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Combination of guar gum derivatives and superplasticizers, impact on properties of Portland cement-pastes

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Abstract: The study focused on competitive or synergetic effects induced by the combination of stabilizing agents based on hydroxypropyl guar (HPG) and superplasticizers on the properties of cement pastes. Two polycarboxylate superplasticizers (PCE) exhibiting different charge densities and two HPGs with different molar substitution ratios (MS_{HP}), were studied. First, a method allowing the quantification of both kinds of admixture was developed. The results show that the adsorption of HPGs is significantly affected by the presence of PCE, while only the adsorption of the PCE with the lowest charge density is slightly modified by the HPG. The combination of HPG with PCE superplasticizer strongly modifies the rheological behavior of cement pastes. Despite the presence of HPG, the viscosity of the pastes strongly decreased with increasing dosage of PCE. The viscosity was even close to the viscosity of a cement paste with PCE only. However, the use of HPG in combination with PCE allows maintaining a significant yield stress compared to PCE alone. The charge density of the PCE seemed to affect the drop of the viscosity and the gain on the yield stress induced by HPG.

Keywords: Admixtures, rheology, polysaccharides, guar derivatives, superplasticizers.

1. Introduction

In order to obtain specific properties from the fresh state to the hardened material, the formulations of cementitious materials become more and more complex due to combining several groups of admixtures. For many years, cementitious materials with high fluidity have been developed, thanks to their economic and technical advantages. For this purpose, high-range-water-reducing (HRWR) admixtures, also known as superplasticizers, are commonly introduced in the formulations of cementitious materials. These admixtures can dramatically reduce the amount of mixing water, while maintaining or increasing workability at identical or similar performance (1), (2), (3). Today, polycarboxylate ethers (PCE) are commonly used as superplasticizers to disperse cement particles in concretes and mortars (4). Through the anionic charges of the backbone chain, the PCEs can be adsorbed on surfaces of cement phases and hydrates. Through the side chains and the main chain they induce steric repulsion forces between the particles, leading to improved dispersion (2),(5). However, inhomogeneities such as segregation or bleeding may occur for highly flowable mixtures with negative effects on the durability. To overcome this adverse effect, viscosity-enhancing admixtures (VEA) or stabilizing agents (STA) can be introduced into the formulation (6), (7), (8), (9). Natural polysaccharides or their derivatives, such as sphingane gums, starch derivatives, cellulose ethers or guar gum derivatives, are frequently used as STA. These admixtures induce modifications of the rheological behavior of the cementitious materials by usually increasing the yield stress and the apparent viscosity and by supplying shear thinning behavior (10) (11).

It is worth noting that the yield stress and the viscosity are very important properties for the flow of concrete, since the both affect its workability and casting properties. The viscosity is an important parameter during casting and application of concrete since it influences the filling velocity, the resistance to flow and the segregation stability during the flow process. The yield stress, which is responsible of the stability at rest (no segregation) and the maintaining of the shape at rest, is more linked to the properties of flowable concrete after casting. The rheological parameters of concrete are generally dependent of the solid volume fraction and the rheological properties of the fluid surrounding the aggregates, i.e. the cement paste.

The consideration of environmental concerns, the reduction of greenhouse gas emissions and energy consumption lead the cement and concrete industry to develop more and more complex formulations. Consequently, a greater control of the formulation and a better understanding of the effects of all admixtures in a formulation are necessary. Indeed, an understanding of the mechanism of action of the

admixtures is a way to improve the selection of admixtures in relationship with the practical applications. However, most of the academic studies focused on the effect of individual admixture, despite competitive adsorption which can occur inhibiting the intended effect (12) or positive interaction which can promote the efficiency of the polymers (13), (14).

The objectives of this paper are to propose a method allowing the quantification of the specific adsorption of hydroxypropyl guar and polycarboxylate-based superplasticizers when they are introduced together in the mix, and to improve the understanding of synergetic or competitive effects between these two admixtures on the rheological aspect.

2. Materials and methods

2.1. Mineral products

The cement used for this study was an ordinary Portland cement, referenced as CEM I 42.5 R (CEMEX) according to the European standard EN 197-1. The chemical composition was determined by means of X-ray fluorescence spectroscopy and the resulting clinker composition according to the modified Bogue calculation according to Taylor (15) is given in Table 1.

Table 1. Oxide composition (% weight) of the investigated cement determined by XRF and clinker phase composition according to the modified Bogue calculation.

Chemical composition (% wt)				Phase composition (% wt)	
Oxides	XRF	Oxides	XRF	Phases	XRD (Rietveld)
CaO	62,80	Na ₂ O	0,28	C ₃ S	61,8
SiO ₂	20,56	K ₂ O	0,95	C ₂ S	20,5
Al ₂ O ₃	4,36	TiO ₂	0,2	C ₃ A	6,2
Fe ₂ O ₃	2,27	SO ₃	3,45	C ₄ AF	7,7
MgO	2,14	LOI	2,40		

2.2. Organic admixtures

Hydroxypropyl guar (HPGs) are obtained from the original guar gum via a nucleophilic substitution, using propylene oxide in the presence of an alkaline catalyst (Figure 1). Guar gum is a natural polysaccharide extracted from the endospermic seed of *Cyamopsis tetragonolobus*. The guar gum is considered as a non-ionic polymer in water. The guar gum exhibits a high molecular weight and hydrophilic properties. The structure of the guar consists of a D-mannopyranose backbone with random branchpoints of galactose. This branched-chain structure and the high amount of hydroxyl groups lead to the guar gum a high chemical reactivity and an easy dissolution in cold water. The HPGs manufacturing hardly impacts the environment, since the extraction of the guar gum requires only a simple thermo-mechanical process and the chemical modification of the original guar gum requires normal reaction conditions of temperature and pressure, which does not generate large quantity of by-products, and requires minimal purification procedure (16).

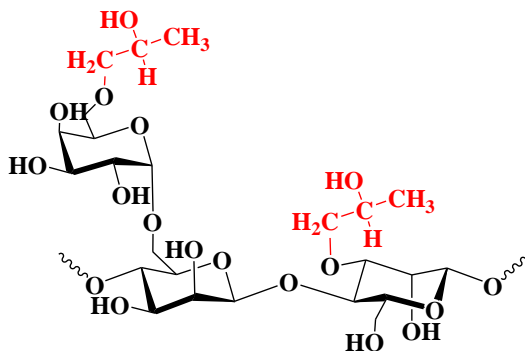


Figure 1. Molecular structure of HydroxyPropyl Guar.

In this paper, two different HPG, provided by Lamberti S.p.A., were studied. They are hereafter referred to HPG1 and HPG3. The only difference between the both HPGs is the molar substitution ratio, which increases from HPG 1 to HPG 3. The molar substitution ratio (MS_{HP}) represents the number of hydroxypropyl units per hexose unit (mannose or galactose), which is, according to the manufacturer, less than 3 for the investigated HPGs. Since the two different HPGs are originated from the same original guar gum, they exhibit roughly the same molecular weight, around $2 \cdot 10^6 \text{g} \cdot \text{mol}^{-1}$ (17). These HPGs were chosen because they are able to adsorb on the cement particles (18).

Two polycarboxylate-based superplasticizers (PCE) were studied (Glenium Master Sky 591 called PCE_{LC} and Glenium Master Sky 595 called PCE_{HC}). Since these two polymers are commercial products, no details of the chemical composition were given by the manufacturer (BASF). A qualitative description is given in Table 2. These superplasticizers were chosen because of their difference in the charge density, since it is one of the major influencing parameters for the performance of superplasticizers (12). For the following, LC and HC mean low charge and high charge density, respectively.

Table 2. Qualitative description of the PCEs used.

	PCE_{LC}	PCE_{HC}
Backbone	Polycarboxylate ether (PCE)	
Side chains	Polyethylene oxide (PEO)	
Side chain length	Medium + low	Medium
Grafting degree	High	Low
Backbone charge density	Low	High
Solid content (%)	30	20

2.3 Preparation of fresh pastes

The investigations were carried out on pastes from cement and water. The water-to-cement ratio (W/C) was kept constant at 0.4. Deionized water was used for all the experiments. The hydroxypropyl guar was dry-blended with the cement, hand-premixed during one minute, before adding liquid. When superplasticizers were used, they were added into the dry mix with the water. The amount of water contained into the PCE solution was deduced from the mixing water in order to keep constant the liquid-to-solid ratio. The mixing was made in a blender in accordance to EN 196-1. All the dosages in admixture were expressed in percent by weight of cement (% bwoc). The studied dosages were 0.1, 0.2 and 0.3% bwoc and 0.1% bwoc for PCEs and HPGs, respectively.

All tests were carried out at a controlled temperature of 20 ± 2 °C since rheological behavior of the cement paste and adsorption measurements are temperature-dependent. A reference test was also performed with cement without admixture.

2.4 Rheological behavior

The rheological measurements were performed with a Rheometer Viskomat NT (Schleibinger Geräte), in a room thermostated at 20 °C. The rheological properties of fresh pastes were investigated with a double gap cell and a basket probe composed of a structured grid (Vogel cell). The gap thickness was about 6 mm.

The paste was introduced into the measurement system at the end of the mixing cycle and was then held at rest. At 9 min the experiment was started. The mortar was first pre-sheared for 1 min at 100 s^{-1} in order to re-homogenize the sample and to eliminate its shear history because of potential thixotropic character of cementitious materials (19), (20). After a period of rest of 5 min, the rheological measurements were started. The imposed shear profile consisted of 14 decreasing steps from 100 s^{-1} to 0.06 s^{-1} . The measuring time was adjusted for each shear rate, in order to obtain a steady state.

The shear stress (τ) was expressed as a function of the shear rate ($\dot{\gamma}$) and the Herschel-Bulkley model was applied to fit the experimental data and used to describe cement rheological behavior (21):

$$\tau = \tau_0 + K\dot{\gamma}^n \quad (1)$$

where τ_0 corresponds to the yield stress, K to the consistency coefficient and n to the fluidity index which characterizes shear-thinning or shear thickening behavior of the paste. In addition, the residual viscosity, as defined by Hot (22), was determined.

$$\text{residual viscosity}_{(\dot{\gamma})} = \mu_{app} - \frac{\tau_0}{\dot{\gamma}} \quad (2)$$

Where μ_{app} is the apparent viscosity ($= \tau/\dot{\gamma}$), τ_0 is the yield stress.

The residual viscosity does not take into account the contribution of the energy needed to overcome the attractive interaction colloidal forces and to destroy the inter-particle network, characterized by the yield stress (22).

2.5 Adsorption measurements

The adsorption isotherms were determined using the depletion method. The non-adsorbed polymers remaining within the pore solution was quantified. The pore solution was extracted from the cement pastes by means of centrifugation, 15 min after contact between water and cement. Around 150 g of cement paste were centrifuged at 5000 rpm for 5 min. Afterwards, the supernatant was centrifuged again at 14500 rpm for 10 min. It is worth noting that the amount of missing polymer into the pore solution was called "adsorbed" for the rest of the paper, despite that a small part of polymer could be intercalated into hydrates due to early chemical interactions (23). Moreover, adsorption does not mean that the polymer becomes active in dispersing due to possible multilayer adsorption.

2.5.1 Total Organic Carbone (TOC) measurements:

The supernatant was diluted with hydrochloric acid solution at 0.1 mol.L⁻¹. The Total Organic Carbone (TOC) was determined by combustion at 850 °C with a Vario-TOC Cube (Elementar). The device was calibrated thanks to reference solutions of HPG and PCE.

2.5.2 Size Exclusion Chromatography (SEC) measurements:

Since the TOC measurements give the global amount of carbon in the solution, this method does not allow to quantify the amount of each polymer separately. An original method, involving the Total Organic Carbone (TOC) measurements and the Size Exclusion Chromatography analysis (SEC) was thus developed to achieve this objective. The SEC analysis was used to separate the two polymers (superplasticizer and polysaccharide) and to quantify the amount of PCE only, in the pore solution. After calibrating of the both analysis methods, the subtraction of the SEC results to the TOC results gives the amount of polysaccharide in the pore solution.

Size Exclusion Chromatography analyses were carried out on a Waters apparatus equipped with a pump Waters 916. The eluent was a 0.5 mol.L⁻¹ NaCl solution, on-line degassed. The flow rate was set to 0.5 mL.min⁻¹. A column Shodex OHpak SB-806M-HQ was used and kept at 50 °C in an oven. Detection was achieved thanks to a refractometer-type detector Waters 2410.

3. Results and discussion

3.1 Adsorption measurements

It was first checked if the SEC method is a suitable method to quantify the adsorption of PCE. For this purpose, adsorption measurements were carried out without polysaccharide, and the concentration in PCE, remaining into the pore solution, was determined by the both analysis methods. The concentrations obtained by Size Exclusion Chromatography (SEC) analysis were compared to those obtained by Total Organic Carbone (TOC) measurements (Figure 2). The results show a good correlation between the both methods (slope very close to 1 and correlation coefficient higher than 0.99), validating the suitability of the Size Exclusion Chromatography method for quantifying the amount of PCE remaining in the pore solution.

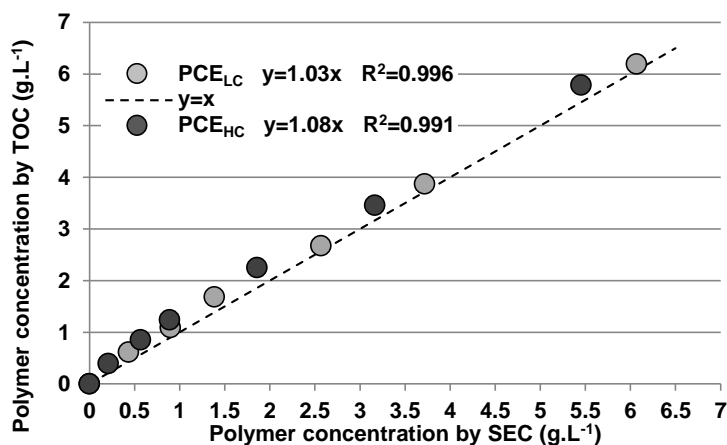


Figure 2. Comparison of SEC and TOC methods for the quantification of PCE adsorption.

The adsorption isotherms obtained by Size Exclusion Chromatography analysis for the both PCEs (high charge and low charge) are shown in Figure 3. The adsorption measurements of PCEs are represented by Langmuir model (solid line). The results show that the adsorption of PCE_{HC} is higher than that of PCE_{LC}, which is coherent with the charge density of the two PCEs (12), (24) and the greater size of PCE_{LC} molecules in the pore solution (result not shown here).

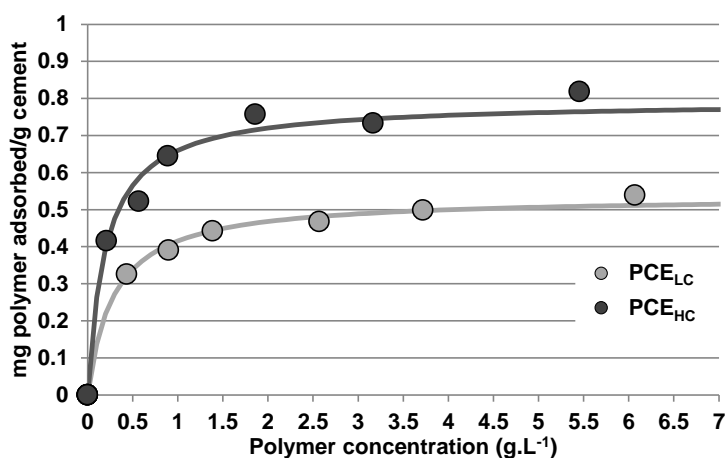


Figure 3. Adsorption isotherm of PCE_{LC} and PCE_{HC} alone determined by SEC analysis.

The amounts of PCEs adsorbed in presence of a constant amount of HPG1 or HPG3 are shown in Figure 4 and Figure 5. The adsorption isotherms of PCEs, HPG1 and HPG3 alone are also represented for comparison. The adsorption of HPGs (0.1%) is of 0.74 mg/g and 0.53 mg/g for HPG1 and HPG3, respectively, whereas the adsorption of 0.3% of PCEs reaches 0.55 mg/g and 0.82 mg/g for PCE_{LC} and PCE_{HC}, respectively. However, due to the great difference in molecular weight between HPG and PCEs, more molecules of PCE are adsorbed than HPG. The increase in hydroxypropyl substitutions on the guar (increasing MS_{HP} from HPG1 to HPG3) leads to a decrease in the adsorption of the admixture onto the solid surfaces. This result is consistent with previous studies conducted on HPGs and cellulose ethers (CE) in cementitious materials (25),(18) and can be ascribed to the decrease in the polarity of the polysaccharide and to the increase in the size of the molecules.

The results highlight that both admixtures (PCE and HPG) are able to adsorb even when they are added together in the cement pastes. The combination of the PCE, exhibiting the lowest charge density (PCE_{LC}), with HPG1 leads to a modification of the adsorption of the two polymers (Figure 4). Indeed, for the both admixtures, their amounts adsorbed are lower when the two polymers are introduced together in the mix

than when they are introduced separately. By increasing the dosage of PCE_{LC} from 0.1% to 0.3% bwoc, the adsorption is reduced from 7% to 5% and 13% to 20% for PCE_{LC} and HPG1, respectively.

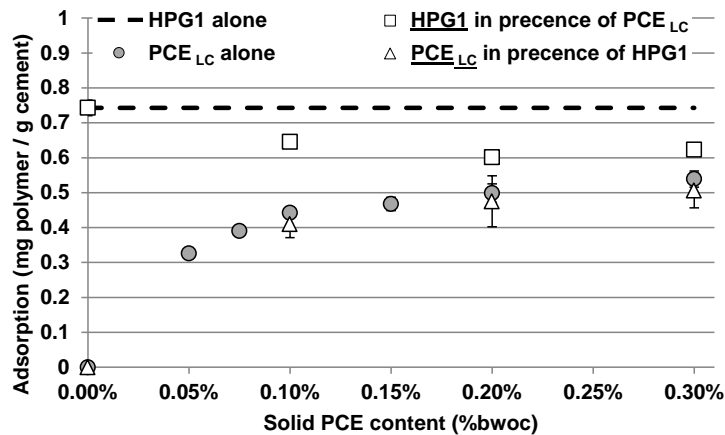
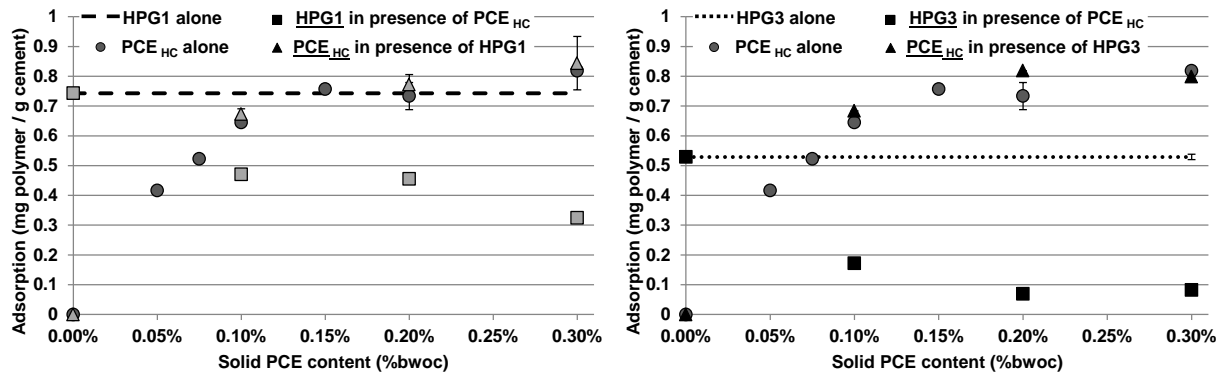


Figure 4. Adsorption isotherm of HPG1 alone, PCE_{LC} alone, HPG1 and PCE_{LC} when they are combined.

When the charge density of PCE increases (PCE_{HC}), the adsorption of the PCE seems to be unmodified by the presence of the HPG1 (Figure 5 (a)). It appears as if the adsorption of the HPG1 is strongly reduced by the presence of the PCE_{HC} . The drop of adsorption ranges from 37% to 56% when the dosage of PCE increases from 0.1% to 0.3% bwoc. These values correspond approximately to three times those obtained with the low charge density PCE.



(a) Adsorption isotherm of HPG1 alone, PCE_{HC} alone, HPG1 and PCE_{HC} when they are combined.

(b) Adsorption isotherm of HPG3 alone, PCE_{HC} alone, HPG3 and PCE_{HC} when they are combined.

Figure 5. Adsorption isotherm of HPGs alone, PCE_{HC} alone, HPGs combined with PCE_{HC} .

The combination of HPG3 with PCE_{HC} leads also to a low impact on the adsorption of PCE_{HC} but to a great reduction of the HPG3 adsorption (Figure 5(b)). The adsorption of HPG3 is reduced by 0.36 and 0.46 mg/g, for PCE concentrations of 0.1 and 0.2%, respectively. In comparison, the losses in adsorption are equal to 0.27 and 0.29 mg/g for HPG1. Despite a lower adsorption of HPG3 alone than HPG1 alone, HPG3 appears to be more sensitive to the presence of the PCE. This result tends to indicate that the bonding energy, involved in the adsorption mechanism between the HPG and the surface of cement phases, decreases when the MS_{HP} increases. However, the presence of 0.3% of PCE_{HC} leads to a reduction of approximately 0.45 mg/g in adsorption for the both polysaccharides, seeming to indicate an insufficient available surface for these latter.

All the measurements were realized with a high dosage in PCE (>0.1% bwoc) leading to a high surface coverage of the cement particles. This surface coverage becomes more and more close to the surface

saturation when the dosage in PCE increases (Figure 3). In these conditions, competitive adsorption between organic admixtures should occur (14). The results show clearly that the affinity of the polymer with the cement particles is a key factor in the competitive adsorption. The polymer with the highest affinity adsorbs first, leaving the remaining surface available for the second admixture. In the case of increasing dosage in PCE_{HC}, the available surface for the polysaccharide decreases, leading to a decreasing adsorption of HPG. When the charge density of the PCE is lower, the gap of affinity between the PCE and the polysaccharide is reduced, and competitive adsorption occurs.

3.1 Impact of admixtures on the rheological properties of fresh pastes

Figure 6 and Figure 7 show the evolution of the relative yield stress, extracted from Herschel-Bulkley model, and the relative residual viscosity for all the studied pastes (with and without admixture). The relative value (yield stress or residual viscosity) corresponds to the ratio of the value obtained for the admixed pastes to the value determined for the non-admixed cement paste. The use of increasing dosage in PCEs leads to continuous decrease in the yield stress and residual viscosity. The charge density of PCE impacts the evolution of the yield stress and the residual viscosity. Indeed, pastes admixed with PCE_{HC} exhibit a lower yield stress and a lower residual viscosity than pastes mixed with PCE_{LC}. This result is in agreement with the higher adsorption of PCE_{HC} which improves the steric repulsions and limits the contacts between cement particles. In our case, cement pastes admixed with 0.1% and 0.2% of PCE_{HC} give similar rheological behaviors than cement pastes mixed with 0.2% and 0.3% of PCE_{LC}, respectively. Consequently when the charge density of PCE decreases, higher dosage in PCE is required to obtain the same rheological behavior, and thus same slump flow (26).

The results show also that the presence of 0.1% of HPG (HPG1 or 3) leads to an increase in both yield stress and residual viscosity compared to the non-admixed paste. The results indicate that HPG is able to bridge two cement particles, which results in an increase of the yield stress (18). However, despite a strong drop of the adsorption with the increase in the MS_{HP} (from HPG 1 to 3) the yield stress increases. This suggests that the non-adsorbed polymer may be responsible for the yield stress increase. The rise in the polymer concentration in the pore solution induces an increase in the pore solution viscosity and/or depletion flocculation, which could compensate the loss of bridging.

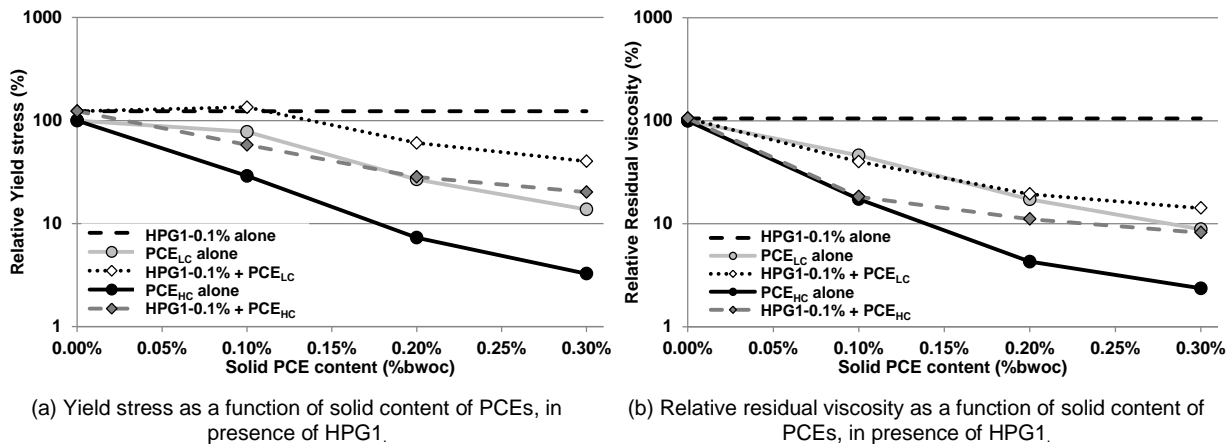


Figure 6. Effect of PCEs in presence of HPG1 on the rheological behavior of cement pastes.

When the PCEs are combined with HPGs, a general decrease in the yield stress and the residual viscosity is observed with increasing dosage in PCE. However, the yield stress is always higher than with PCE alone. In presence of HPG1, the impact of the dosage in PCE depends on the charge density of the PCE. For PCE_{HC}, a continuous decrease in the yield stress is observed, whereas a plateau followed by a decrease is noticed for PCE_{LC}. These tendencies are consistent with the adsorption results. The significant reduction in HPG adsorption induced by PCE_{HC}, leads to the progressive replacement of the bridging by the steric repulsions, and consequently, to the drop of the yield stress. In the case of the lowest dosage in PCE_{LC}, we showed that the reduction in adsorption of HPG and PCE was low. The

reduction in HPG adsorption could be sufficiently low to maintain enough bridging and thus a similar yield stress than with HPG alone. At higher dosage in PCE_{LC} , the steric repulsion induced by the superplasticizer adsorbed could be responsible to the decrease in the yield stress.

The combination of HPG with PCE_{LC} induces a low modification of the residual viscosity compared to the use of PCE_{LC} alone. However, the viscosity of the pore solution is quite similar than that obtained with HPG alone (results not shown here). This result indicates that the modifications of the colloidal and electrostatic forces induced by the PCE are greater than the modification of the hydrodynamic forces induced by the polysaccharide. For highly charged PCE, the increase in the pore solution viscosity induced by the reduction in HPG adsorption can justify the greater residual viscosity observed when the pastes are admixed with the combination of PCE and HPG compared to the PCE alone.

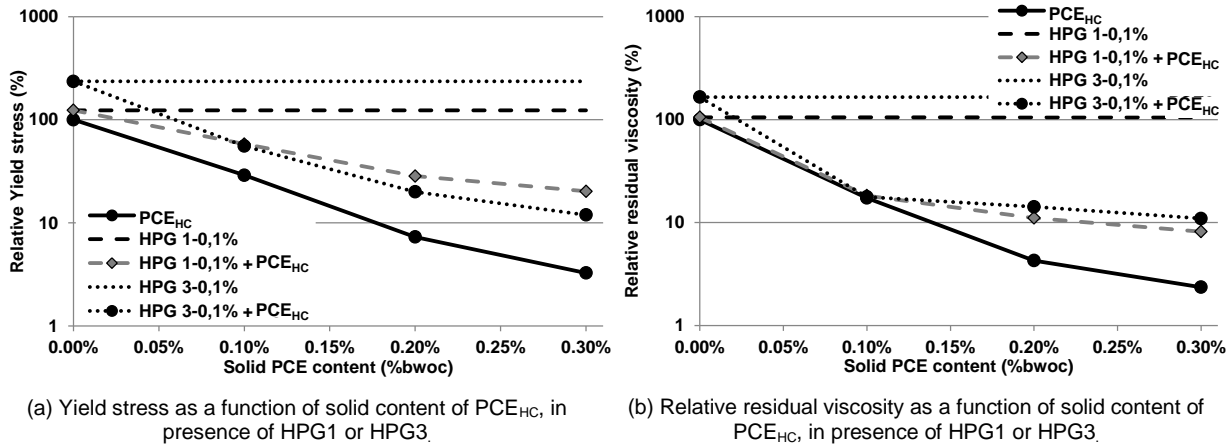


Figure 7. Effect of HPG1 and HPG3 in presence of PCE_{HC} on the rheological behavior of cement pastes.

Figure 7 shows the impact of HPG3 on the rheological behavior of cement paste admixed with PCE_{HC} . The results obtained with the combination of HPG1 with PCE_{HC} are also given for comparison. It appears clearly a strong decrease in the yield stress and the residual viscosity for increasing dosage in PCE. Despite that HPG3 provides a greater initial yield stress than HPG1, the yield stress decreases faster when PCE_{HC} is added. This signifies that the increase in the amount of HPG3 solubilized in the pore solution, resulting from the huge reduction in the adsorption of HPG3, is not sufficient to compensate the loss of bridging, and the steric repulsion induced by the PCE. However, this leads to an increase in the residual viscosity, in comparison with HPG1.

4. Conclusion

This paper deals with the effect of the combination of PCEs and HPGs on the adsorption and rheological behavior of cement pastes. An original method allowing the quantification of the adsorption of two admixtures was proposed. The results show that the combination of HPG with PCE superplasticizer strongly affects the adsorption of the polymers, more specially, leads to a decrease in the adsorption of the polysaccharide. Moreover, the combination of both admixtures modifies the rheological behavior of cement pastes. Despite the presence of HPG, the relative viscosity of the pastes decreased with increasing dosage in PCE. However, it allows maintaining a significant yield stress in the cement paste compared to PCE alone. The increase in the charge density of the PCE seemed to amplify the drop of the viscosity and to reduce the gain on the yield stress induced by HPG. The MS_{HP} seems also to slightly affect the rheological behavior by leading to a supplementary decrease in the yield stress and a supplementary increase in the viscosity.

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