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Effect of Guar Gum Derivatives on Fresh State Properties of Portland Cement-Based Mortars

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Abstract: Mortars are traditionally made from a mixture of sand, a binder and water. However, modern factory-made mortars are currently, very complex materials. Indeed, to exhibit various properties from the fresh paste to the hardened material, mortar formulations are composed of many mineral and organic admixtures. Among organic admixtures, polysaccharides are widely used in mortar formulation to improve water retention capacity of the freshly-mixed materials. The water retention capacity is an essential property of mortars to enhance cement hydration and its adhesion to a substrate. Moreover, many polysaccharide admixtures, acting as viscosity-enhancing agents, prevent segregation and improve the homogeneity and workability of cement-based system. Indeed, the viscosity of the system strongly increases using polysaccharides. Nevertheless, polysaccharides, as sugars, act on cement hydration. The main drawback is the retarding effect in hydration mechanism and setting-time of the cement.

The aim of this study is to focus on the effect of guar gum derivatives on fresh state properties of Portland cement-based mortars, such as water retention, rheological behavior and the hydration delay. This work focuses on the guar gum derivatives since their manufacturing process is low pollutant and they provide very good properties to cement-based mortars. The results highlight that the chemical composition of guar gum derivatives (MS, DS, additional alkyl chain) are the key levers to improve water retention of mortars and to adapt the rheological behavior of the cementitious paste to a specific application.

Keywords: Cement; HydroxyPropyl Guar; Mortar; Rheology; Water retention.

1. Introduction

Modern factory-made mortars are complex materials, in which several kinds of admixtures are added in order to obtain specific properties, from the fresh state to the hardened material. Indeed, since many years, concretes, mortars or cement grouts with high fluidity have been developed, since their use implies many economical and technical advantages. However, the use of highly flowable mixtures may lead to segregation or excessive bleeding and subsequently, durability issues. In order to overcome this problem by enhancing the segregation resistance while maintaining high fluidity, viscosity-enhancing admixtures (VEA) are frequently introduced within the formulation (1,2,3,4). Among these admixtures, natural polysaccharides or their derivatives (such as welan gum, starch derivatives or cellulose ethers) are the most widely used. Moreover, the incorporation of these VEAs in shotcrete or render mortar is useful to ensure sagging resistance for thick application on vertical support, and to allow sufficient fluidity for normal pumpability by supplying shear thinning rheological behavior (5). Indeed, these admixtures provide, generally, high yield stress and apparent viscosity at low shear rate but low resistance to flow at high shear rate (6). However, their mode of action is not fully understood, since results are sometimes contradictory. Water retention (WR) is another essential property of monolayer render at fresh state. Indeed, high water retention improves the cement hydration and limits the absorption of the mixing water by a substrate and thus provides good mechanical and adhesive properties to the mortar (7). Among admixtures enhancing water retention capacity of the freshly-mixed mortars, cellulose ethers (CE) are the most widely used. Nevertheless, hydroxypropyl guar (HPG) are now also well-established in the construction industry as water retention agent for mortars (8,9,10,11). Since HPGs improve two main properties of mortar, they appear as suitable admixtures to be used in render formulation.

The aim of this study is to provide an understanding of the effect of chemical composition and structure of HPGs and its dosage on macroscopic properties of mortars. For this purpose, an original guar gum and five HPGs with specific chemical modifications, such as increase in MS_{HP} or substitutions by hydrophobic

units, were selected. The impact of admixtures on the water retention capacity, on cement hydration and on the rheological behavior of mortars was investigated.

2. Materials and methods

2.1 Mineral products

Mineral products used in this study consist in blend Portland cement (Holcim), lime (Holcim), calcium carbonate (Calcitec V60, Mineraria Sacilese S.p.A.) and dolomite (Bombardieri and Leidi 0.1-0.4mm). The mineral compositions of the commercial Portland cement, CEM II/B-LL 32.5 R according to the European standard EN 197-1 (12), used are given in Table 1.

Table 1. Mineral composition (% weight) of the investigated cement determined by XRF and XRD-Rietveld refinement.

Chemical composition (% wt)				Phase composition (% wt)			
Oxides	XRF	Oxides	XRF	Phases	XRD (Rietveld)	Phases	XRD (Rietveld)
CaO	57.87	SO ₃	3.95	C ₃ S	54.3	Calcite	28.9
SiO ₂	12.31	Na ₂ O	0.99	C ₂ S	3.5	Gypsum	3.0
Al ₂ O ₃	5.25	K ₂ O	1.66	C ₃ A	4.7	Quartz	0.9
MgO	1.19	TiO ₂	0.16	C ₄ AF	4.6	Free CaO	0.8
Fe ₂ O ₃	4.05	LOI	13.7				

The phase composition was determined by Rietveld refinement method (Siroquant V2.5 software) after XRD analysis (D5000, Siemens) and the oxide composition was quantified by means of X-ray fluorescence spectroscopy. 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) was 5, 15, 20, 300 and 600 μ m for lime, cement, calcite and both dolomite fine aggregates, respectively.

2.2 Organic admixtures

Guar gum is a natural polysaccharide extracted from the seed endosperm of *Cyamopsis tetragonolobus*. This polymer consists in a $\beta(1-4)$ -linked D-mannopyranose backbone with random branchpoints of galactose via an $\alpha(1-6)$ linkage (Fig. 1(a)). Hydroxypropyl guar (HPGs) are obtained from the original guar gum via an irreversible nucleophilic substitution, using propylene oxide in the presence of an alkaline catalyst (Fig. 1(b)).

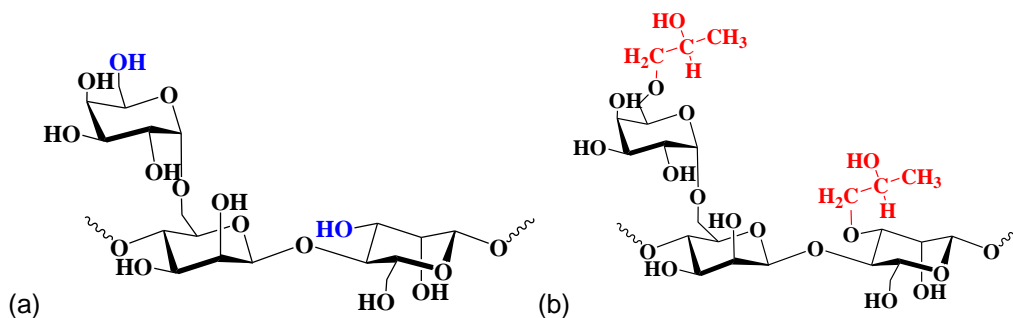


Figure 1. Molecular structure of original guar gum (a) and HydroxyPropyl Guar (b)

The manufacture of HPGs has the advantage of having a more reduced impact on the environment than cellulose derivatives. Indeed, guar gum is extracted by simple thermo-mechanical process, exhibits a higher chemical reactivity and is soluble in cold water thanks to its branched-chain structure with a lot of hydroxyl groups. Thus, the chemical modification of the original guar gum requires normal reaction conditions of temperature and pressure, does not generate large quantity of by-products, and requires minimal purification procedure (8). In this paper, five HPGs and an original guar gum provided by Lamberti S.p.A were studied. They exhibit roughly the same molecular weight, around $2 \cdot 10^6$ g.mol⁻¹ since they are

all from the same original guar gum (noted HPG 6 in the paper) (13). Table 2 provides a qualitative description of the polymers used. The qualitative substitution degrees are provided by the manufacturers. The molar substitution ratio (MS_{HP}) represents the number of hydroxypropyl units per anhydroglucose unit and is less than 3 for the investigated HPGs. The degree of substitution (DS_{AC}) represents the amount of alkyl chain per anhydroglucose unit. The only difference between HPGs 1 and 3 is the molar substitution ratio, which increases, while HPG 4 exhibits an additional substitution (short alkyl chains).

Table 2. Qualitative description of the HPG used.

	MS_{HP}	DS_{AC}	Additional substitution
HPG 1	Low	-	
HPG 3	High	-	
HPG 4	High	Low	Short alkyl chain
HPG 6	-	-	-

2.3 Methodology

Mortars were prepared according to the following mixture proportions: 12% of cement, 3% of lime, 18% of calcium carbonate, 43% of dolomite Bombardieri and 24% of dolomite Leidi (by weight). The admixtures were in addition to the total dry mixture (i.e. cement, lime, calcium carbonate and dolomite) and are expressed in weight percent by weight of binder (% bwob). Dry mixture was blended in a shaker (Wab, Turbula, Germany) for 10 min. Deionised water was added in order to obtain a liquid-to-solid ratio $L/S = 0.22$. The mixing procedure was in accordance with EN 196-1 (14). All tests were carried out, at least, in triplicate and at a controlled temperature. A control test was also performed with a mortar without admixture.

2.4 Water retention measurements

The water retention capacity of freshly-mixed mortar was assessed using ASTM C1506-09 standard method (15). It had to be performed 15 min after mixing to measure the water loss of a mortar under partial vacuum. The standardized apparatus was submitted to a vacuum of 50 mm of mercury ($6.6 \cdot 10^3$ Pa) for 15 min. Then, the water retention capacity, WR, was calculated using the following equation:

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

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

All the experiments were carried out at 23 °C. Three classes of water retention can be specified according to the DTU 26.1 (16). The first class (low WR category) contains mortars that exhibit WR lower than 86%. The second class (medium) corresponds to WR ranging from 86% to 94%. The last one (high) is defined by WR higher than 94%, corresponding to the required values in the field of rendering application.

2.5 Rheological behavior

The rheological measurements were performed with Rheometer MCR 302 (Anton-Paar), thermostated at 20 °C. The rheological properties of fresh mortars were investigated with vane-cylinder geometry (17,18). The mortar was introduced into the measurement system at the end of the mixing cycle. At 10 min, the mortar was pre-sheared for 30 s at 100 s^{-1} in order to re-homogenize the sample and to eliminate its shear history (19,20). After a period of rest of 5 min, the rheological measurements were started (total time = 15 min). The imposed shear rate was decreased by step from 300 to 0.06 s^{-1} . At each shear rate, the measuring time was adjusted in order to obtain a steady state whatever the formulation. The samples were systematically submitted to high shear rate (100 s^{-1}) for 30 s before each imposed shear rate in order to resuspend particles of mortar within the mortar mixtures. The results were expressed as shear stress τ according to shear rate $\dot{\gamma}$ and the Herschel-Bulkley (HB) model was applied to fit the experimental data and used to describe mortars rheological behavior (21):

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

where τ_0 correspond to the yield stress, K the consistency coefficient and n the fluidity index which characterizes shear-thinning behavior of mortar.

2.6 Adsorption curves of HPGs on binder

The adsorption isotherms were determined using the depletion method. The non-adsorbed polymer remaining within the pore solution was quantified by means of Total Organic Carbon (TOC) measurements. Prior to analysis, the pore solution was extracted from admixed or non-admixed mortar. The extraction was performed by means of two centrifuging steps. The first step consisted in the centrifugation of around 150 g of mortar at 5000 rpm for 5 min. The supernatant was, afterward, centrifuged again at 14500 rpm for 10 min in order to avoid the presence of mineral particles within the solution. The supernatant was diluted with hydrochloric acid solution at 0.1 mol.L⁻¹. The total organic carbon was determined by combustion at 850 °C with a Vario-TOC Cube (Elementar). The adsorbed amount of polysaccharides was calculated from the difference of TOC content of the HPG reference solution and the TOC content of the supernatant.

2.7 Conductimetric measurement

Characterization of the delay induced by the studied admixtures on the cement hydration was performed by conductivity measurements. Conductivity measurements were carried out in lime suspension in order to obtain hydration kinetics close to that observed in cement pastes, in spite of a high liquid-to-solid weight ratio (L/S). Conductivity curves were interpreted according to explanations proposed by Comparet et al. (22). As soon as cement came in contact with liquid, the electrical conductivity increased as a consequence of the dissolution of the anhydrous phases. Then, nucleation of hydrates on the grain surface leads to a period where the conductivity evolves weakly. Conductivity then accelerated more quickly. The conductimetric slope is related to the growth rate of the hydration products. Meanwhile, cement dissolution still continued. The conductivity increases to the supersaturation with respect to portlandite and decreases rapidly due to its precipitation. Thus, an electrical conductivity drop is caused by the portlandite precipitation. The portlandite precipitation time was used as a benchmark to classify and to quantify the relative retardation ability of admixtures on cement hydration.

Experiments were performed in lime solution (20 mM), thermostated at 25 °C and continuously stirred. The liquid-to-solid weight ratio (L/S) used was equal to 10. Polymer-to-binder weight ratio (P/B) was fixed to 0.5%. Binder GUM 01 and admixture powders were blended in a shaker (Turbula, Wab) for 10 min before contact with the liquid phase. The control corresponds to the neat binder.

3. Experimental results

3.1 Impact of HPGs on the water retention property of fresh mortars

Fig. 2 represents the evolution of the water retention capacity of fresh admixed mortars, according to the polymer dosage. The non-admixed mortar exhibits a low water retention capacity of about 72% ± 0.3%. Then, as expected, the water retention increases with the use of HPGs and with increasing polymer dosage, until reaching a plateau with very high WR values (>97%). In the range of polymer dosage studied, the WR values reached for HPGs 3 and 4 are greater than 94% and therefore belong to the high WR class. The original guar gum and, to a lesser extent HPG 1, highlight a very limited impact, regardless of dosage until 0.2%. These results suggest that the substitution of hydroxyl units from original guar gum by hydroxypropyl units increases the WR of mortars. Furthermore, the increase in the MS_{HP} (from HPG 1 to 3) improves the WR capacity of mortar, since HPG 3 provides the higher WR despite lower dosage.

The results highlight moreover the positive impact of additional alkyl chain on WR. Indeed, the highest WR are obtained with HPG 4 for the lowest polymer dosages. Moreover, concerning the shape of WR curves, an abrupt change in slope can be noticed for mortars admixed with HPGs 3 and 4, and with HPG1 but only above 0.15%. This occurs for a decreasing polymer dosage from HPG 3 to HPG 4.

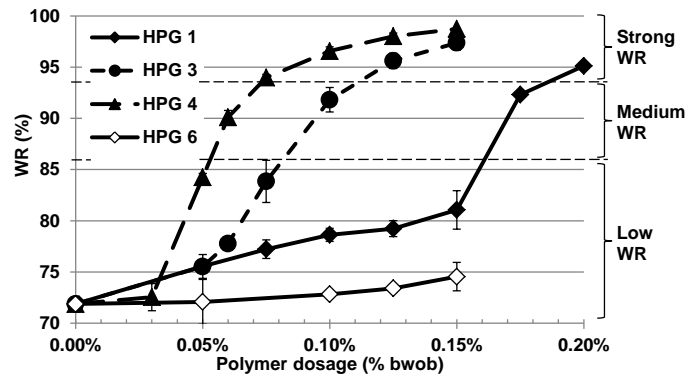


Figure 2. Impact of polymer dosage on water retention capacity of fresh admixed mortars

3.2 Modification of cement hydration by HPGs

The conductimetric data highlights the impact of HPGs on the kinetics of hydration (Fig. 3(a)). By focusing on the portlandite precipitation time, it appears a wide range of delays induced by the admixtures. Among HPGs, HPG 4 exhibits the weaker delay (4.5 h) (Fig. 3(b)). The most important delay is observed for HPG 1 (17.8 h). The native guar gum induces the lowest delay in the portlandite precipitation. The increase in MS_{HP} (from HPG 1 to 3) leads to a decrease in the portlandite precipitation time. The comparison between HPG 3 and HPG 4 suggests the low impact of the alkyl chain on the delay of the portlandite precipitation.

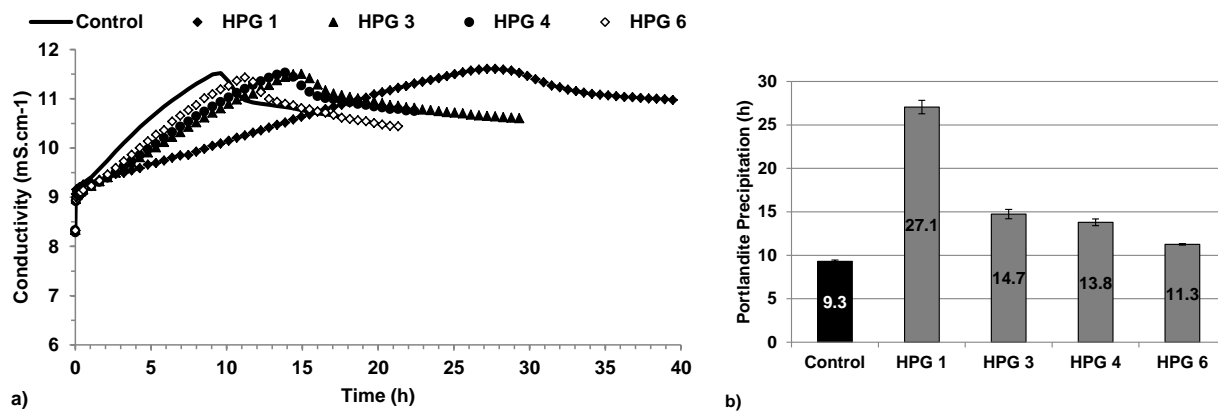


Figure 3. Influence of HPGs on conductimetric curves (a) and on portlandite precipitation time (b), $[Ca(OH)_2]=20$ mM, L/S=10, P/B=0.5%

The conductimetric curves reveal a very low extension of the duration of the “period of low increase in conductivity” (Fig. 3(a)). This result highlights the weak influence of admixtures on the nucleation of the first cement hydrates. The same results were obtained by Poinot et al. (9). The delay of portlandite precipitation is mainly due to the slope decrease. The slope of the conductimetric curve, being linked to the growth rate of the hydrated cement phases, suggests that HPGs act preferentially on the growth of hydrates, rather than on their nucleation.

3.3 Adsorption curves of HPGs on binder

Fig. 4(a) shows the adsorption isotherms of the admixtures on Portland based-mortars. The results confirm the adsorption of original guar gum and HPGs on cementitious materials. It has been shown that the adsorption mechanism of galactomannose polysaccharides at solid–liquid interfaces involves strong hydrogen bonding (23). In the range of polymer dosage used in the study, no plateau was reached, and this, whatever the admixture. For the original guar gum (HPG 6), the adsorption is the highest of all the tested polymers and corresponds to a total adsorption higher than 98.5% of the introduced polymer. The presence of hydroxypropyl substitutions on the guar leads to a decrease in the affinity of the polymer with the binder since the adsorption of HPG 1 is lower by 35% than the original guar gum. Moreover, the

adsorption is further reduced by increasing values of MS_{HP} (64% for HPG 3 compared to HPG 6). This tendency is consistent with previous studies on HPGs and cellulose ethers (9, 24). Fig. 3(a) highlights also the effect of the additional alkyl chain on the adsorption. It appears that the hydrophobic side chains slightly intensify the adsorption of the hydrophobically modified HPG on surface of grains with respect to HPG 3.

From the TOC measurements, the real polymer concentration within the extracted pore solution was determined. Fig. 4(b) shows the evolution of this concentration versus the introduced polymer dosage. Excepted HPG 6, the amount of non-adsorbed polymer increases with increasing polymer dosage. According to the HPG, the concentration rises following this order: HPG 6 < HPG 1 < HPG 4 < HPG 3.

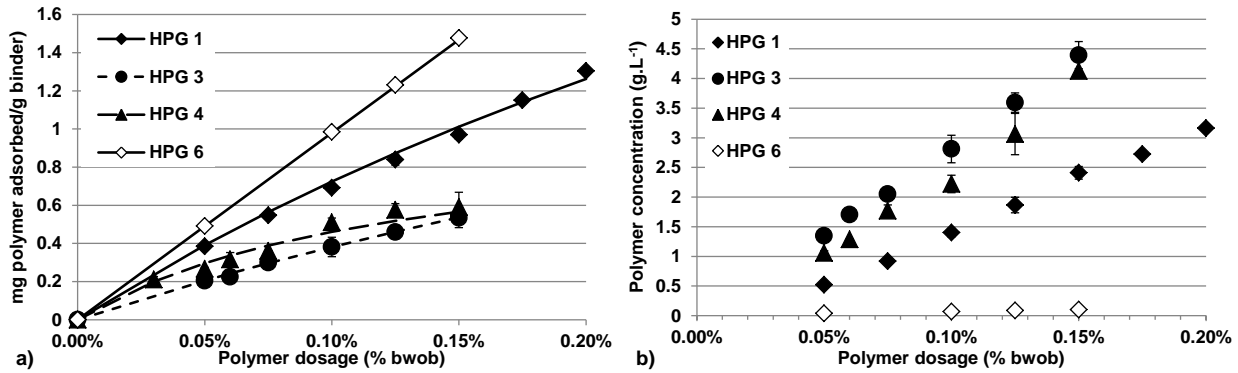


Figure 4. Adsorption isotherms of HPGs 1, 3, 4 and original guar gum (HPG 6) (a) and concentration of HPGs in extracted mortar pore solution (b)

3.4 Impact of HPGs on the rheological properties of fresh mortars

Fig. 5(a) shows the evolution of the yield stress, extracted from Herschel-Bulkley model, for all the studied mortars with and without admixture. The mortar without admixture exhibits a yield stress value of around 45 Pa. From the presented results, three different classes of HPG, inducing different evolution of the yield stress with the polymer dosage, can be highlighted for admixed mortars. The first category is only composed of the original guar gum (HPG 6), which induces a low and quasi linear decrease in the yield stress of mortar when HPG dosage increases. On the contrary, HPGs 1 and 3 lead to a continuous rise of the yield stress of mortars from 50-60 Pa to around 120 Pa with the increase in the HPG dosage from 0.05% to 0.15%. Finally, HPG 4 constitutes the third class of admixture. The use of this admixture leads an improvement of the yield stress compared to the non-admixed mortar, whatever the dosages tested in the study. However, the increase is not proportional to the admixture dosage. Indeed, our first dosage (0.05% bwob) leads to an increase in the yield stress. Beyond this dosage, increasing the dosage provides a slow and low decrease, before reaching a plateau. The value of the yield stress reached on the plateau is still higher than that of the mortar without admixture.

The evolution of the consistency coefficient (K from Herschel-Bulkley equation) during the increase of polymer dosage is presented Fig. 5(b). As in the case of the yield stress, the results can be divided into three classes of polymer. The first class is only composed of the original guar gum which provides a very low or negligible modification of the consistency coefficient with increasing polymer dosage compared to non-admixed mortar. HPGs 1 and 3, constituting the second group, induce first an increase followed by a plateau in the consistency coefficient. Finally, HPG 4 leads to a continuous increase in the consistency coefficient of admixed mortars.

Fig. 5(c) shows the evolution of the fluidity index (n) versus the polymer dosage for all the studied mortars. It is worth to note that whatever the mortars, the values of the fluidity index are lower than 1, meaning that they are all shear thinning. Due to the high standard deviation, the value of the fluidity index of mortars admixed with HPGs 1 and 3 and 6 seem to be unchanged as the dosage of HPGs increase. However, HPG 4 leads to a low increase followed by a continuous decrease in the fluidity index until reaching values around 0.5. This means that the shear thinning behavior of mortars becomes more and more pronounced.

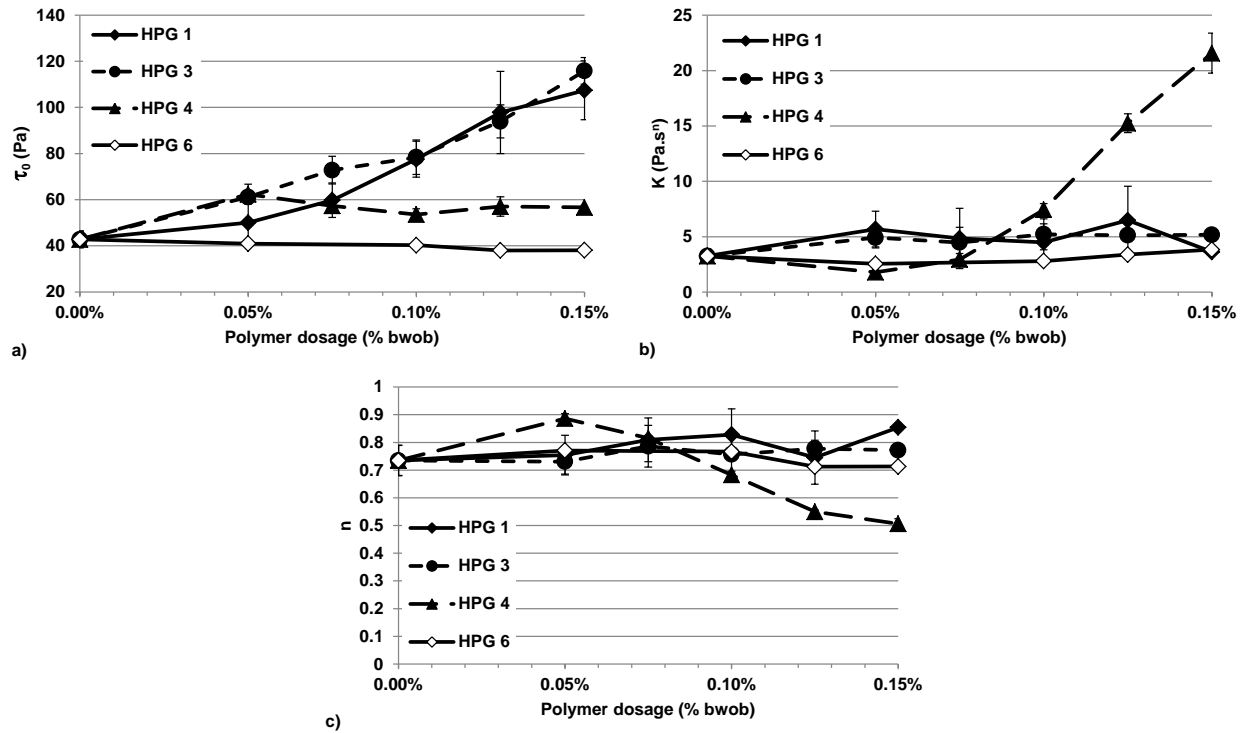


Figure 5. Impact of polymer dosage on yield stress (a), consistency coefficient (b) and fluidity index (c) of fresh admixed mortars (HPGs 1, 3, 4 and original guar gum (HPG 6))

4 Discussion

The effect of the original guar gum (HPG 6) is negligible from the WR point of view. Since the adsorption is higher than 98.5% of the initial amount of polymer, very few molecules are still in the pore solution. The composition of pore solution is thus close to that of the non-admixed mortar, leading to similar WR.

Concerning the hydroxypropyl guar, the results from WR experiments are consistent with those of previous studies performed with HPGs or CEs and with the proposed mechanism. Indeed, the WR of admixed mortars is mainly governed by the ability of polysaccharidic admixtures to form an associated polymer molecules network and to induce overlapping of polymer coils within the pore solution (10,25,26). When the polymer concentration in solution increases, the isolated polymer coils, existing at low concentration, begin to come into contact between them. This concentration is defined as the coil-overlap concentration (noted C^*). Above this critical concentration, the polysaccharide aggregates stop the water flow by plugging the porous network of a thin polysaccharide-enriched filter cake at the interface mortar-substrate resulting in a sudden and sharp rise in WR curves (10). The abrupt change in slope is reached for a decreasing polymer dosage from HPG 1 to HPG 3. The only difference between these HPGs is the increasing substitution degree. According to literature, the increase in MS_{HP} does not lead to a change in C^* (27). However, the increasing substitution degree leads to a decrease in polymer adsorption on mortar components and hence an increase in polymer amount in pore solution (Fig. 4). Consequently, the coil overlapping occurs at lower dosage. The results highlight furthermore the positive impact of additional alkyl chain on WR. The presence of additional alkyl chains (HPG 4), despite slightly higher adsorption than HPG 3, leads to the formation of polymer associates at lower polymer dosage. Indeed, the interconnection between alkyl chains creates intramolecular and intermolecular interactions through specific hydrophobic interactions which cause a decrease in the coil-overlapping concentration (28,29). Consequently, the abrupt change in slope is reached for a lower polymer dosage of HPG 4 than HPG 3.

It is generally admitted that cement hydration delay induced by admixtures is due to adsorption of these molecules onto surfaces of the hydrating cement particles and/or surfaces of hydration products (30,31). Polysaccharides are molecules which contain a lot of polar functional groups (-OH). Therefore, strong interactions, through electrostatic forces and hydrogen-bonding, can occur between polysaccharides and the highly polar hydrated phases (31). This interpretation is consistent with our results, especially for

HPGs 1 and 3. Indeed, the increase in the MS_{HP} leads to a decrease in the amount of free hydroxyl groups on the backbone chain and in the polarity of the molecule. Therefore a drop in both adsorption onto the surfaces and delay of the portlandite precipitation, is observed. However, in the case of HPG 4, and more especially for HPG 6, the adsorption of the admixture is higher than that of HPG 3 but the delay in the portlandite precipitation is lower. Therefore, a competitive adsorption of admixture could occur between the constituents of the binder, promoting adsorption onto non-reactive phases (dolomites and/or calcite). To answer to this question, the conductimetric analysis should be carried out only with cement.

The rheological results (Fig. 5) highlight that HPGs 1 and 3, HPG 4 and HPG 6 behave quite differently. Indeed, HPGs 1 and 3 lead to a continuous increase in the yield stress, while HPG 4 modifies mainly the consistency coefficient and the fluidity index. HPGs 1 and 3 affect the rheological behavior of the admixed mortars in the same way, i.e. an increase in the yield stress, a low increase followed by a plateau in the consistency coefficient and a negligible modification of the fluidity index when the polymer dosage rises. Fig. 4(a) shows that HPGs adsorb onto particles constituting the mortar. Prima facie, this adsorption could be responsible for the increase in the yield stress because of bridging flocculation (24). However, despite a strong drop of the adsorption (50%) with the increase in the MS_{HP} (from HPG 1 to 3) the yield stress also increases. This suggests that the non-adsorbed polymer may be responsible for the yield stress increase. The potential loss of bridging can be compensated by an increase in the pore solution viscosity induced by the rise in the polymer concentration and/or by the depletion flocculation induced by the non-adsorbed coils (32). Moreover, the presence of HPG coils within the pore solution leads to an increase in the consistency coefficient (K) compared to non-admixed mortars. However, the expected increase in K due to the rise of pore solution viscosity with the polymer dosage can be compensated by steric hindrance, leading to a plateau for K.

Since the adsorption of original guar gum is higher than 98.5%, one expects to detect a very strong increase in the yield stress compared to non-admixed mortar. However, the rheological behavior of the admixed mortar with HPG 6 is very close to that of the non-admixed mortar. This result suggests that the entire molecule of HPG 6 could be mainly adsorbed onto the surface of only one particle, limiting therefore the bridging flocculation. Moreover, the adsorption of the guar molecule onto a single particle leads to an increase in both steric hindrance and dispersion effects, leading to a low but continuous decrease in the yield stress. For dosages higher than 0.1% bwob, the concentration in polymer coils into the pore solution begins to slightly increase, leading to the beginning of the increase in K and of the decrease in n .

The additional alkyl chain also modifies the rheological properties of mortars. Contrary to HPG 3, HPG 4 leads to a strong and continuous increase in the consistency coefficient and a decrease in the fluidity index. These results highlight that mortars become more and more shear-thinning since the fluidity index decreases from 0.8 to 0.5. This rheological behavior gets more pronounced as the HPG dosage increases. These results are consistent with the fact that the hydrophobically modified HPG leads to the formation of coil overlapping at lower HPG dosage (0.05% in this study) since the presence of additional alkyl chains enhances the entanglement. Above this 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 shear thinning behavior of the solution, and thus of the mortars, amplify with the increasing polymer dosage. The yield stress is also impacted by the additional alkyl chain. Indeed, τ_0 , of mortar admixed with HPG 4, increases for a dosage equal to 0.05% bwob then slowly decreases for dosages up to 0.075% bwob, before reaching a plateau for higher dosages. This result could be explained by a change in the HPG conformation due to the presence of additional alkyl chains. Indeed, as previously mentioned, alkyl chain creates intramolecular and intermolecular interactions through specific hydrophobic interactions. Intramolecular association of hydrophobic units tends to force the polymer chain into a more compact conformation (29,33). Moreover, the conformation of hydrophobically modified polymers in aqueous solution involves the presence of alkyl chains inside the coils in order to limit contacts between hydrophobic chains and water (29). Consequently, the hydrophilic groups, such as hydroxyl and hydroxypropyl, are preferentially on the outskirts of the coils, promoting the adsorption onto the surface of particles and therefore steric hindrance which implies a prevention of direct contacts between particles. Moreover, due to a more compact conformation and avoidance between water and hydrophobic units, the bridging ability of hydrophobically modified HPG should decrease. All these points should lead to a decrease in the yield stress.

5. Conclusions

In this paper, we studied the effect of several guar gum derivatives on water retention property and rheological behavior of mortars. Based upon the results, it was found that the original guar gum was totally adsorbed onto particle surface, leading to a negligible modification of WR and rheological behavior with respect to the non-admixed mortar. Depending of the chemical structure of HPGs, it is possible to promote the water retention according to two different ways. First, by increasing the MSHP of HPGs, the amount of adsorbed polymer drops, which leads to an increase in the HPG concentration within the pore solution and therefore to lower HPG dosage necessary to reach coil overlapping. Second, by enhancing overlapping, the hydrophobically modified HPGs improve the effectiveness of WR agent at low dosage. HPGs also modify the rheological behavior of the mortars. As in the case of WR, the hydrophobic characteristic of HPGs is the preponderant parameter. Indeed, it was shown that additional alkyl chain mainly leads to a more shear thinning behavior of the mortar and to a rise in the consistency coefficient, while classical HPGs strongly increases the yield stress.

7. References

1. Rols S., Ambroise J., Péra J., "Effects of different viscosity agents on the properties of self-leveling concrete", Cement and Concrete Research, 29 (2), 1999, pp 261-266.
2. Khayat K.H., Yahia A., "Effect of welan gum-high-range water reducer combinations on rheology of cement grout", ACI Materials Journal, 94(5), 1997, pp 365-372.
3. Lachemi M., Hossain K.M.A., Lambros V., Nkinamubanzi P.-C., Bouzoubaâ N., "Self-consolidating concrete incorporating new viscosity modifying admixtures", Cement and Concrete Research, 34(6), 2004, pp 917-926.
4. Sonebi M., "Rheological properties of grouts with viscosity modifying agents as diutan gum and welan gum incorporating pulverised fly ash", Cement and Concrete Research, 36(9), 2006, pp 1609-1618.
5. Paiva H., Silva L.M., Labrincha J.A., Ferreira V.M., "Effects of a water-retaining agent on the rheological behaviour of a single-coat render mortar", Cement and Concrete Research, 36(7), 2006, pp 1257-1262.
6. Khayat K.H., "Viscosity-enhancing admixtures for cement-based materials - an overview", Cement and Concrete Composites, 20(2-3), 1998, pp 171-188.
7. Jenni A., Holzer L., Zurbruggen R., Herwegh M., "Influence of polymers on microstructure and adhesive strength of cementitious tile adhesive mortars". Cement and Concrete Research. 35(1), 2005, pp 35-50.
8. Biasotti B., Giudici M., Langella V., Pfeiffer U., "Highly substituted hydroxypropylguar: a strong contribution to construction chemistry", International Dry mix Mortar Conference, Nürnberg, Germany, 2011.
9. Pointot T., Govin A., Grosseau P., "Impact of hydroxypropylguars on the early age hydration of Portland cement", Cement and Concrete Research, 44, 2013, pp 69-76.
10. Pointot T., Govin A., Grosseau P., "Importance of coil-overlapping for the effectiveness of hydroxypropylguars as water retention agent in cement-based mortars", Cement and Concrete Research, 56, 2014, pp 61-68.
11. Cappellari M., Daubresse A., Chaouche M., "Influence of organic thickening admixtures on the rheological properties of mortars: Relationship with water-retention", Construction and Building Materials, 38, 2013, pp 950-961.
12. Standard EN 197-1, "Cement-Part 1: Composition, specifications and conformity criteria for common cements", 2012.
13. Pointot T., Benyahia K., Govin A., Jeanmaire T., Grosseau P., "Use of ultrasonic degradation to study the molecular weight influence of polymeric admixtures for mortars", Construction and Building Materials, 47, 2013, pp 1046-1052.
14. Standard EN 196-1, "Methods of testing cement-Part 1: Determination of strength", 2006.

15. Standard C1506-09, "Standard test Method for Water Retention of Hydraulic Cement-Based Mortars and Plasters". American Society for Testing and Material, 2009.
16. NF DTU 26.1, "Travaux d'enduits de mortiers ", 2008.
17. Bouras R., Kaci A., Chaouche M., "Influence of viscosity modifying admixtures on the rheological behavior of cement and mortar pastes", Korea-Australia Rheology Journal, 24(1), 2012, pp 35-44.
18. Barnes H.A., Nguyen Q.D., "Rotating vane rheometry - a review", Journal of Non-Newtonian Fluid Mechanics, 98(1), 2001, pp 1-14.
19. Phan T.H., Chaouche M., Moranville M., "Influence of organic admixtures on the rheological behaviour of cement pastes", Cement and Concrete Research, 36(10), 2006, pp 1807-1813.
20. Roussel N., Ovarlez G., Garrault S., Brumaud C., "The origins of thixotropy of fresh cement pastes", Cement and Concrete Research, 42(1), 2012, pp 148-157.
21. Herschel W.M., Bulkley R., "Measurements of consistency as applied to rubber-benzene solutions", Proceedings of the American Society for the Testing of Materials, 26, 1926, pp 621-633.
22. Comparet C., Nonat A., Pourchet S., Guicquero J.P., Gartner E., Mosquet M., Chemical interaction of di-phosphonate terminated monofunctional polyoxethylene superplasticizer with hydrating tricalcium silicate, Proceedings, 6th International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Nice, France, 2000, pp 61-74.
23. Wang J., Somasundaran P., Nagaraj D.R., "Adsorption mechanism of guar gum at solid-liquid interfaces", Minerals Engineering, 18(1), 2005, pp 77-81.
24. Brumaud C, Baumann R, Schmitz M, Radler M, Roussel N., "Cellulose ethers and yield stress of cement pastes", Cement and Concrete Research, 55, 2014, pp 14-21.
25. Bülichen D., Kainz J., Plank J., "Working mechanism of methyl hydroxyethyl cellulose (MHEC) as water retention agent", Cement and Concrete Research, 42(7), 2012, pp 953-959.
26. Marliere C., Mabrouk E., Lamblet M., Coussot P., "How water retention in porous media with cellulose ethers works", Cement and Concrete Research, 42(11), 2012, pp 1501-1512.
27. Volpert E., Selb J., Candau F., "Influence of the Hydrophobe Structure on Composition, Microstructure, and Rheology in Associating Polyacrylamides Prepared by Micellar Copolymerization", Macromolecules, 29, 1996, pp 1452-1463
28. Cheng Y., Brown K.M., Prud'homme R.K., "Characterization and Intermolecular Interactions of Hydroxypropyl Guar Solutions", Biomacromolecules, 3(3), 2002, pp 456-461.
29. Simon S., Dugast J., Le Cerf D., Picton L., Muller G., "Amphiphilic polysaccharides. Evidence for a competition between intra and intermolecular associations in dilute system", Polymer, 44(26), 2003, pp 7917-7924.
30. Cheung J., Jeknavorian A., Roberts L., Silva D., Impact of admixtures on the hydration kinetics of Portland cement, Cement and Concrete Research, 41 (12), 2011, pp 1289-1309.
31. Jolicoeur C., Simard M.A., Chemical admixture-cement interactions: phenomenology and physico-chemical concepts, Cement and Concrete Composites, 20 (2-3), 1998, pp 87-101.
32. Palacios M., Flatt R.J., Puertas F., Sanchez-Herencia A., "Compatibility between Polycarboxylate and Viscosity-Modifying Admixtures in Cement Pastes", Proceedings, 10th International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Prague, Czech Republic, 2012, pp 29-42.
33. Aubry T., Moan M., "Rheological behavior of a hydrophobically associating water soluble polymer". Journal of Rheology, 38(6), 1994, pp1681-1692.