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Effect of the repartition of the PEG side chains on the adsorption and dispersion behaviors of PCP in presence of sulfate

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We studied how the repartition of the negatively charged groups/PEG side chains along the polycarboxylate comb-like copolymers influences the dispersant behavior of these comb copolymers. Performing a RAFT copolymerization allowed providing well defined copolymers differing only in the repartition (gradient or random) of the charged groups along the backbone. Calcite suspensions were used to mimic early age cementitious materials. Our results highlight how the distribution of the comonomers modifies PCP adsorption behavior: the "gradient" PCP is less sensitive to the sulfate competitive adsorption. This has a strong effect on the PCP dispersant behavior. Indeed, we confirmed that the dispersion efficiency is very well correlated with the amount of adsorbed PCP: a unique relationship "yield stress–amount of PCP adsorbed" was found whatever PCP microstructure and sulfate concentration (12 to 140 mmol/L), indicating that PCP microstructure and sulfate concentration should not significantly modify the conformation of the adsorbed PCP.

1. Introduction

Comb-like copolymers made of a polymethacrylate backbone partially esterified with polyethyleneglycol (PEG) chains are widely used in order to improve the rheology of the concentrated particle suspensions such as suspensions obtained in cement or concrete [1,2]. Added to the concrete these polymers allow the facilitation of its placement. They are also used to decrease the initial amount of water added in order to produce a concrete more durable and with better mechanical performances. The dispersion ability of these polycarboxylate polymers (PCP) is due to their adsorption on cement grains. The PCP adsorption induces a steric repulsion between the grains because of the PEG teeth extended away from the particles [3]. As a consequence the distance separating the mineral particles is increased, and then the attractive Van der Waals and ionic correlation forces acting between the mineral surfaces are strongly reduced [4–7]. This dispersion effect was also reported when these polymers are added to barium titanate suspension [8], limestone suspension [9] or silica suspension [10].

The effect of polycarboxylate polymers on the fluidity of the concrete paste has been studied and it was concluded that the anionic carboxylate groups located in the polymer backbone strongly interact with the positive mineral surface of the cement particles giving rise to their adsorption on the cement particles [11]. Namely, because of the alkaline pH of the cement suspension ($pH > 12$), the non-esterified methacrylic groups (MAA) are ionized. On the other hand, as soon as the cement grains are in contact with water, anhydrous phases hydrate generating new positive mineral surfaces as the aluminate hydrates carrying an intrinsic positive charge, or as the silicate surfaces which also present a positive surface because of the strong affinity of the Ca^{2+} ions for the mineral surface. Consequently the adsorption of these polymers on the cement grains results from the strong interaction of the anionic carboxylate (MAA) groups with the Ca^{2+} covered mineral surfaces [12]. These interactions are therefore obviously dependent on the ionic conditions of the suspension and on the chemical structure of the polymer.

In accordance with these conclusions, the polymer adsorption was shown to be very sensitive to the concentration of divalent ions like sulfate ions as a consequence of their competitive adsorption. The initial rheology of the cement paste made with PCP is consequently dramatically affected in the presence of high sulfate ion concentrations [13]. Such effects were therefore studied and reported as PCP–cement incompatibility [14]. On the other hand, the effects of the different structural parameters of the PCP, such as the PCP molar mass, the number and the length of the PEG side chains which also determines the global charge density of the polymer, were also studied on their ability to adsorb on the cement grains [15–18] confirming again the role of the anionic carboxylate (MAA) groups in the polymer adsorption. However, whereas the role of the number and the length of the PEG side chains in the PCP adsorption and in its subsequent dispersion ability has been widely studied, there is no study dedicated to the effect of the comb-like PCP microstructure. Nevertheless the repartition of the comonomers on the chains is an important parameter likely to govern both the global conformation of the macromolecule accounting for the

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bulkiness of the graft PEG [19] and the polymer adsorption ability: for example, the mode of interaction of acrylamide–acrylic acid copolymers with multivalent cations as calcium was previously shown to depend on the repartition of the charged units along the chain. The repartition of the charged units was then approached by experimental measurements of the number of acrylic diads [20].

The purpose of this work is then to examine how the distribution of the anionic (MAA) groups and PEG side chains along the PCP backbone, modifies the ability of the polymer to adsorb on the Ca^{2+} covered mineral surfaces and to disperse the grains. For this study, two PCPs were synthesized by performing a RAFT copolymerization of PEG methacrylate (PEGMA) with methacrylic acid (MAA) [21]. This type of polymerization provides polymers having low polydispersity and a controlled distribution of the PEG side chains along the PCP chains. Both types of PCP have a very similar number of PEG side chain per chain and their molar masses are very close. Nevertheless whereas the PEG side chains are randomly distributed along the chains in the “random PCP”, they are located according to a gradient distribution along the chains of the “Grad PCP”. Consequently these two PCPs differ from each other only in the distribution of anionic carboxylate groups/ PEG side chains along the PCP backbone.

This study was carried out using aqueous calcite ($CaCO_3$) suspensions as an inert system model for early age cementitious materials. Indeed, as soon as cement grains are mixed with water, hydration reactions take place giving rise to water consumption, temperature increase, creation of new surfaces and also changes in the ionic composition of the pore solution [22]. All these parameters obviously govern the PCP adsorption and the rheological behavior of the cement paste. Moreover PCP itself is known to also act on the hydration rate [2,15,23–27]. Consequently in order to control these different parameters and to avoid side effects due to cement hydration, this study was carried out using an inert model suspension. Calcite suspensions in equilibrium with different interstitial solutions representative of cement pore solutions were previously shown to accurately mimic early age cement paste [28,29], this mineral presenting also a Ca^{2+} covered surface under these conditions. The polymer adsorption on calcite was then determined for the two PCPs using calcite suspensions made with saturated solutions with respect to calcium hydroxide and containing different concentrations of sulfate ions (12, 65 and 140 mmol/L) representative of the sulfate concentrations found in the interstitial solution of a fresh cement paste. The rheology of these different suspensions was then evaluated through static rheological experiments which yielded key rheological parameters as the yield stress (τ_0), allowing a comparison of the effectiveness of the two PCPs. Namely, the layer of the adsorbed polymers is reported to decrease the attractive Van der Waals and ionic correlation forces acting in cement suspensions that give rise to the formation of the rigid network and prevent the cement from flowing [30]. Kjeldsen and co workers [31] also showed how the thickness of the adsorbed PCP layer estimated from the length of the PEG side chains, appears to control the rheological properties of MgO suspensions. Furthermore these authors proposed in this paper a scaling approach to quantitatively link the surface coverage (for low or intermediate coverage) with the interparticle forces. In our study the magnitude of these attractive forces will then be estimated from the yield stress value τ_0 that is defined as the shear stress below which the cementitious material stops flowing [32]. It is worth noting that the empirical tests commonly used in the construction industry such as slump test or test derived from slump test which consists of the measurement of the paste spread are well correlated to the yield stress [33–36]. Previous studies carried out with cement and superplasticizers have shown a linear relation between Log(τ_0) [37,38]or the paste-spread [39,40] and the amount of adsorbed polymer on cement grains, whereas Flatt and coworkers [41] found that Log(τ_0) varies linearly with the inverse of the adsorbed amount. Consequently this study will conclude about the effect of the anionic groups repartition along the PCP backbones, on the polymer adsorption and dispersion ability. Rheological behavior will then be discussed in the light of the adsorption results.

2. Materials and methods

2.1. Materials

2.1.1. Mineral products

The calcite betocarb P2-OG was supplied by OMYA France. According to OMYA, this calcite has a specific surface area determined by Blaine's method of $0.395\,m^2\,g^{-1}$ and a diameter D50 of 7 μm. The specific surface area determined from nitrogen adsorption using the BET equations was found to be equal to $0.77\,m^2\,g^{-1}$.

To adjust the sulfate concentration of the different solutions, Normapur analytical grade Na_2SO_4 and $CaSO_4$ (gypsum) from Prolabo were used. The CaO was obtained by thermal decarbonation (10 h at 1000 °C) of pure $CaCO_3$ (Prolabo Normapur).

2.1.2. PCP

The two copolymers were synthesized according to the literature [21] with methacrylic acid (MAA) and poly(ethylene glycol) methyl ether methacrylate 1100 (PEGMA). 1100 denotes the average molecular weight of the macromonomer. These two samples are based on the same polymerization degree (DP = 100) and the same ester group ratio (PEGMA/(PEGMA + MAA) = 41% mol). The polymerization is carried out by a living/controlled radical polymerization technique (RAFT) which allows microstructure differences by changing the polymerization process. Thanks to this technique, the same polymer chains are growing during all the polymerization procedure. This means that we can induce intra-chain composition shift by changing the monomer composition during the reaction time. For the random PCP copolymer, all the monomers are introduced into the reaction vessel before initiation. For the gradient copolymer, the polymerization started with a mixing of monomers containing all the MAA monomers and a part of the PEGMA monomers (MAA/PEGMA initial molar ratio 70/30). The rest of the PEGMA is added continuously after 35 min during 20 min which induces a monomer composition drift and the gradient microstructure. The reaction is stopped by cooling after 120 min and the polymers are diluted to 20% solid contents before use without further purification. The 2 polymers are schematically represented in Fig. 1.

The polymers were analyzed performing Aqueous SEC (ASEC) using a Water equipment composed of Waters 515 HPLC pump, a refractometric detector (Waters 410) and three Polymer Laboratories columns (2 Aquagel-OH 30 and 1 Aquagel-OH mixed). $NaNO_3$ (0.1 N) was used as eluent (flow rate of 1 mL.min^{-1}). Molar masses and molar mass distributions were determined on the basis of a poly(ethylene oxide) (PEO) standard calibration curve.

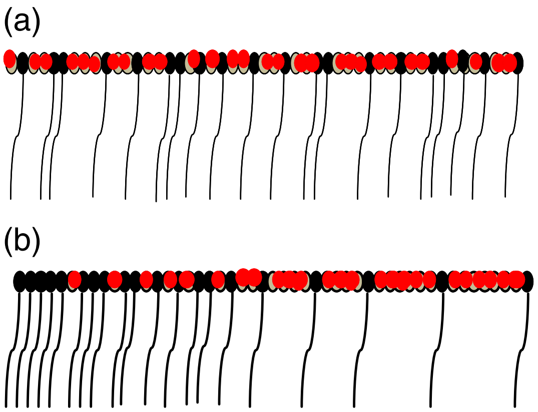

Fig. 1. A schematic representation of random PCP (a) and gradient PCP (b).

For the SEC analyses, 5 drops of the reaction medium were dissolved in 1 mL of $NaNO_3$ buffer, filtered (0.45 μm filter) and directly injected into the SEC device.

The ASEC curves presented in Fig. 2 show similar molar masses distribution for the targeted polymers. Moreover, as expected for a RAFT polymerization, they display a low polydispersity in comparison with the PCP obtained by conventional free radical polymerization. In the case of the random PCP, Aqueous SEC analysis displays some free PEGMA monomers in the final polymer. As the reaction conditions induce a random reactivity between the 2 monomers [21], this is not affecting the final composition of the polymer (PEGMA/(PEGMA + MAA) = 41%mol). The molar mass of the random PCP is just a bit lower than targeted (Fig. 2, comparison between grad and random PCP) and one has to manage purity close to 85% for this polymer.

2.2. Methods

2.2.1. Preparation of the initial solutions

All the solutions used are saturated with respect to calcium hydroxide in order to remain the surface charge of calcite unchanged. For the initial solutions, this is done by adding 0.5 g of CaO to 250 mL of distilled deionised water. In order to evaluate the effect of the sulfate ions on the performances of the two PCPs, three solutions containing different sulfate concentrations were prepared. The first solution consists in a solution saturated with respect to gypsum by adding 0.86 g of gypsum to the previous 250 mL of CaO saturated solution. The solutions with higher sulfate concentrations were obtained by adding 2.84 g and 5.32 g of Na_2SO_4 respectively to 250 mL of the CaO saturated solution. These suspensions were continuously stirred during 10 h at 25 °C and then filtered through 0.3 μm millipore filters. The ionic concentrations were then determined by atomic emission spectroscopy (ICP OES).

The appropriate amount of PCP was then added to these initial ionic solutions in order to obtain solutions containing varying concentrations of PCP (0.2 g/L to 2 g/L). A small part of this solution was removed, acidified with H_3PO_4 to avoid carbonation, and then analyzed by a carbon analyzer (TOC 5000A Shimadzu) in order to determine the initial concentration of the PCP in each solution.

2.2.2. Preparation of the calcite suspensions

The suspension is prepared using a warring blender and according to the following procedure:

- 23 mL of initial solution is poured into the 50 mL blender.
- 80 g of calcite and 150 mg of calcium hydroxide (added to compensate calcium consumption due to Ca^{2+} adsorption on calcite) were mixed dry for about 5 s by hand outside the blender.
- The powder is then poured into the blender and the paste was mixed for about 10 s by hand.

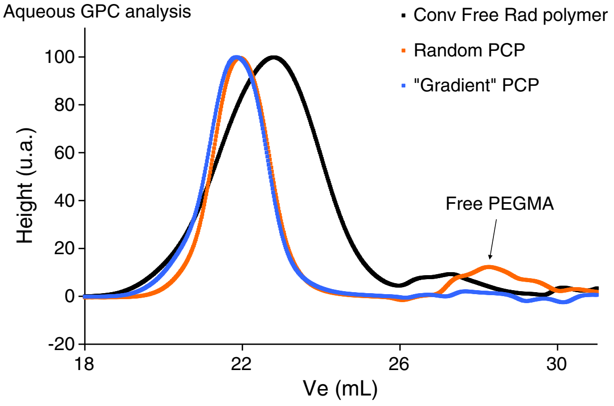

Fig. 2. Aqueous ASEC analysis of random and gradient PCPs and comparison with a traditional PCP obtained by conventional free radical polymerization.

- Mixing is then performed according to the next procedure: 1 min speed 5000 rpm, 1 min without mixing, 1 min speed 5000 rpm. The temperature of the suspension after the mixing was measured and does not exceed 27 °C.

Using this procedure, the solid fraction of the suspension is equal to 0.56. Preliminary experiments were performed to optimize the solid fraction of the suspension in order to avoid sedimentation during the rheology experiments and to be in accordance with the sensitivity of the rheometer.

2.2.3. Measurements of ion concentrations

A small part of the initial ionic solution was removed before the calcite addition, and acidified with hydrochloric acid to avoid carbonation. Calcium and sulfate concentrations were then determined by Atomic Emission Spectrometry (ICP-OES Vista Pro Varian).

Immediately after the rheology experiment, a part of the suspension used for the rheology test was removed, centrifuged (9000 rpm, 5 min) and the supernatant was filtered through 0.3 μm millipore filters. This solution was also acidified by hydrochloric acid. Calcium and sulfate ion concentrations of the pore solution were then determined by Atomic Emission Spectrometry (ICP OES, Varian Vista Pro).

2.2.4. PCP adsorption measurements

The PCP adsorption onto the mineral particles in the different pastes was determined by measuring the residual concentration of polymer in the liquid phase of the suspensions. Again, immediately after the rheology experiment, a part of the paste was centrifuged and the filtered supernatant was also acidified with H_3PO_4 to avoid carbonation. The total organic carbon (TOC) of the pore solution was then measured by using a Shimadzu TOC analyzer 5000A. The amount of PCP adsorbed is therefore deduced from the reference TOC measurements of initial solution prepared before the calcite addition. Thus the amount of adsorbed polymer cannot be accurately determined by this method when a small fraction of it is adsorbed. It is worth noting that a previous experiment was carried out on the calcite suspension prepared without polymer in order to evaluate and to take into account the low content of carbon released by the calcite.

2.2.5. Rheology experiments

The rheological behavior of the suspensions was investigated at 25 °C, using a controlled strain rheometer (ARES Rheometrics Scientific, USA) and a non conventional geometry as represented in Fig. 3. This mixing-type tool is composed of a helicoidal ribbon and a cell and allows maintaining a saturated water atmosphere within the cell. The surfaces of the ribbon and cell [42,43] were serrated to avoid the slippage. The suspensions were poured into the cell and a 30-second preshearing cycle was applied at a shear rate of 100 s^{-1} to break the particle agglomerates.

The flow curves are then obtained by measuring the stress as the shear rate was decreasing by step from 30 to 0.03 s^{-1}. As suggested by Geiker [44] the measuring time was adjusted to be long enough to obtain a steady state, and short enough to prevent sedimentation. The following procedure for testing the rheological properties of the investigated calcite suspensions was then applied (Table 1).

3. Results and discussion

3.1. Ionic composition of the pore solution

Calcium and sulfate concentrations of the pore solution in equilibrium with the calcite were measured by atomic emission spectroscopy in all the calcite suspensions just after performing rheological tests. Ionic compositions of the different pore solutions are reported in Table 2. Compositions of the initial ionic solutions used to make the calcite suspension are also reported in Table 2. No trends in the calcium and

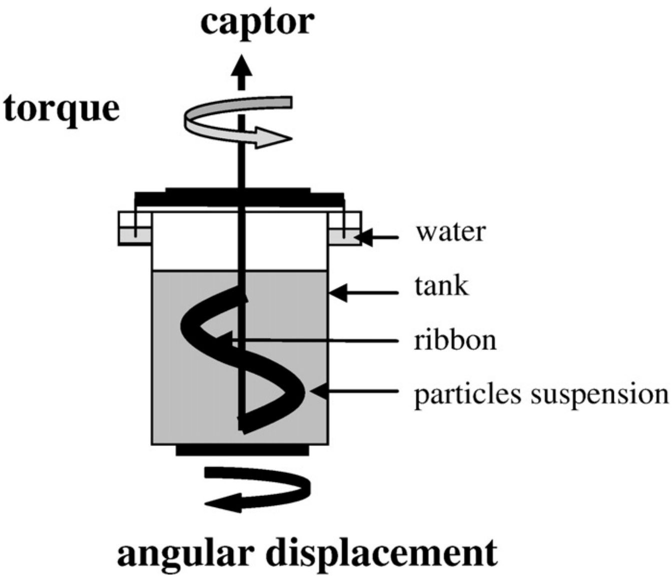

Fig. 3. Non conventional geometry used for rheological investigations [42,43].

sulfate concentrations after PCP adsorption have been observed for a given sulfate solution. Else, constant values within the accuracy reported in Table 2 have been obtained whatever the PCP content. Therefore, only the average values and corresponding precision for each series have been reported in Table 2.

In accordance with the solubility equilibrium of gypsum, the addition of increasing amount of sodium sulfate obviously gives rise to a calcium concentration decrease due to a common ion effect. As previously indicated, adding a small amount of calcium hydroxide (150 mg) to the calcite suspensions was necessary to maintain the pore solution saturated with respects to calcium hydroxyde: without this addition, a significant decrease of the calcium concentration would be measured in the pore solution after the calcite addition, this was attributed to the calcium ions adsorption onto the calcite [45] and this effect is obviously enhanced by the high solid fraction. Furthermore, calcium concentrations measured in the different calcite suspensions containing PCP (after adsorption) are slightly higher than calcium concentrations of the initial ionic solution made without PCP. This difference can be explained by a complexation effect of calcium ions with the PCP carboxylate functions [46] inducing then a slight increase of the solubility of calcium hydroxide and thus of the total amount of calcium ($[Ca^{2+}]_{free}+[Ca\text{–}PCP]_{complex}$) measured in the pore solution by spectroscopy ICP OES. Total calcium and sulfate concentrations experimentally found in the initial solution (Table 2) are consistent with the predicted values determined using PHREEQC speciation calculations. It is also worth noting that in the presence of sulfate ions, a non-negligible part of the calcium concentration measured corresponds to the $CaSO_4$ complex present in solution. According to PHREEQC speciation calculations, $[Ca^{2+}]_{free}$ decreases respectively from 22 mmol/L (solution1) to approximately 7 mmol/L and less than 5 mmol/L for the solutions 2 and 3.

3.2. Adsorption results

Preliminary experiments were carried out to verify that adsorption equilibrium was reached under experimental conditions. Consequently four different mixing procedures were tested and compared in terms of adsorption (reference procedure: 1 min blender 5000 rpm, 1 min without mixing and 1 min blender 5000 rpm, second procedure: 3 min hand mixing, third procedure: 4.5 min blender speed 5000 rpm, 1 min without mixing and 4.5 min blender speed 5000 rpm, fourth procedure: 1 min blender speed 5000, 1 min without mixing 1 min blender speed 5000 rpm and 12 h on the vibrating table). It was found that the adsorption remains the same whatever the mixing procedure used, therefore we concluded that the adsorption equilibrium was reached within the reference procedure.

Table 1
Program applied for the rheology experiments.

Shear rate s^{-1}	30	12	5.6	2.6	1.2	0.5	0.24	0.11	0.06	0.03
Duration s	15	10	10	5	10	10	20	30	30	30

The amount of adsorbed PCP (in mg per gram of calcite) is plotted as a function of the free PCP concentration measured in the pore solution for the two PCPs and for the three different sulfate concentrations (Fig. 4). In order to account for the residual monomers of the random PCP (15% in mass, see Section 2.1.2) the adsorption isotherm was recalculated assuming that all the residual monomers are unadsorbed and remain in the solution (Fig. 4). It obviously appears that this correction does not modify the plateau value and only induces a low shift at the beginning of the isotherm curve (Fig. 4, PCP random corrected).

The three gradient PCP adsorptions ([sulfate] = 12, 65 and 140 mmol/L) and the two random PCP adsorptions ([sulfate] = 12 and 65 mmol/L) clearly follow a Langmuir-type isotherm (Fig. 5). For the highest sulfate concentration the amount of random PCP adsorbed cannot accurately be measured. Indeed in this case because a low fraction of the initial polymer is adsorbed (less than 10%) the method used to determine the amount of adsorbed polymer cannot be accurate (see Methods Section 2.2.4).

As expected the quantity of adsorbed polymer is strongly reduced as sulfate ion concentration increases. Indeed the amount of adsorbed PCP found at the adsorption plateau turns down from approximately 0.35 mg of PCP per gram of calcite in presence of 12 mmol/L of sulfate ions and whatever the PCP microstructure, to less than 0.05 mg of random PCP adsorbed per gram of calcite when the sulfate concentration reaches 140 mmol/L. This effect has been previously attributed to a competition of the sulfate anions with the polyanionic PCP interacting with the Ca^{2+} covered surfaces [13]. Moreover it is worth noting that the addition of sulfate salt to the solution induces a significant decrease of the concentration of the calcium ions. This decrease results from the lower concentration of Ca^{2+} in connection with the gypsum solubility. The strong decrease of $[Ca^{2+}]_{free}$ from 22 to 5 mmol/L as previously indicated, can then obviously modify the calcite interface and leads to a lowering of its “adsorption site” density active for the carboxylate adsorption. Indeed Ca^{2+} ion is known to be a zeta-potential determining ion for calcite [45,47] and then the Ca^{2+} concentration plays a role in the PCP adsorption on calcite as earlier reported [48]. Consequently the influence of sulfate ions on the interaction between PCP and calcite could result from a competitive adsorption of the sulfate ions and also maybe from a modification of the calcite interface.

The most important point in the adsorption results is the role of the PCP microstructure: PCP having a “gradient” distribution of anionic carboxylate functions is less sensitive towards the sulfate concentration increase than the usual “random” PCP. “Gradient” PCP behaves then like a usual “random” PCP which would be less esterified. Namely the sensitivity of the PCP adsorption towards sulfate concentration was shown to clearly decrease with lower ester ratio [49]. In an earlier work [41] Flatt proposed a way to quantify the sulfate sensibility of the PCP and in particular the effect of the sulfate concentration on the PCP adsorption. This theoretical approach takes into account the PCP structure and again this clearly highlights the impact of both ester ratio and side chain length of the PCP in the competitive adsorption. However in the present case these two parameters are the same for both PCP and thus their estimated sulfate sensitivity parameter is also the same. However this model involves that the backbone conformation of the PCP studied is the same (flexible worm backbone). This is a limitation for that model to explain our results: indeed, according to Gay and Raphael [19], changing the PCP ester ratio from 30% (= less esterified part of the

Table 2
Ionic composition of the $^{(1)}$ initial solution prepared without PCP used for making the calcite suspensions $^{(2)}$ pore solution obtained after centrifugation of the suspensions used to perform rheological tests.

PCP type	Sol. 1		Sol. 2		Sol. 3	
	(Sulfate12 mmol/L)		(Sulfate 65 mmol/L)		(Sulfate140 mmol/L)	
	pH = 12.5 ± 0.1		pH = 12.7 ± 0.1		pH = 12.8 ± 0.1	
	$[Ca^{2+}]$ mmol/L	$[SO_4^{2-}]$ mmol/L	$[Ca^{2+}]$ mmol/L	$[SO_4^{2-}]$ mmol/L	$[Ca^{2+}]$ mmol/L	$[SO_4^{2-}]$ mmol/L
Initial $^{(1)}$ solution without PCP	33 ± 1	12.5 ± 1	15 ± 2	63 ± 3	13 ± 2	130 ± 5
Grad PCP $^{(2)}$ (after ads)	41 ± 3	13.7 ± 1	21 ± 1.5	67 ± 4	21 ± 4	147 ± 4
Stat PCP $^{(2)}$ (after ads)	37 ± 2	12 ± 0.5	21 ± 2	67.5 ± 2.5	22 ± 3	141 ± 5

gradient PCP) to 40% or more (= random PCP or second part of the gradient PCP) should modify the backbone conformation regime of the PCP used for this study and then makes the model inappropriate for our study.

Thus, the differences observed in the adsorption behavior reveals the major role of the repartition of the charged carboxylate functions along the backbone. Conversely to the "random" PCP, a gradient distribution of the carboxylate leads to the formation of chain parts with a higher charge density than the mean charge density of the PCP and in the same chain, part of it is more esterified and then less charged. In accordance with the synthesis procedure, the part of the "gradient" PCP which is less esterified should contain at least 30% of ester. In order to go further, the repartition of the carboxylate groups has been estimated in a simple probability model assuming $r_{MAA} = 1.03$ and $r_{PEGMA} = 1.02$ [50]. The repartition of the carboxylate groups was then estimated from the calculations of the probability to form the different triads and tetrads applying the stationary process [51,52] and taking into account the instantaneous monomer composition during all the polymerization duration. The results reported in Table 3 allow a comparison of the monomer sequences along the backbone in both polymers. This confirms that as expected in a gradient PCP, the groups are less uniformly distributed along the backbone leading to a decrease of the number of diads or isolated carboxylate groups (ECCE and ECE) and thus a subsequent increase of the number of carboxylate functions in sequences containing a larger number of carboxylate groups as triad (ECCCE) or tetrad (ECCCCE) or pentad (ECCCCCE) etc. This result shows that for the same global number of charged carboxylate groups integrated in the chain, isolated or diad carboxylate groups are then less efficient to compete with sulfate adsorption on calcium covered surfaces. It is likely that the mode of interaction between the calcium cations present at the calcite surface and the carboxylate groups depends on the distance separating the anionic groups.

3.3. Rheology results

The flow curves were obtained for calcite suspensions with varying PCP concentrations by measuring the stress as the shear rate was decreasing from 30 to 0.03 s^{-1} according to the procedure previously described (experimental part). Fig. 6 shows a typical curve: the stress measured decreases as a function of the shear rate until reaching a constant value which was taken to be equal to the yield stress (0.33 Pa in this case: $[SO_4^{2-}] = 65$ mmol/L and 0.23 mg grad $PCP_{ads}/g_{calcite}$). These experiments were carried out for all the different calcite suspensions allowing the determination of the yield stress.

No visible segregation was detected during testing. Supplementary tests were performed with the most fluid suspensions to ensure that no disturbing sedimentation occurs during the rheology measurements: the previous test was then repeated two times adding one minute delay between the two tests and suppressing the preshearing cycle. The same stress–shear rate curve was again obtained confirming that there is no sedimentation disturbing the measurements (Fig. 6).

Then the same program including preshearing cycle was successively repeated three times to insure the reproducibility of the experiment.

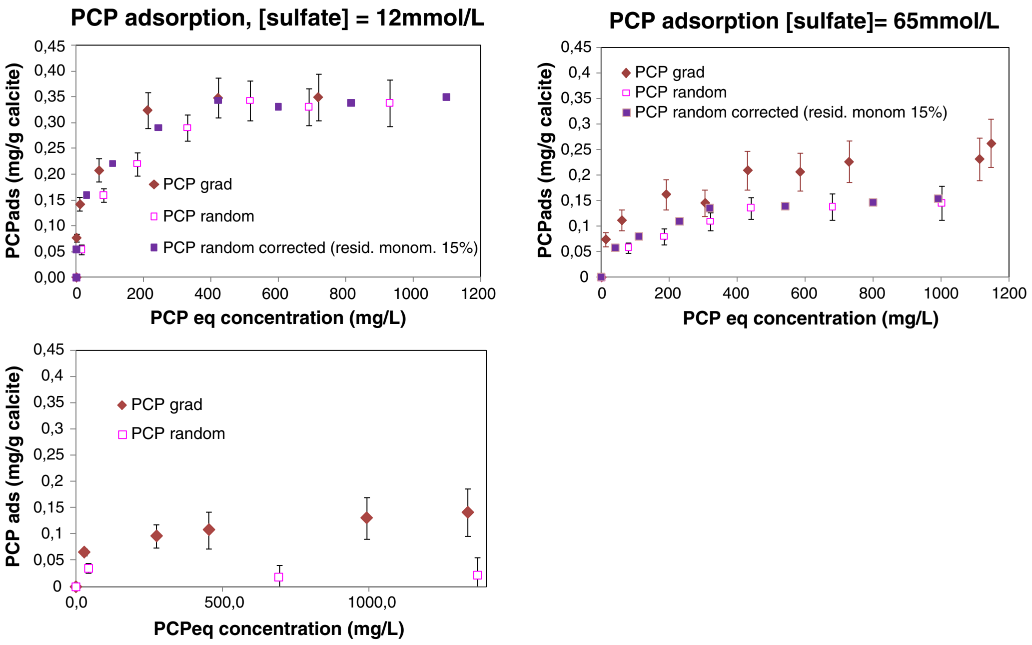

Fig. 4. Effect of the PCP microstructure and of the sulfate concentration on the PCP adsorption. Solid fraction = 0.56. N_2 BET surface area of calcite: 0.77 $m^2\ g^{-1}$.

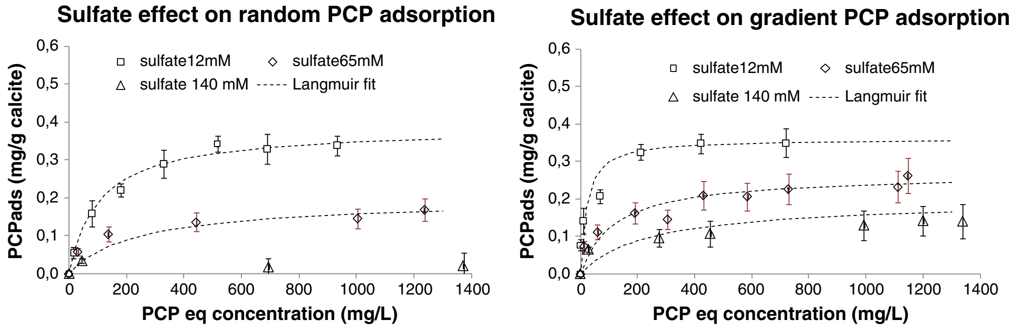

Fig. 5. Effect of the sulfate concentration on the random (left) and gradient (right) PCP adsorption. Solid fraction = 0.56. N_2 BET surface area of calcite: 0.77 $m^2 g^{-1}$.

3.3.1. Relationship of the yield stress with the PCP adsorption

3.3.1.1. Effect of the sulfate concentration on the relationship yield stress–adsorption. The evolution of the logarithm of the yield stress was reported as a function of the “gradient” PCP adsorption (Fig. 7). It clearly appears that the logarithm of yield stress linearly decreases with the PCP adsorption proving a strong effect of the adsorbed PCP layer on reducing the attractive forces acting between the calcite particles.

This relationship remains the same whatever the sulfate concentration (12 mmol/L < $[SO_4^{2-}]$ < 140 mmol/L) indicating that the sulfate ions present in the pore solution do not modify the dispersion ability of the adsorbed polymer. It is interesting to note that in a previous study based on direct force measurements, Laarz [53] showed a significant modification of the conformation and thickness of the adsorbed PCP by addition of $CaSO_4$ compared to the thickness measured in presence of monovalent ions. He then suggested an effect of the divalent ions leading these comb copolymers to at least partly collapse. In the present work divalent ions are always present, their concentrations only vary, then the ionic strength of these three experiments increased then from 8×10^{-2} to 4.3×10^{-1} mmol/L. The present results are consistent with the conclusions of Borget [54] who found that the hydrodynamic radius of different PCP in alkaline solution remains the same if the ionic strength exceeds 10^{-2} mmol/L and in a large range of ionic strength ($3 \times 10^{-2} <$ I mmol/L $< 4 \times 10^{-1}$) obtained by modifying the sulfate concentration for example. He concluded then that electrostatic interactions between the carboxylate groups are completely screened under these conditions. Conversely, Yamada in an earlier study [13] concluded to shrinkage of the PCP due to the ionic strength increase. As he measured the same steric size of PEO irrespective of ionic strength he attributed this effect to shrinkage of the polycarboxylate backbone in higher ionic strength. Nevertheless it is worth noticing that the size measurements were then performed in pure water containing varying contents of salt (Na_2SO_4 or NaCl). The dissociation degree of the carboxylic groups could therefore vary from an experiment to another according to pH variation induced by different ionic strengths, inducing itself a change in the polymer conformation. This is not the case for the present work as the solutions are saturated with respect to calcium hydroxide.

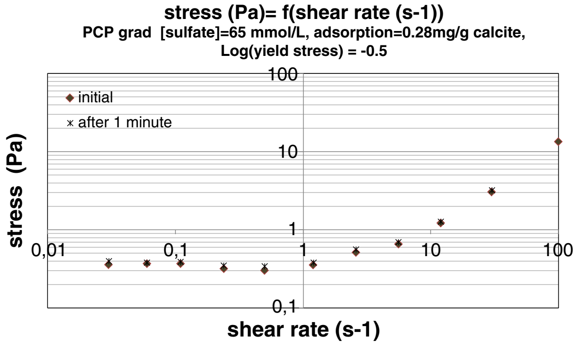

Fig. 6. Typical flow curve obtained with the calcite suspensions. The test was repeated two times, adding one minute delay between the tests: no difference is observed. The stress measured decreases as a function of the shear rate until reaching a constant value corresponding to the yield stress (0.33 Pa in this case).

The only observed effect of the sulfate concentration increase is then related to the PCP adsorption. As seen on the adsorption isotherms, the maximum adsorption is three times lower when sulfate concentration is ten times more (140 mmol/L instead of 12 mmol/L). This adsorption decrease obviously induces a subsequent increase of the yield stress of two orders of magnitude.

It is also worth noting that the yield stress seems to be insensitive to the various amounts of free PCP present in the pore solution, contrary to the conclusions of Sugamata et al. [55] To bring this point to light we can for example consider the three experiments that lead roughly to the same yield stress (Log Yield stress = 1) and also to the same adsorption (0.14 mg/g of calcite) as indicated in Fig. 6. Considering the previous isotherm curves (Fig. 4) we conclude that the same yield stress is obtained whereas the pore solution contains either 0.011 g/L of free PCP (12 mmol/L of sulfate), 0.30 g/L of free PCP (65 mmol/L of sulfate) or 1.34 g/L of PCP (140 mmol/L of sulfate).

Consequently the only parameter acting on the yield stress of the calcite suspensions prepared with different amounts of the same PCP is the amount of adsorbed polymer, and this is true for both PCPs studied whatever the amount of sulfate in the pore solution ranging from 12 to 140 mmol/L and whatever the “free” (unadsorbed) PCP amount.

3.3.1.2. Effect of the microstructure of the PCP on the relationship yield stress–adsorption. Yield stress of the calcite suspensions was plotted as a function of the amount of adsorbed PCP for the both PCP and the three sulfate concentrations.

These three figures (Fig. 8) allow one to conclude that the efficiency of the adsorbed PCP to decrease the yield stress of calcite suspensions is very similar whatever the PCP microstructure. However the monomer distribution along the backbone obviously acts on the charge spacing and on the POE vicinity. Thus, the PCP microstructure (gradient-random) could affect the conformation of the adsorbed polymer. In a model based on the Flory free energy approach, Gay and Raphael [19] predicted how the structure of the PCP, in particular its ester ratio, acts on the conformation of the polymer in a good solvent. According to this model, changing the PCP ester ratio from 30% (= less esterified

Table 3
Estimation of the repartition of the carboxylate groups in the gradient PCP and in the random PCP. E is used for the PEGMA comonomer and C for the MAA comonomer.

Repartition of the carboxylate groups (%)	Gradient PCP	Random PCP
% of carboxylate groups present as isolated carboxylate groups (ECE)	11.7	13.1
% of carboxylate groups present as diad (ECCE)	11.3	13.9
% of carboxylate groups present as triad, tetrad and other (ECCCE, ECCCCE…)	77.5	72.9

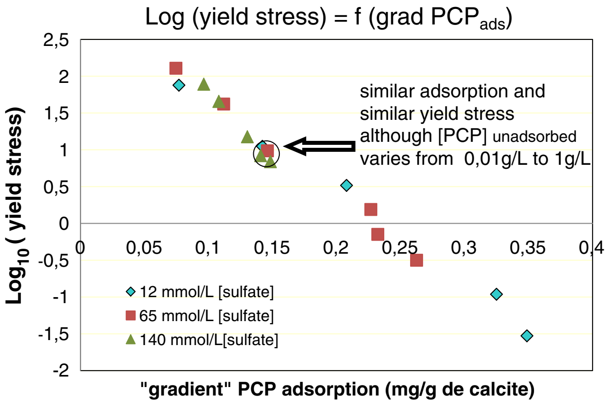

Fig. 7. Evolution of the yield stress of the calcite suspensions as a function of the “gradient” PCP adsorption. An increase of the sulfate concentration of the pore solution strongly decreases the PCP adsorption but has no effect on the dispersion ability of the adsorbed “gradient” PCP. (N_2 BET calcite surface area: 0.77 $m^2\ g^{-1}$).

part of the gradient PCP) to 40% or more (= random PCP or second part of the gradient PCP) should modify the backbone conformation regime of the PCP used for this study (flexible backbone worm to stretched backbone worm). Furthermore an extension of this model to adsorbed PCP on C–S–H [7] was found to be consistent with experimental data obtained by atomic force measurements. Nevertheless all these studies were carried out in sulfate-free solutions, whereas Laarz [53] in an earlier study has shown a strong effect of the $CaSO_4$ addition on the conformation of the adsorbed PCP. This could explain why the only effect observed of the PCP microstructure concerns its ability to adsorb on calcite particles in the presence of sulfate ions. For example because the “random” PCP adsorption becomes quite negligible when the sulfate concentration reaches 140 mmol/L, its effectiveness in terms of dispersing calcite particles also becomes negligible, whatever the initial amount of “random” PCP added (from 0.2 g/L to 2 g/L) to the calcite suspension. Under these conditions the addition of the same amount of “gradient” PCP gives rise to a more significant dispersing effect due to its stronger ability to compete with the sulfate ions for the adsorption.

All these data are now reported on the same graph (Fig. 9). As indicated in this figure, the logarithm of the yield stress linearly decreases with the amount of adsorbed PCP according the same straight line. This means that under the experimental conditions the yield stress can simply be expressed as an exponential decrease of the amount of adsorbed PCP, and this relation remains the same whatever the PCP microstructure studied and the ionic strength of the calcite suspension ranging from 0.08 to 0.43 mol/L by varying the Na_2SO_4 contents. From these results we can suspect that the PCP microstructure and the increase of the ionic strength resulting from the sulfate ions increase (from 12 to 140 mmol/L) do not affect the adsorbed polymer layer which only depends on the amount of adsorbed polymer. Conversely, the PCP microstructure strongly affects its ability to adsorb and compete with sulfate ions for adsorption on Ca^{2+} covered surfaces.

4. Conclusions

Calcite suspensions in equilibrium with respect to calcium hydroxide and containing varying amounts of sulfate ions were used to study how the repartition of the anionic (MAA) groups and PEG side chains along the PCP backbone affects the polymer behavior in terms of adsorption and dispersion ability.

This work clearly shows that the repartition of the anionic carboxylate groups along the backbone has a strong effect on the PCP adsorption ability in the presence of sulfate ions. A significant decrease of the PCP adsorption was observed as the sulfate concentration increased, in connection with both the sulfate competitive adsorption on the Ca^{2+} covered surfaces and the subsequent decrease of calcium ions present in the solution inducing a modification of the calcite interface. Furthermore, compared to the usual random repartition of the comonomers PEGMA 41%–MAA 59% along the PCP comb-polymer, a gradient repartition of the comonomers strongly enhances the polymer adsorption, especially when the sulfate ion concentration increases. The adsorption of the equivalent “gradient” polymer studied is therefore significantly less sensitive to the sulfate competitive adsorption.

In terms of adsorption a “gradient” PCP behaves like a “random” PCP copolymer having a lower esterification ratio τ proving the contribution of the less esterified part of the gradient polymer in its adsorption.

The logarithm of the suspension yield stress was shown to linearly decrease with the PCP adsorption in the ranges studied, proving the efficiency of the adsorbed PCP layer to decrease the attractive forces acting between the calcite particles. This linear relation remains the same with both PCP microstructures studied (random or gradient). This study shows that the only parameter acting on the yield stress of

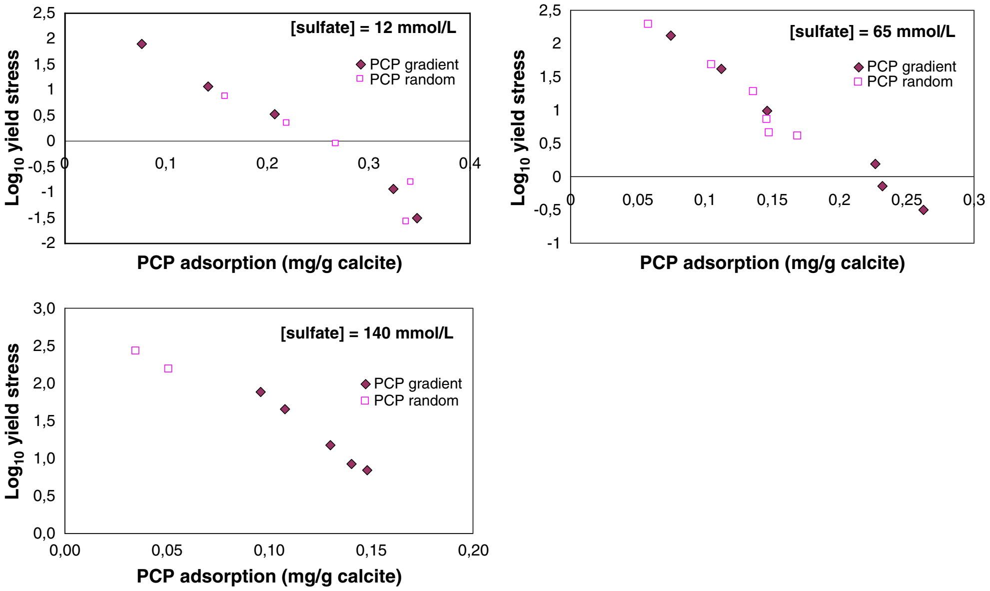

Fig. 8. Effect of the PCP microstructure (random or gradient) on the yield stress–adsorption relationship. It clearly appears that the PCP microstructures studied have no effect on the efficiency of the adsorbed PCP to decrease the yield stress.

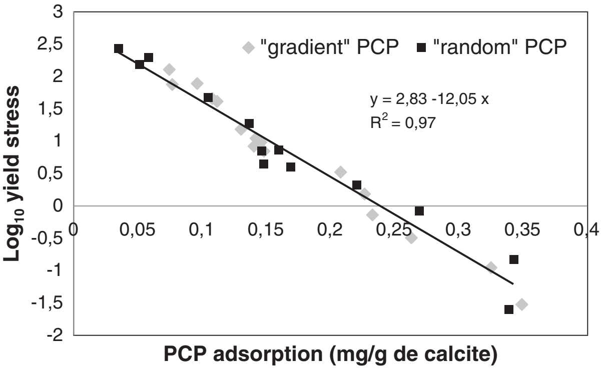

Fig. 9. Log$_{10}$ (yield stress) decreases linearly as a function of the amount of adsorbed PCP. This relationship remains the same whatever the microstructure of the PCP studied and the sulfate concentration.

the calcite suspensions prepared with different amounts of the "gradient" and "random" PCPs studied is the amount of adsorbed PCP whatever the microstructure of the PCP studied, whatever the sulfate concentration of the pore solution ranging from 12 to 140 mmol/L and whatever the amount of "free" (unadsorbed) PCP in the pore solution. This well agrees with previous studies showing that the dispersion effect of PCP is well correlated to the amount of adsorbed polymer and can be interpreted in terms of surface coverage.

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