Interaction of polycarboxylate ether with silica fume

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Abstract

The interaction of silica fume with negatively charged polycarboxylate ethers in comparison to a polyacrylate and two non-ionic polyethylene glycols is investigated by adsorption and streaming potential measurements at slight alkaline pH value. The results indicate that polyethylene glycol is adsorbed on the silica fume in a flat conformation. Increased molecular weight however favours network formation. In contrast, the polyacrylate is adsorbed only in a very low amount due to a mutual electrostatic repulsion of the negative charged silica surface and the carboxylate groups. Polycarboxylate ether, which combine both structural features, a negative charged backbone and non-ionic polyethylene glycol side chains, adsorb via hydrogen bonding mechanism of the side chains with the silica particles. The adsorption rate of the polycarboxylate ethers predominantly increases with decreasing carboxylic equivalent. However, the adsorption affinity is determined by both, the carboxylic equivalent and the side chain length of the polycarboxylate ether.
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1. Introduction

In the last decades progress has been made in the refractory industry concerning the formulation of castables. This development resulted in, for example, low-cement castables wherein silica fume, also known as microsilica, plays an important role. On the one hand, microsilica acts as micro-filler yielding in an optimized granulometry down to sub-micrometer levels due to its small particle size. On the other hand, microsilica contributes to the formation of mullite as high-temperature phase, providing strength and improved abrasion and thermal shock resistance in refractories.[1] A typical bonding system of this class of refractory concrete consists of calcium aluminate cement, silica fume (each approximately 5–8% by weight of the castable), very fine calcined or reactive alumina and a dispersant.

Enormous progress has been made in the field of dispersants as well, making dispersants with novel architecture available. A new generation of plasticizers are the so-called polycarboxylate ether which are graft polymers based on an anionic backbone and non-ionic side chains. Originally, this type of superplaticiser has been applied in construction engineering. In Portland cement based systems they provide high-fluidity and high-strength due to their superior dispersing force for cement, especially at low water-cement ratios. A significant amount of research has been devoted toward increasing the understanding of Portland cement – dispersant interactions, focussing on, e.g. adsorption behaviour, mixing conditions for concrete, rheology control and so on.[2–10] In the meanwhile, polycarboxylate-type superplasticisers are applied in the refractory industry as well and it turned out that they are also very effective dispersants for calcium aluminate cement based systems.[11] In the past, several investigations proved the very positive impact of these polycarboxylate ethers on mainly microsilica-free and low silica containing castables in terms of water reduction, workability and strength.[12–15] Other experiments, however, revealed that polycarboxylate ethers could not always display their efficacy in castable formulations which contain silica fume in higher proportions.

The purpose of the present work is to study in a first approach the interaction of polycarboxylate ethers with silica fume in order to get a more fundamental insight into the reactions taking place in this type of binder system. Therefore, several structural different polycarboxylate ethers have been synthesised and their interaction with the solid silica surface has been analysed by adsorption and streaming potential measurements. A commonly available polyacrylate and two polyethylene glycols of different

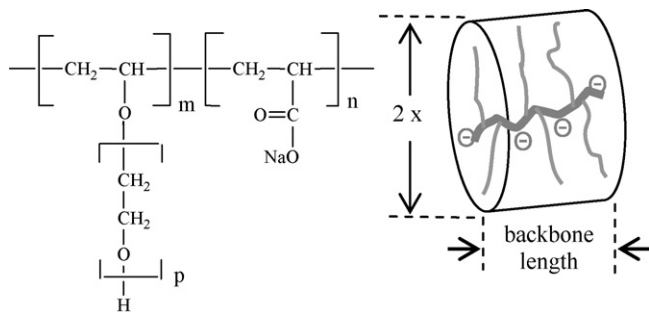* Tel.: +49 8621 86 3250 fax: +49 8621 86 2166.
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Fig. 1. Schematic structure of the polycarboxylate ethers. The diameter is twice the side chain length x.

Table 1
Chemical composition of silica fume.[a]

	Typical	Max.
SiO$_2$ (diff)	97.0%	
SiC	0.5%	1.1%
MgO	0.3%	0.4%
Al$_2$O$_3$	0.15%	0.3%
CaO	0.2%	0.3%
Na$_2$O	0.05%	0.1%
K$_2$O	0.8%	1.0%
Fe$_2$O$_3$	0.03%	0.1%

[a] As stated in the technical data sheet from the supplier.

molecular weight have been chosen as reference which should mimic the negatively charged backbone of the carboxylate ethers and the non-ionic side chains, respectively.

2. Experimental procedure

2.1. Starting materials and their characteristics

Polycarboxylate ether (PCE) of different carboxylic equivalents and side chain length as shown in Fig. 1 have been synthesised by radical polymerisation technique in aqueous medium and neutralized as sodium salt.[16] A detailed description of the composition of the polymers is given in Table 2. The molecular weight was evaluated by size exclusion chromatography (SEC) equipment from Waters & Co, using chromatography columns from Shodex calibrated with polyethylene oxide standards. A polyacrylate sodium salt (NaPA) with an average molecular weight $Mn = 5100$ was purchased from Aldrich Chemicals & Co and used as backbone model. The polyethylene glycols ($Mn = 2000$ Da and 20 kDa) which are used as side chain model are commercial products from Clariant GmbH, Germany.

The silica fume "RW-Füller Q1" used in this study is a commercial product from RW Silicium GmbH, Pocking, Germany, with a purity of >97 % and off-white appearance. The size of the primary particles is in the range of approximately 0.1–0.3 μm according the statements in the technical data sheet from the supplier. The amount of secondary particles, which are often generated during filtration and collection, is 30 % for particles below 1 micron and 5 % below 10 micron, respectively. The specific surface area as determined by nitrogen adsorption (BET) is stated to be in the range of 16–20 m^2/g. In the present study an average BET surface of 18 m^2/g was assumed for the calculation of the surface coverage. The entire chemical composition of microsilica is given in Table 1.

2.2. Adsorption isotherms

The adsorption measurements have been conducted at the native pH value of the silica suspensions, which scarcely changed after the polymer solution was added (around 8–8.5) and in the absence of any added electrolyte. This pH value is approximately 1 unit below a typical aqueous castable binder

matrix and should sufficiently reflect castable conditions. Aqueous suspensions containing 15 wt% of microsilica have been prepared with polymer concentrations up to 5% by weight of substrate. After ultrasonic treatment for 10 min at 120 W, the samples have been stirred for 1 h at ambient temperature. Preliminary tests revealed that this period of time is sufficient to reach adsorption–desorption equilibration. Afterwards, the suspensions have been filtered over a 0.45 μm syringe filter and the filtrate was injected into the columns of the SEC equipment. Polymer adsorption onto silica fume was deduced from data obtained from the areas of the SEC signals. A calibration curve ($R^2 > 0.99$) of each sample set was generated by injecting the initial polymer concentrations. The amount of polymer adsorbed was finally calculated by subtracting the residual amount in solution from the initial amount charged. For each polymer type, the adsorption isotherm has been determined from at least 16 different polymer concentrations.

2.3. Streaming potential measurement

The streaming potential as a function of pH has been measured by a particle charge detector PCD-03-pH (Mütec Analytic GmbH, Herrsching, Germany) of a 1 % suspension of silica fume in 0.01 n NaNO$_3$ solutions which was used as background electrolyte. At this concentration, the ionic strength should be sufficiently high so that the amount of additional ions deriving from the additives (Na as counter ion) and adjustment of the pH value can be neglected. On the other hand, higher concentrations of NaNO$_3$ have been avoided since it is known that a too high electrical conductivity can perturb the streaming potential measurement. For control, the electrical conductivity of the silica suspension was monitored during adjustment of the pH value. The conductivity of the silica suspension in 0.01 m NaNO$_3$ solution was 1.25 ± 0.05 mS/cm at the native pH of ca. 8 and increased during the adjustment by about 0.15 mS/cm towards a pH value of 3.5 and 11, respectively.

The polycarboxylate ethers and the polyethylene glycol have been added at a fixed concentration of 2.0% by weight of the substrate, which is near the saturation level of adsorption, while the polyacrylate has been added at 0.1% by weight of substrate, respectively. Staring from two individual samples, the pH value of the silica suspensions has been adjusted by the addition of either HNO$_3$ or NaOH prior to the filling of the measuring cell in order to achieve a stable pH value. The potential was read
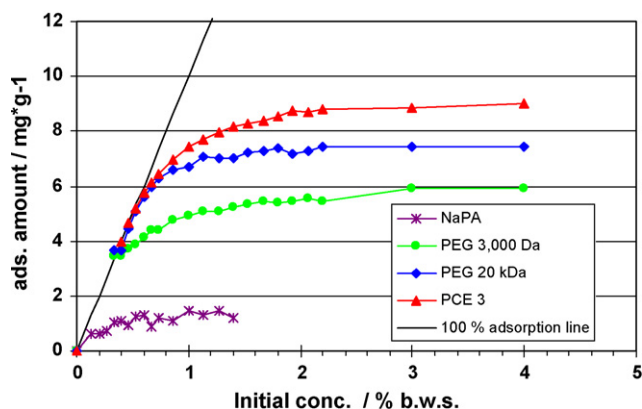
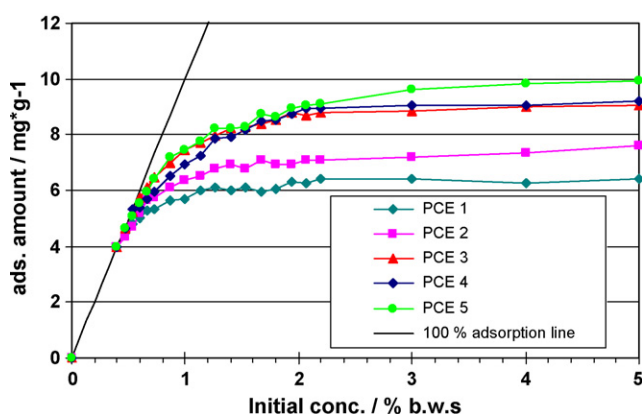Fig. 2. Adsorption isotherms for NaPA, PEG and PCE 3.

Fig. 3. Adsorption isotherms for PCE 1 to PCE 5.

after approximately two minutes, when it was sufficiently stable in most cases.

3. Results and discussion

3.1. Adsorption measurements

The adsorption isotherms of the polyacrylate and the two polyethylene glycols as well as the polycarboxylate ether PCE 3 (chosen as reference among the PCE types) are shown in Fig. 2. The adsorption behaviour of the modified polycarboxylate ethers PCE 1–PCE 5 is depicted in Fig. 3. The polycarboxylate ethers and the high molecular weight polyethylene glycol are com-

pletely adsorbed at concentrations up to approximately 0.5 wt%, the low molecular weight polyethylene glycol up to 0.2%, respectively. At higher concentrations, the amount of adsorbed polymer levels out until a plateau is reached. The shape of these adsorption isotherms suggests a monolayer adsorption of the polymers. The amount of adsorbed polycarboxylate ether increases in the series PCE 1–PCE 5 (see below for discussion). It is interesting to note, that rather similar adsorption rates are found for PCE 2 and PEG 20,000 Da ($\sim$7.5 mg/g$_{substrate}$) as well as for PCE 1 and PEG 3000 Da ($\sim$6 mg/g$_{substrate}$).

The adsorbed amount of polyacrylate on silica is rather low (<1 mg/g$_{substrate}$) which is in accordance with results reported in the literature.[18–20] At the pH value where the experiments have been conducted, the carboxylic groups are mostly deprotonated and therefore the polyacrylate is negatively charged. This leads to a mutual repulsion between carboxylate groups and the negatively charged silica surface, which impedes the accumulation of polymer chains on the silica surface. It might be argued, that the low adsorption amount derives from isolated hydrogen bonding between surface hydroxyl and carboxylate groups (SiOH $\leftrightarrow$ $^-$OOC– resp. SiO$^-$ $\leftrightarrow$ HOOC–) still present at the native pH value.

In contrast, the non-ionic polyethylene glycols adsorb on the silica whereby the adsorbed amount increases as the molecular weight increases. This interaction of the non-ionic polyethylene glycol can be explained by hydrogen bonding of the polyether units with the silanol groups on the silica surface.[21] Considering the dimensions of silica fume (average particle size 200 nm) and PEG 20 kDa in a stretched conformation (125 nm; see Table 2) it is very likely that polyethylene glycols of high molecular weight act as a flocculation agent by bridging several silica particles as depicted in Fig. 4.[22]

Regarding the polycarboxylate ethers PCE 1 to PCE 5, a different structural arrangement has to be considered. If the polycarboxylate ether molecule is stretched sufficiently in an aqueous environment, the backbone of the polymer can freely rotate around the C–C bonds and it can be expected that the entire molecule forms a brush like conformation with the charged backbone in the centre (longitudinal axis), whereas the side chains themselves are more or less helically looped. On the basis of a stretched conformation as depicted in Fig. 1 (right) and the molecular weight of the macromolecule, the size of the polymers was calculated in order to get an impression of the size ratios of polymers and silica particle. The length of the back-

Table 2
General characteristics and estimated dimensions of the polymers used.

Polymer	p (resp. mol wt)[a]	–COO$^-$ equiv. (/mol%)	mol wt (g mol^{-1})	Backbone length (nm)	Side chain length (nm)
Polyacrylate		100	5,100	15	0
PEG 3000 Da		0	3,000	0	20
PEG 20 kDa		0	20,000	0	125
PCE 1	135 (6000)	95	29,200	17	38
PCE 2	135 (6000)	92	30,600	17	38
PCE 3	135 (6000)	85	46,600	17	38
PCE 4	68 (3000)	85	25,200	17	19
PCE 5	135 (6000)	85	38,600	12	38

[a] p is the average number of ethylene oxide segments in the side chain. The average molecular weight is given in parenthesis.
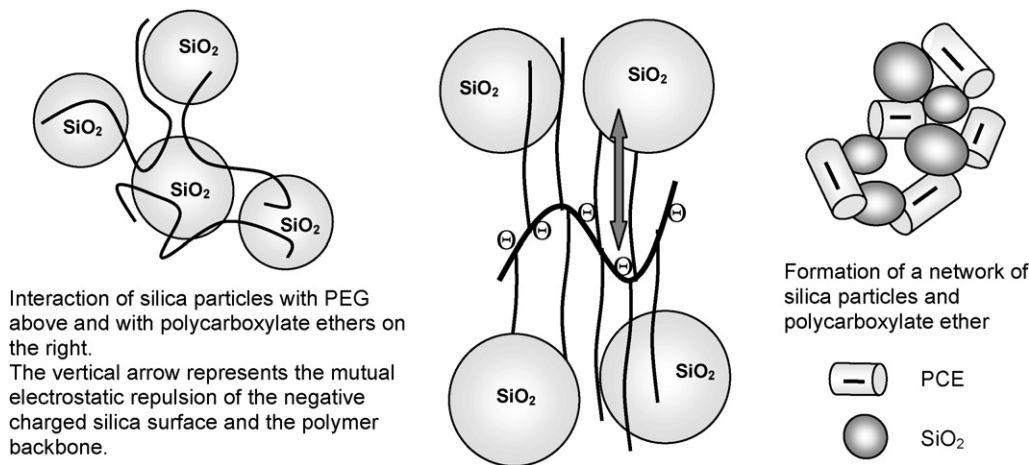
Fig. 4. Interaction mechanism of silica fume with PEG and polycarboxylate ether (PCE).

bone was calculated assuming a maximum stretched length of C–C–C in the main chain to be 2.51 Å.[17] The length of an ethylene glycol side chain was estimated on the basis of 19.5 Å for a 7-unit chain elongated in a stable conformation.[17] Accordingly, the dimensions of the two polyethylene glycol molecules as well as the polyacrylate in a stretched conformation were estimated. In Table 2 the corresponding data are listed.

As previously mentioned, polycarboxylate ether adopt a brush like conformation in aqueous environment. Due to the mutual electrostatic repulsion of the charged backbone and the silica surface only the polyglycol side chains, especially the terminal ethylene oxide units, are able to interact with the silica surface as depicted in Fig. 4. This leads to a bridging of the particles by the polycarboxylate ether, while PCE with long side chains should favour flocculation. Based on this interaction mechanism, both carboxylic equivalent and side chain length should determine the adsorption behaviour of polycarboxylate ether on microsilica. It can be argued that polymers with high carboxylic equivalents should lead to lower adsorption rates as polymers with low carboxylic equivalent. Indeed, as it can be seen from Fig. 3, the adsorbed amount of polycarboxylate ether increases with decreasing carboxylic equivalent (PCE 1–PCE 3).

Within the series of polycarboxylate ether of equal carboxylic equivalent the adsorbed amount of polymer at the saturation level is slightly higher if the backbone of the polycarboxylate ether is shorter (PCE 3 vs. PCE 5). A reduction of the side chain length from 6000 to 3000 Da has no significant influence (PCE 3 vs. PCE 4) on the adsorption rate. Apparently, a side chain length of 3000 Da is still long enough for bridging the silica particles.

For the polycarboxylate ethers and the polyethylene glycols the Langmuir model is found to be applicable in interpreting the adsorption behaviour. The Langmuir adsorption isotherm is expressed by the following equation[23]:

$$C_{ads} = \frac{kC_{max}C_{sol}}{(1 + kC_{sol})} \tag{1}$$

where C_{sol} is the equilibrium concentration of the polymer in solution (g/l), C_{max} the amount of adsorbed polymer for mono-

layer coverage (mg/g$_{substrate}$) and k a constant (l/g). This equation may be rewritten using a linear-raised form:

$$\frac{1}{C_{ads}} = \frac{k}{C_{max}} \frac{1}{C_{sol}} + \frac{1}{C_{max}} \tag{2}$$

Plotting $1/C_{sol}$ vs. $1/C_{ads}$ a straight line is obtained. The maximum adsorption concentration can be calculated from the intercept with the ordinate ($1/C_{max}$) and the constant k from slope of the line $1/kC_{max}$.

The initial slope of the adsorption curve, called the adsorption affinity Γ is given by the following equation:

$$\Gamma = \lim_{C \to 0} \frac{d}{dC}\left(\frac{kC_{max}C_{sol}}{1 + kC_{sol}}\right) = kC_{max} \tag{3}$$

Therewith, the adsorption affinity can be calculated from the obtained data C_{max} and k. The linear-raised plots for both, the polyethylene glycols and the polycarboxylate ethers, showed acceptable regressions lines with a correlation coefficient $R^2 > 0.94$. Due to the large scattering of data points in the case of the polyacrylate the linear fit was not applicable and, hence, the corresponding data have not been calculated.

In Table 3 the adsorbed polymer concentration at the plateau, C_{max}, obtained from the experiment as well as all calculated data are summarized. The calculated values for the maximum amount adsorbed, C_{max}, according to the Langmuir model are slightly higher but fit well to the values obtained by the experiment.

When looking at the data of adsorption affinity it is found that the adsorption affinity decreases as the carboxylic equivalent of the polycarboxylate ether decreases, while the opposite trend is observed for the adsorbed amount C_{max} within this series of polymers. For an explanation of this finding, it might be helpful to consider the side chain density of the polycarboxylate ether, which is related to the carboxylic equivalent of the polymers. If the carboxylic equivalent of the polymer is reduced, the side chain density is consequently increased, and vice versa. In this context, the side chain density is the lowest for PCE 1 with the highly carboxylic equivalent and the highest for PCE 3 (and as well for PCE 4 and PCE 5 which are composed of the same monomer ratio on molar basis). As a consequence of the lower

Table 3
Data obtained from the adsorption measurements; n.a. = not applicable. The error of the adsorption affinity Γ is estimated from the graphical plot to be ±0.1.

Polymer	–COO⁻ equiv. (mol%)	C_{max} (exp.) (mg/g)	C_{max} (calc.) (mg/g)	C_{max} (calc.)[a] (mg/m²)	k (calc.) (l/g)	$\Gamma = kC_{max}$ (mg l/g m²)
Polyacrylate			n.a.	n.a.	n.a.	n.a.
PEG 3000	0	5.9	6.3	0.4	1.7	0.8
PEG 20 kD	0	7.5	8.4	0.5	2.8	1.4
PCE 1 ($p = 135$)[b]	95	6.4	6.8	0.4	3.2	1.3
PCE 2 ($p = 135$)	92	7.6	8.1	0.5	2.2	1.1
PCE 3 ($p = 135$)	85	9.1	10.8	0.6	1.4	0.8
PCE 4 ($p = 68$)	85	9.2	11.2	0.6	1.0	0.6
PCE 5 ($p = 135$)	85	10.0	12.0	0.7	0.9	0.6

[a] Calculation based on an average surface area of 18 m²/g as indicated in the technical data sheet of the silica fume.

[b] p is the number of ethylene oxide segments in the side chain.

side chain density, the polyglycol side chains of PCE 1 should be more flexible which enhances the "end-on" adsorption of the side chains on the silica particles as displayed in Fig. 4. In this context, it is further interesting to compare the adsorption affinity of polycarboxylate ether PCE 3 and PCE 4, which differ only in their side chain length. As it can be seen by this example, the adsorption affinity is lower for PCE 4 which can be attributed to the increased electrostatic repulsion. It is worth to mention that these two PCE with different side chain length show similar adsorption rates C_{max}. Hence, it might be concluded that the adsorption affinity is predominantly influenced by the side chain length. Furthermore, among the investigated polymers, PCE 4 and PCE 5 reveal the lowest adsorption affinity, which is even lower than for PEG 3000 Da. The adsorption affinity of the highly charged PCE 1 is of the same magnitude as PEG 20 kDa, while PCE 3, PCE 4 and PCE 5 are at the level of PEG 3000 Da.

3.2. Streaming potential measurement

Streaming potential measurements of the pure silica fume suspension as well as with some selected polymers have been conducted in order to support the results obtained by the adsorption experiments. Therefore, measurements have been carried out at a fixed polymer concentration as a function of the pH value. A superposition of the curves is show in Figs. 5 and 6. The streaming potential of silica fume is negative over the whole pH range due to the negative surface charge and declines smoothly in the pH range from 2.5 to 8. The isoelectric point (IEP) of silica

is known to be generally in the range of 1.5–2.5, depending on the nature and concentration of present salts. A more detailed discussion regarding the IEP of silica can be found elsewhere in the literature.[24]

In the presence of polyacrylic acid, the streaming potential is less negative at a pH value below 5.5 than it is for the pure silica sample. At higher pH values, the streaming potential decreases down to −1000 mV. It can be argued that at pH < 5 the carboxylic groups of the polyacrylate are predominately protonated, favouring an interaction of the –COOH groups with the silanol groups of the silica surface. This interaction reduces the particle surface charge and as consequence the streaming potential is less negative. When increasing the pH value, the carboxylic groups get deprotonated and the charge density gradually increases. Hence, a mutual repulsion of both, particle and polymer occurs and the streaming potential can be regarded in first approximation as sum-parameter of the particle and the polymer charge.

In the case of the non-ionic polyethylene glycol the streaming potential is shifted to higher values and rather constant in the pH range of 4.5–8.5. This indicates that the adsorption of the polyglycol shields the negative surface charge of the silica particles. It can be further deduced that the adsorption behaviour of PEG should not be affected much by the variation of the pH value within this range. Considering the adsorption affinity Γ for both polyethylen glycols (PEG 3 kDa and PEG 20 kDa) calculated from the adsorption experiments, a flocculation mechanism as depicted in Fig. 4 is very likely, whereby the higher molecular weight PEG is more suited for flocculation.
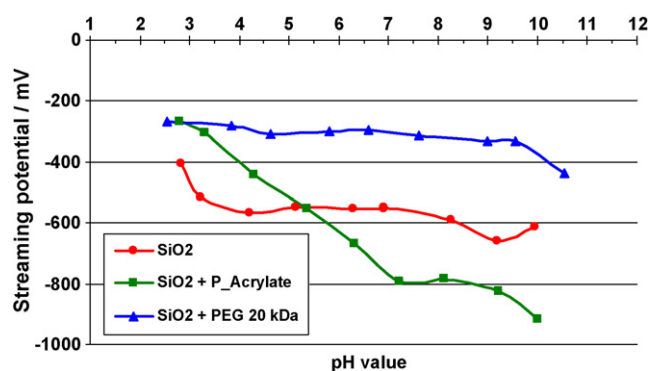

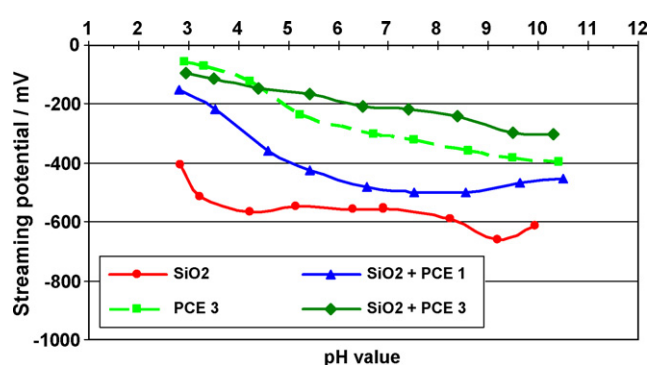Fig. 5. Streaming potential of SiO₂ and in presence of polyacrylate and PEG 20 kDa.

Fig. 6. Streaming potential of SiO₂ and in presence of PCE 1 and PCE 3. For comparison the curve of the pure PCE 1 is included as dashed line.

For the polycarboxylate ether PCE 1 and PCE 3 which combine both carboxylic groups and non-ionic polyglycol as structural units, it can be supposed that the streaming potential is a superposition of both reference polymers. Similarly to polyacrylic acid, the carboxylic groups of polycarboxylate ether are protonated at low pH value and the entire polymer itself is non-ionic. But with increasing the pH value, the carboxylic groups get continuously deprotonated and a brush-like conformation as depicted in Fig. 1 can be expected. At the native pH of the silica suspension, which is of interest here, only the polyglycol side chains of the polymer are able to adsorb onto the silica surface, while both the negatively charged carboxylate groups as well as the silica surface mutually repel as in the case for polyacrylic acid. Hence, the strength of the interaction of polcarboxylate ethers and silica is determined by the attractive forces of the side chains of the polymer and the repulsive forces of the negative charged backbone as shown in Fig. 4. Indeed, the streaming potential of the silica samples with PCE 1 and PCE 3 differs significantly in the range of pH $\sim$ 7 to 8.5, whereas the latter sample with PCE 3 shows in the entire pH range the lowest potential overall. It can be argued that the electrostatic repulsion between polymer and silica surface is less for the polycarboxylate ether with the lowest carboxylic equivalent (PCE 3), favouring the adsorption of the polyethylene glycol side chains. This leads to a better "shielding" of the of the silica surface with the consequence that the streaming potential decreases. In contrast, if the electrostatic repulsion forces are dominating as it the case for PCE 1, the adsorption of the polyglycol side chains is less favoured and the potential is rather similar to the pure silica sample. At this point it is interesting to recall the results of the adsorption measurements where the adsorbed amount of polymer increases as the carboxylic equivalent of the polymer decreases. In this context, the results of the streaming potential measurements are consistent and support the discussed adsorption model.

4. Conclusion

From the results obtained it can be concluded that polycarboxylate ether adsorb within the given pH-range via their polyethylene glycol side chains on silica fume. A low carboxylic equivalent in the polymer backbone favours the adsorption. In contrast, adsorption is low for polycarboxylate ethers with high carboxylic equivalent in their backbone and impeded for polyacrylic acid in particular, which possesses no side chains. This is due to the mutual electrostatic repulsion of the negative backbone and the silica surface.

However, the adsorption affinity is a function of both, the side chain length of the polymer and its carboxylic equivalent. If the side chain of the polycarboxylate ether is sufficient long, the adsorption affinity increases as the carboxylic equivalent of polycarboxylate ether increases. This is due to the more flexible side chains, which enhances the "end-on" adsorption of the side chains on the silica particles.

Considering the results, polycarboxylate ethers with both high carboxylic equivalent and short side chains (less than 3000 Da) should be more suited as dispersants for microsilica containing refractory concretes, which is currently under investigation.

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