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Effects of the molecular architecture of comb-shaped superplasticizers on their performance in cementitious systems

Frank Winnefeld [a,*], Stefan Becker [b], Joachim Pakusch [b], Thomas Götz [b]

[a] *Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Concrete/Construction Chemistry, Überlandstrasse 129, 8600 Dübendorf, Switzerland*

[b] *BASF AG, GKD/C-B1, Carl-Bosch-Strasse 38, 67056 Ludwigshafen, Germany*

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Abstract

The objective of this study is to link the molecular structure of polycarboxylate-ether-type superplasticizers with the performance of cementitious systems in order to develop new products with enhanced properties, e.g. improved water reduction with a wide range of cements or a reduced retardation of cement hydration. Different experimental superplasticizers have been synthesized varying length and density of the polyether chains as well as the molecular weight of the polymer. The influence of these polymers on the properties of cement pastes and mortars was determined using various characterization methods like mortar flow, rheological and calorimetric measurements, adsorption measurements and mortar compressive strength.

Characteristic connections between molecular structure of the polycarboxylate-type water reducers, adsorption behaviour, workability and retarding effect have been determined allowing the synthesis of new superplasticizers with improved performance.
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1. Introduction

Superplasticizers are nowadays commonly used in concrete technology to improve the workability of cementitious systems. On one hand, they enable the production of concretes with special flow properties like self-compacting concrete. On the other hand, superplasticizers allow concrete mix designs with very low water/cement ratios. Thus, high performance concretes with very high strength and durability can be achieved.

Among the first generation superplasticizers are sulphonated naphthalene–formaldehyde condensates, sulphonated melamin–formaldehyde condensates and modified lignosulphonates; the new generation products with enhanced properties are based on comb-shaped polycarboxylate-based polymers. The superplasticizers are adsorbed on the cement particles and act as dispersants by electrostatic and/or steric repulsion effects as demonstrated by Uchikawa et al. [1].

The workability properties of cement pastes, mortars and concretes containing superplasticizers are depending on various parameters. On one hand, the type, the chemical composition and the molecular structure of the admixture [2–10] influence the rheological properties (e.g. apparent yield stress, viscosity, concrete slump). On the other hand, the chemical composition of the cements (especially C_3A-content and availability of soluble sulphates during workability time), their specific surface, the presence of mineral additions or of other types of admixtures as well as the hydrate phases formed during early hydration affect the behaviour of superplasticizers in pastes, mortars and concretes [11–20].

Despite the increasing number of ongoing research projects, there are still many unsolved problems when using superplasticizers in cementitious systems. Effects like poor

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[*] Corresponding author. Tel.: +41 44 823 4535.
E-mail address: frank.winnefeld@empa.ch (F. Winnefeld).

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flow behaviour, early slump loss, strong retardation or flash set may be the result of an incompatibility between the binder and the superplasticizer.

Many papers on superplasticizer–cement interactions do not present the molecular structure of the admixtures used. This paper is aimed to be a contribution to close this gap by presenting a parametric study involving systematic variations of the molecular structure of the admixtures. The objective of this study is to link the structural parameters of polycarboxylate-ether type superplasticizers with their performance in cementitious systems in order to develop new products with enhanced properties; e.g. improved water reduction with a wide range of cements and/or reduced retardation of cement hydration.

2. Materials

2.1. Superplasticizers

Different experimental superplasticizers of polycarboxylate ether (PCE) type (copolymers of methylpolyethyleneglycole-methacrylate and methacrylic acid) have been synthesized with varying length and density of the polyether chains and varying molecular weight. Fig. 1 shows the chemical structure of the experimental superplasticizers used in this study. They were applied as sodium salts.

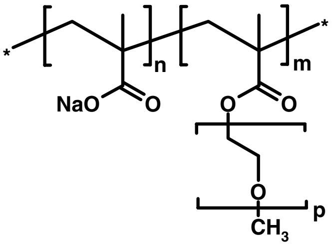

Fig. 1. Chemical structure of the experimental superplasticizers (copolymers of methylpolyethyleneglycole-methacrylate and methacrylic acid, sodium salts); m:n = 1:2, 1:3, 1:4, $p = 9$, 23, 45.

In principle two different access routes to comb-shaped PCEs are known: (i) radical polymerization of (meth)acrylic acid and optional other comonomers to form the backbone followed by polymer analogue linking of mono end-capped polyethylene glycoles ("alkyl-PEG") [21], and (ii) preformation of mono unsaturated "teeth" via linking of (meth)acrylic acid units with alkyl-PEGs followed by radical copolymerization of these macromonomers with additional (meth)acrylic acid and optional other comonomers [22,23].

The model PCEs used in this study have been synthesized according to the second path. During the polymerization step the molar concentrations of all monomers were kept constant to ensure the same reaction kinetics in all examples. Due to the molecular weight difference of the macromonomers used here, this led to different final solids contents, which was compensated in all paste and mortar tests. Therefore, all dosages given in this paper are referring to the dry matter of the admixture.

In total, 11 superplasticizers based on polycarboxylic acid with systematic structural variations (length of side chains, density of side chains and molecular weight of polymer) have been synthesized. As reference polymer polymethacrylic acid (= backbone polymer without side chains) was used. Molecular weight of the polymers was determined by size exclusion chromatography (SEC). Table 1 shows the characteristic properties of the polymers. It is important to note, that the charge density of the polymer increases with decreasing side chain density and with decreasing side chain length, leading to an increasing amount of free carboxylic groups. This is supported by experimental data of Plank et al. [24], who determined the anionic charge densities of various PCEs of similar molecular architecture. It is expected that the adsorption of the polymers is enhanced with increasing charge density.

Table 1
Characterization of the polycarboxylate ether superplasticers

Polymer	Length of EO chain l (see Fig. 1)	Density of side chains m:n (see Fig. 1)	Molecular weight M_n[a] (g/mol)	Molecular weight M_w[b] (g/mol)	PDI[c] M_w/M_n	Solid content (mass%)
PMA	–	–	3900	9100	2.3	40.1
PCE 9-1:2	9	1:2	9700	17,900	1.8	13.1
PCE 9-1:3	9	1:3	9600	18,800	1.8	11.4
PCE 9-1:4	9	1:4	9400	18,600	1.9	10.0
PCE 23-1:2	23	1:2	12,100	28,300	2.3	25.7
PCE 23-1:3	23	1:3	11,300	24,500	2.2	20.4
PCE 23-1:4	23	1:4	11,400	23,000	2.0	16.6
PCE 45-1:2	45	1:2	12,700	47,100	3.7	44.2
PCE 45-1:3	45	1:3	13,300	39,400	3.0	34.0
PCE 45-1:4	45	1:4	12,200	35,500	2.9	28.3
PCE 23-1:4-L	23	1:4	9500	17,600	2.4	17.5
PCE 23-1:4-H	23	1:4	14,200	33,900	1.9	17.6

[a] M_n = number-average molecular weight.
[b] M_w = mass-average molecular weight.
[c] PDI = M_n/M_w = polydispersity index.

Table 2
Chemical composition of the used ordinary Portland cement CEM I 42.5 N

CaO (wt.%)	MgO (wt.%)	SiO_2 (wt.%)	Al_2O_3 (wt.%)	Fe_2O_3 (wt.%)	Na_2O (wt.%)	K_2O (wt.%)	SO_3 (wt.%)	CO_2 (wt.%)	LOI[a] (wt.%)	Free lime (wt.%)
63.3	1.7	20.0	4.8	2.4	0.09	1.15	2.98	2.20	2.74	0.64

[a] LOI = loss on ignition.

Before the superplasticizers were used in the experiments, a defoaming agent (fatty alcohol alkoxylate) and a biocide (water based combination of chloromethyl-/methylisothiazolone (CMI/MI) and N-/O-formals) were added to all polymers. The dosages were 0.8 wt.% referring to the solid content of the PCE for the defoaming agent and 0.2 wt.% referring to the PCE solution for the biocide.

2.2. Portland cement

An ordinary Portland cement CEM I 42.5 N according to European Standard EN 197-1 with a specific surface of 2900 cm^2/g (Blaine method) was used. The chemical composition is given in Table 2.

3. Methods

3.1. Mortar tests

The mortar tests were carried out with a polymer dosage of 0.20% referring to cement weight. Standard quartz sand 0–2 mm according to European Standard EN 196-1 was used as aggregate. Cement/aggregate ratio was 1:3 by mass, water/cement ratio was set to 0.45. The admixtures were dissolved in the mixing water.

A mixer according to EN 196-1 at stage I (62.5 rpm) was used to prepare the fresh mortars. Cement and sand were mixed for 1 min. The mixing water was added progressively during the next 30 s. After continuing the mixing for 90 s it was stopped for 15 s in order to scrape off the material that had adhered to the sides of the mixing bowl with a plastic spatula. After that, the mixing was continued for 90 s.

Density and air content of the fresh mortars were tested according to EN 1015-6 and EN 1015-7, respectively. A cone according to EN 1015-3 with an upper diameter of 70 mm, a lower diameter of 100 mm and a height of 60 mm was used to perform the mortar flow test by measuring the resulting mortar flow (maximum spread diameter). The test was carried out on the same mixture 5 min, 30 min, 60 min and 90 min after starting the mixing process. Between the measurements the fresh mortar was stored in the mixing bowl covered by a damp cloth to prevent the material from drying out.

Compressive and flexural strength were tested according to EN 196-1 at various sample ages. Standard prisms 40 mm × 40 mm × 160 mm were prepared. The samples were demoulded after 24 h and afterwards cured under water until testing.

3.2. Rheology

For the rheological experiments a Paar Physica MCR 300 rheometer was used. A cylindrical measuring geometry according to ISO 3219 with a cup and a rotating bob was applied (Searle geometry) to measure the flow curves. The measuring gap was 1.13 mm with a ratio outer to inner radius of 1.0847.

To blend the cement with water and superplasticizer, a mixer according to European standard EN 196-1 was used. 300 grams of cement were taken for each measurement. The water/cement ratio was kept at 0.35. The polymer–cement ratio was varied between 0.10% and 0.50% of cement weight, the admixtures were dissolved in the mixing water. The mixing water was filled into the mixing bowl. Afterwards the cement was added, and the mixing process was started.

The mixing procedure was set at 90 s of mixing at stage I (62.5 rpm), a 30 s pause to mix the paste by hand and then 90 s of mixing at stage I again. The pause was necessary to scrape off the paste, which sticked to the bowl. Afterwards the cement paste was transferred into the rheometer cup with a spoon. The measuring system was then lowered into the cup, and the cup was covered with a solvent trap to keep humidity high during the experiment. The temperature of the paste was controlled by a water bath and kept constant at 20 °C.

The measurement started 5 min after water or the admixture containing solution was added to the cement. First, 1 min of pre-shearing at a shear rate of 100 s^{-1} was performed to break the particle agglomerates in the suspension. After that, a flow curve with shear rates between 100 and 0.1 s^{-1} was recorded using ramp times of 5 s in the shear rate range 100–1 s^{-1} and of 10 s for shear rates below 1 s^{-1}. Apparent yield stress and plastic viscosity were calculated according to the Bingham model.

3.3. Conduction calorimetry

The measurements were carried out on cement pastes with a water/cement ratio of 0.40. A conduction calorimeter (Thermometric TAM Air) was used for the experiments. 6.00 grams of cement were weighed into a flask and 2.40 ml of water or the admixture containing aqueous solution were added. The mixing was done by a small stirrer for 2 min. The flask was then capped and placed into the calorimeter. Due to the external mixing, the initial heat peak (first maximum right after the addition of water to cement) could not be measured. The heat flow was then recorded for 72 h. Measuring temperature was 20 °C. The influence of different dosages (0.10%, 0.20%, 0.30% of cement) of each superplasticizer on the rate of heat liberation was examined. From the calorimetric curve the onset of the acceleration period was derived in the following way: (i) the minimum heat flow during the dormant period was determined, (ii) 0.25 J/(g · h) was added to this value; this was defined as the heat flow at the onset of the acceleration period, and (iii) the corresponding hydration time was defined as the onset of the acceleration period.

The start of the acceleration period determined from heat flow calorimetry using the described method corresponds roughly to the initial setting determined by the Vicat needle test according to European Standard EN 196-3. Thus it can be used as a comparative value for initial setting of the different superplasticizer–containing cement pastes.

3.4. Size exclusion chromatography

The molecular weight of the polymers and its distribution were determined by size exclusion chromatography. All samples were filtered through a 0.2 μm filter before measurement. 100 μl solution with a polymer concentration of about 2 g/l were injected into the column. A combination of three columns – TSK G 4000 PWxl (size exclusion PEG/PEO 2000–3,000,000 g/mol), TSK G3000 PWxl (size exclusion $\leqslant$50,000 g/mol) and TSK 2500 PWxl (size exclusion <3000 g/mol), was used as stationary phase. The length of each column was 30 cm with an inner diameter of 7.8 mm. The column temperature was set at 30 °C. As solvent 0.08 mol/l tris(hydroxymethyl)-aminomethan-buffer pH 7.0 in distilled water with 0.15 mol/l Cl^- and 0.001 mol/l NaN_3 added was applied. The number of exchange plates at the applied flow rate of 0.5 ml/min was around 40,000. As detectors a differential refractometer and a UV-photometer (wavelength 225 nm) were used. From the obtained elution curves the molecular weight distribution was calculated using a calibration with polyethylene glycol standards.

GPC was also applied to determine the amount of polymer adsorbed on the cement particles by the solution depletion method. 50 g of cement and 20 ml of water or the admixture containing aqueous solution (water/cement ratio 0.40) were placed in a plastic container and mixed by hand with a spatula for 2 min. Superplasticizer dosage was 0.20% of cement (or 2.00 mg per g cement). After 5, 30 and 60 min the pore solution was removed through a 0.45 μm filter by vacuum filtration. The alkaline pore solution was stabilized by adding nitric acid; the pH was adjusted to 2–3. These solutions were measured by GPC as described above. The percentage of polymer adsorbed on the cement was calculated from the integrals of the molecular weight distributions using a reference measurement of the aqueous polymer solution.

In contrast to a determination of polymer adsorption by measurement of the total organic content (TOC) in the pore solution, the GPC measurement also reveals, which molecular weight fractions of the polymers preferably adsorb on the cement.

4. Results and discussion

4.1. Air content and density of fresh mortar

Entrained air may significantly influence for instance the rheological properties or the compressive strength. In order to compare the workability of different mixtures, their air content should be within a narrow range. Therefore, a defoaming agent was added to all superplasticizers before use. The air content (see Table 3) of the reference mixture without admixture is 5.4 vol.%, and for the mixtures with superplasticizers between 4.4 vol.% and 6.7 vol.%. Corresponding to this, the fresh mortar densities of all mortars are in a comparable range between 2220 kg/m^3 and 2263 kg/m^3. Thus it can be assumed, that the results of

Table 3
Influence of superplasticizers on fresh mortar properties, SP dosage 0.20 mass% of cement

Polymer	Air content/vol.%	Density /kg/m^3	Spread diameter/cm			
			5 min	30 min	60 min	90 min
Reference	5.4	2243	12.6	n.d.[a]	n.d.[a]	n.d.[a]
PMA	4.4	2263	14.6	13.2	12.8	13.0
PCE 9-1:2	6.5	2223	16.7	16.4	16.3	16.3
PCE 9-1:3	5.5	2245	16.3	16.8	16.9	16.6
PCE 9-1:4	5.0	2243	16.5	16.3	16.6	16.4
PCE 23-1:2	6.1	2230	15.0	15.2	15.3	15.4
PCE 23-1:3	5.8	2220	17.1	18.2	18.3	18.0
PCE 23-1:4	6.7	2203	17.8	18.6	18.4	18.1
PCE 45-1:2	5.4	2243	14.3	14.5	14.5	14.5
PCE 45-1:3	5.1	2247	17.3	17.5	17.7	17.4
PCE 45-1:4	5.5	2227	18.5	18.4	18.4	18.1
PCE 23-1:4-L	5.1	2238	18.4	18.4	18.3	18.2
PCE 23-1:4-H	5.0	2251	16.9	17.5	17.7	17.5

[a] n.d.: not determined (mortar too stiff to perform flow test).

the mortar workability tests and strength measurements are only slightly influenced by different air contents.

4.2. Mortar flow test

The results are given in Table 3. The reference mortar without admixture shows a spread diameter of 12.6 cm when tested 5 min after start of mixing. After 30, 60 and 90 min the slump flow could not be determined, because the mortar became too stiff to perform a reliable measurement.

All superplasticizers improved workability compared to the plain mortar. The spread diameter of all PCE-containing mortars remained mainly constant over time. Therefore the slump tests performed after 30, 60 and 90 min are not discussed any further.

The mortar with added polymethacrylic acid (PMA) causes the slightest improvement of workability when all polymers are compared. This could be expected, as this polymer has no polyethylene-oxide (PEO) side chains. Its dispersing effect can be regarded as mainly electrostatic.

Concerning short side chains with 9 ethylene-oxide (EO) units, the workability does not seem to depend on the side chain density. For medium (23 EO units) and long (45 EO units) side chains there is a trend that a lower side chain density improves the flow. As a tendency, an increasing length of the side chain influences flow positively for side chain densities 1:3 and 1:4. In general, short side chains (9 EO units) and high side chain densities (1:2 molar ratio between methylpolyethyleneglycole-methacrylate and methacrylic acid monomers) lead to only minor improvement of workability. In the first case, this is probably related to a poor steric repulsion effect due to the short PEO chains. In the second case, the low charge density of the polymer may lead to a poor adsorption of the polymer on the cement particle surface.

There is only a slight influence of the polymer molecular weight on mortar workability in the case of the examined polymers. The mortars with PCE 23-1:4-L, PCE 23-1:4, and PCE 23-1:4-H added show almost the same spread diameters.

4.3. Rheology

The workability measurements of standard mortars as described above may be influenced by segregation of the aggregates or bleeding. Also only one superplasticizer dosage has been examined in the experiments. Thus, rheological measurements on cement pastes have been performed with different PCE concentrations between 0.10% and 0.50% of cement weight. The results obtained for apparent yield stresses and plastic viscosities from Bingham evaluation of the flow curves are given in Fig. 2.

With increasing side chain density of the superplasticizer the dosage, which is needed to reduce the apparent yield stress below 1 Pa, increases. Concerning the polymers with side chain density 1:2, an apparent yield stress below 1 Pa was not reached even at a dosage of 0.5% of cement weight. This effect is probably related to a poor adsorption behaviour. Polymethacrylic acid (which can be regarded as a polycarboxylate with an infinite low side chain density) also shows a plasticizing effect; apparent yield stress is reduced below 1 Pa at concentrations of 0.3%. Hence, there must be an optimum polymer structure with respect to the side chain density beyond 1:4 in the case of the examined cement.

The length of the side chains has only a minor influence on the rheology of the examined cement-PCE-combinations for side chain densities 1:3 and 1:4. In the mortar slump flow test, however, a slight increase in slump flow can be found for polymers with longer side chains (e.g. for polymers with side chain density of 1:4 slump flow after 5 min is 16.5 cm, 17.8 cm, and 18.5 cm for side chain lengths of 9, 23, and 45 PEO units, respectively). But the correlation between flow of cement paste and mortar flow after 15 times shocking on the shocking table seems not to be trivial. Schober and Flatt [10] e.g. found no correlation between the mortar flow with shocking and the mini-slump flow of pastes without shocking. While the latter is directly correlated to the yield stress [25,26], the authors state that the influence of the shocking is dependent on other factors like mortar density and plastic viscosity. Also segregation and bleeding phenomena may influence mortar slump flow.

The results for the polymers with side chain densities of 1:2 reveal that longer PEO chains lead to higher values of apparent yield stress and viscosity. This effect seems surprisingly as longer side chains are expected to cause higher repulsion forces. Also other authors found the opposite effect, e.g. Yamada et al. [2] used superplasticizers with a related structure; methallyl sulfonic acid was also copolymerized into the backbone chain of their molecules. They found in their system that longer PEO chains gave lower apparent yield stresses and lower plastic viscosities. In the present case the charge density of the polymers has to be taken into account. PCEs with side chain densities of 1:2 generally exhibit a low charge density of the backbone. The overall charge density of the polymers decreases with increasing side chain length; the charge density of the PCEs is related to their adsorption behaviour. Thus, the increase of apparent yield stress and plastic viscosity at a given polymer dosage with increasing side chain length can be explained by the fact that less polymer is adsorbed.

4.4. Conduction calorimetry

Besides the workability improvement, the influence of superplasticizers on cement hydration (generally retardation) is of special importance in concrete technology.

Fig. 3 gives the influence of the PEO side chain length (side chain density 1:3) on the development of hydration heat of cement pastes with 0.3% of superplasticizer added. The plain cement without any addition of PCE shows a dormant period associated with a relatively low heat flow

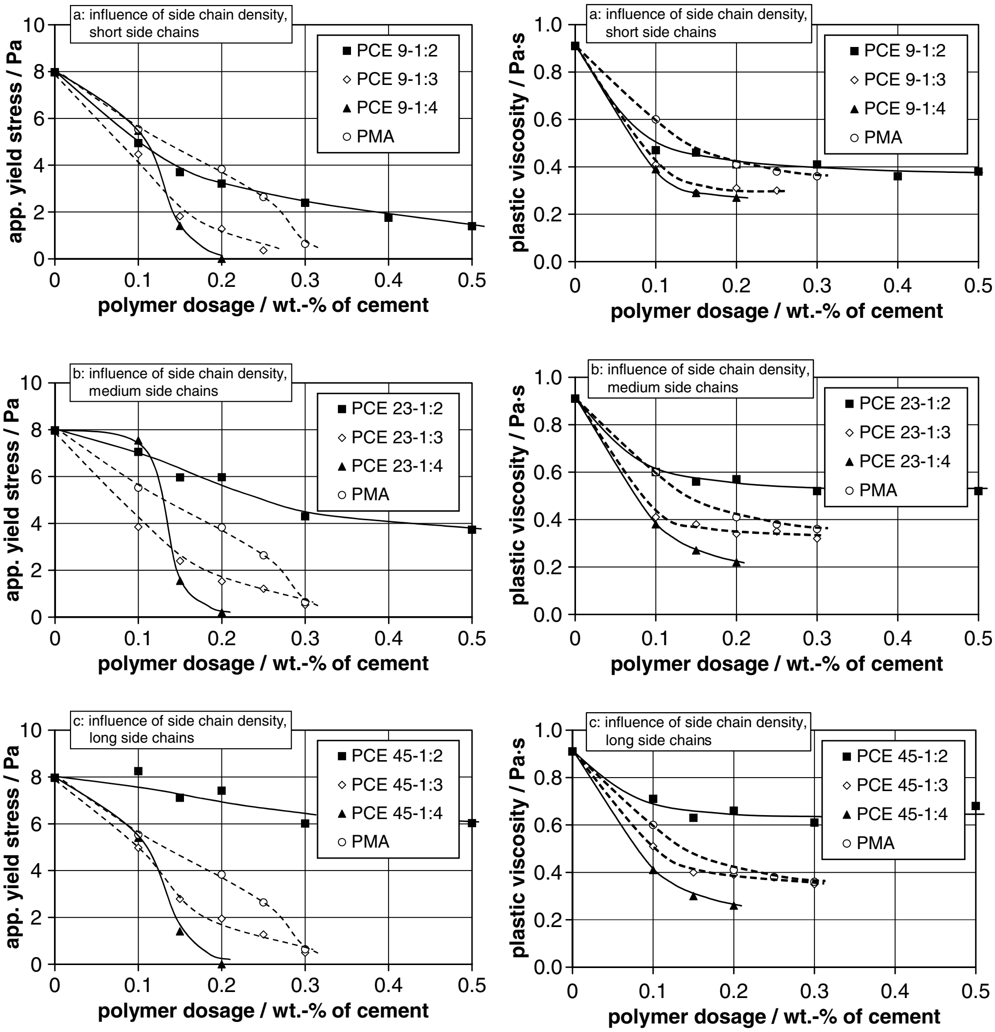

Fig. 2. Apparent yield stress (left column) and plastic viscosity (right column) of the cement pastes. (a) Influence of side chain density, short side chains (9 EO units), (b) influence of side chain density, medium side chains (23 EO units), (c) influence of side chain density, long side chains (45 EO units).

until about 2 h of hydration time. This is followed by an increase in heat evolution over several hours towards a maximum after about 11 h, mainly due to the effects of alite hydrating to calcium silicate hydrates. An additional peak (more or less a shoulder) is observed after about 15 h. It represents the time when the calcium sulphate is consumed and the remaining tricalciumaluminate phase reacts no longer to ettringite but to other phases like monosulphate, calcium aluminate hydrates or monocarbonate. After this peak, there is a steady decrease in the evolution of heat oh hydration (deceleration period), which soon reaches a constant, but low value (final period).

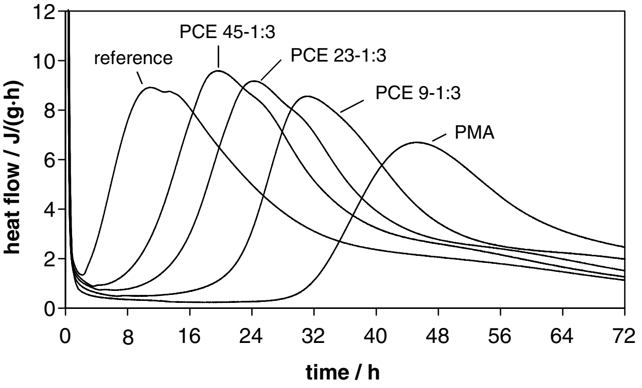

Fig. 3. Influence of side chain length of superplasticizers with side chain density 1:3 on the hydration heat flow of cement paste; polymer dosage 0.30% of cement.

In general, all superplasticizers retard the hydration of the cement compared to the plain cement paste. The retardation mainly affects the hydration of the alite phase, as shown by X-ray diffraction and thermal analysis in the Portland cement system, as well as by conduction calorimetry of pure alite [27,28]. In the case of additions of 0.3% polymer, the dormant period is prolonged between about 3 and 17 h for the grafted polymers and 26 h for the polymethacrylic acid. Furthermore, the main hydration peak seems to be broader compared to the plain paste. The time between the main hydration peak and the shoulder attributed to the consumption of calcium sulphate seem prolonged as well.

Fig. 3 illustrates the effect of PEO side chain length on the early hydration kinetics. A decreasing side chain length of the grafted polymers leads to an increase of the retarding effect. This was found for all examined side chain densities. As an extrapolation of this chain length effect, polymethacrylic acid (PMA), which has no side chains, has the strongest retarding effect. Similar results are reported by Yamada et al. [2], who found an increase of the final setting of cement pastes containing polycarboxylate-based PCEs with decreasing PEO chain length. Kirby and Lewis [3] determined an increasing retardation of the onset of the acceleratory period with decreasing PEO chain length. Fig. 4 shows the influence of the PEO side chain density (side chain length 23 EO units) on the development of hydration heat of cement paste with 0.3% of superplasticizer added. A lower side chain density causes a stronger retardation of cement hydration. Similar curves were obtained from measurement of the polymers with shorter (9 EO units) and longer (45 EO units) side chains. Again, the behaviour of polymethacrylic acid (PMA) is an extrapolation of this chain density effect. The molecular weight of the polymers (comparison between the polymers PCE 23-1:4-L, PCE 23-1:4 and PCE 23-1:4-H) does not have a strong influence. From Fig. 5 it can be seen, that a decrease in molecular weight leads only to a slight prolonged dormant period. Yamada et al. [2] found a similar result. They determined only slightly shorter setting times with increasing molecular weight of polycarboxylate-ether-type superplasticizers.

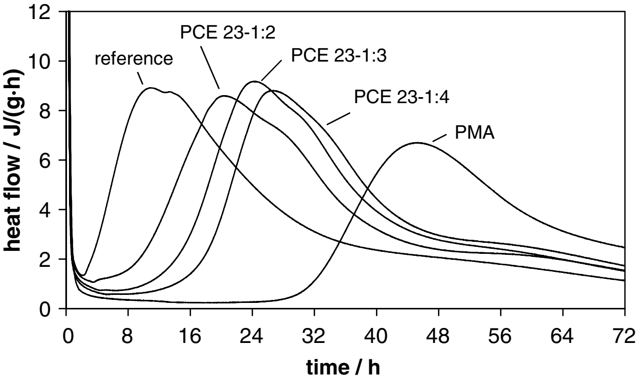

Fig. 4. Influence of side chain density of superplasticizers with side chain length of 23 ethyleneoxide units on the hydration heat flow of cement paste; polymer dosage 0.30% of cement.

The PCE/cement ratio influences the start of the acceleration period as well, see Fig. 5. Increasing additions of superplasticizers lead to a stronger retardation of cement hydration. The influence of PCE dosage on retardation is more pronounced for shorter side chains and for lower side chain densities. The polymer with the longest side chains and the highest side chain density (PCE 45-1:2) shows almost no retardation even at an addition of 0.3%, whereas polymethacrylic acid (PMA) shows the strongest dosage dependence of the retarding effect. Again, the molecular weight of the polymer has no significant influence.

Mollah et al. [14] proposed three different mechanisms for the retarding effects of superplasticizers on cement hydration (i.e. alite hydration): (i) adsorbed superplasticizer molecules hinder the diffusion of water and calcium ions at the cement-solution interface, (ii) calcium ions form

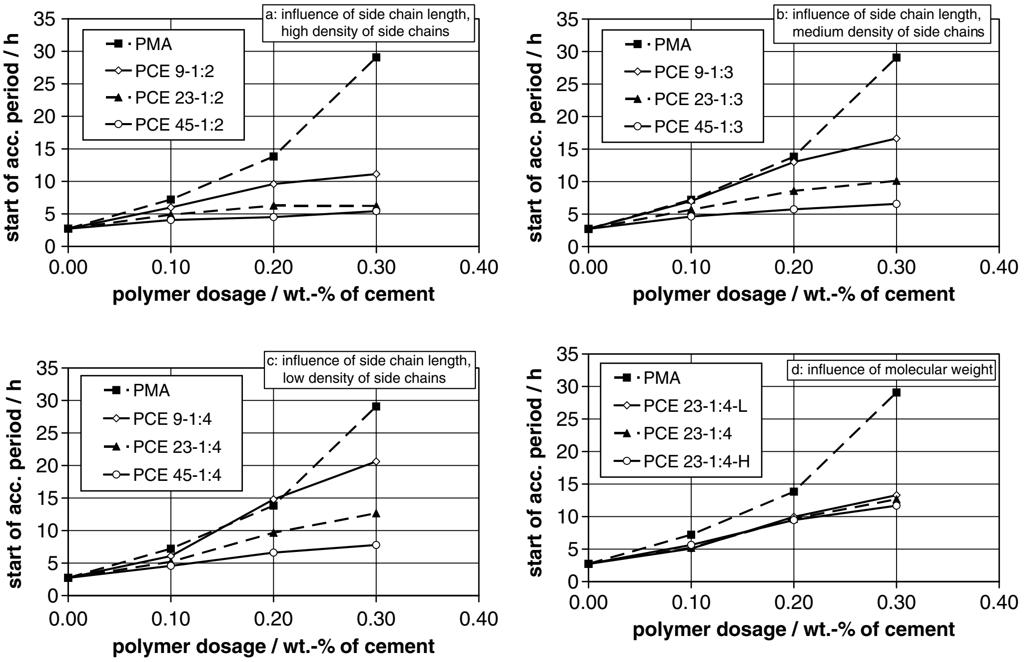

Fig. 5. Influence of polymer type and dosage on the start of the acceleration period. (a) Influence of side chain length, high side chain density (1:2), (b) influence of side chain length, medium side chain density (1:3), (c) influence of side chain length, low side chain density (1:4), (d) influence of molecular weight, side chains 23 EO units, side chain density 1:4.

complexes with the polymer molecules which prevent nucleation and precipitation of calcium containing hydrate assemblages, and (iii) the dispersive action of superplasticizers changes growth kinetics and morphology of hydrate phases.

From literature [29–32] it is known that polyacrylates and PEO-grafted polyacrylates form complexes with calcium ions that are able to bind reasonable amounts of calcium ions. The complexation causes a decrease in the particle size of dispersed swollen particles of these polymers [30]. The calcium binding capacity is related to the amount and the accessibility of the carboxylate groups in the polymer [30,32], and thus decreases with increasing amount and length of the PEO side chains. However, according to Richter and Winkler [29], not only the binding capacity towards calcium, but also the stability constants of the complexes, which are dependent on the ionic composition of the solution have to be taken into account. The authors reported only low stability constants in the range of 10^2 and 2×10^5 for complexes between Ca^{2+} and polyacrylic acids. These low stability constants are confirmed in a study by Lothenbach and Winnefeld [28] involving the examination of the pore solution chemistry of a PCE-modified cement paste at different hydration times (1 h–2 years) in comparison to a plain paste. It was found that the PCE superplasticizer did not affect the composition of the pore solution, i.e. the calcium content. This indicates that there is no significant complexation of calcium ions by PCEs. Thus, the retarding effect of PCEs is probably not caused by the interaction with dissolved calcium ions.

From these results it seems more likely that the retardation mechanism is due to adsorption of the polymers or due to changes in nucleation and growth kinetics of the hydrate phases. Adsorption, which is related to the charge density of the polymer, clearly plays an important role (see Section 4.5), especially when the surface coverage of the cement particles is taken into account. Thus, i.e. the only slight retarding effect of PCEs with long side chains can be explained in a way that in the PCEs with long side chains most of the mass of the polymer is concentrated in the non-adsorbing backbone. Thus, the coverage of the surface of the cement with a PCE with long side chains is much less compared to a PCE with short side chains, assuming that the total amount of polymer adsorbed is the same in both cases. A cement particle with a less covered surface should exhibit a faster setting.

Ridi et al. [33] examined the hydration of alite in the presence of superplasticizers by means of differential scanning calorimetry and determined in-situ the amount of free (freezable) water. They found a strong increase of the activation energy for the acceleration period in the presence of superplasticizers compared to the plain alite paste. The authors concluded and confirmed by SEM investigations that superplasticizers modify the hydration process, probably related to the morphology of the hydrate phases. Rieger et al. [34] examined the precipitation of $CaCO_3$ from a mixed $Na_2CO_3/CaCl_2$ solution without and in the presence of polycarboxylates by transmission X-ray microscopy. Without superplasticizer, precursors (amourphous and/or Vaterite) form as beads of several μm diameter, that may consist of agglomerated nanoparticles. These precursors dissolve and recrystallize as calcite. In the presence of polycarboxylates the $CaCO_3$ nanoparticles (diameter less than 100 μm) are fixed in a network of polymers. As long as these nanoparticles are covered completely they remain dispersed. If the amount of polymer is not sufficient (i.e. if less polymer is present or the polymer is consumed) the nanoparticles dissolve and recrystallize as calcite. It seems to be possible that similar effects of hindered (re)crystallization occur during the hydration of alite and the precipitation of hydrate phases in cementitious systems in the presence of superplasticizers.

4.5. *Adsorption of superplasticizers*

On one hand, the enhancement of flow of cement pastes, mortars and concretes is influenced by electrostatic and/or steric repulsion effects of the superplasticizers as shown by Uchikawa et al. [1]. On the other hand the adsorption characteristics of the polymers at the surface of the cement particles are important. Strictly speaking "adsorption" is not the correct term, as a part of the consumed polymer is coprecipitated with early cement hydration products as shown by Plank et al. [35] and thus according to Flatt and Houst [15] not effective for dispersion. The retarding effect of superplasticizers on cement hydration is strongly related to the amount of adsorbed and non-adsorbed polymer as well [14]. The results of the adsorption measurements (dosage 0.2% PCE referred to cement weight) are given in Table 4.

The amount of polymer adsorbed does not change significantly between 5 min and 30 or 60 min, respectively. Hence, it can be assumed that the PCEs adsorb rapidly on the selected cement. This results correlates well with the almost constant spread diameters in the mortar tests between 5 min and 90 min after mixing.

In general, PCEs with shorter side chains and lower side chain density adsorb to a larger extent on the cement particles. This could be expected when the charge density of the polymers is taken into account, which increases with decreasing side chain length and with decreasing side chain density [24]. Polymethacrylic acid (PMA) adsorbs to 100%, the added amount of 0.2% is obviously below the saturation point. From another test series [27] it is known, that for the other products this concentration is near or above the saturation point.

The PCEs with side chain density 1:2 show a very low adsorption, thus explaining the only slight improvement of rheological properties when applying these polymers. As suggested above, the increase of apparent yield stress and plastic viscosity at a given PCE dosage of the 1:2 series with increasing side chain length is caused by a decrease of the amount of polymer adsorbed (1.11, 0.82, and 0.75 mg/g

Table 4
Superplasticizer consumption in cement pastes determined by GPC

Polymer	Polymer consumption/%			Polymer consumption /mg/g cement		
	5 min	30 min	60 min	5 min	30 min	60 min
PMA	100	100	100	2.00	2.00	2.00
PCE 9-1:2	56	55	56	1.11	1.09	1.11
PCE 9-1:3	72	72	74	1.43	1.44	1.47
PCE 9-1:4	78	83	85	1.56	1.66	1.69
PCE 23-1:2	44	42	41	0.89	0.83	0.82
PCE 23-1:3	63	63	59	1.26	1.25	1.19
PCE 23-1:4	77	78	77	1.54	1.56	1.55
PCE 45-1:2	49	47	37	0.99	0.94	0.75
PCE 45-1:3	63	57	56	1.25	1.15	1.12
PCE 45-1:4	73	79	75	1.45	1.58	1.51
PCE 23-1:4-L	64	67	69	1.29	1.33	1.38
PCE 23-1:4-H	82	87	86	1.63	1.74	1.73

cement after 60 min for PCE 9-1:2, PCE 23-1:2, and PCE 45-1:2, respectively).

Polycarboxylate ethers with higher molecular weight adsorb stronger compared to polymers with lower molecular weight and same molecular architecture. This can be derived from the comparison of the polymers PCE 23-1:4 L, PCE 23-1:4 and PCE 23-1:4 H (number-average molecular weights 9500, 11,400 and 14,200 g/mol, respectively).

To address this effect further, the molecular weight distributions of the polymers before and after interaction with the cement suspensions have been evaluated in more detail. Fig. 6 displays the molecular weight distributions of aqueous solutions of the two polymers PCE 23-1:2 and PCE 23-1:4 before and after 60 min interaction with cement. On one hand, it can be derived from the graph, that PCE 23-1:2 adsorbs to a less extent to the cement particle surfaces than PCE 23-1:4. On the other hand, the molecular weight distributions of the polymers in the cement pore solution are shifted to a lower molecular weight compared to the original polymer solutions. This means that polymer fractions with a high molecular weight adsorb preferentially on the cement particles. This effect was generally found for all examined PCEs after 5, 30 and 60 min of interaction with cement. Fig. 7 shows some examples for the percentage of polymer adsorbed after 60 min depending on the molecular weight fraction. It can be derived from this figure—as discussed above—the general trend, that a decreasing side chain density and a decreasing side chain length favours adsorption of polycarboxylates on cement particle surfaces. Furthermore, the percentage of a certain polymer fraction, which is adsorbed on the cement particle, increases, when its molecular weight increases.

Similar results concerning this polydispersity effect are reported by other authors for PCEs [36,37] and also other types of superplasticizers like lignosulfonates [6–9]. Flatt et al. [36] found a stronger adsorption for the higher molecular weight fractions of a PCE-based superplasticizer by means of HPLC analysis. Magarotto et al. [37] separated a polycarboxylate type superplasticizer into different molecular weight fractions by ultrafiltration. They found a higher adsorption as well as also a better performance with increasing molecular weight of the polymer.

The results of the influence of polymer polydispersity are also in good agreement with experimental data obtained from other systems with different polymers and substrates, e.g. [38–40]. Also referring to theoretical considerations

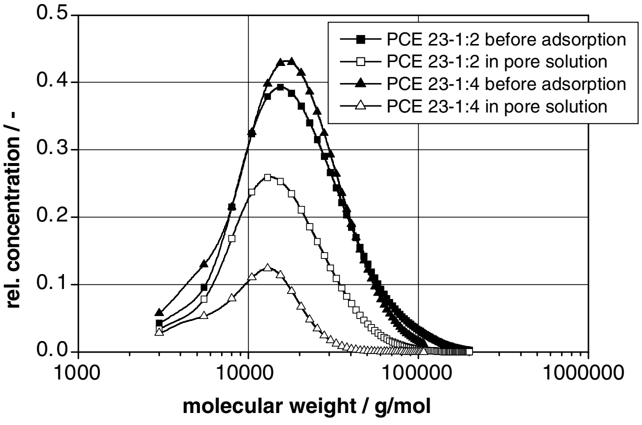

Fig. 6. Molecular weight distribution of solutions of PCE 23-1:2 and PCE 23-1:4 before adsorption and in the pore solution 60 min after mixing.

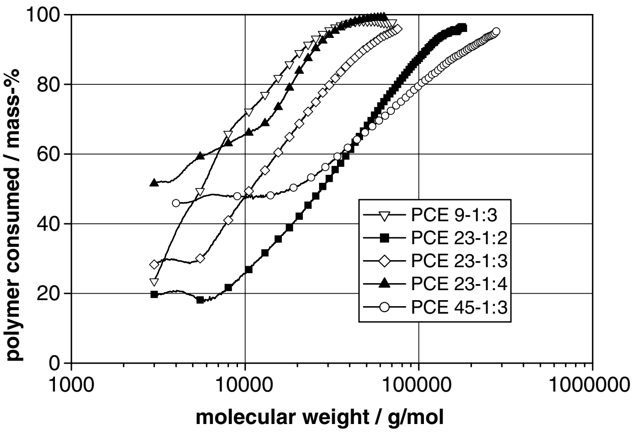

Fig. 7. Influence of polymer molecular weight fraction on amount of polymer consumed 60 min after mixing.

Table 5
Strength development of cement mortars, superplasticizer dosage 0.20 mass% of cement

Polymer	Flexural strength/MPa					Compressive strength/MPa				
	16 h	1 d	2 d	7 d	28 d	16 h	1 d	2 d	7 d	28 d
Reference	2.2	4.5	6.1	8.2	9.0	7.1	17.2	30.5	46.3	54.6
PMA	n.d.	2.6	6.1	8.8	10.2	n.d.	8.8	31.3	53.7	63.5
PCE 9-1:2	0.5	3.3	6.7	9.0	9.8	1.3	10.4	32.7	54.6	63.9
PCE 9-1:3	n.d.	2.8	6.6	8.0	8.7	n.d.	8.8	32.3	50.8	60.5
PCE 9-1:4	n.d.	2.4	4.8	7.6	8.2	n.d.	7.4	26.6	47.6	56.0
PCE 23-1:2	1.1	4.0	6.7	9.0	9.5	2.7	13.3	33.3	52.4	60.4
PCE 23-1:3	0.4	2.7	5.5	7.3	8.0	1.4	9.0	25.8	42.2	48.6
PCE 23-1:4	0.3	2.8	5.3	6.4	6.9	1.1	9.1	24.3	38.1	44.6
PCE 45-1:2	1.6	4.4	7.1	8.8	9.1	4.4	16.0	33.8	50.5	59.8
PCE 45-1:3	1.2	3.9	5.9	6.6	7.5	3.3	13.2	27.3	41.2	47.0
PCE 45-1:4	0.9	3.8	5.9	7.0	7.7	3.1	14.4	28.2	39.9	46.0
PCE 23-1:4-L	0.2	2.7	5.0	6.5	7.3	1.1	13.5	33.3	50.2	58.8
PCE 23-1:4-H	0.3	4.1	6.9	8.2	8.9	1.0	9.4	23.9	34.4	39.4

n.d.: not determined (strength too low for measurement).

and models, a preferred adsorption of the high molecular weight fraction is expected in dilute systems due to thermodynamic reasons [41–44]. According to Aubouy [44], the free energy of a polymer layer adsorbed at a surface in the dilute regime is a decreasing function of the polymerization index. This means that the interface will lower its energy when shorter polymer chains are replaced by longer ones. The adsorption of smaller polymer fractions is not favourable because the loss in translatory entropy causes an increase in free energy of adsorption, as pointed out by Janardhan [42].

4.6. Compressive and flexural strength

The results of the compressive and flexural strength measurements are given in Table 5. Some of the mortars – especially those containing the most plasticizing PCEs – tended to bleed or segregate. This has to be kept in mind when interpreting the strength results.

All PCE containing mortars show lower strengths after 16 h and 1 d than the reference mortars. It was not possible to perform strength tests after 16 h of mortars with the most retarding polymers (PMA, PCE 9-1:3 and PCE 9-1:4), because the samples were not solid enough for the measurement. Early strengths (16 h, 1 d) of the mortars increase with increasing side chain length and increasing side chain density of the PCE. This correlates well with the retarding effect determined by heat flow calorimetry. There is no clear trend visible that PCE enhance 28 d strength as shown for example by Şahmaran et al. [45]. Longer side chain lenghths and lower side chain densities tend to decrease 28 d strengths, however the influence of segregation and/or bleeding has to be taken into account.

5. Conclusions

In this study the effects of different superplasticizers based on polycarboxylate-ethers with varying structure (different lengths and densities of side chains, different molecular weight) on workability and early hydration of cement pastes and mortars had been examined.

It was found, that a decreasing density of the PEO side chains enhances workability (increased mortar spread diameter, lowering of apparent yield stress and plastic viscosity of cement pastes). The lengths of the side chains and the molecular weight of the polymers had only a minor influence. The minor effect of side chain lengths is probably due to the conformation of the PEO chains, which is not stretched but more "mushroom"-like especially in aqueous solutions with high ionic strengths [30,46]. Thus, a proportional increase of the steric repulsion force with increasing lengths of the side chains cannot be observed.

The adsorption of polymers on the surfaces of the cement particles plays an important role in cementitious systems concerning the enhancement of workability. The adsorption measurements revealed that polymers with higher charge densities adsorb to a larger extent compared to polymers with lower charge densities. The charge density of the comb-shaped PCEs increases with the presence of an increasing number of free carboxylic groups, i.e. with decreasing side chain length and with decreasing side chain density. Thus, polymers with lower charge densities having long PEO side chains and high side chain densities are adsorbing less than polymers with higher charge densities; this correlates well with the rheological measurements.

All superplasticizers retarded the hydration of the normal Portland cement used in this study. The dormant period was prolonged with increasing charge density of the PCE, i.e. with decreasing length and decreasing density of the PEO side chains. The molar weight of the polymer was found to have no significant influence on the setting time. It is important to note that PCEs mainly retard the dissolution of alite [27,28]. The amount of adsorbed polymer and the surface coverage of the cement particles by the PCEs can be linked to the retardation effect. Possible hydration mechanisms discussed in literature, e.g. [14], are that (i) adsorbed polymer molecules hinder the diffusion of water and calcium ions at the surface of the cement clinker grains, (ii) complexes form between calcium ions and polymers in the pore solution, and (iii) the dispersive action of superplasticizers changes growth kinetics and morphology of hydrate phases. There is not much evidence from literature that calcium ions form strong complexes with PCE-based superplasticizers. Thus, it can be concluded that the retardation of cement hydration by PCEs is mainly due to adsorption of the polymers on the surface of the cement particles and due to growth kinetics and morphology of early hydrates, which is supported by investigations of Ridi et al. [33] and Rieger et al. [34].

The polymer adsorption showed a strong dependency on the molecular weight fraction (so-called polydispersity effect). It was found that fractions of higher molar weight are adsorbed to a larger extent than fractions of lower molecular weight. The polydispersity effect is reported from various polymer–substate combinations an in agreement with theoretical models, but still not well described in superplasticizer–cement systems.

The results presented in this paper show, how the structure of a PCE-based superplasicizer controls rheology and setting of cement paste, mortar and concrete. Adsorption plays a key role; it is controlled by molecular weight, side chain density, and side chain length of the polymers. PCEs with higher molecular weight, lower side chain densities and shorter side chains adsorb stronger. Rheological properties and retardation depend on adsorption behaviour.

This information can be used to improve the molecular design of PCE-based superplasticizers. To enhance the properties of a superplasticizer to be used e.g. in a precast concrete fabrication plant, where good workability and not too prolonged setting times are important, the following guidelines can be extracted from this study: (i) use a low density of side chains to achieve good workability, (ii) use long side chains to avoid undesirable retardation, and (iii) optimize the molecular weight distribution of the polymer.

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