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Combination of superplasticizers with hydroxypropyl guar, effect on cement-paste properties

Alexandre Govin[a*], Marie-Claude Bartholin[a], Wolfram Schmidt[b], Philippe Grosseau[a]

[a] École Nationale Supérieure des Mines, SPIN-EMSE, CNRS: UMR 5307, LGF, F-42023 Saint-Étienne, France

[b] Bundesanstalt für Materialforschung und -prüfung (BAM), Unter den Eichen 87, 12205 Berlin, Germany

[*] Corresponding author: Tel: +33 4 77 42 02 53

E-mail address: govin@emse.fr

Viscosity-modifying agent (VMA) are used in several applications of concrete, such as underwater concrete, Self-Compacting Concrete (SCC) or Self-Levelling Underlayments (SLU) in order to improve the washout resistance and the stability. The study focuses on the modifications of cement pastes properties implied when a VMA (hydroxypropyl guars or HPG) and a superplasticizer are introduced together. For reaching this objective, two chemically different polycarboxylate-based superplasticizers (PCE) and two HPGs exhibiting different molar substitution ratios (MS_{HP}), were studied. A method, combining total organic carbon and size exclusion chromatography, was developed in order to quantify the adsorption of the both admixtures. The adsorption of HPGs appears being significantly lowered by the presence of PCE, while only the adsorption of the less charged PCE is slightly affected by the HPG. As consequence, strong modifications of the rheological properties of cement pastes were noticed when HPG and PCE are combined. The desorption of HPG leads to higher yield stress and residual viscosity than with PCE alone.

Keywords: Admixture; Rheology; Adsorption; Polymers; Pore solution.

1. Introduction

For many years, cementitious materials exhibiting high fluidity have been developed motivated by their economic and technical advantages. In order to achieve this high fluidity, special admixtures were designed and introduced in the formulations of cementitious materials. Among the admixture classes, superplasticizers, also known as high-range-water-reducing (HRWR) admixtures, are commonly used for this purpose. These admixtures allow to dramatically reduce the amount of mixing water, while maintaining, or even enhancing the workability and the performances [1-3]. Today's typically used superplasticizers (SPs), based on polycarboxylate ethers (PCE), exhibit a comb-like structure. They consist of a polyanionic backbone partially esterified with non-ionic side chains of polyethylene oxide (PEO). The ionic charges, conferred by the deprotonated carboxylic groups in the backbone, allow the PCE to adsorb on the positively charged surfaces of cement particles and hydrated phases. The non-adsorbing side chains are responsible for the dispersing effect through steric repulsion forces between particles [2, 4-5]. According to Flatt et al., the adsorption of these admixtures depends mainly on the amount of free carboxylic groups, while the steric repulsions are influenced by the number and the length of the side chain [5]. However, inhomogeneities or poor stability, such as segregation or bleeding, may occur for highly flowable cementitious materials, which can compromise durability of concrete. To overcome this adverse effect, viscosity-modifying admixtures (VMA) are often introduced into the formulation [6-9]. VMA are widely used to improve stability, cohesion and robustness of many concrete applications, such as self-compacting concrete, self-leveling underlayment concrete, under water concrete, shotcrete… VMA may be classified as organic or inorganic-based materials as proposed by Kawai [10]. Inorganic VMAs consist in high specific surface area powders such as colloidal silica, fine silica fume, fly ash or calcium carbonate which increase the stability of highly flowable concrete, or swelling

materials such as bentonite for improving water retention. The organic VMAs are hydrophilic and water soluble polymers often classified into three classes, i.e. natural, semi-synthetic and synthetic polymers. Synthetic VMAs include mainly polyethylene oxide (PEO) or polyacrylamides, while natural and semi-synthetic VMAs consist mainly in natural polysaccharides (starch, welan gum, diutan gum, guar gum, xanthan gum, alginate, agar…) and their derivatives (cellulose ethers, modified starch, gar gum derivatives…). Among them, sphingan gums (welan and diutan gum), starch, cellulose ethers (hydropropyl methyl cellulose, hydroxylethyl cellulose, carboxymethyl cellulose), are the most frequently used. These admixtures cause modifications of the rheological behavior of the cementitious materials by increasing both the apparent viscosity and the yield stress [11-13]. The admixed cementitious materials generally exhibit a shear-thinning behavior. The viscosity mainly influences the properties of concrete during the flow process (casting and application), such as the filling velocity, the resistance to flow and the segregation stability during the flow. The yield stress is more linked to the properties of flowable concrete after casting by improving the stability at rest (no segregation) and the maintaining of the shape at rest.

The present paper is focusing on the influence of Hydroxypropyl Guar (HPG) as VMA in presence of PCE. HPGs are semi-synthetic polymers already widely used in many industrial fields, such as textile printing, hydraulic fracturing process, oil production or paper manufacturing [14,15]. These admixtures provide high water retention capacity in cementitious materials, making these admixtures suitable for the construction industry. Several studies were devoted to the estimation of the water retention capacity induced by the HPGs and to their mechanism of action [16-20]. The chemical structure of the HPGs, such as the molecular mass, the amount of hydropropyl groups grafted on the backbone, characterized by the MS (MS_{HP}), and the nature of the grafting, appear as crucial parameters for the water retention properties

[20, 21]. Indeed, these structural parameters affect the dosage necessary to reach the coil overlapping concentration, corresponding to the concentration from which, the isolated polymer coils, existing at low polymer concentration, come into contact. This overlapping leads to the establishment of polymer aggregates in the aqueous phase, which is responsible to the improvement of the water retention of cementitious materials [18, 20]. The HPGs also have capacity to enhance the stability of cementitious materials through the increase in either the yield stress and/or the viscosity [19, 20]. HPGs have the advantage of being less expensive than the microbial polysaccharides such as welan and diutan gum, and less impacting the environment than cellulose derivatives. Indeed, thanks to its chemical structure, guar gum is extracted by simple thermo-mechanical process and the chemical modification of the guar gum requires normal reaction conditions of temperature and pressure, generates less by-products and requires minimal purification procedure [22].

Since formulations developed by concrete industry become more and more complex and contain several admixtures, a better understanding of the effects induced by admixtures is essential. A sound interpretation of the mechanism is required for tailoring concrete performances for special practical applications. It was previously shown that the combination of admixtures may lead to competitive adsorption which can cause unintentional effects [23] but also enhance the effectiveness of the admixtures [24, 25]. Üzer and Plank studied the impact of welan gum on the dispersing ability of PCE [26]. The authors showed that the welan gum strongly reduced the fluidity induced by the PCE. According to them, the loss of fluidity is caused by the increase in the liquid phase viscosity, and no competitive adsorption between PCE and welan gum occurred. On the contrary, it is reported that competitive adsorption could occur when PCE is combined with cellulose ether [25]. Indeed, depending on PCE dosage, cellulose ether could be partially or totally desorbed by the presence of PCE, leading to

modification of the rheological behavior of cement pastes (decrease in the yield stress and increase in the viscosity).

The objective of this paper is to provide improvement in the understanding of synergetic or competitive effects between polycarboxylate-based superplasticizers and hydroxypropyl guars, by focusing on adsorption and rheology. In order to quantify the specific adsorption onto cement particles of both admixtures (HPG and PCE) upon combined addition to the mix, a suitable method is proposed. The method consists in a combination of total organic carbon (TOC) measurements and size exclusion chromatography (SEC) experiments. The consequence of the adsorption on the rheological properties of the cement paste is highlighted through the yield stress and the viscosity. The effect of the chemical composition and structure of HPGs is studied. For this purpose, two HPGs with an increasing amount of hydroxypropyl groups grafted were selected. Also two different PCEs were chosen in order to highlight the influence of the charge density of PCE.

2. Materials and methods

2.1. Mineral products

Ordinary Portland cement (CEM I 42.5 R CEMEX according to the European standard EN 197-1) was used for all the study [27]. The chemical composition and the phase composition of the cement were determined by X-ray fluorescence spectroscopy and XRD analysis (D5000, Siemens) combined with Rietveld refinement method (Siroquant V2.5). The results are given in Table 1.

Table 1 Oxide composition and clinker phase composition of cement (%, weight).

Chemical composition (% wt)									
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	free CaO	LOI
20.56	4.36	2.27	62.80	2.14	0.28	0.95	3.45	1.2	2.60

Phase composition (% wt)						
C_3S	C_2S	C_3A	C_4AF	CŠ	CŠ,0.5H	CČ
68.1	12.8	8.7	6.6	1.8	0.8	1.2

2.2. Organic admixtures

In this paper, two different commercial polycarboxylate-based superplasticizers (PCE), provided by BASF, were studied and labeled PCE_{LC} and PCE_{HC} respectively. Further details are given in Table 2. The main difference between the two superplasticizers lies in their charge density, which may strongly affect their performance [23]. Indeed, a high charge density should promote the adsorption of the admixture onto the cement surface [28, 29]. The carboxylate groups present in each PCE was determined by conductimetric titration using a 0.1 M NaOH solution. The anionic charge density supplied by carboxylate sites of superplasticizers (SPs) was expressed in mmol of charge per g of polymer. Between the two superplasticizers, PCE_{LC} and PCE_{HC} exhibit the lowest and the highest charge density, respectively (Table 2). This is consistent with the decreasing grafting degree from PCE_{LC} to PCE_{HC} and characterized by a decrease in the b/a ratio (Fig. 1(a)).

Table 2 Qualitative description of the PCEs and HPGs used.

	PCE_{LC}	PCE_{HC}	HPG1	HPG3
Backbone	Methacrylic acid, identical for both		-	-
Side chains	Polyethylene oxide (PEO)		-	-
Side chain length	Medium + low	Medium	-	-
Grafting degree	High	Low	-	-
Backbone charge density [a]	Low	High		
Backbone charge density [b] (mmol/g)	0.86	1.19	-	-
Solid content (%)	30	20	-	-
MS_{HP}	-	-	Low	High
Hydrodynamic radius (nm) *	13	10	26	35

[a] Given by the provider

[b] Determined by conductimetric titration

* Hydrodynamic radius (nm) was determined by Dynamic Light Scattering (DLS) (Zetasizer Nano ZS, Malvern Instrument) in 1M NaOH solution at 0.5g/L

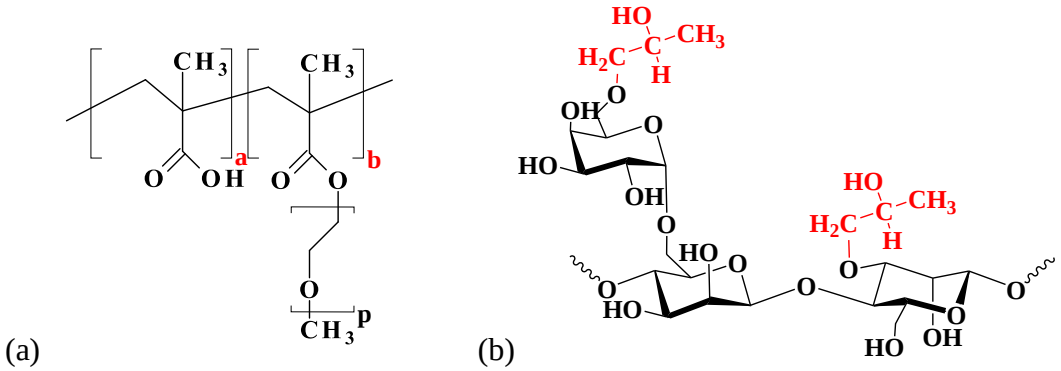


Fig. 1. Molecular structure of polycarboxylate ether (PCE) superplasticizer (methacrylic acid backbone and polyethylene oxide side chain) (a) and Hydroxypropyl Guar (b).

Briefly, the guar gum is a hydrophilic and non-ionic natural polysaccharide extracted from the endosperm of *Cyamopsis tetragonolobus* seed. Guar gum is composed of D-mannopyranose backbone (β(1-4) bond) with random branchpoints of galactose via an α(1–6) linkage. The manufacture of HPGs is more environmentally friendly than for cellulose derivatives since its extraction requires a simple thermo-mechanical process and its branched-chain structure, with a lot of hydroxyl groups, provides a high chemical reactivity and solubility in cold water [22].

Two hydroxypropyl guars (HPGs) were studied and provided by Lamberti S.p.A. They are qualitatively described in Table 2 and Fig. 1(b). The both polysaccharides exhibit similar molecular weight, around $2.10^6 g.mol^{-1}$[21]. The number of hydroxypropyl groups per anhydroglucose unit, characterized by the molar substitution (MS_{HP}) was less than 3 for the two HPGs (value provided by the manufacturers). However, HPG 1 and HPG 3 differ by their molar substitution ratio (MS_{HP}), which increases from HPG 1 to HPG 3 (qualitative description).

2.3. Preparation of cement pastes

The effect of admixtures was investigated on water-cement system, i.e. cement pastes, with a constant deionized water to solid ratio W/C=0.4. Prior to add water, the hydroxypropyl guar was hand-premixed with cement during one minute. The superplasticizers were added into the dry mix at the same time as the water. In order to maintain a constant water-to-cement ratio, the water contained into the PCE solution was taken into account and deduced from the total mixing water.

All admixtures were studied without pre-dissolution in order to be the closest to the application. The mixing was made in a blender according to EN 196-1 standard [30]. All the dosages in admixture were expressed in percent by weight of cement (% bwoc). The dosage in HPGs was fixed to 0.1% bwoc while the dosage in PCEs was ranged from 0.1% bwoc to 0.3% bwoc.

All tests were carried out in triplicate and at a controlled temperature (20 ± 2 °C). Cement without admixture was also studied and was considered as reference.

2.4. Rheological behavior

The rheological properties of cement pastes were investigated thanks to a Rheometer Viskomat NT (Schleibinger Geräte) equipped with a double gap cell and a basket probe made of a structured grid (Vogel cell). The room was thermostated at 20 °C.

At the end of the mixing procedure, the paste was introduced into the measurement cell and held at rest for several minutes. 9 min after contact between water and cement, the rheological protocol was started. The cement pastes were sheared at 100 s^{-1} for 1 min in order to homogenize the sample and to remove its shear history (potential thixotropic character) [31, 32]. The rheological tests were performed and recorded at 15 min (after 5 min of rest). The experimental protocol consisted in applying 14 decreasing shear rate steps, ranging from 100 s^{-1} to 0.06 s^{-1}, on the cement pastes. Since steady state is necessary to obtain valuable data, the duration of each step was adjusted.

The cement paste rheological properties was correctly described by Herschel-Bulkley (HB) model [33]:

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

where τ_0, K and n are the yield stress, the consistency coefficient and the fluidity index, respectively.

The fluidity index represents the shear-thinning or shear-thickening characteristic of a suspension.

The viscosity was examined through the residual viscosity. The residual viscosity was determined according to the following equation, as previously defined by Hot et al. [34].

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

Where μ_{app} corresponds to the apparent viscosity ($\mu_{app}=\frac{\tau_{(\dot{\gamma})}}{\dot{\gamma}}$) and τ_0 is the yield stress previously determined by Herschel-Bulkley model.

The advantage of the residual viscosity lies in the fact that the effect of the yield stress on the apparent viscosity is subtracted [34]. The contribution of the energy required to break the inter-

particle network, responsible of the yield stress, and to overcome the van der Waals attractive force are deducted. Consequently, the residual viscosity becomes more representative of the energy dissipation when the suspension flows.

2.5. Viscosity of the aqueous phase

The rheological properties of the supernatant was investigated by means of a rheometer (MCR 302, Anton-Paar) equipped with cone and plate geometry (2° cone angle, 50 mm diameter), thermostated at 20°C. The supernatant was extracted as described in the next section (section 2.6. dedicated to the adsorption measurements). The steady shear flow of aqueous phases was investigated using decreasing logarithmic ramps in the 10^3 - 1 s^{-1} range.

Flow curves ($\eta = f(\dot{\gamma})$), exhibiting typical shear thinning behavior with a Newtonian region in the low shear rate range, were correlated with the Cross model [35]:

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

where η_0 is the zero-shear rate viscosity, η_∞ the infinite rate viscosity, α a relaxation time and n a non-dimensional exponent.

The aqueous phase viscosity was characterized by the zero-shear rate viscosity which represents the viscosity at the Newtonian plateau occurring at low shear rate.

2.6. Adsorption measurements

In order to obtain the adsorption isotherms, the non-adsorbed polymer remaining within the aqueous phase was quantified. The adsorption was calculated using the depletion method. The aqueous phase of fresh cement paste (around 150 g) was first extracted, 15 min after the mixing start, by means of a centrifugation step (5000 rpm for 5 min). A second centrifugation step (14500 rpm for 10 min) was applied to the previously extracted supernatant for avoiding the

presence of particles in the solution. Despite that a small amount of polymer could be intercalated into the hydrates due to early chemical interactions [36], the amount of missing polymer in the aqueous phase was considered as “adsorbed” for the rest of the paper.

Total Organic Carbon (TOC) measurements:

Prior to analysis, the extracted supernatant was diluted 10 times with 0.1 mol.L^{-1} hydrochloric acid solution. The total organic carbon content in the extracted solutions was determined by combustion under pure oxygen at 850°C (Vario-TOC Cube, Elementar). Reference solutions of HPG (250mg/L) and PCE (650mg/L) were used to calibrate the device for each experimental series. The initial organic carbon contained in pure cement, such as grinding aids, was taken into account and deduced after its quantification in cement aqueous phase without admixture.

Size Exclusion Chromatography (SEC) measurements:

In the present paper, two kinds of admixtures containing carbon (HPG and PCE) were introduced in the cement pastes. TOC analysis is a suitable method for quantifying the adsorption of each admixture when they are introduced separately. However, when the two admixtures are introduced together in the cement paste, TOC method is not able to differentiate the origin of the carbon content. A specific method was therefore developed to determine the concentration of the two admixtures in the aqueous phase. In order to quantify solely the amount of PCE in the aqueous phase, size exclusion chromatography (SEC) was selected. This chromatographic method separates molecules relating to their size and hydrodynamic radii. Fig. 2(a) shows that thanks to the high difference in the molecular weight of the both kind of admixtures (HPGs and PCEs) studied here, the respective peaks are sufficiently separated for a suitable integration of the peak area ascribed to PCE (from 16.4 to 21 min). As all

chromatographic analysis, the peak area is proportional to the polymer concentration. The calibration curves obtained by SEC for the both PCEs are given Fig. 2(b).

These highlight a great proportionality between the integrated signal given by the refractive index detector and the PCE concentration. After calibrating of the both analysis methods (SEC and TOC), the PCE concentration was first quantified by SEC and subtracted to the TOC concentration. This allows to calculate the HPG concentration remaining in the aqueous phase.

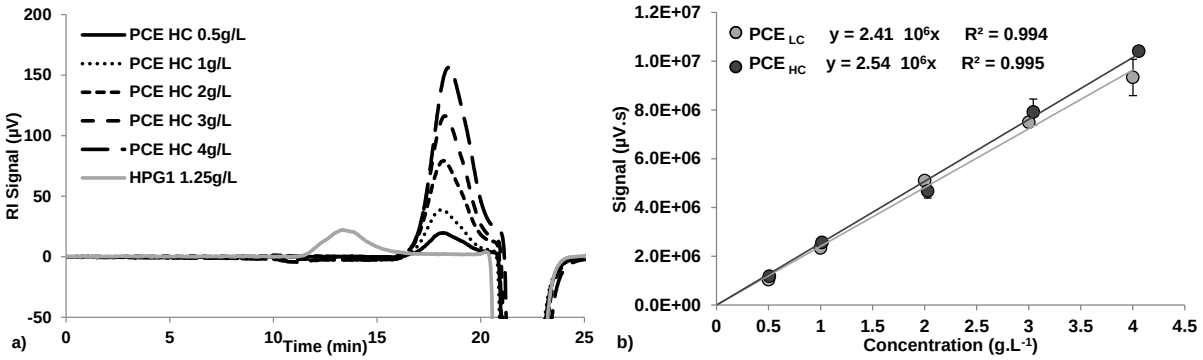


Fig. 2. Illustration of SEC analysis for different concentrations in PCE_{HC} (0.5 to 4 g/L) and for HPG1 (1.25g/L) (a), calibration curves obtained from chromatograms for PCE_{LC} and PCE_{HC} (b).

SEC investigations were performed on a Waters apparatus (pump Waters 916). A 0.5 $mol.L^{-1}$ NaCl solution, on-line degassed, was used as eluent. The flow rate was fixed at 0.5 $mL.min^{-1}$. The separation module consisted in Shodex column (OHpak SB-806M-HQ) heated at 50 °C. A refractometer detector (Waters 2410) was used to achieve the detection.

3. Results and discussions

3.1. Adsorption curves and discussion

The methodology was first validated by comparing the concentration of each PCE (introduced alone) given by SEC and by TOC analyses, which is the commonly technique used for quantifying organic polymer adsorption onto cement particles. The results in Fig. 3 confirm that the concentrations of PCEs obtained by SEC and by TOC are identical. This validates the use of SEC as a suitable method for quantifying the amount of PCE remaining in the aqueous phase and thus its adsorption.

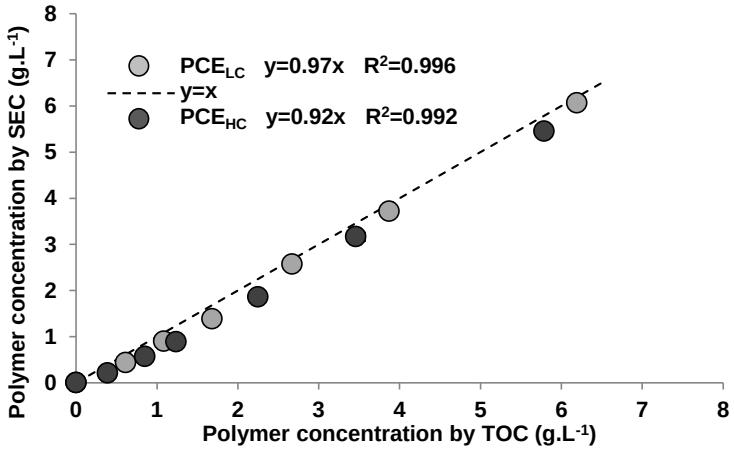


Fig. 3. Validation of the quantification method by correlating the PCE adsorption determined by TOC and SEC methods.

The adsorption isotherms for the two PCEs and for the two HPGs are depicted in Fig. 4. Here the amount of polymer consumed (or adsorbed) was plotted versus the equilibrium polymer concentration in the aqueous phase. The resulting curves were obtained after fitting of the experimental data through the Langmuir equation (solid and dash lines) written as follow:

$$Q_{ads} = Q_{plateau} \frac{Kc}{1+Kc} \quad (4)$$

Where Q_{ads} (mg of polymer /g of cement) is the amount of polymer adsorbed, $Q_{plateau}$ the maximum amount of polymer adsorbed, K (L/g) the Langmuir sorption equilibrium constant corresponding to the ratio of adsorption and desorption rates ka and kd (the rates are equal at the equilibrium), and c (g/L) the equilibrium concentration in solution.

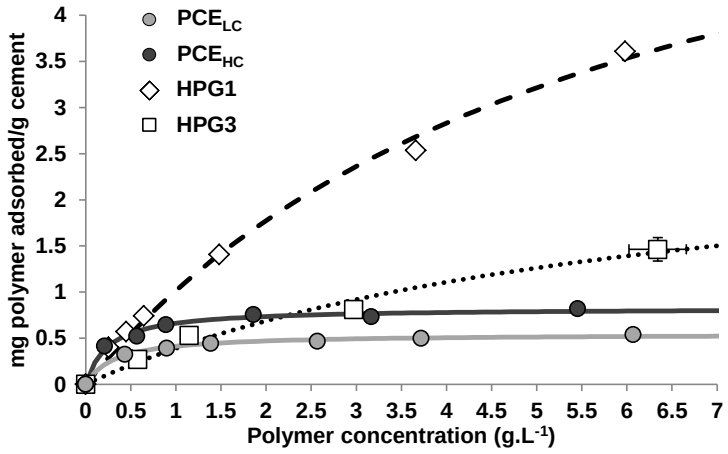


Fig. 4. Adsorption isotherm for PCE_{LC} (⊙), PCE_{HC} (●), HPG1 (◇) and HPG3 (□).

The maximum adsorbed amount ($Q_{plateau}$) and the Langmuir constant (K) are summarized in Table 3 for the four polymers

The Fig. 4 and Table 3 highlight the higher adsorption of PCE_{HC} than PCE_{LC}. Indeed, PCE_{HC} exhibits higher affinity and plateau value than PCE_{LC}, which is coherent with the difference in the charge density, the grafting degree and the molecule size of the two PCEs. Indeed, lower side chain density and higher charge density promote the adsorption of PCEs on cement surface [23, 28, 37-39].

Table 3 Langmuir parameters for adsorption of PCEs and HPGs after fitting of experimental data.

	PCE_{HC}	PCE_{LC}	HPG1	HPG3
Maximum adsorbed amount $Q_{plateau}$ (mg/g)	0.83	0.55	7.01	2.86
Langmuir equilibrium constant K (L/g)	4.01	3.09	0.17	0.16

For HPGs, it is important to point out that no real plateau was reached and the given value was determined by extrapolation for comparison (Fig. 4, Table 3). It has been previously showed that HPGs can also adsorb on mineral surface, and therefore on cement particles and the depleted amount of HPG determined by the depletion method was not the result of physical entrapment of polymer molecules into the inter-particles space during the centrifugation step [20, 40]. However, it can be mentioned here that the nature of the interaction, i.e. electrostatic interaction or hydrogen bonding with the polar cement phases, is not fully known.

The increase in hydroxypropyl substitutions grafted on the guar (increasing MS_{HP} from HPG1 to HPG3) results in a drop in the adsorption plateau without significantly changing the Langmuir constant. These results are consistent with previous studies conducted on HPGs or cellulose ethers (CE) in cementitious materials [20, 41] and may be attributed to conformational differences induced by the decrease in the polarity of the polysaccharide, and to the increase in the hydrodynamic radius of the molecules.

HPGs exhibit greatly lower Langmuir constant than PCEs. This result highlights the better affinity of PCEs with the surface of cementitious particles than HPGs. The difference in affinity between the two admixtures may result from their strongly different chemical nature and their behavior in alkaline media. Indeed, many parameters may influence the adsorption and/or competitive adsorption of polymers, such as their chemical composition, molecular structure, molecular mass, the pH, the ionic strength… [42-44]. The difference in affinity was checked

by zeta potential measurements carried out on admixture solutions. In order to be close to real cementitious solution in term of composition, ionic strength, pH…, the admixture (HPG or PCE) was dissolved into a cement pore solution (without cement particles). The pore solution was previously extracted by centrifuging a non-admixed cement paste (W/C=0.4) as described in section 2.6. Then, admixture was dissolved in the pore solution in order to reach a concentration of 1 $g.L^{-1}$. The zeta potential of HPG-based fluid was around -15mV. The negative zeta potential indicated that the guar gum molecules contained chemical groups that could produce negative charges. As proposed by Wang et al. [45], this negative zeta potential indicates that, in alkaline media, the guar gum molecules interact with OH^- anions to form hydrogen bonds, leading to negatively charged side chains. This is consistent with the large amount of polar groups on HPGs, such as hydroxyl groups, leading to interactions between the admixtures and the polar cement phases [40, 46]. However, a strongly lower zeta potential (around -60mV) was obtained when the PCE was dissolved in the cement pore solution (without cement particles). This is coherent with the fact that polymethacrylic acid should be fully deprotonated at pH higher than 10 [47]. As consequence, in aqueous phase of fresh cement paste, which is highly alkaline (pH $\approx$ 12.5), the PCEs can strongly chelate with Ca^{2+} ions as counter-ions on the mineral surface [29] promoting its adsorption on the surface of cement particles through electrostatic interactions [48].

The adsorption isotherms for the two PCEs (PCE_{LC} and PCE_{HC}), in presence of 0.1% of HPG (HPG1 or HPG3), are depicted in Fig. 5, Fig. 6 and Fig. 7. In addition, the adsorption values of each admixture (PCE_{LC}, PCE_{HC}, 0.1% of HPG1 and 0.1% of HPG3) introduced alone in the cement paste was represented for comparison.

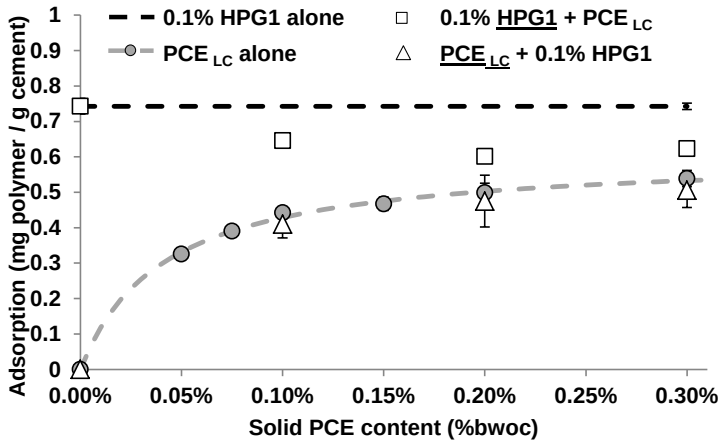


Fig. 5. Adsorption isotherms of HPG1 alone (▬ ▬.), PCE_{LC} alone (-○-), HPG1 (□) and PCE_{LC} (△) when they are combined.

The most important point is that PCE and HPG adsorb onto the surface of cement particles, even when they are introduced together in the pastes (Fig. 5, Fig. 6 and Fig. 7). However, the absence of adsorption regimes where both admixtures adsorb as they are alone in the cement paste is noticed. This regime could exist but at lower dosages than those tested in this paper because it requires low surface coverage to avoid competitive adsorption [49]. By increasing the dosage in admixtures, the surface coverage becomes sufficiently high to expect competitive adsorption between admixtures [25, 49]. It is why all the experiments in this study, were carried out with high admixture dosages (> 0.1% bwoc for the PCE and 0.1% bwoc for HPG) in order to enforce a high surface coverage of the cement particles and then to promote competitive adsorption.

The combination of PCE_{LC} with HPG1 leads to reduction in the adsorption of the two polymers in comparison with when they are introduced alone (Fig. 5). The results are depicted in Fig. 8 and expressed in mg of polymer adsorbed per g of cement, and in percentage in relation to the adsorption of the admixture introduced alone in the mix. The reduction in adsorption ranges

from 7% to 5% for PCE_{LC} and from 13% to 20% for HPG1, with increasing dosage in PCE_{LC} (from 0.1% to 0.3%).

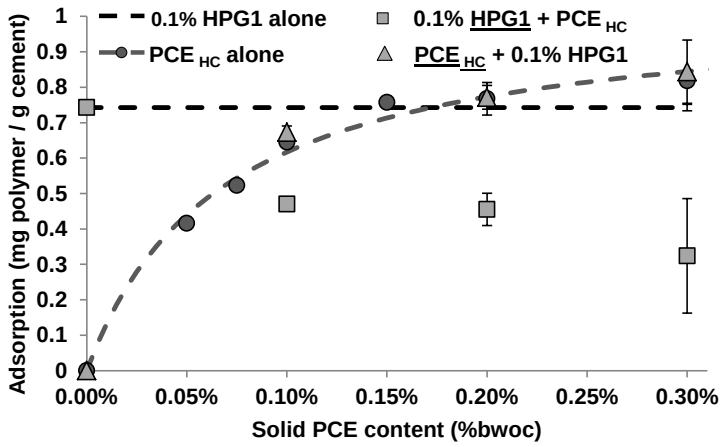


Fig. 6. Adsorption isotherms of HPG1 alone (▬ ▬), PCE_{HC} alone (●), HPG1 (□) and PCE_{HC} (△) when they are combined.

The effect of the charge density of PCE is highlighted in Fig. 6. It appears obvious that the charge density of the superplasticizer affects the behavior of the admixtures. Indeed, when the charge density of PCE increases (PCE_{HC}), its adsorption is unmodified by the presence of HPG1. On the contrary, a strong reduction in the adsorption of HPG1 is pointed out in presence of PCE_{HC}. The reduction in adsorption ranges from 37% to 56% with increasing dosage in PCE (from 0.1% to 0.3%). These values are approximately three times higher than those obtained with the low charge density PCE (Fig. 8).

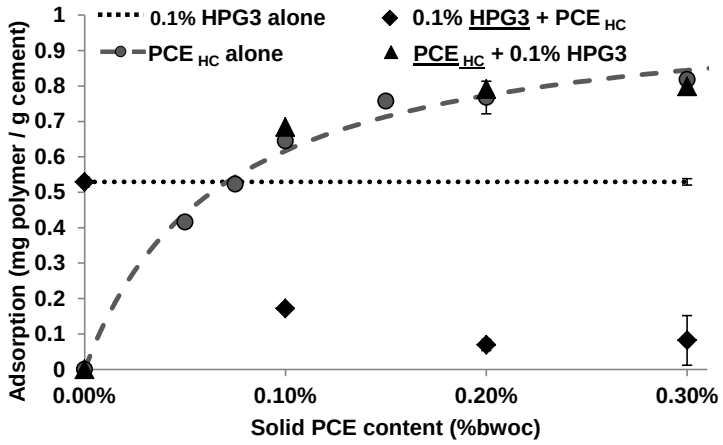


Fig. 7. Adsorption isotherms of HPG3 alone (**.....**), PCE_{HC} alone (-●--), HPG3 (◆) and PCE_{HC} (▲) when they are combined.

The combination of PCE_{HC} with HPG3 (higher MS_{HP} than HPG 1) leads also to a negligible modification of the adsorption of PCE_{HC} but to a huge reduction of HPG3 adsorption (Fig. 7). For PCE concentrations of 0.1 and 0.2 %, the adsorption of HPG3 is reduced of about 0.36 mg/g and 0.46 mg/g, respectively. These values correspond to a strong drop in adsorption of about 67 % and 87%, respectively (Fig. 8). In comparison, for the same concentrations in PCE_{HC}, the reduction in adsorption was only of 37% and 39% (0.27 mg/g and 0.29 mg/g) for HPG1, respectively. Despite a lower adsorption of HPG3 without PCE, than HPG1, HPG3 appears to be more sensitive to the presence of the PCE. This result may indicate a decrease in the bonding energy, involved in the adsorption mechanism between the HPG and the surface of cement phases, induced by the MS_{HP} increases. The presence of 0.3% of PCE_{HC} leads to a reduction in adsorption of approximately 0.45 mg/g for the both HPGs (HPG3 and HPG1), indicating an insufficient surface available for the polysaccharide, whatever the HPG.

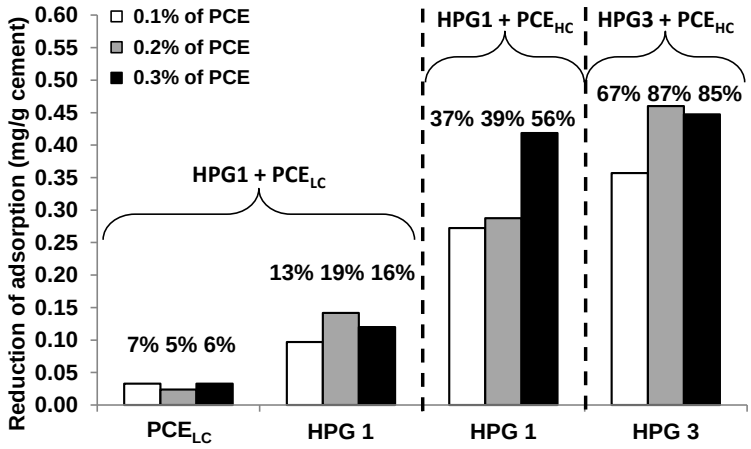


Fig. 8. Reduction in the adsorption of: PCE_{LC} and HPG1 when they are introduced together, and HPG1 and HPG3 when they are combined with PCE_{HC}. The results are expressed in mg/g of cement and in percentage in relation to the adsorption of the admixture introduced alone.

From the results, it appears clearly that the affinity of the polymer with the cement particles is a key factor in the process of competitive adsorption. Indeed, the polymer with the highest affinity and/or diffusion mobility adsorbs first, leaving only the remaining surface or adsorption sites, available for the second admixture. Here, the PCEs exhibit higher affinity than the HPGs (Table 3), causing that the PCE adsorbs first followed by the HPG.

When the dosage in PCE_{HC} increases the steric hindrance and the reduction of free adsorption sites lead to a decreasing surface available for the polysaccharide. As consequence, the adsorption of this latter is reduced. It is worth noting that even at 0.3% bwoc of PCE_{HC}, the HPG is able to adsorb since its adsorption is not null. This result suggests that either the dosage in PCE is not enough to completely inhibit the adsorption of the HPG, or a low adsorption of HPG is still possible through a potential change in conformation of the adsorbed molecule, or interactions between the HPG and the adsorbed PCE occur, or a low amount of HPG is entrapped during the hydration process. Furthermore, the cement hydrates continue to grow

providing additional free surfaces for adsorption. More investigations are needed to conclude on this point.

It can also not be excluded that the adsorption of PCE is favored in comparison to the guar gum because of the higher mobility of PCE in the aqueous phase. Indeed, the kinetic aspects of the adsorption were neglected here. The initial adsorption rate may contribute to the preferential adsorption of the PCE compared to the HPG. Indeed, Hoogeveen et al. showed that initial adsorption rate is usually controlled by the rate of transport, and then by the diffusion coefficient, of the non-adsorbed polymer from the bulk solution to the surface which is promoted by the small size of molecules [43]. As consequence, the adsorption of PCE may be kinetically stimulated, since PCE exhibited a lower size than HPG (Table 2). The dissolution kinetic of admixtures was also neglected. In the present study, the HPG was not pre-dissolved in the mixing water, whereas the PCEs were provided in aqueous solution (20 or 30% of PCE solid in water depending on the PCE). Obviously, the HPG needs first to dissolve prior to adsorb onto the surface of cement particles. The dissolution step could, therefore, limit the amount of HPG adsorbed at 15 min despite that at least 85% of HPG is dissolved after the 5 min of the mixing protocol [20].

Competitive adsorption between the PCE and the polysaccharide may occur if the PCE charge density decreases. In this case, the gap of affinity between each admixture and the surface of cement particles is reduced. Therefore, the two admixtures tend to adsorb together, leading to steric hindrance and a drop in the surface available for the both admixtures.

3.2. Rheological properties of fresh cement pastes

This section is dedicated to the impact of the competitive adsorption on the rheology of the cement pastes. The evolution as a function of the PCE dosage of the two rheological parameters

studied in this paper, i.e. the yield stress obtained from Herschel-Bulkley model and the residual viscosity, are represented in Fig. 9 and Fig. 10.

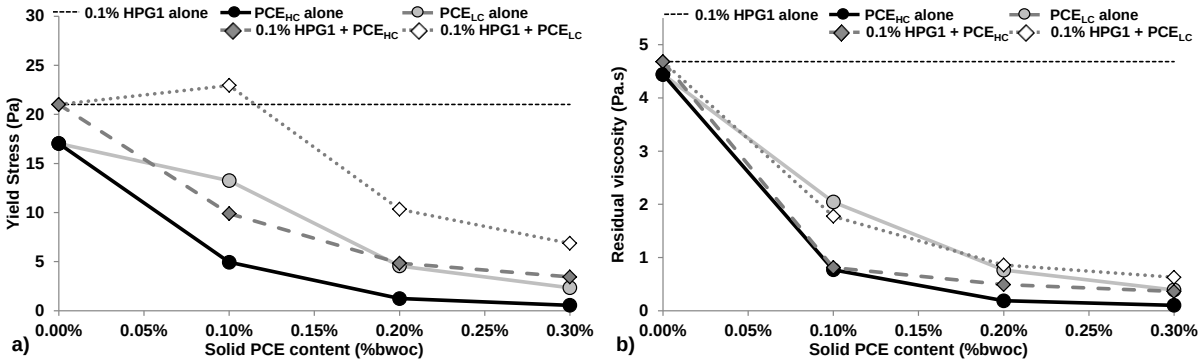


Fig. 9. Effect of the PCE charge density (PCE_{LC} and PCE_{HC}) on the yield stress (a) and the residual viscosity (b), with or without 0.1% of HPG1.

0.1% HPG1 alone (▬ ▬), PCE_{HC} alone (●—), PCE_{LC} alone (○—), 0.1% HPG1 + PCE_{HC} (◆ ▬ ·) and 0.1% HPG1 + PCE_{LC} (◇ ···)

As expected, the yield stress, as well as the residual viscosity, decreases by adding PCE into the cement pastes (Fig. 9). Moreover, higher is the PCE dosage; lower are the two rheological parameters. The steric repulsive forces induced by the adsorbed PCE lead to a reduction of the Van der Waals attractive forces, which causes the reduction of the yield stress. The increase in adsorbed PCE with its dosage contributes to the rise of the inter-particle distance, which may be responsible to the drop in the residual viscosity. The yield stress, as well as the residual viscosity, is also affected by the charge density of PCE. Indeed, for a given dosage, the two rheological characteristics are lower for the pastes admixed with PCE_{HC} than with PCE_{LC}. This is consistent with the greater adsorption of PCE_{HC} (Fig. 4). Indeed, steric repulsions and limitation of contacts between cement particles are improved by high adsorption. It is interesting to note that higher dosage in PCE is required in order to reach similar rheological

behavior when the charge density of PCE decreases. This is in accordance with a previous study [50]. In our study, the addition of 0.1% bwoc of PCE_{HC} leads to same values of yield stress and residual viscosity than 0.2% bwoc of PCE_{LC}. For 0.2% bwoc of PCE_{HC}, 0.3% bwoc of PCE_{LC} is required.

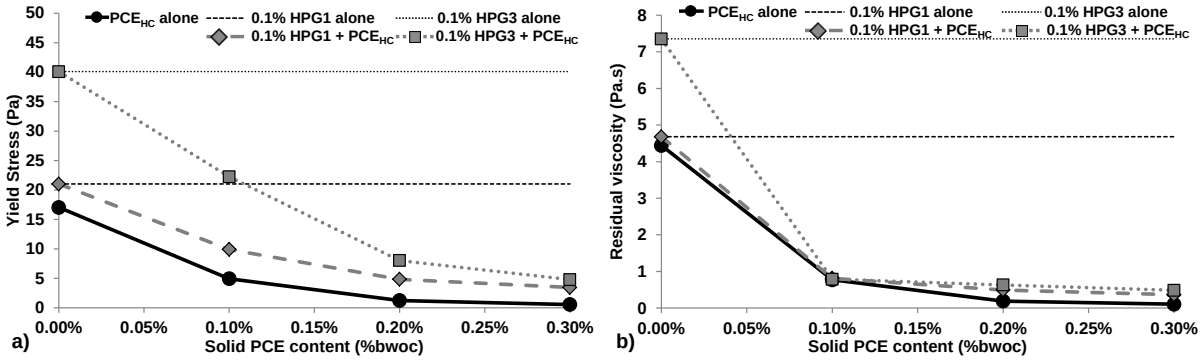


Fig. 10. Effect of the MS_{HP} of the HPG on the yield stress (a) and the residual viscosity (b) when the HPGs (0.1% of HPG1 and 0.1% of HPG3) are combined with PCE_{HC}.

PCE_{HC} alone (—●—), 0.1% HPG1 alone (▬ ▬), 0.1% HPG3 alone (.....), 0.1% HPG1 + PCE_{HC} (—◆— ·) and 0.1% HPG3 + PCE_{HC} (···■···)

Fig. 9 and Fig. 10 also show the increase in both yield stress and residual viscosity when 0.1% bwoc of HPG is introduced alone into the cement paste. This finding is consistent with the observation that polysaccharides, such as HPGs or cellulose ethers, can adsorb on cement particles, increasing the yield stress through bridging flocculation [20, 41]. However, a strongly higher yield stress is obtained with the HPG exhibiting the highest MS_{HP} (HPG3), despite an important reduction in its adsorption, and therefore in its possible bridging capacity (Fig. 10). The decrease in adsorption of the HPG3 leads to the rise in the concentration of the non-adsorbed polysaccharide molecules remaining in the aqueous phase. This rise in the non-adsorbed HPG coils could compensate the loss of bridging by increasing either the viscosity of

the aqueous phase and/or attractive depletion flocculation forces [51]. The increase in viscosity of the interstitial fluid is highlighted in Fig. 11(b), where the zero-shear viscosity of the aqueous phase of the cement paste admixed with HPG3 is twice higher than that obtained with HPG1. The increase in the residual viscosity is also a consequence of the partial adsorption of HPG. Indeed, as mentioned previously, the viscosity of the aqueous phase, and therefore the viscous dissipation, is promoted by the non-adsorbed HPG coils [46, 52-53]. However, it can be noted that polysaccharides could induce specific additional repulsive forces which lead to a lower increase in cement pastes viscosity than expected by the rise of the aqueous phase viscosity [46, 52-53].

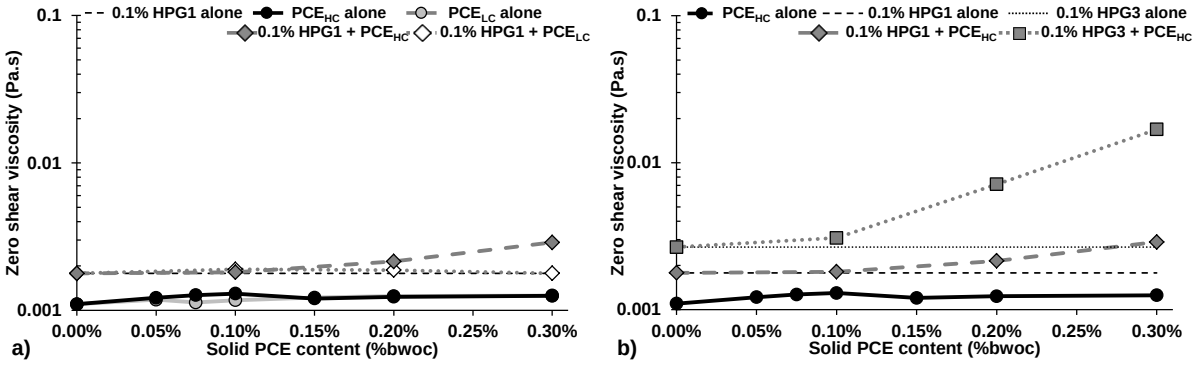


Fig. 11. Evolution of the aqueous phase zero-shear viscosity as a function of the PCE dosage: (a) HPG1 with PCE_{HC} and PCE_{LC} (0.1% HPG1 alone (- - -), PCE_{HC} alone (—●—), PCE_{LC} alone (—○—), 0.1% HPG1 + PCE_{HC} (—◆ ·) and 0.1% HPG1 + PCE_{LC} (···◇···)), (b) HPG1 and PHG3 with PCE_{HC} (0.1% HPG1 alone (- - -), 0.1% HPG3 alone (.....), PCE_{HC} alone (—●—), 0.1% HPG1 + PCE_{HC} (—◆ ·) and 0.1% HPG3 + PCE_{HC} (···■···))

When an increasing dosage in PCE is combined with 0.1% of HPG, a general decrease in both yield stress and residual viscosity is observed (Fig. 9 and Fig. 10). However, whatever the PCE dosage, the combination of the two admixtures leads always to a higher yield stress than PCE

alone. This could be the result of the attractive depletion force induced by the non-adsorbed polysaccharide. Depletion forces are the results of osmotic effect induced by differences in concentration of non-absorbing polymer in a suspension. In order to reach equilibrium, the polymer molecules move to the lower concentration zone, leading to attractive or repulsive depletion forces between particles. A recent paper was dedicated to the study of the effect of depletion forces induced by the non-adsorbing polymer on the yield stress [54]. The authors showed that in a system containing a superplasticizer, as well as, polyethylene oxide glycol (PEG), the non-adsorbing polymer coils (PEG) could be at the origin of attractive depletion forces between particles. In this case, the attractive depletion forces participate to the flocculation mechanism, characterized, at macroscopic scale, by an increase in the yield stress. The charge density of the PCE also affects the evolution of the rheological parameters when PCE is combined with HPG. The yield stress continuously decreases with increasing dosage in PCE_{HC}, while a plateau followed by a decrease is observed with PCE_{LC}. These evolutions are coherent with the gradual reduction in HPG adsorption induced by PCE_{HC} (Fig. 5 and Fig. 6). Consequently, the bridging created by the adsorbed HPG is gradually replaced by the steric repulsive forces induced by the adsorbed PCE. In the case of PCE_{LC}, it may be assumed that the drop in HPG adsorption could be sufficiently low to preserve bridging and the low desorption of PCE_{LC} limits the steric repulsive forces. These two effects allow to maintain a comparable yield stress than with HPG1 alone. When the dosage in PCE_{LC} is higher than 0.1% bwoc, the steric repulsion forces implied by the PCE leads to the decrease in the yield stress.

The residual viscosity of the cement paste is also affected by the combination of HPG1 and PCE_{LC}. However, the residual viscosity is slightly different than that obtained with PCE_{LC} alone, while the aqueous phase exhibits similar viscosity than with HPG1 alone (Fig. 11(a)).

These results indicate that the rise of the hydrodynamic forces induced by the non-adsorbed polysaccharide is not sufficient to overcome the modifications of the colloidal and electrostatic forces induced by the PCE. When the charge density of the PCE rises, it was previously shown that the concentration of non-adsorbed HPG increases (Fig. 8), as well as the viscosity of the aqueous phase (Fig. 11(a)). This can justify the greater residual viscosity of the pastes obtained with the combination of PCE and HPG than with the PCE alone.

The impact of the MS_{HP} on the rheological behavior of cement paste admixed with PCE_{HC} and HPG is illustrated in Fig.10. In presence of HPG3, a strong reduction in the yield stress, as well as the residual viscosity, can be observed for increasing dosage in PCE_{HC}. Despite HPG3 provides a greater initial yield stress than HPG1, the yield stress decreases faster when PCE_{HC} is added. This means that the increase in the amount of non-adsorbed HPG3 in the aqueous phase, resulting from its huge desorption and which may promote attractive depletion forces, is not sufficient to compensate the loss of bridging, and the steric repulsion induced by the PCE. However, the high amount of HPG coils in the aqueous phase contributes to the great increase in the aqueous phase viscosity (Fig. 11(b)), and therefore to the residual viscosity of cements pastes compared to cement paste admixed with PCE alone.

4. Conclusions

This paper deals with the effect of the combination of PCEs and HPGs on their adsorption and on the rheological behavior of admixed cement pastes. A suitable method composed of TOC and SEC analyses is proposed. This method allows the quantification of the relative adsorption of the two different admixtures present in a cement paste. This method could be used, in further

researches, to study the effect of the combination of superplastisizers and VMA in flowable industrial applications, such as Self-Compacting Concrete (SCC) or Self-Levelling Underlayments (SLU). The results show that the adsorption of the two polymers may be affected when HPG is combined with PCE superplasticizer. More specially, the adsorption of the polysaccharide decreases. However, if the charge density of the PCE decreases, this admixture becomes sensitive to the presence of the polysaccharide and its desorption may occur.

The consequences of the adsorption/desorption of admixtures on rheological properties of cement pastes are studied. It was shown that the rheological properties are strongly modified by the addition of the two kinds of admixtures. Despite the introduction of the HPG, the relative viscosity of the cement pastes decreased when the dosage in PCE increases. However, the residual viscosity is higher than with PCE alone. This may be the consequence of the increase in concentration of the non-adsorbed HPG coils in the aqueous phase resulting from the reduction in adsorption. The mixture of PCE with HPG allows preserving a significant yield stress to the cement paste in comparison to PCE alone. The charge density of the PCE seems to affect the rheological properties by amplifying the drop of the viscosity and by reducing the improvement of yield stress induced by HPG. The MS_{HP} mainly affects the yield stress of the cement paste and the viscosity of the pore solution but leads to lower effect on the viscosity of the cement paste. According to the results, HPG3 (high MS) may be more suitable for SCC application than HPG1 since the yield stress could be sufficiently low to allow the flow while the viscosity of the paste is greater in order to improve the stability.

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