HPMC-admixed mortars.

#### 4.2 Pore solution viscosity

The effect of pre-dissolution on pore solution viscosity was investigated. By means of centrifugation, the pore solution was extracted. Then its viscosity was determined and characterized by the zero-shear viscosity. Fig. 7 shows the pore solution viscosity of mortars admixed with dry and pre-dissolved admixture at three polymer dosages (0.3, 0.5 and 0.66% bwoc). For a dosage equivalent to 0.66% bwoc (i.e. 6.66 g.L<sup>-1</sup>), polymers were also dissolved in real pore solution extracted from the control mortar. The viscosity is represented as a diamond in the Fig. 7.



**Fig. 7:** Impact of pre-dissolution on pore solution viscosity as a function of polymer dosage.

As expected, the pore solution viscosity increases with the dosage. It appears that the pore solution viscosities of HPMC 2-admixed mortars are not affected by the method of introduction. The pore solution viscosity is slightly lower when HPG 3 is added dry than when it is pre-dissolved in the mixing water. For HPG 1, the pore solution viscosity is strongly different according to the method of introduction. For a dosage of 0.66% bwoc for example,  $\eta_0$  is about  $8 \cdot 10^{-3}$  Pa.s for the dry addition, and about  $36 \cdot 10^{-3}$  Pa.s for the pre-dissolved addition. With the same polymer, dissolved in the same media, a difference of viscosity reflects a difference of polymer concentration. This result means therefore that there are clearly more polymers remaining into the pore solution when HPG 1 is added pre-dissolved.

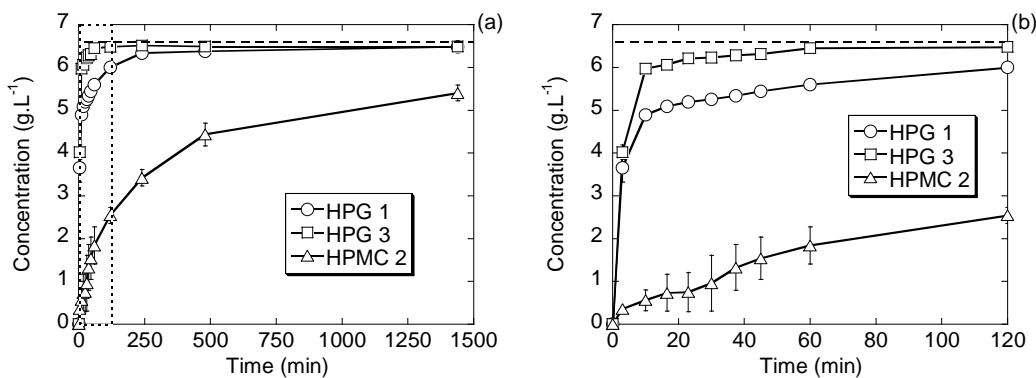
### 4.3 Dissolution kinetics of polysaccharides

In order to explain the results exhibited above, the admixture dissolution kinetics was investigated. On the one hand, the dissolution kinetics was characterized in nearly saturated lime solution, which may represent a very simplified pore solution model. On the other hand, the polymer dissolution after mixing was determined by means of viscosity measurements. To overcome the potential effect of cement-polysaccharide interaction, this experiment was carried out only in 100% sand system.

#### 4.3.1 In lime solution

The dissolution kinetics of the admixtures studied was determined in 20 mM lime solution. Concentration was calculated from viscosity measurements thanks to parameters  $C^*$ ,  $b_1$  and  $b_2$  (see Table 2) obtained from calibration curves.

The final concentration expected is  $6.66 \text{ g.L}^{-1}$ . This concentration is reached quickly for the two HPG, while HPMC 2 is still partially dissolved after 24h (Fig. 8a). Nevertheless, by focusing on the first two hours of dissolution (Fig. 8b), it appears that the dissolution kinetics of HPG 3 is faster than HPG 1. After 10 min, 90% of HPG 3 is dissolved while 73% of HPG 1 is actually in solution. At the same time, only 8% of HPMC 2 is dissolved.



**Fig. 8:** Dissolution kinetics of admixture in lime solution ( $[\text{Ca}(\text{OH})_2]=20\text{mM}$ ).

#### 4.3.2 After mortar mixing without cement

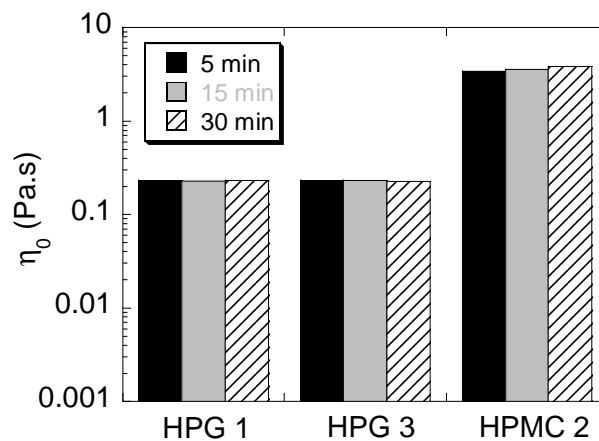
For this experiment, all the solid phases of the mortar were substituted by sand. The dry admixture was first added to the sand and the dry mixture was homogenised. The amount of polymer was the same than for dosage of 0.66% bwoc in mortars. Then, deionized water was added, keeping a liquid to solid ratio of 0.3 (i.e. similar to the mortars L/S ratio). This mixture



of sand, polymer and water were mixed for 4 min in accordance with EN 196-1 [36], as mortars.

At 5 min (i.e. 1 min after the end of the mixing), the mixture was centrifuged and the viscosity of the supernatant was determined, as described in section 3.1.4. The same procedure was repeated 15 and 30 min after the beginning of the mixing.

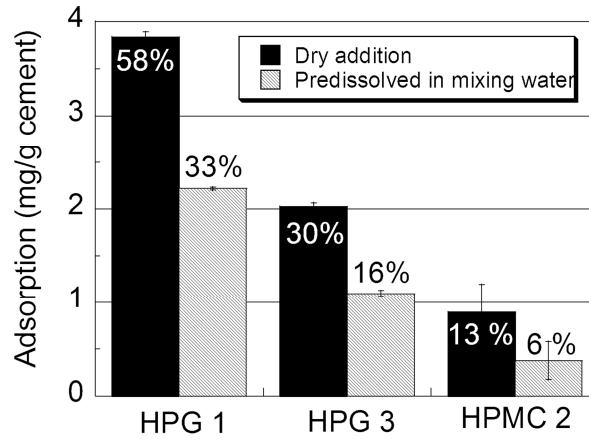
Whatever the admixture, no evolution of the interstitial solution viscosity over time is observed, suggesting that after mixing with water, the total dissolution of each polymer occurs within the first 5 min (Fig. 9).



**Fig. 9:** Pore solution viscosity 5, 15 and 30 min after mixing, reflecting the dissolution kinetics of admixtures added dry in granular media.

#### 4.4 Adsorption of polysaccharide on cement

The adsorption ability of the admixtures studied on cement was also investigated since it reflects in some way the admixture-cement interaction. The amount of polymer adsorbed on cement in the mortar (polymer dosage of 0.66% bwoc) was determined from TOC analyses. Measurements were carried out 15 min after the contact between cement and water. The results are shown in Fig. 10.



**Fig. 10:** Impact of pre-dissolution on the amount of admixture adsorbed on cement.

Whatever the method of introduction, HPMC 2 is the admixture that adsorbs less on cement. The adsorption ability of HPG 1 is higher than HPG 3. In the case of the dry method of addition for example, 58% of HPG 1, 30% of HPG 3 and 13% of HPMC 2 is adsorbed on the cement. The same ranking is obtained for the pre-dissolved method of addition. Moreover, the amount of polymer adsorbed is higher in the case of dry addition than in case of pre-dissolved addition whatever the polymer. It is worth noting that in the case of HPMC 2, high standard deviations were obtained. Therefore the difference in adsorption ability according to the method of addition is not significant.

## 5 Discussion

The polymer concentration is a parameter of primary importance in controlling rheological properties of polysaccharide solutions [43]. At low polymer concentration, i.e. dilute solution state, individual polymer molecules are present as isolated coils. As the concentration of polymer is increased, the coils begin to bring into contact with one another leading to the formation of polymer aggregates. In this semi-dilute solution state, the polysaccharide solutions exhibit shear-thinning behaviors and their zero-shear viscosity increase highly with the dosage.

Previous studies highlighted the importance of the polysaccharide solution state on macroscopic mortar properties. Aggregates of HPG [24] and cellulose derivatives [4,5], present in the pore solution because of polymer coils overlapping in the semi-dilute solution state, were found to be responsible of the increase in WR by plugging the porous network. Moreover, for a polysaccharide dosage corresponding to the dilute solution state, mortar

exhibits a Binghamian rheological behavior (i.e. fluidity index equal to 1.0) and the increase in consistency is slight [25]. Above the critical dosage, the pore solution and so the mortar becomes shear-thinning and the consistency increases strongly with the dosage.

The impact of method of polysaccharide addition on pore solution viscosity was investigated in the current paper (Fig. 7). It appears clearly that, for a given dosage, the pore solution viscosity is lower when the polymer is added dry than when it is pre-dissolved. This suggests that the amount of polymer in the pore solution is lower in the case of dry addition. A higher dosage is therefore necessary in order to reach the critical concentration and thus to improve macroscopic mortar properties.

In the case of HPG 1 previously dissolved in the mixing water, above a threshold dosage of 0.3% bwoc, the WR (Fig. 3) and the consistency (Fig. 4) of the admixed mortar increase suddenly, while the fluidity index starts to decrease (Fig. 6) meaning that the mortar becomes shear-thinning. The same behavior is observed when HPG 1 is added dry, but for a higher dosage of 0.5% bwoc (+ 0.2% bwoc). In the same way, the critical polymer dosages of HPG 3 are 0.3% and 0.4% bwoc, for dry and pre-dissolved addition respectively (+ 0.1% bwoc). There is no difference for HPMC 2 which exhibits a critical polymer dosage of 0.1% bwoc whatever the method of addition. These observations are consistent with the impact of method of polysaccharide addition on pore solution viscosity, which is strong for HPG 1, medium for HPG 3 and non-existent for HPMC 2 (Fig. 7).

Therefore the method of addition influences the amount of polymer present in pore solution which shifts the boundary between dilute and semi-dilute solution states and so the improvement of mortar properties. Two hypotheses can be considered to explain this phenomenon: polymer dissolution kinetics or adsorption ability.

A lower amount of polymer dissolved in the pore solution without pre-dissolution than with pre-dissolution may be due to slow dissolution kinetics. In the aim to test this hypothesis, the dissolution kinetics of the three admixtures was investigated in nearly saturated lime solution (which represents a very simple model for pore solution with high alkalinity and strong concentrations of calcium ions) for a final concentration of  $6.66 \text{ g.L}^{-1}$  (which represents the highest amount of polymer, i.e. a dosage of 0.66% bwoc). Effectively, HPG 1 exhibits slower dissolution kinetics than HPG 3 (Fig. 8). According to Cheng et al. [49], the increase in  $MS_{HP}$  leads to a decrease in the intermolecular interactions of HPG. Therefore the dissolution of HPG 3 (high  $MS_{HP}$ ) is easier than the dissolution of HPG 1 (low  $MS_{HP}$ ). Nevertheless, HPMC 2 exhibits by far the slowest dissolution rate while there is no difference in pore solution viscosity with or without pre-dissolution (Fig. 7). This measurement thus characterizes well

the dissolution kinetics but not what is really happen in the mixer. Indeed, the results from Fig. 7 suggest that, although a very slow dissolution rate, HPMC 2 is completely dissolved at the end of the mixing.

In order to focus on dissolution kinetics during the mixing and to overcome the likely adsorption of polymer on cement, all the solid phases were substituted by sand. It appears that whatever the admixture, the polymer is completely dissolved at the end of the mixing since the pore solution viscosities are exactly the same at 5, 15 and 30 min after the mixing with water (Fig. 9). The strong shear forces induce in the mixer and the friction with the granular media allow therefore the complete dissolution of polysaccharide, even of cellulose derivatives known for their slow dissolution rate. Thus dissolution kinetics cannot be responsible for the impact of pre-dissolution.

A second hypothesis would be a difference in the amount of adsorbed polymer according to the method of addition. To test this assumption, the adsorption ability of the three admixtures was investigated by means of TOC analyses. Effectively, it appears that the amount of polymer adsorbed is higher in the case of dry addition than in case of pre-dissolved addition (Fig. 10). Moreover, the adsorption ability of HPG 1 is the greatest. These results are in good agreement with the measurements of pore solution viscosity where a large loss of viscosity was obtained for HPG 1 between the two methods of addition (Fig. 7). For a given polymer dosage, a loss of viscosity was also observed between the “reference” (polymer dissolved in the pore solution of un-admixed mortar) and the real pore solution (extracted from the admixed mortar). The same trend can be observed for HPG 3 but with slighter differences. The viscosity loss can be attributed also to a loss of polymer in solution because of adsorption.

It is worth mentioning that according to Bülischen et al. [4], adsorption of anionic polysaccharides on cement should be excluded. The TOC measurements would reflect the amount of polymer retained as agglomerates plugged in the porous network rather than the adsorbed amount.

We are certainly in agreement that at such polymer dosage (0.66% bwoc), agglomerates are present in the pore solution. Nevertheless, if TOC measurements reflect only a physical retention of polymer agglomerates, and based upon the water retention mechanism which is linked to presence of agglomerates, higher is the “retained amount”, higher should be the water retention capacity. Our experimental results are contradictory since values of retained polymer (obtained from TOC) are higher for the dry addition than for the polymer pre-dissolved in mixing water (Fig. 10) but the water retention capacity is lower (Fig. 3).

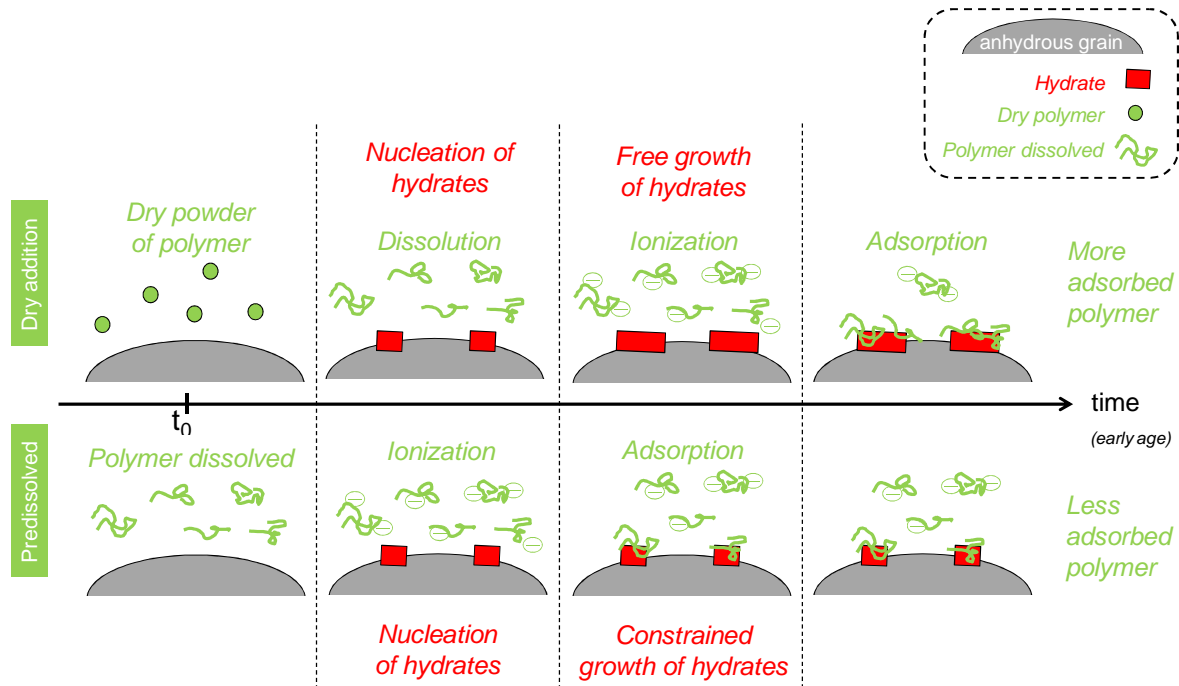
Moreover, pore solution extracted by centrifugation exhibit a shear-thinning behavior which is characteristic of polymer coils overlapping. We therefore believe that the high speed centrifugation would be able to extract some agglomerates but not to trap all of them in the pellet.

Furthermore, it was previously assumed that the mechanism responsible for the cement hydration delay induced by HPG [26] is the adsorption of these molecules on the hydrated cement phases. Indeed, HPG are molecules which contain a lot of polar functional groups (-OH). Therefore, interactions through Van der Waals forces and hydrogen-bonding can occur between polysaccharides and the highly polar hydrated phases [50]. Moreover, the hydrated cement phases exhibit a high surface charge density [53]. The ionization of the hydroxyl groups of HPG in the alkaline pore solution [54] would enhance the adsorption through strong electrostatic forces.

The adsorption ability of polysaccharide at the surface on the cement grains is therefore matter of debate but in our mind and for the specific case of HPG, this is the only valid theory to explain all the experimental results of the influence of HPG on mortars properties. Since adsorption is measured by depletion method, our results not allow confirming or invalidating the incorporation of the admixture in an organo-mineral phase during the early age hydration of the cement as suggested by Flat and Houst [34] regarding the superplasticizers. Nevertheless, if this occurs, this should accentuate the consumption of polymer when it is added as dry powder.

Fig. 11 is a schematic representation of the polysaccharide-cement interaction. On the abscissa, the time at early age is arbitrary represented. The two cases, dry and pre-dissolved addition, are also shown. Once the cement is in contact with water, the anhydrous cement grains dissolve rapidly in the first seconds after wetting [53,54] and nucleation of the first hydrates occurs at very early times, close to the time of mixing [55]. The dissolution of cement leads to a strong increase of calcium hydroxide concentration in the pore solution [56,57] and thus the ionization of hydroxyl groups of polysaccharide. In the case where polymer is previously dissolved, the polysaccharide is able to adsorb rapidly on the first hydrates and to constrain their growth. The slowdown of hydrates growth rate in presence of polysaccharides has been highlighted in the past [17,20,26,58–60]. Nevertheless, when the polymer is added as dry powder, it has to dissolve first before to be able to adsorb on hydrates. Therefore the hydrates have more time to grow and the surface area available for adsorption is higher. Once dissolved, more polymers can be adsorbed or consumed leading to less polymer in solution in comparison with the pre-dissolution state. Ultimately, it has been

shown in a previous paper that pre-dissolution of HPG leads to a greater hydration delay than when admixture is introduced as a powder in the dry-mix [26].



**Fig. 11:** Schematic representation of the polysaccharide-cement interaction regarding the method of addition.

The adsorption ability of polysaccharide is linked to the substitution degree. Lower the substitution degree is, higher the content of hydroxyls is and thus stronger the adsorption ability is. This can explain the difference between HPG 1 and HPG 3. The adsorption ability of HPG 1 (low  $MS_{HP}$ ) is so high that the difference induced by the method of addition is amplified.

The yield stress values (Fig. 5) are consistent with this theory. Indeed, because of its very long chains, the same HPG molecule can adsorb on separate cement particles and bound them together. This phenomenon is well known as polymer bridging flocculation [61–63]. According to some authors [9,64,65], this bridging effect between cement particles would be one of the cause responsible for the cement-based materials yield stress induced by polysaccharide. A linear correlation between the amount of adsorbed polymer and the yield stress was even established [65]. This allows understanding the lower yield stress values when the polymer is pre-dissolved (Fig. 5) since the pre-dissolution reduces the amount of adsorbed polymers (Fig. 11).

At low dosage, i.e. without entanglement and formation of agglomerates, the mortars admixed with dry HPG exhibit better WR (Fig. 3) and higher consistency (Fig. 4) than mortars

admixed with pre-dissolved admixture. Moreover, in the case of dry addition, the mortars present a strong shear-thinning behavior (Fig. 6) meaning a high viscosity at low shear rate. Thus, it can be assumed that the enhancement of bridging effect leads to improve yield stress, but also slightly the water retention ability, the consistency and the shear-thinning behavior of the admixed mortars.

## **6 Conclusions**

Based upon this study, it appears that the method of addition of polysaccharidic admixtures may influence their impact on the fresh state properties of mortars. It is obvious for HPG 1 which has a low degree of substitution.

This pre-dissolution effect is due to a difference of the amount of polymer in the pore solution regarding the method of addition. Indeed, a greater amount of polymer in solution was noticed when the polymer is pre-dissolved in the mixing water rather than when the polymer is added as dry powder to the other solid phases of the mortar as usual.

The pre-dissolution of the polymer may accelerate the adsorption on hydrated cement phases. Therefore the growth of hydrates is rapidly constrained leading to a reduction of the surface area available to the adsorption. Contrariwise, the common addition of polymer as dry powder leads to a greater amount of polymer adsorbed.

By consuming polymer on the surface of cement grains, this common addition requires a greater dosage in order to achieve the overlapping of polymer coils. At equivalent dosage, in comparison with the pre-dissolved addition, the dry addition leads thus to mortars with lower water retention capacity and lower consistency but higher yield stress value and weaker cement hydration delay.

This study of method of addition allows highlighting the importance of cement-polysaccharide interaction on macroscopic properties of admixed mortars. Moreover, this paper confirms the fundamental influence of coil overlapping on polysaccharides effectiveness as admixtures for cement-based materials.

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## 8 References

- [1] J. Desbrieres, Cement cake properties in static filtration. Influence of polymeric additives on cement filter cake permeability, *Cem. Concr. Res.* 23 (1993) 347–358.
- [2] J. Pourchez, B. Ruot, J. Debayle, E. Pourchez, P. Grosseau, Some aspects of cellulose ethers influence on water transport and porous structure of cement-based materials, *Cem. Concr. Res.* 40 (2010) 242–252.
- [3] L. Patural, P. Marchal, A. Govin, P. Grosseau, B. Ruot, O. Devès, Cellulose ethers influence on water retention and consistency in cement-based mortars, *Cem. Concr. Res.* 41 (2011) 46–55.
- [4] D. Büllichen, J. Kainz, J. Plank, Working mechanism of methyl hydroxyethyl cellulose (MHEC) as water retention agent, *Cem. Concr. Res.* 42 (2012) 953–959.
- [5] C. Marliere, E. Mabrouk, M. Lamblet, P. Coussot, How water retention in porous media with cellulose ethers works, *Cem. Concr. Res.* 42 (2012) 1501–1512.
- [6] M. Lasheras-Zubiate, I. Navarro-Blasco, J.M. Fernández, J.I. Álvarez, Effect of the addition of chitosan ethers on the fresh state properties of cement mortars, *Cem. Concr. Res.* 34 (2012) 964–973.
- [7] L. Bertrand, S. Maximilien, R. Guyonnet, Wedge Splitting Test: A test to measure the polysaccharide influence on adhesion of mortar on its substrate, in: *Proceedings of the 11<sup>th</sup> International Congress on Polymers in Concrete*, Berlin, Germany, (2004) 569–576.
- [8] A. Jenni, L. Holzer, R. Zurbruggen, M. Herwegh, Influence of polymers on microstructure and adhesive strength of cementitious tile adhesive mortars, *Cem. Concr. Res.* 35 (2005) 35–50.
- [9] K.H. Khayat, Viscosity-enhancing admixtures for cement-based materials - An overview, *Cem. Concr. Comp.* 20 (1998) 171–188.
- [10] K.H. Khayat, A. Yahia, Effect of Welan Gum-High-Range Water Reducer Combinations on Rheology of Cement Grout, *ACI Mater. J.* 94 (1997) 365–372.
- [11] S. Rols, J. Ambroise, J. Péra, Effects of different viscosity agents on the properties of self-leveling concrete, *Cem. Concr. Res.* 29 (1999) 261–266.
- [12] M. Lachemi, K.M.A. Hossain, V. Lambros, P.-C. Nkinamubanzi, N. Bouzoubaâ, Self-consolidating concrete incorporating new viscosity modifying admixtures, *Cem. Concr. Res.* 34 (2004) 917–926.
- [13] H. Paiva, L.M. Silva, J.A. Labrincha, V.M. Ferreira, Effects of a water-retaining agent on the rheological behaviour of a single-coat render mortar, *Cem. Concr. Res.* 36 (2006) 1257–1262.
- [14] M. Sonebi, Rheological properties of grouts with viscosity modifying agents as diutan gum and welan gum incorporating pulverised fly ash, *Cem. Concr. Res.* 36 (2006) 1609–1618.
- [15] A. Leemann, F. Winnefeld, The effect of viscosity modifying agents on mortar and concrete, *Cem. Concr. Comp.* 29 (2007) 341–349.
- [16] M. Cappellari, A. Daubresse, M. Chaouche, Influence of organic thickening admixtures on the rheological properties of mortars: relationship with water-retention, *Constr. Build. Mater.* 38 (2013) 950–961.
- [17] A. Peschard, A. Govin, P. Grosseau, B. Guilhot, R. Guyonnet, Effect of polysaccharides on the hydration of cement paste at early ages, *Cem. Concr. Res.* 34 (2004) 2153–2158.



- [18] F. Ridi, E. Fratini, F. Mannelli, P. Baglioni, Hydration process of cement in the presence of a cellulosic additive. A calorimetric investigation, *J. Phys. Chem. B.* 109 (2005) 14727–14734.
- [19] D.A. Silva, P.J.M. Monteiro, The influence of polymers on the hydration of portland cement phases analyzed by soft X-ray transmission microscopy, *Cem. Concr. Res.* 36 (2006) 1501–1507.
- [20] J. Pourchez, A. Peschard, P. Grosseau, R. Guyonnet, B. Guilhot, F. Vallée, HPMC and HEMC influence on cement hydration, *Cem. Concr. Res.* 36 (2006) 288–294.
- [21] J. Pourchez, P. Grosseau, B. Ruot, Current understanding of cellulose ethers impact on the hydration of C3A and C3A-sulphate systems, *Cem. Concr. Res.* 39 (2009) 664–669.
- [22] E. Knapen, D. Van Gemert, Cement hydration and microstructure formation in the presence of water-soluble polymers, *Cem. Concr. Res.* 39 (2009) 6–13.
- [23] B. Biasotti, M. Giudici, V. Langella, U. Pfeiffer, Highly substituted hydroxypropylguar: a strong contribution to construction chemistry, in: *Proceeding of the 3<sup>rd</sup> International Drymix Mortar Conference, Nürnberg, Germany, (2011) 2–9.*
- [24] T. Poinot, A. Govin, P. Grosseau, Importance of coil-overlapping for the effectiveness of hydroxypropylguars as water retention agent, *Cem. Concr. Res.* 56 (2014) 61–68.
- [25] T. Poinot, A. Govin, P. Grosseau, Influence of hydroxypropylguars on rheological behavior of cement-based mortars, *Cem. Concr. Res.* 58 (2014) 161–168.
- [26] T. Poinot, A. Govin, P. Grosseau, Impact of hydroxypropylguars on the early age hydration of Portland cement, *Cem. Concr. Res.* 44 (2013) 69–76.
- [27] G.M. Bruere, Importance of Mixing Sequence when using Set-Retarding Agents with Portland cement, *Nature.* 199 (1963) 32–33.
- [28] H.M. Jennings, H. Taleb, G. Frohnsdorff, J.R. Clifton, Interpretation of the effects of retarding admixtures on pastes of C3S, C3A plus gypsum and Portland cement, in: *Proceedings of the 8<sup>th</sup> International Congress on the Chemistry of Cement, Rio de Janeiro, Brasil, (1986) 239–243.*
- [29] G. Luke, K. Luke, Effect of sucrose on retardation of Portland cement, *Adv. Cem. Res.* 12 (2000) 9–18.
- [30] 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.
- [31] 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 (1999) 1159–1165.
- [32] I. Aiad, S. Abd El-Aleem, H. El-Didamony, Effect of delaying addition of some concrete admixtures on the rheological properties of cement pastes, *Cem. Concr. Res.* 32 (2002) 1839–1843.
- [33] I. Aiad, Influence of time addition of superplasticizers on the rheological properties of fresh cement pastes, *Cem. Concr. Res.* 33 (2003) 1229–1234.
- [34] R.J. Flatt, Y.F. Houst, A simplified view on chemical effects perturbing the action of superplasticizers, *Cem. Concr. Res.* 31 (2001) 1169–1176.
- [35] T. Poinot, K. Benyahia, A. Govin, T. Jeanmaire, P. Grosseau, Use of ultrasonic degradation to study the molecular weight influence of polymeric admixtures for mortars, *Constr. Build. Mater.* 47 (2013) 1046–1052.
- [36] EN 196-1, Methods of testing cement — Part 1: Determination of strength, 2006.
- [37] Standard C1506-09, Standard test Method of Water Retention of Hydraulic Cement-Based Mortars and Plasters, *Am. Soc. Test. Mat.*, 2009.

- [38] A. Ait-Kadi, P. Marchal, L. Choplin, A.S. Chrissémant, M. Bousmina, Quantitative analysis of mixer-type rheometers using the Couette analogy, *Can. J. Chem. Eng.* 80 (2002) 1166–1174.
- [39] L. Choplin, P. Marchal, La rhéologie systémique ou une rhéologie au service d'un génie des procédés et des produits, *Rhéologie*. 12 (2007) 9–18.
- [40] S. Pourchet, S. Liautaud, D. Rinaldi, I. Pochard, Effect of the repartition of the PEG side chains on the adsorption and dispersion behaviors of PCP in presence of sulfate, *Cem. Concr. Res.* 42 (2012) 431–439.
- [41] M.R. Geiker, M. Brandl, L.N. Thrane, D.H. Bager, O. Wallevik, The effect of measuring procedure on the apparent rheological properties of self-compacting concrete, *Cem. Concr. Res.* 32 (2002) 1791–1795.
- [42] W.M. Herschel, R. Bulkley, Measurements of consistency as applied to rubber–benzene solutions, *Am. Soc. Test. Mat. Proc.* 26 (1926) 621–633.
- [43] E.R. Morris, A.N. Cutler, S.B. Ross-Murphy, D.A. Rees, J. Price, Concentration and shear rate dependence of viscosity in random coil polysaccharide solutions, *Carbohydr. Polym.* 1 (1981) 5–21.
- [44] D. Risica, A. Barbeta, L. Vischetti, C. Cametti, M. Dentini, Rheological properties of guar and its methyl, hydroxypropyl and hydroxypropyl-methyl derivatives in semidilute and concentrated aqueous solutions, *Polymer*. 51 (2010) 1972–1982.
- [45] M.M. Cross, Rheology of non-Newtonian fluids: a new flow equation for pseudoplastic systems, *J. Colloid Sci.* 20 (1965) 417–437.
- [46] Q. Wang, P.R. Ellis, S.B. Ross-Murphy, Dissolution kinetics of guar gum powders. I. Methods for commercial polydisperse samples, *Carbohydr. Polym.* 49 (2002) 131–137.
- [47] W.W. Graessley, The entanglement concept in polymer rheology, in: *The Entanglement Concept in Polymer Rheology*, Springer Berlin Heidelberg, 1974: pp. 1–179.
- [48] G. Robinson, S.B. Ross-Murphy, E.R. Morris, Viscosity-molecular weight relationships, intrinsic chain flexibility, and dynamic solution properties of guar galactomannan, *Carbohydr. Res.* 107 (1982) 17–32.
- [49] Y. Cheng, K.M. Brown, R.K. Prud'homme, Characterization and Intermolecular Interactions of Hydroxypropyl Guar Solutions, *Biomacromolecules*. 3 (2002) 456–461.
- [50] C. Jolicoeur, M.-A. Simard, Chemical admixture-cement interactions: phenomenology and physico-chemical concepts, *Cem. Concr. Comp.* 20 (1998) 87–101.
- [51] B. Jönsson, A. Nonat, C. Labbez, B. Cabane, H. Wennerström, Controlling the Cohesion of Cement Paste, *Langmuir*. 21 (2005) 9211–9221.
- [52] A. Izaguirre, J. Lanás, J.I. Álvarez, Characterization of aerial lime-based mortars modified by the addition of two different water-retaining agents, *Cem. Concr. Comp.* 33 (2011) 309–318.
- [53] P. Barret, D. Ménétrier, Filter dissolution of C3S as a function of the lime concentration in a limited amount of lime water, *Cem. Concr. Res.* 10 (1980) 521–534.
- [54] P. Barret, D. Ménétrier, D. Bertrandie, Mechanism of C3S dissolution and problem of the congruency in the very initial period and later on, *Cem. Concr. Res.* 13 (1983) 728–738.
- [55] J.W. Bullard, H.M. Jennings, R.A. Livingston, A. Nonat, G.W. Scherer, J.S. Schweitzer, et al., Mechanisms of cement hydration, *Cem. Concr. Res.* 41 (2011) 1208–1223.
- [56] S. Garrault-Gauffinet, A. Nonat, Experimental investigation of calcium silicate hydrate (C-S-H) nucleation, *J. Cryst. Growth*. 200 (1999) 565–574.
- [57] D. Damidot, A. Nonat, P. Barret, Kinetics of Tricalcium Silicate Hydration in Diluted Suspensions by Microcalorimetric Measurements, *J. Am. Chem. Soc.* 73 (1990) 3319–3322.

- [58] H.J. Weyer, I. Müller, B. Schmitt, D. Bosbach, A. Putnis, Time-resolved monitoring of cement hydration: Influence of cellulose ethers on hydration kinetics, *Nucl. Instr. Meth. Phys. Res. B.* 238 (2005) 102–106.
- [59] A. Peschard, A. Govin, J. Pourchez, E. Fredon, L. Bertrand, S. Maximilien, et al., Effect of polysaccharides on the hydration of cement suspension, *J. Eur. Cera. Soc.* 26 (2006) 1439–1445.
- [60] J. Pourchez, P. Grosseau, B. Ruot, Changes in C3S hydration in the presence of cellulose ethers, *Cem. Concr. Res.* 40 (2010) 179–188.
- [61] E. Dickinson, L. Eriksson, Particle flocculation by adsorbing polymers, *Adv. Colloid Interface Sci.* 34 (1991) 1–29.
- [62] F. Lafuma, K. Wong, B. Cabane, Bridging of Colloidal Particles Through Adsorbed Polymers, *J. Colloid Interface Sci.* 143 (1991) 9–21.
- [63] J. Swenson, M.V. Smalley, H.L.M. Hatharasinghe, Structure of bridging polymers, *J. Chem. Phys.* 110 (1999) 9750–9756.
- [64] M. Collepardi, Self-Compacting Concrete: what is new?, in: *Proceedings of the 7th CANMET/ACI Conference on Superplasticizer and Other Chemical Admixtures in Concrete*, Berlin, Germany, (2003) 1–16.
- [65] C. Brumaud, R. Baumann, M. Schmitz, M. Radler, N. Roussel, Cellulose ethers and yield stress of cement pastes, *Cem. Concr. Res.* 55 (2014) 14–21.