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A new class of organosilane-modified polycarboxylate superplasticizers with low sulfate sensitivity

Wei Fan [a,b,c], François Stoffelbach [b], Jutta Rieger [b], Laure Regnaud [c], Angélique Vichot [c], Bruno Bresson [a], Nicolas Lequeux [d,*]

[a] *Laboratoire de Physico-Chimie des Polymères et des Milieux dispersés (PPMD), UMR 7615, UPMC Sorbonne Universités and CNRS, ESPCI – ParisTech, 10 rue Vauquelin 75231 Paris cedex 05, France*
[b] *Laboratoire de Chimie des Polymères (LCP), UMR 7610, UPMC Sorbonne Universités and CNRS, 3 rue Galilée, 94200 Ivry sur Seine, France*
[c] *CTG Italcementi Group, Les Technodes – BP 01, 78931 Guerville, France*
[d] *Laboratoire de Physique et d'Etude des Matériaux (LPEM), UMR 8213, UPMC Sorbonne Universités and CNRS, ESPCI – ParisTech, 10 rue Vauquelin 75231 Paris cedex 05, France*

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ABSTRACT

It is well-established that a competitive adsorption exists between polycarboxylate superplasticizers (SP) and sulfate ions solubilized in the interstitial solution of cement paste, which may cause a loss of the dispersing properties. This has been explained by competitive weak ionic interactions between functional carboxyl groups and sulfate ions with cement grains. In this study, SPs including trialkoxysilane functional groups have been synthesized. Adsorption and dispersing properties of these SPs were evaluated in the presence of different concentrations of Na_2SO_4 added in aqueous solution. It appeared that a partial substitution of carboxyl groups by trialkoxysilane in the polymer makes them more resistant to sulfate ions. We suggested that the high adsorption capacity of these SPs results from the formation of strong bonds between hydroxysilane groups and calcium silicate hydrate phases. The improved compatibility of these new silylated SPs has been demonstrated through the formulation of two different concrete equivalent mortars.

1. Introduction

Polycarboxylate-type superplasticizers (SP) with polyethylene glycol (PEG) side chain are very efficient in the formulation of high-performance concrete due to their excellent water reducing capacity [1]. The dispersing mechanism of these superplasticizers is generally thought to be related to the adsorption of the polymer backbone via carboxylic functional groups and the steric hindrance effect generated by PEG side chains [2–5]. However, it is known that the dispersing performance of SPs is significantly affected by many parameters such as cement composition and mixing conditions [6–8]. It is thus hard to control or to predict the concrete workability with these particular plasticizers [9]. Sulfate ions dissolved in the interstitial solution of cement paste seem to be one of the most important parameters having an adverse impact on SP adsorption [10,11]. Yamada *et al.*[12] demonstrated that polycarboxylate polymer can desorb when the sulfate concentration in the interstitial solution is raised by addition of Na_2SO_4, and then causes a loss in fluidity. Conversely, when the sulfate concentration is reduced by precipitation of gypsum using $CaCl_2$, the fluidity is improved due to an increase of polymer adsorption. These observations suggest that a competition between SO_4^{2-} and COO^- adsorption occurs on the cement surface. The influence of the SP structure on the sulfate-polycarboxylate competition has been studied by Zimmermann et al. [13]. It was found that the sulfate sensitivity depends mainly on the polymer composition and architecture and is correlated to the adsorption equilibrium: by decreasing the polyethylene glycol (PEG) side chain length and the PEG/carboxylate molar ratio, the adsorption is enhanced and the adsorption competition with sulfate is reduced [14]. However, polymers exhibiting an excessive adsorption due to a high carboxyl group concentration are detrimental for fluidity retention with time because the residual concentration of non-adsorbed polymers is too low to compensate the increase of solid surface because of hydration [15]. Consequently, SP are generally adapted to each type of cement, and the use of a SP designed for particular high alkali cement may cause problems when used for low alkali cements, such as variations of dispersing properties, rheological behavior, fluidity retention, setting time, etc. So, there is an urgent need to improve the performance of SP to make this admixture more robust with respect to the composition of raw materials.

To circumvent the sulfate–carboxylate competition, one solution would be to include functional groups into the polymer backbone able to form sufficiently strong bonds to be unaffected by sulfate ions. In a previous work, we have found that a new layered calcium organosilicate hybrid can be formed with covalently linked organic functionalities [16,17], and that silylated hydrosoluble polymers can be covalently bonded to calcium silicate hydrate (CSH) [18]. Organosilane functions

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[*] Corresponding author. Tel.: +33 1 40 79 44 41; fax: +33 1 40 79 46 40.
E-mail address: nicolas.lequeux@espci.fr (N. Lequeux).

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incorporated into SPs would be a solution to limit the problem of sulfate-carboxylate compatibility. For this purpose, a series of polycarboxylates modified by insertion of trimethoxysilane functions have been synthesized [19] and their adsorption and dispersing properties has been investigated as well as their adsorption resistance against sulfate ions.

2. Experimental

2.1. Materials

Methacrylic acid (MAA, 99%, Acros, stabilized with 250 ppm of methylethylhydroquinone), poly(ethylene glycol) methyl ether methacrylate (MAPEG, M_n~1100 g mol^{-1}, Aldrich), 3-(trimethoxysilyl) propyl methacrylate (MAPTMS, 98%, Acros), 4,4′-azobis(4-cyanovaleric acid) (ACPA, ≥98%, Fluka), 1-butanethiol (BuSH, 99%, Aldrich), tetrahydrofuran (THF, >99%, Acros), diethyl ether (Et_2O, pure, Acros), $Al_2(SO_4)_3 \cdot 16H_2O$ (Fluka) and $CaCO_3$ (Aldrich) were used as received without further purification.

2.2. Synthesis of poly(poly(ethylene glycol) methyl ether methacrylate-co-methacrylic acid-co-3-(trimethoxylsilyl) propyl methacrylate), P (MAPEG-co-MAA-co-MAPTMS)

Radical copolymerizations of MAPEG, MAA and MAPTMS were initiated by ACPA at 70 °C, in the presence of a chain transfer agent (BuSH)A typical experiment for the polymerization procedure (Table 1, P(PEG_{40}-MAA_{30}-Si_{30})) is as follows: in a 100 mL one-neck round-bottom flask, MAA (1.1809 g, 0.0136 mol), MAPEG (20.0112 g, 0.0182 mol), MAPTMS (3.3866 g, 0.0136 mol) and ACPA (0.1281 g, 0.4545 mmol) were mixed with 40 mL of THF. The solution was bubbled under argon for 30 min at room temperature to remove free oxygen. BuSH (0.97 mL, 0.009 mol) was then injected into the mixture, using a microsyringe. A small amount of trioxane was used as an internal reference to determine monomer conversion by ^1H NMR. The flask was then immersed in an oil bath thermostated at 70 °C and the reaction was maintained for 24 h under argon. Polymers were directly isolated by evaporation of THF and then dried at room temperature under vacuum to yield a fine white powder.

2.3. Cements and C_3S used

Two Portland cements named C1 and C2 were used for this study. Chemical compositions are given in Table 2. The main difference between the two cements comes from the sulfate alkali content which is much higher in C2 than in C1.

Tricalcium silicate, C_3S, was synthesized at CTG Italcementi Group by calcination of stoechiometric mixture of $CaCO_3$ and silica. C_3S was ground to a specific surface Blaine of 3900 cm^2 g^{-1}.

2.4. Synthesis of ettringite

Ettringite was obtained by precipitation from solution containing stoechiometric mixture of burned CaO (obtained by calcination of $CaCO_3$ for 12 h at 1000 °C) and $Al_2(SO_4)_3 \cdot 16H_2O$ in excess of deionized water. The reaction is as follows:

$$6CaO + Al_2(SO_4)_3 \cdot 16H_2O + 16H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$$

After 7 days, the precipitate was washed with deionized water, filtered and then dried at 35 °C for one day. X-ray diffraction (XRD) analysis confirmed the product to be ettringite. A specific surface area of 10.4 m^2 g^{-1} was determined by N_2 BET measurement after drying at 45 °C under vacuum for 20 hours.

2.5. Preparation of cement pastes

All cement pastes were prepared at room temperature with a water/cement ratio (W/C) of 0.44, using a IKA Labortechnik mixer equipped with a 4-bladed propeller stirrer. First of all, aqueous SP solutions were prepared with deionized water for the reference polycarboxylate P(PEG_{60}-MAA_{40}) or with 0.1 N NaOH solution for all silylated SPs. Na_2SO_4 were added to the starting polymer aqueous solutions in order to study the effect of sulfate ions on the adsorption and rheological behaviors. Then, the pastes were prepared by mixing the cement powder with the polymer solution for 1 min at low speed and a further 2 min at high speed. The same procedure was used for C_3S with W/C = 1. For ettringite, the sample was prepared with W/C = 5 and sample suspension was stirred for 15 min before being extracted.

2.6. Analytical methods

2.6.1. Nuclear magnetic resonance (NMR)

^1H NMR spectra of polymers was performed in $CDCl_3$ at 25 °C with a Bruker Avance 200 (200 MHz) spectrometer. Liquid and solid state ^{29}Si NMR experiments were carried out on a Bruker Avance 500 MHz spectrometer in a 7 mm diameter probe. Triethylsilane and Q8M8 were used as reference for liquid and solid state experiments, respectively. For solid state NMR, cross-polarization magic angle spinning (CP-MAS) spectra were performed with a typical pulse length of 4 μs at spinning rate of 7 kHz.

2.6.2. Size exclusion chromatography

The weight-average molar masses (M_W, absolute values) and their distribution (PDI = M_w/M_n, the polydispersity index) were measured by size exclusion chromatography (Viscotek GPCmax) coupled with three detectors (light scattering, viscosity and refractive index) [20–21]. The measurements were performed at 35 °C using a 0.5 mol L^{-1} $LiNO_3$ aqueous solution (pH adjusted to 12.6 with NaOH) as eluent.

Table 1
Structural characteristics of synthesized polymers.

	Initial mol%			^1H NMR	Acid–base titration	^{29}Si NMR[a]		TGA		M_w (kDa)	PDI M_w/M_n
	MAPEG	MAA	MAPTS	PEG mol%	COOH mol%	Expected MAPTMS/TES ratio	Measured MAPTMS/TES ratio	wt.% SiO_2 calculated [b]	wt.% SiO_2 measured		
P(PEG_{40}-MAA_{60})	40	60	0	42	61	–	–	–	–	78	1.9
P(PEG_{40}-MAA_{55}-Si_5)	40	55	5	–	–	0.03	0.03	0.56–0.58	0.54	83	1.4
P(PEG_{40}-MAA_{50}-Si_{10})	40	50	10	–	–	0.05	0.05	1.18–1.20	1.15	69	1.3
P(PEG_{40}-MAA_{40}-Si_{20})	40	40	20	–	–	0.16	0.15	2.29–2.35	2.32	56	1.6
P(PEG_{40}-MAA_{30}-Si_{30})	40	30	30	–	–	0.26	0.27	3.33–3.46	3.37	67	1.9
P(PEG_{40}-MAA_{20}-Si_{40})	40	20	40	–	–	0.31	0.30	4.50–4.65	4.54	92	1.8
P(PEG_{40}-MAA_{10}-Si_{50})	40	10	50	–	–	0.38	0.37	5.63–5.82	5.67	97	1.9
P(PEG_{40}-Si_{60})	40	0	60	–	–	0.44	0.42	6.75–6.98	6.71	133	1.9

[a] ^{29}Si NMR analysis was performed on the final solution of polymerization using triethylsilane (TES) as internal standard.

[b] Theoretical mass of SiO_2 calculated with hypothesis of no hydrolysis and complete hydrolysis of alkoxysilane functions, respectively.

Table 2
Phase and chemical composition of the Portland cement used.

Cement type	C_3S (wt.%)	C_2S (wt.%)	C_3A (wt.%)	C_4AF (wt.%)	Na_2O_{eq} (wt.%)	SO_3 (wt.%)	Specific surface Blaine ($cm^2\ g^{-1}$)	Sulfate concentration[a] ($mmol\ L^{-1}$)
C1	57.6	20.5	3.6	13.1	0.15	2.5	4120	26
C2	67.1	8.7	14	4	0.79	3.58	4440	142

[a] Sulfate concentration in interstitial solution after 15 min measured by ICP (W/C = 0.44).

Polyethylene oxide (Mw = 21.917 kg mol^{-1}, PDI = 1.03 and Intrinsic Viscosity = 0.384) was used as reference.

2.6.3. Thermogravimetric analysis

Thermogravimetric measurements (TGA) were carried out using an SDT 2960 analyzer from TA Instruments equipped with a flow gas system. Experiments were performed under N_2 up to 600 °C then under air up to 1000 °C, at a heating rate of 10 °C min^{-1}.

2.6.4. Adsorption isotherms

Adsorption of SP on cement, C_3S and ettringite was measured using a total organic carbon analyzer (TOC-V, Shimadzu). 15 min after the contact between the polymer solutions and the powders, the interstitial solution was extracted from the paste by centrifugation at 4200 g for 10 min, and filtered with a 0.45 µm nylon filter. The adsorbed amount of SP was calculated from the difference between the organic content in the initial mixing aqueous solution and in the filtrated interstitial solution. Values were corrected from the carbone amount released by cement mixed with pure water. SP adsorption measurements on cement were repeated twice using a new fresh paste each time.

2.6.5. Rheological measurements

Rheological measurements were conducted with an AR 1000 N controlled stress rheometer (TA Instruments), equipped with a helix type geometry. The measurements were performed 15 min after mixing by preshearing the paste at a shear rate of 100 s^{-1} for 1 min, followed by a steady-state measurement at several stress values decreasing from the stress value corresponding to a shear rate of 100 s^{-1} to 0.01 Pa. The yield stress was calculated by fitting the rheogram data according to the Hershey–Buckley model [22]. The detection limit was estimated to 1 Pa.

2.6.6. Setting

The hydration of Portland cement paste was followed at 20 °C with a high sensitivity (0.1 µW) isothermal Tian-Calvet type microcalorimeter (TAM AIR, TA Instruments). Before starting the experiment, the cement paste was prepared in a plastic cell with 2 g of cement at W/C = 0.44 and at a dosage of SP/C equal to 0.1 or 0.3 wt.%. The cell was quickly introduced in the calorimeter before measurement.

2.7. Concrete equivalent mortar (CEM)

Concrete equivalent mortars were prepared with C1 and C2 cements to examine the influence of the sulfate alkali content included in cement powder on dosage requirement for SP. The mortar was prepared with 1350 g of normalized CEN sand, 679 g of cement and 303.3 g of water (20.9 g of water was used for pre-wetting the sand). The mixing protocol used was described by A. Schwartzentruber et al. [23] The minimum dosage of SP required to obtain a slump of 210 mm ± 10 mm was determined for all mortars. Slump flow was measured by pull out spread of the mortar from a cone of top diameter 50 mm, bottom diameter 100 mm and height 150 mm after 7 min of mixing. The spread was calculated from the average of three crossing diameters.

3. Results and discussion

3.1. Synthesis and characterization of SPs

A series of poly(poly(ethylene glycol) methyl ether methacrylate-*co*-methacrylic acid-*co*-trimethoxylsilyl proyl methacrylate), P(MAPEG-*co*-MAA-*co*-MAPTMS) or P(PEG-MAA-Si), with various compositions has been synthesized by radical copolymerization in THF in the presence of a chain transfer agent. Chemical structures of the synthesized polymers are shown in Fig. 1. The substitution of MAA by MAPTMS has been varied from 0 to 100 mol% and the percentage of PEG side chains has been fixed to 40 mol% for all polymers. The extreme compositions of the series correspond to reference polymethacrylate copolymer, P(PEG_{40}-MAA_{60}), on one side, and methacrylic acid-free SP, P(PEG_{40}-Si_{60}), on the other side. The principal characteristics (M_w and PDI) of the different SPs are summarized in Table 1.

The monomer conversion was determined by ^{1}H NMR spectroscopy in $CDCl_3$ by the relative integration of the protons of 1,3,5-trioxane at 5.1 ppm and the vinylic protons of monomers. For the reference copolymer P(PEG_{40}-MAA_{60}), the consumption of both monomers followed the same kinetics during the polymerization suggesting a random distribution of carboxylic acid and PEG side chains along the polymer backbone. The attempt to extrapolate this result to the terpolymers P(MAPEG-*co*-MAA-*co*-MAPTMS) was more complex due to the overlapping of the vinyl proton peaks of MAPTMS with the other monomers. We observed in all cases a conversion of monomers more than 96% after 24 h of reaction by comparing the integration of all the vinyl protons peaks relative to those of the methoxy protons of PEG side chains ($-$O-C**H**$_3$). The conversion yield close to 100% justifies that SPs may be used directly after evaporation of the solvent without further purification. We suppose that the residual polymerization reagents present after drying have no influence on the properties of the polymers.

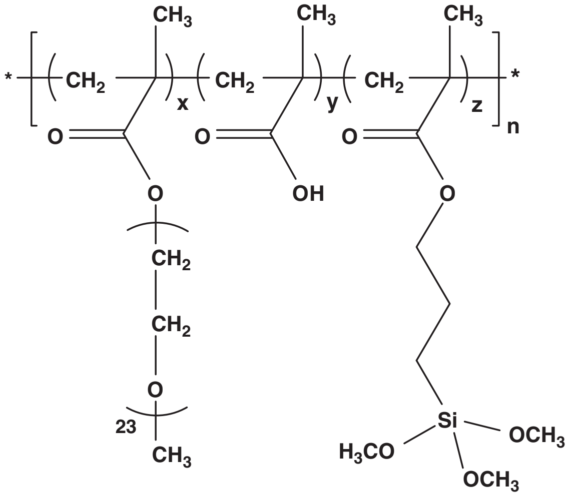

Fig. 1. Chemical structure of poly(poly(ethylene glycol) methyl ether methacrylate-*co*-methacrylic acid-*co*-3-(trimethoxylsilyl) proyl methacrylate), P(MAPEG-*co*-MAA-*co*-MAPTMS).

The expected amount of alkoxysilanes included in SPs has been confirmed by TGA and by quantitative ^{29}Si NMR carried out on the crude reaction medium. During polymerization, the formation of a little amount of methanol was observed by ^{1}H NMR indicating a partial hydrolysis of the trimethoxysilane functions into silanols. Such hydrolysis could not be avoided even in dry condition using water-free THF as solvent. ^{29}Si NMR spectroscopy was carried out to characterize the condensation of partially hydrated trialkoxysilane in the crude reaction mixture and then after drying (see Fig. 2). Before drying, the ^{29}Si NMR spectrum is characterized by a main peak at −42.7 ppm corresponding to uncondensed T^0 (C–Si(OR)$_3$; R = CH$_3$ or H) species. After drying, in addition to the T_0 environment, several condensed organosilanes are observed as T_1 (C-Si(OSi)$_1$(OR)$_2$,δ = −50.1 ppm) and T_2 (C–Si(OSi)$_2$ (OR)$_1$, δ = −59.1 ppm) species [24]. It appears that the drying step under reduced pressure caused inevitably the formation of inter- or intrachain siloxane bridges. The condensation of alkoxysilane may explain why the dried silylated polymers can neither be redispersed in THF nor in pure water. However, aqueous dispersion of the polymers is possible by using NaOH solution at pH between 12 and 13 due to the instability of siloxane bridges in basic medium. Moreover, hydrolysis of residual trimethoxysilane is mainly facilitated at high pH [25]. The good dispersion of silylated SPs in NaOH solution was confirmed by comparing the hydrodynamic radii determined by dynamic light scattering measurements of P(PEG$_{40}$-Si$_{60}$) and reference PC. Very similar hydrodynamic radii, 4.5 nm and 5.2 nm, were obtained for both copolymers respectively, confirming the disappearance of interchain siloxane bonds in alkaline medium.

3.2. Adsorption isotherms

The adsorption isotherms of P(PEG$_{40}$-MAA$_{60}$) and P(PEG$_{40}$-MAA$_{40}$-Si$_{20}$) on the low sulfate alkali C1 cement after 15 minutes of reaction are shown as examples in Fig. 3. The amount of adsorbed polymers increases gradually with the concentration of superplasticizers and then tends to saturate at SP/C higher than 0.2 wt.%. In the following and in order to limit the number of experiments, measurement were all performed at SP/C = 0.3 wt.% to access the adsorption capacity of each polymer in different experimental conditions.

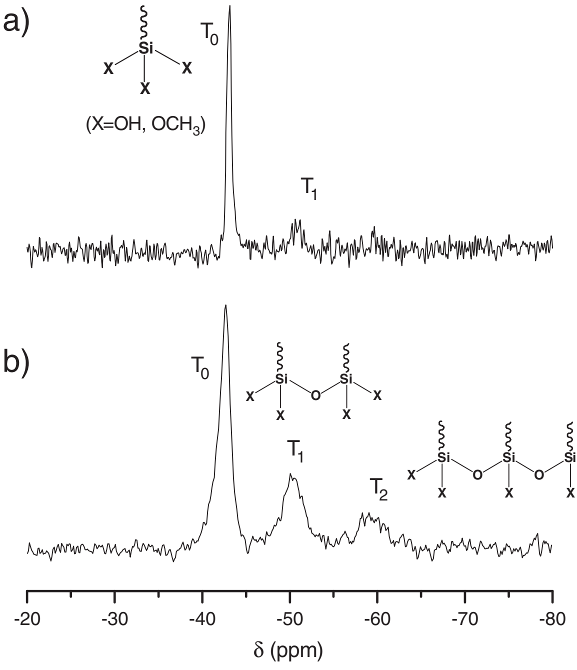

Fig. 2. (a) Liquid ^{29}Si NMR of crude THF solution of P(PEG$_{40}$-MAA$_{30}$-Si$_{30}$) after polymerization. (b) Solid ^{29}Si MAS NMR of P(PEG$_{40}$-MAA$_{30}$-Si$_{30}$) after evaporation of THF.

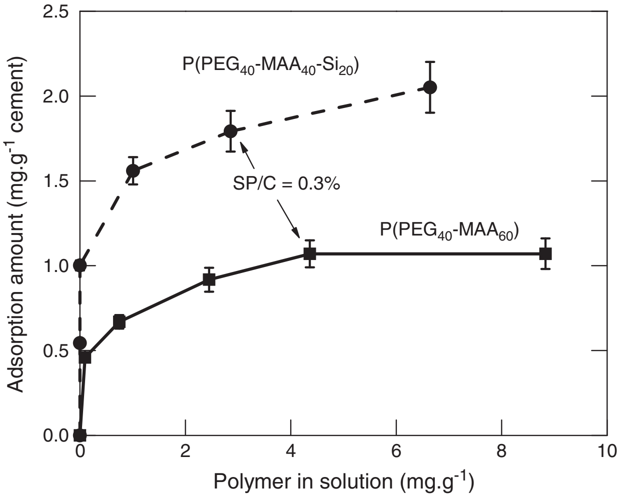

Fig. 3. Adsorption isotherms of P(PEG$_{40}$-MAA$_{60}$) and P(PEG$_{40}$-MAA$_{40}$-Si$_{20}$) on C1 cement (W/C = 0.44, t = 15 min).

3.3. Effects of alkoxysilane groups on SP adsorption

The substitution of carboxyl by trialkoxysilane groups has a strong impact on the adsorbed amount of SPs on cement. As seen in Fig. 4, the adsorption is enhanced by more than 1.5 for a carboxyl–organosilane substitution of about 20% and then gradually decreases for higher substitution. The adsorption of carboxyl-free polymer, P(PEG$_{40}$-Si$_{60}$), is slightly lower than for the reference PC. To characterize the influence of sulfate ions on the adsorption properties, measurements have been repeated in presence of 140 mmol L^{-1} and 200 mmol L^{-1} of Na$_2$SO$_4$ added to the starting aqueous solution. To access the real sulfate amount in cement paste during adsorption, which depends on the chemical equilibrium reaction during hydration and on the initial content of sulfate alkali in cement powder, interstitial solution has been extracted after 15 min and analyzed by Inductively Coupled Plasma (ICP). These experiments have been conducted on polymer-free mixtures and it was assumed that the obtained values were not influenced by the presence of SP. After an extra addition of 140 mmol L^{-1} or 200 mmol L^{-1} of Na$_2$SO$_4$,, the sulfate ion concentration, which is initially equal to 26 mmol L^{-1} for the C1 cement, reaches after 15 min 145 mmol L^{-1} and 195 mmol L^{-1}, respectively. As expected [12], an increase of the sulfate ion concentration induced a partial desorption of the reference PC P(PEG$_{60}$-MAA$_{40}$); by addition of 140 mmol L^{-1} of sodium sulfate the adsorbed amount falls from 1.1 to less than 0.5 mg of PC per g cement. However, with increasing substitution of carboxyl groups by alkoxysilane groups, the adsorption is less and less influenced by the presence of sulfate ions. This important result shows that the modification of polycarboxylate superplasticizers by the insertion of a few trimethoxysilane groups improves essentially the tolerance of SP to sulfate ions present in the interstitial solution.

3.4. Adsorption on pure phases

In order to improve the understanding of the adsorption mechanism of silylated SP on cement, adsorption experiments have been investigated on silicate tricalcium C$_3$S and ettringite phases. These both phases have been chosen as representative of silicate phases on one side and aluminate phases on the other. Because anhydrous tricalcium aluminate, C$_3$A, and tetracalcium aluminoferrite, C$_4$AF, phases are highly reactive in water, we preferred to use ettringite which is the principal aluminate hydrate formed at the early stage of hydration. As shown in

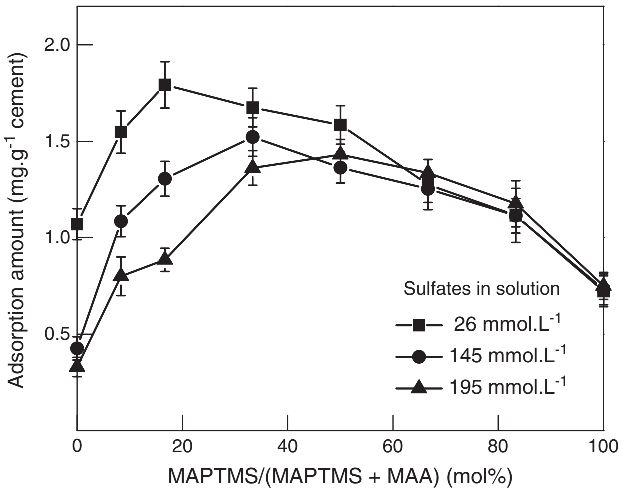

Fig. 4. Adsorption of P(MAPEG-*co*-MAA-*co*-MAPTMS) on C1 cement vs. the substitution percentage of MAA by MAPTMS and for different amount of sulfate ions in solution. Solid squares: adsorption on cement without extra addition of Na_2SO_4 to starting solution. Solid circles; adsorption on cement initially mixed with a 140 mmol L^{-1} of Na_2SO_4 solution. Solid triangles; adsorption on cement initially mixed with a 200 mmol L^{-1} of Na_2SO_4 solution. All the measurements have been done with a W/C = 0.44 and a SP/C = 0.3 wt.% after 15 min of hydration. The concentration of sulfate measured by ICP after 15 min is given in the figure.

Fig. 5, reference PC strongly adsorbs on ettringite probably via electrostatic interaction between carboxyl groups (COO^-) with the positively charged surface of ettringite [26]. The interaction of hydroxysilane groups, partially deprotonated at high pH, with ettringite is less effective and the polymer adsorption decreases by a factor more than 3 for the fully silylated polymer, P(PEG_{40}-Si_{60}). Whatever the composition of SPs, the adsorption onto ettringite decreases with the addition of sulfate ions, which compete with the carboxyl and hydroxysilane groups for the electrostatic interaction with ettringite. Interestingly, the adsorption behavior on C_3S is radically different. The adsorption of SPs on C_3S is improved by the substitution of carboxylate by silylated functions suggesting a stronger interaction of the second species compared to the first ones. Moreover, with the addition of sodium sulfate (100 mmol L^{-1}) in the aqueous solution, the adsorption of the reference PC drops to zero, whereas it remains high in silylated SPs. For these modified SPs the adsorption value does not depend on the level of substitution. These results are coherent with data published earlier by Franceschini et al. [18] on the adsorption of trialkoxysilane-modified polymers, such as polyvinylpyrrolidone or polydimethylacrylamide, onto CSH. It was demonstrated in this work the formation of covalent bonds between the silicate inorganic chains of CSH and silylated functions. Moreover, the efficiency of the linkage is such that only a few percents of these functions were sufficient to ensure strong adsorption on CSH. In contact with water, the surface of C_3S is quickly hydroxylated and covered by CSH grains [27]. The hydration reactivity of synthesized C_3S was confirmed by the increase of the specific surface area measured by BET from 0.7 to 1 m^2 g^{-1} after 15 min of hydration. Due to the strong similarities between the adsorption behavior of silylated polymers onto pure C_3S and synthesized CSH, it is likely that covalent bonds are formed between siloxane groups and the hydrated layer present at the surface of C_3S. In contrast to the ionic interactions formed between carboxyl groups and C_3S, which are easily displaced by sulfate ions, siloxane bonds are strong enough to resist to the addition of sulfate ions due to the “covalent” character of the bond.

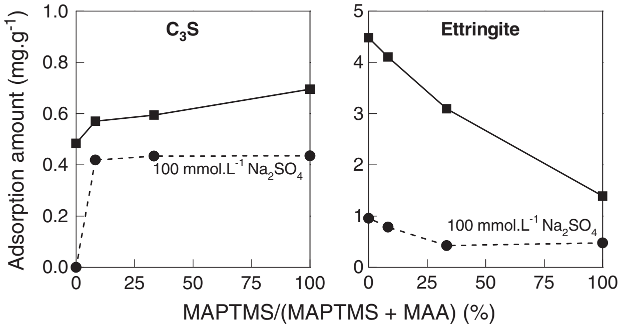

Fig. 5. Adsorption of SPs on C_3S and ettringite without addition of soluble sulfate ions (squares); and with addition of 100 mmol L^{-1} of Na_2SO_4 (circles). Measurements have been done with W/C = 1 and SP/C = 0.2 wt.% for C_3S and W/C = 5 and SP/C = 1 wt.% for ettringite. All polymers were dissolved in 0.1 M NaOH solution.

Thanks to adsorption measurements on C_3S and ettringite, it becomes possible to explain the adsorption behavior of silylated SPs on cement. By replacing a low fraction of carboxylate by alkoxysilane, the adsorption of SP on C_3S is improved by formation of strong bonds with C_3S. In contrast, the adsorption on positively charged aluminates is mainly driven by electrostatic interaction with carboxylate groups. Here, the addition of sulfate ions induces a partial desorption of the polymers. An increase of alkoxysilanes functions causes a partial loss of adsorption due to reduced electrostatic interactions via COO^- with aluminates. As the adsorption occurs now mainly on silicate phases, the displacement by sulfate ions is strongly suppressed.

3.5. Rheological properties

The effects of silylated SP on the fluidity of cement paste in function of the sulfate concentration have been investigated (Fig. 6). Without extra addition of sodium sulfate (data corresponding to sulfate concentration of 26 mmol L^{-1}), all the cement pastes containing polymer show good dispersing properties (yield stress < 5 Pa) compared to polymer-free paste (yield stress = 92 Pa), except for fully silylated SP, P(PEG_{40}-Si_{60}). As discussed above, P(PEG_{40}-Si_{60}) is preferentially adsorbed onto silicate phases. It is likely that an inhomogeneity of adsorption is responsible for flocculation to occur. As expected, when extra sulfate ions are introduced, the dispersing ability of reference PC decreases significantly due to a reduced adsorption. The dispersing abilities of silylated SP is less impacted by sulfate competition, especially for the SPs made with more than 20 mol% of trialkoxysilane, which is consistent with an adsorption which is less affected by sulfates in solution. The yield stress vs. the polymer adsorption amount at different sulfate content is shown in Fig. 7. We observe that the logarithm of the yield stress decreases linearly with the adsorbed mass independently of the level of MAA substitution by MAPTMS, except for the fully substituted polymer, P(PEG_{40}-Si_{60}), which has lesser performance, and for the

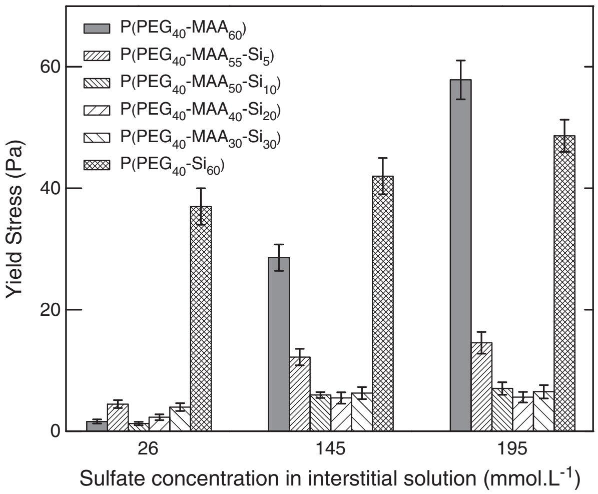

Fig. 6. Yield stress values of C1 cement paste formulated with 0.3 wt.% of SPs (SP/C = 0.3) vs. the sulfate concentration in solution.

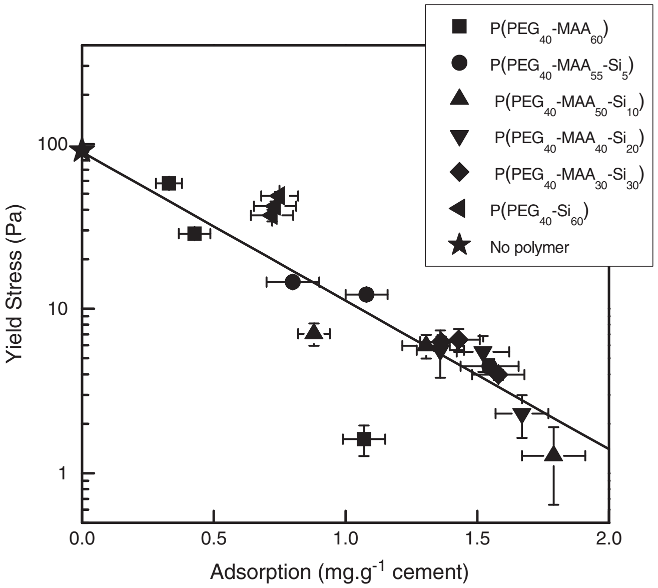

Fig. 7. Yield stress of C1 (0.3 wt.% of SPs) vs. the adsorbed amount of the polymers at different sulfate content.

silane-free copolymer, P(PEG_{40}-MAA_{60}) which is more efficient only at lower sulfate concentration.

3.6. Setting

To complete this work, the influence of polymer composition on the setting time of C1 cement has been carried out at a SP dosage of 0.1 and 0.3 wt.% (Table 3). For the low dosage in polymer and compared to the polymer-free cement paste, the setting is delayed for a few hours (about 5 hours), but depends weakly on the carboxyl-alkoxysilane ratio. However, at a dosage of 0.3 wt.%, a more significant retardation is observed for silylated SPs compared to reference PC. Curiously, the setting time is becoming shorter as the organosilane substitution increases. However, this effect seems to be correlated to the adsorption behavior which follows the same trend; superplasticizers incorporating too much alkoxysilane adsorb less effectively and then the retard effect, which is impacted by adsorption, is less important.

3.7. Concrete equivalent mortar

We have shown that the modification of SP by insertion of trialkoxysilane groups mainly reduced the problem of sulfate competition. However, this assertion has been demonstrated using only single cement. To make these admixtures attractive for practical use, the compatibility with different cements must be established. In order to demonstrate that for a required rheological property the SP dosage is independent of the amount of sulfate initially included in cement powder, concrete equivalent mortars have been designed with two Portland cements differing by their sulfate alkali content (namely C1 and C2 cement, see Table 2). P(PEG_{40}-MAA_{60}) and P(PEG_{40}-MAA_{40}-Si_{20}) have been used to improve workability and the amount of each SP has been determined in order to achieve a slump of 210 mm ± 10 mm. The required dosage of P(PEG_{40}-MAA_{60}) in mortar increases more than twice for the high alkali cement C2 compared to the low alkali cement C1 (see Fig. 8). On the contrary, the dosage of P(PEG_{40}-MAA_{40}-Si_{20}) remains the same for both mortars demonstrating the excellent performance of silylated SP with respect to the sulfate compatibility.

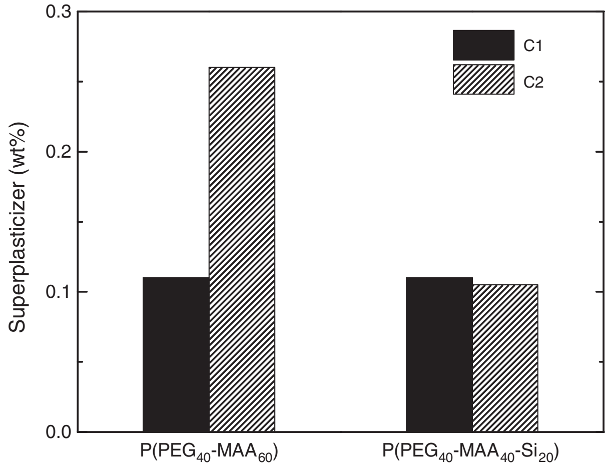

Fig. 8. Percentage of SPs (relative to cement) required in mortar formulated with a low C1 and a high C2 sulfate alkali cement to achieve a constant slump of 210 ± 10 mm.

Table 3
Setting time of C1 cement (W/C = 0.44) mixed with superplasticizers (SP/C = 0.1 and 0.3 wt.%).

Sample	Setting time (h)	
	SP/C = 0.1 wt.%	SP/C = 0.3 wt.%
Polymer-free paste	2.6	
P(PEG_{40}-MAA_{60})	7.8	13.3
P(PEG_{40}-MAA_{40}-Si_{20})	6.5	16.7
P(PEG_{40}-MAA_{20}-Si_{40})	7.1	15.5
P(PEG_{40}-MAA_{10}-Si_{50})	7.3	14.3

4. Conclusion

A series of polycarboxylate based superplasticizers modified with trialkoxysilane functions have been successfully synthesized by radical copolymerization. The adsorption on cement and the dispersing properties have been investigated in function of the polymer composition and at different concentration of sulfate ions in solution. It was found that a partial substitution of carboxyl by trialkoxysilane groups enhances the adsorption. However, an excess of silylated functions is detrimental for the adsorption. Insertion of a small amount of alkoxysilanes into polycarboxylate polymers greatly reduced the competition of adsorption with sulfate ions. It was found that silylated functions interact essentially with silicate phases and form strong bonds, which are insensitive to sulfate ions. The strong correlation between the adsorption level and dispersing ability makes the silylate-modified polycarboxylates very promising candidates that may improve the formulation robustness of concretes made with cements containing various amounts of sulfate alkali.

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