

Superplasticizers and Other Chemical Admixtures in Concrete

Proceedings
Thirteenth International Conference
Milan, Italy

July 2022

Denny Coffetti
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Terence C. Holland



American Concrete Institute

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Superplasticizers and Other Chemical Admixtures in Concrete— Conference Proceedings

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Thirteenth International Conference
Milan, Italy
July 10-13, 2022

Editors:
Denny Coffetti,
Luigi Coppola, and
Terence Holland



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First printing, June 2022

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Editorial production: Gail Tatum

ISBN-13: 978-1-64195-185-2

Preface

In May 1978, the Canada Centre for Mineral and Energy Technology (CANMET), in association with the American Concrete Institute (ACI) sponsored a 3-day conference in Ottawa, ON, Canada, on the use of superplasticizers in concrete. Selected papers from the conference were published as ACI SP-62.

In 1981, CANMET, again in association with ACI, sponsored a second 3-day international conference in Ottawa on the use of the superplasticizers in concrete. Proceedings of the conference were published as ACI SP-68.

The purpose of the third international conference in Ottawa in 1989 was to review the progress made since the meetings in 1978 and 1981, and to bring together representatives of the chemical admixtures, cement, and concrete industries to exchange information and delineate new areas of needed research. The scope of this conference was expanded to include chemical admixtures other than superplasticizers. Proceedings of the conference were published as ACI SP-119.

In October 1994, CANMET in association with ACI and several other organizations sponsored the fourth conference in Montreal, QC, Canada. The objective of this conference was to bring attention to new developments in chemical admixture since the last conference in 1989. The proceedings of the conference were published as ACI SP-148.

In October 1997, the Committee for the Organization of CANMET/ACI International Conference, (ACI Council), in association with ACI and several cement and concrete organizations in Italy, sponsored the fifth conference in Rome, Italy. The conference was aimed at transferring technology in the fast-moving field of chemical admixtures. The proceedings of the conference were published as ACI SP-173.

In October 2000, Committee for the Organization of CANMET/ACI International Conferences, (ACI Council), in association with several organizations in Canada and France, sponsored the sixth conference in Nice, France. More than 50 papers from more than 20 countries were received and reviewed by an ACI review panel, and 37 were accepted for publication in the proceedings of the conference. The proceedings were published as ACI SP-195.

In October 2003, the Committee for the Organization of CANMET/ACI International Conferences (ACI Council) in association with several organizations in Canada and Germany, sponsored the seventh conference in Berlin, Germany. The conference attracted more than 275 delegates and proceedings of the conference consisting of 39 papers, were published as ACI SP-217.

In October 2006, the Committee for the Organization of CANMET/ACI International Conferences, (ACI Council), sponsored the eighth conference in Sorrento, Italy. More than 60 papers from more than 25 countries were received, and peer reviewed by the CANMET/ACI review panel in Budapest, and 36 were accepted for publication as ACI SP-239.

In October 2009, the Committee for the Organization of International Conferences (COIC) (formerly CANMET/ACI International Conferences) sponsored the ninth ACI International Conference in Seville, Spain. More than 50 papers from more than 20 countries were

received and peer reviewed, and 35 were accepted for publication in the proceedings of the conference. The proceedings were published as ACI SP-262.

In October 2012, COIC sponsored the Tenth International Conference on Superplasticizers and Other Chemical Admixtures in Concrete in Prague, Czech Republic. More than 70 papers from all over the world were peer reviewed, and 33 were accepted for publication in the proceedings of the conference. The proceedings were published as ACI SP-288.

In July, 2015, the COIC in association with ACI sponsored the Eleventh International Conference on Superplasticizers and Other Chemical Admixtures in concrete in Ottawa, ON, Canada. More than 60 papers from the world over were peer reviewed, and 28 were accepted for publication in the proceedings of the conference. Also, additional papers were presented at the conference that were published in the Supplementary Papers Volume.

In October 2018, the Chinese Ceramic Society and the China Academy of Building Research (CABR), Beijing China, in association with ACI, sponsored the Twelfth International Conference on Superplasticizers and other Chemical Admixtures in Concrete in Beijing China. More than 80 papers from all over the world were received and peer reviewed. A total of 36 refereed papers were accepted for publication in the proceedings of the conference. The proceedings were published by as ACI SP-329. The proceedings were published as ACI SP-302. Also, 54 additional papers were presented at the conference, and were published in the Supplementary Papers Volume.

In July, 2022, after a postponement for the COVID-19 pandemic, the ACI Italy Chapter and the University of Bergamo, Italy, sponsored the Thirteenth International Conference on Superplasticizers and Other Chemical Admixtures in Concrete in Milan, Italy. The proceedings of the conference consisting of 35 refereed papers were published by ACI as SP-354. In addition to the refereed papers, about 20 other papers were presented at the conference, and were published in a supplementary papers volume.

The main topics of the papers presented at the conference are related to superplasticizers, accelerating admixtures, retarding admixtures, air-entraining agents, shrinkage-reducing agents, superabsorbent polymers, and self-healing admixtures, and their influence on the properties of the concrete in fresh and hardened state. These properties include: workability, slump-loss, time of setting, heat of hydration, strength, durability, shrinkage, and creep of the concrete mixtures.

Thanks are extended to the reviewers for the valuable efforts in reviewing all the manuscripts published in the conference proceedings and in the supplementary volume.

The guidance from Dr. V. M. Malhotra and Prof. M. Collepardi, the Honorary Chairpersons of the conference, is sincerely appreciated.

Also, acknowledged is the support of ACI International for the publication of the proceedings (ACI SP 354).

The Editors
Dr. Denny Coffetti
Prof. Luigi Coppola
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Experimental and theoretical investigation on the adsorbed layer thickness of PCE comb polymers

Johann Plank, Johannes Stecher, Constantin Tiemeyer

Synopsis: The dosage-dependent development of the adsorbed layer thickness (ALT) of two polycondensates (BNS, AFS), four polycarboxylates (23MPEG6, 45MPEG6, 52IPEG2, 52IPEG6) and one phosphate comb polymer (45MPEG-P3) was investigated via dynamic light scattering technique using cationic polystyrene nanoparticles as substrate. It was found that polycondensates develop very thin adsorbed layers [0.3 - 0.6 nm ($1.2 - 2.4 \times 10^{-8}$ in)] whereas PCEs produce layers of $\sim 2.5 - 8$ nm ($9.8 - 31 \times 10^{-8}$ in). These values are larger than those reported previously from AFM and XPS measurements, but correlate well with results from molecular dynamics simulations. For PCE molecules, the side chain length exercises the most significant effect on the adsorbed layer thickness while the grafting density has less impact. Furthermore, stronger anchor groups such as the phosphate copolymer produce more dense polymer layers and hence higher ALT values which explain their excellent dispersing effectiveness. Spread flow tests using cement paste revealed a relatively close relationship between paste fluidity and ALT.

Keywords: Polycarboxylate; Superplasticizer; Adsorption; Cement; Steric hindrance; Adsorbed conformation; Molecular dynamics (MD) simulation; Dynamic light scattering (DLS); Nanoparticles

INTRODUCTION

Generally, the dispersing effect of superplasticizers is based on two principle mechanisms: (a) electrostatic repulsion between two particles exhibiting the same surface charge, with the repulsive force being described by the DLVO theory [1, 2]; and (b) the steric hindrance effect, whereby the steric repulsive potential V_{steric} is expressed by the equation introduced by *Ottewill and Walker* [3]:

$$V_{steric}(a) = \frac{4 \pi k T C_v^2}{3 v_1^2 \rho_2^2} (\psi_1 - \kappa_1)(\delta - a)^2 \left(3R + 2\delta + \frac{a}{2} \right) \quad \text{Eq. (1)}$$

where C_v and ρ_2 are the concentration and density of adsorbents present in the layer, v_1 represents the molecular volume of the solvent molecules, ψ_1 and κ_1 represent entropy and enthalpy, R is the radius of adsorbed particles and a the interparticle distance. The adsorbed layer thickness is expressed by δ .

The pivotal role of steric hindrance with respect to PCE dispersing performance was first recognized by Yoshioka et al. as early as in 1997 [4]. According to **equation (1)**, the adsorbed layer thickness δ of the superplasticizer adsorbed on cement presents the most significant of all parameters influencing V_{steric} , as it occurs by the power of three in the equation. Hence, information on the thickness of adsorbed superplasticizer layers is of critical importance to understand their overall dispersing effectiveness and for the design of even more powerful cement dispersants.

Current superplasticizer technology comprises linear, non-branched (e.g. polycondensates) as well as brush-like graft copolymers such as polycarboxylates. The well-known superiority of PCE comb polymers over the linear polycondensates derives from the steric hindrance effect exerted by their bulky pendant groups. When adsorbed on cement, they freely protrude into the cement pore solution and thus generate the steric repulsive effect. Apparently, steric hindrance depends on the extension of the pendant groups into the pore solution. In the past, numerous attempts have been undertaken to quantify the steric effect by assessing how far the PCE side chains reach into the pore solution, in other words, to estimate the layer thickness of the adsorbed polymer.

In a first approach dating back to 2000, the length of the protruding EO side chains was calculated assuming a fully stretched, ideal helix-type conformation for them and ignoring any interaction with ions (especially Ca^{2+}). Based upon this model, side chain lengths as tabulated in **Table 1** were calculated for PCEs containing the most common macromonomers, with 7 EO units assuming a length of 1.95 nm (7.6×10^{-8} in) [5].

Table 1: Calculated lengths of the most common PCE side chains, assuming an idealized stretched conformation.

<i>M_w</i> of macromonomer (Da)	1,000	2,000	2,400	3,000	5,000
Number of EO units	23	45	55	68	114
Calculated lengths [nm (10^{-8} in)]	6.4 (25.0)	12.8 (49.9)	15.3 (59.7)	18.9 (73.7)	31.8 (124.0)

However, this model completely ignored that in the pore solution the polyethylene glycol pendant groups do not attain an ideally stretched conformation and instead are much coiled and tilted, hence the numbers suggested for the adsorbed layer thickness of these polymers appear to be much overstated. In 2010, the coiling effect was first considered in representations of adsorbed PCEs in the form of truncated cones, emphasizing that the actual polymer layer is much thinner than those calculated before (see **Fig. 1**). Second, the early model failed to recognize that PCE polymers can adsorb on a charged surface in different adsorption conformations which are generally referenced to as “train”, “loop” and “tail” mode [6], as is illustrated in **Fig. 2**. Generally, depending on the synthesis process employed in the manufacturing of a polycarboxylate product, its microstructure (repartition of side chains along the main chain, see [7]) can vary significantly which leads to quite different adsorbed conformations and hence adsorbed layer thicknesses, as is exemplified for few polymers in **Fig. 2**.

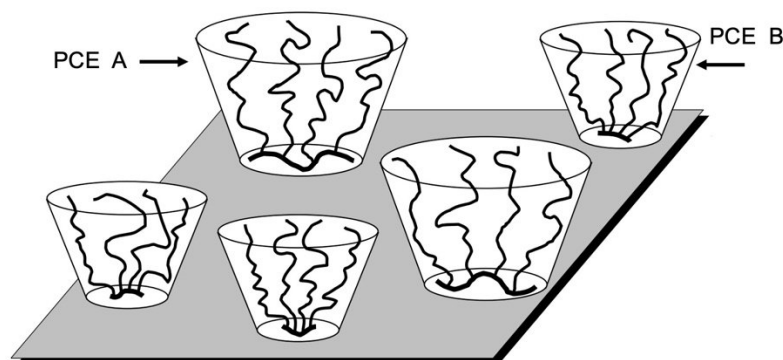


Fig. 1 – Idealized representations of adsorbed PCE molecules of different main and side chain lengths on a charged substrate; PCE A: long main and side chain; PCE B: shorter main and side chain; modified from [8].

In view of the shortcomings of these models, experimental works were initiated to assess the adsorbed layer thickness of specific PCE products. Already in 2005, Kauppi et al. applied atomic force microscopy (AFM) utilizing an MgO sphere as a model substrate for the cement surface glued onto a V-shaped cantilever [9]. As superplasticizers, an acrylic acid-MPEG-acrylate ester copolymer possessing side chains made up of 60 - 80 EO units and another PCE holding pendants comprising of 25 EO units were adsorbed onto the MgO sphere, and using the wet tapping mode the forces were measured at three different KCl concentrations to mimic the ionic strength in the cement pore solution.

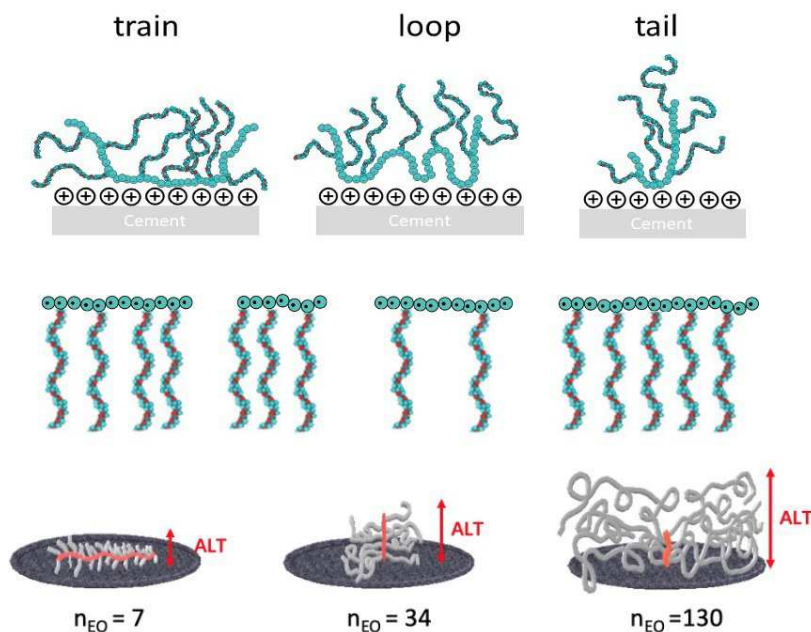


Fig. 2 – Top: principal adsorption modes of negatively charged comb polymer on an oppositely charged surface; middle: potential microstructures present in PCE polymers as a result of specific synthesis conditions; bottom: different adsorbed conformations exemplified on three PCE molecules of different composition; ALT = adsorbed layer thickness.

It was found that the long side chain PCE (80 EO units) produces an ALT of ~ 5 nm (2×10^{-7} in) only which is much less as compared to the theoretical value presented in **Table 1**. Even more, for the second copolymer ($n_{EO} \sim 25$) an ALT of $\sim 1.5 - 2.5$ nm ($5.9 - 9.8 \times 10^{-8}$ in), depending on the KCl concentration, was determined, again showing rather low values. In another attempt Flatt et al. utilized AFM technique to develop force-distance curves from a V-shaped tip coated with C-S-H [10]. Using MPEG PCE superplasticizers ($n_{EO} = 12 - 45$), they determined ALTs of between 3.6 and 6.8 nm (1.4 and 2.7×10^{-4} in) with large differences at different side chain densities, which again suggest densified

layers of adsorbed polymer and extremely coiled side chains. Based upon these findings it was speculated whether such low values consistently generated in AFM experiments resulted from a potential compression of the polymer layer by the tip. Such effect cannot be ruled out completely considering the experimental set-up in this technique.

In the next step, researchers employed X-ray photoelectron spectroscopy (XPS) whereby specific substrates (e.g. silicon or mica) were submerged in a PCE solution, dried and then the thickness of the adsorbed polymer layer was determined utilizing the photoelectron peak of Si 2p, C 1s or Ca 2p. Numerous works based on this technique [11-15] present extremely low values for the ALT of PCEs [$1.2 - 3.9 \text{ nm}$ ($4.7 - 15 \times 10^{-8} \text{ in}$)] which most likely are owed to the drying process of the sample. In fact, by applying XPS technique the thickness of a polymer coating after removal of the solvent, and not in the solvated state, is determined. Unfortunately, such values for the thickness of a dry polymer layer deposited on a surface in no way are representative for the steric expansion of the polymer in a solvent which is driven by entropic forces and results in a loose layer of pendant groups which reach out into the pore space. As such, XPS measurements are not helpful to assess the steric hindrance effect generated by different PCE molecules.

To overcome this problem, researchers then performed atomistic dynamics simulations to determine the ALT of specifically synthesized MPEG, APEG and IPEG PCEs possessing side chains made up of 25 or 34 EO units [16]. First, they noticed that the adsorbed conformation of a PCE is much influenced by the surface charge of the substrate, with increasingly positive surface charge producing a more compressed conformation of the adsorbed polymer, and hence a lower value for the ALT as is illustrated in the Fig. 3.

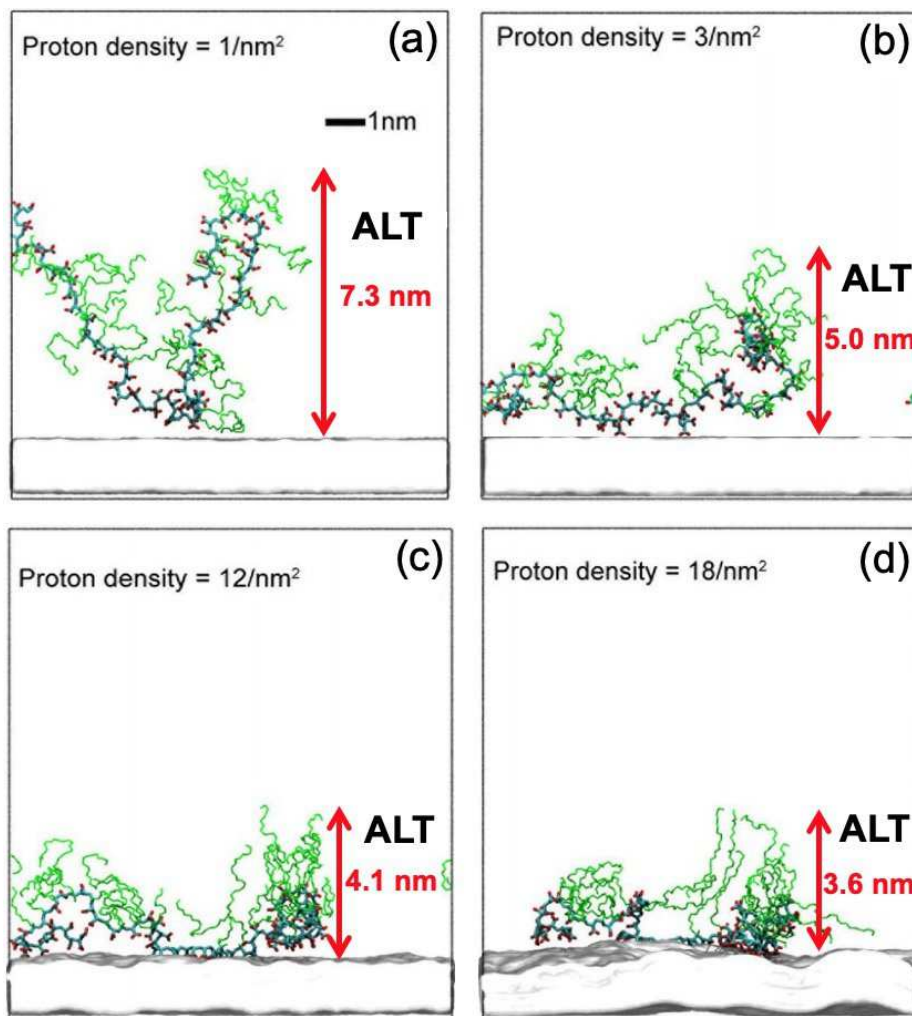


Fig. 3 – Impact of the proton density of an MgO substrate on the ALT of an adsorbed IPEG PCE, adopted from [16]. ($1 \text{ nm} = 3.9 \times 10^{-8} \text{ in}$, $1/\text{nm}^2 = 1/1.5 \times 10^{-15} \text{ in}^2$)

According to these calculations, the ALT of an IPEG PCE exhibiting a molar ratio of 5.7 : 1 (AA: macromonomer)

and holding side chains made up of 25 EO units decreases from 7.3 to 3.6 nm (2.9 to 1.4×10^{-7} in) when the proton density (positive charge) of the MgO surface is increased from $1/\text{nm}^2$ to $18/\text{nm}^2$ (2.6 to $46.8 \times 10^7/\text{in}^2$) (see **Fig. 3**). It was also noticed that significant differences are recorded when the ALT is determined for adsorbed PCEs looked at in parallel or perpendicular view, with values in perpendicular view also being higher than in parallel view (refer to **Table 2**).

Table 2: Comparison of values for ALT obtained from parallel or perpendicular view of individual adsorbed PCE polymers.

PCE sample	ALT [nm (10^{-8} in)]	
	Parallel	Perpendicular
MPEG-PCE (25 EO units)	5.7 (22.2)	8.2 (32.0)
IPEG-PCE (25 EO units)	-	8.1 (31.6)
APEG-PCE (34 EO units)	6.0 (23.4)	9.7 (37.8)

This MD simulation study suggested that (1) the values for the ALTs tend to be higher than previously reported based on AFM and XPS experiments, and (2) that the ALT is strongly impacted by the absolute value of the electrical charge of the substrate. It signifies that the ALTs of PCEs adsorbed on different cement hydrates exhibiting different surface charges as is evidenced by zeta potential measurements (with ettringite being the most positively charged phase, followed by monosulfo aluminate, syngenite and – at great distance – by C-S-H [17, 18] will vary with the charge of the substrate, thus creating non-uniform layers on different hydrates.

Moreover, the study also confirmed that at comparable surface charge the dispersing performance of a PCE is clearly linked to the value of its ALT, thus providing an explanation for the superior performance of IPEG over MPEG PCEs which is generally observed when comparing species from the two groups synthesized at the same molar ratio and with same side chain length. Hence, this simulation work underlines the huge impact of the ALT on PCE performance. Still, an experimental technique providing additional insights into this subject was highly desirable.

RESEARCH SIGNIFICANCE

An experimental method which allows to determine the adsorbed layer thickness of PCE polymers is highly critical to understand their performance with respect to dispersing efficacy in cement. For this purpose, positively charged monodisperse nanoparticles were synthesized, loaded with PCE polymers of different chemical composition and the increase in particle size was captured via dynamic light scattering measurements. From the increase, the adsorbed layer thickness was calculated and correlated with results from cement paste flow experiments. The findings from this study can help to design novel PCE structures with superior dispersing performance in the future.

EXPERIMENTAL PROCEDURES

The ALTs of two polycondensate, four polycarboxylate and one polyphosphate superplasticizer on cationic polystyrene nanoparticles were determined and correlated with their dispersing ability in cement. Polystyrene nanoparticles were selected as substrate based on a description by Kleshchanok and Lang who successfully have tracked the adsorption of PCE on these particles using Total Internal Reflection Fluorescence Microscopy (TIRFM) [19].

Superplasticizer samples

First, a β -naphthalenesulfonate-formaldehyde (BNS) and an acetone-formaldehyde-sulfite (AFS) polycondensate were employed. Both polymers were synthesized according to standard descriptions provided in the literature [20, 21]. Their chemical formula and molecular properties are displayed in **Fig. 4** and **Table 3**, respectively.

As PCE superplasticizers, two MPEG and two IPEG PCEs exhibiting different side chain length at the same molar ratio (MPEG PCEs) or different molar ratio / anionicity at the same side chain length (IPEG PCEs) were chosen. They were self-synthesized according to descriptions provided in [22] and [23]. Their chemical structure and molecular properties are presented in **Fig. 4** and **Table 3**, respectively.

Furthermore, a comb polymer exhibiting phosphate functionalities as anchor groups was employed in the study. Its synthesis followed the procedure described in [24]. For its chemical compositions and properties refer to **Fig. 4** and **Table 3**, respectively.

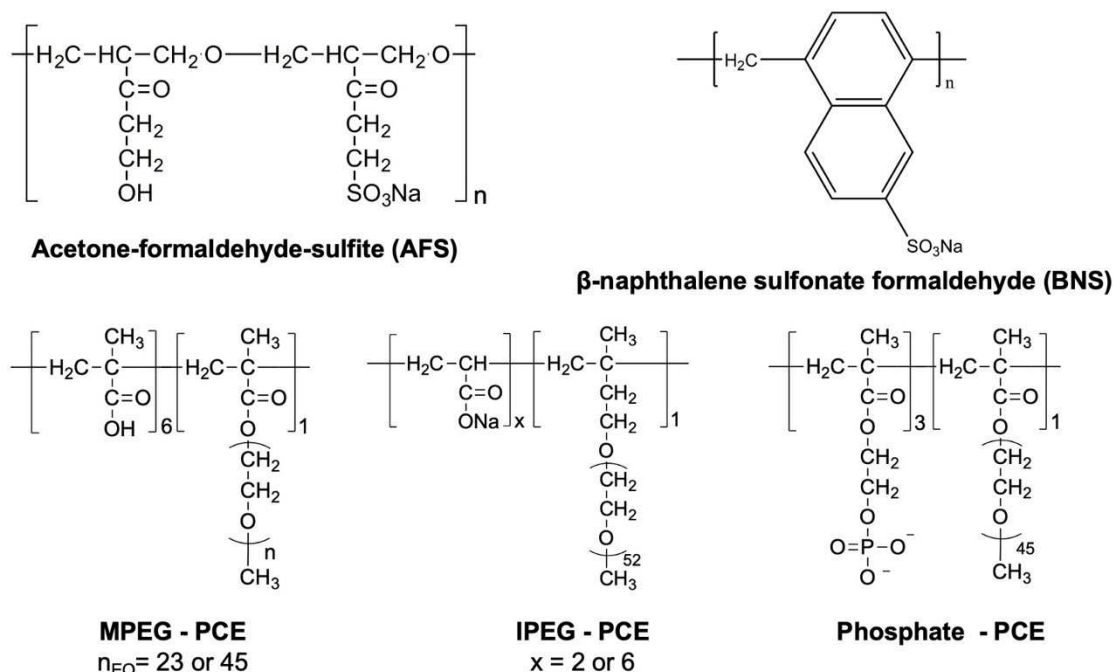


Fig. 4 – Chemical structures of the superplasticizer samples used in this study.

Characterization of polymers

Size exclusion chromatography (Waters Alliance 2695 from Waters, Eschborn, Germany) equipped with a refractive index detector 2414 (Waters, Eschborn, Germany) and an 18° angle dynamic light scattering detector (Dawn EOS from Wyatt Technologies, Santa Barbara, CA) was used. Polymer samples were separated on an Ultrahydrogel™ precolumn and three Ultrahydrogel™ columns (120, 250, and 500; Waters, Eschborn, Germany) with 0.1 M (1.6 × 10⁻⁴ mol/in³) aqueous NaNO₃ (adjusted to pH 12 w/NaOH) as eluant at a flow rate of 1.0 mL/min (0.061 in³/min). The value of dn/dc applied to calculate M_w and M_n for all copolymers was 0.135. (value for polyethylene oxide).

Cationic nanoparticles

As adsorbents, phosphate modified polystyrene nanoparticles [$d \sim 77 \text{ nm}$ ($3.0 \times 10^{-6} \text{ in}$)] were utilized and synthesized according to the method from Kim et al. [25], however with substantial modification: In a closed flask octadecyl phosphate [400 mg (0.014 oz)] dissolved in styrene [20 g (0.71 oz)] under vigorous stirring. In another three neck round bottom flask equipped with nitrogen inlet, reflux condenser and magnetic stirrer, an aqueous solution of NaOH [0.1 molar, 200 mL (6.8 oz)] was placed and heated to 90 °C (194 °F). Into this flask, the solution of octadecyl phosphate was added resulting in a milky emulsion. Furthermore, a solution of sodium persulfate [400 mg (0.014 oz)] in water [5 mL (0.31 in³)] was added and the reaction mixture was stirred for 3 h at 90 °C (194 °F). Thereafter, the reflux condenser was replaced by a distillation bridge to remove styrene while stirring for another 15 minutes at 90 °C (194 °F). After cooling to room temperature, minor amounts of macroscopic agglomerates were removed by centrifugation (8500 rpm, 1 h) to yield a homogeneous dispersion of phosphate modified nanoparticles with a solid content of 6.69 wt. %. The nanoparticle dispersion was stable for at least 2 months when stored in a refrigerator. SEM analysis revealed quite monodisperse polystyrene particles with a diameter of $77 \pm 5 \text{ nm}$ ($30 \pm 2.0 \times 10^{-7} \text{ in}$), as is shown in Fig. 5.

Measurement of adsorbed layer thickness

The layer thicknesses of the polymers adsorbed on the polystyrene (PS) nanoparticles were measured by dynamic light scattering utilizing a ZetaSizer Nano ZS (Malvern Instruments Ltd, Worcestershire, England). The anionic phosphate – modified polystyrene nanoparticles from above were converted to cationic particles through the addition of calcium ions which occupy the surface and induce the charge reversal. To measure the adsorbed layer thickness of polymers in dependence of their concentration, 1 % (by weight) solutions of the anionic polymers were prepared in 0.1 molar aqueous NaOH and mixed with their charge equivalent amounts of Ca²⁺ added as CaCl₂·2H₂O. The anionic charge of the polymers was derived from their molar composition (see Table 3). From these stock solutions, diluted

solutions holding 40 - 1600 mg/L (23 - 918 oz/in³) of polymer (steps were 40, 80, 160, 320, 640, 960, 1280 and 1600 mg/L or 23, 46, 92, 184, 368, 552 and 918 oz/in³) with a volume of 50 mL (3.1 in³) each were prepared and mixed with 50 μ L (3.1×10^{-3} in³) of the phosphate modified nanoparticle dispersion resulting in a PS particle concentration of 66.9 mg/L (38.3 oz/in³). The opaque dispersions holding the polymer, calcium salt and nanoparticles were exposed to ultrasonication for 15 minutes and then kept at rest for 15 minutes before intensity weighted particle diameters were determined via dynamic light scattering on the ZetaSizer Nano ZS instrument. Diameters of the pristine, polymer free PS nanoparticles were determined before each series of polymer measurements was started, and the diameters obtained were averaged. For each polymer concentration, two dispersions were prepared independently, and each dispersion was measured five times at automatically optimized measurement settings [25 °C (77 °F), 15 runs of 10 to 15 s per measurement]. The adsorbed layer thickness at a certain polymer concentration assuming *Langmuir* adsorption was calculated according to the following equation:

$$\text{ALT} = 1/2 \cdot (\text{Particle diameter (z) w/ adsorbed polymer} - \text{Particle diameter (z) w/o polymer}) \quad \text{Eq. (2)}$$

Table 3: Molecular properties of the superplasticizer samples studied.

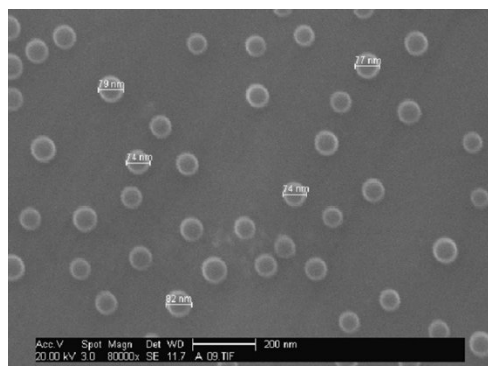
Polymer	<i>M_w</i> (Da)	<i>M_n</i> (Da)	PDI (<i>M_w</i> / <i>M_n</i>)
β -naphthalene sulfonate formaldehyde (BNS)	119,000	-	-
Acetone-formaldehyde-sulfite (AFS)	110,000	18,000	6.1
PCE polymer 23MPEG6	17,300	11,000	1.6
PCE polymer 45MPEG6	31,000	17,200	1.8
PCE polymer 52IPEG2	53,000	22,400	2.4
PCE polymer 52IPEG6	20,200	10,100	2.0
Phosphate polymer 45MPEG-P3	87,500	35,600	2.5

Cement

As cement, an Ordinary Portland Cement sample CEM I 42.5 R provided by Schwenk company, Allmendingen plant, Germany was used. Its phase compositions and physical properties were as follows: C₃S 59.55 %, C₂S 11.08 %, C₄AF 10.07 %, C₃A 6.94 %, anhydrite (CaSO₄) 2.59 %, dihydrate (CaSO₄ • 2H₂O) 3.09 %, hemihydrate (CaSO₄ • 0.5H₂O) 0.10 %, calcite (CaCO₃) 2.34 %, dolomite (CaMg(CO₃)₂) 0.97 %, quartz (SiO₂) 0.42 %, free lime 1.32 %, periklas 0.53 %, portlandit 0.78 %, arcanite 0.22 %. Its *Blaine* value was 3,105 cm²/g (13,476 in²/oz).

Dispersing performance of polymer samples in cement paste

For evaluation of the dispersing effectiveness of superplasticizers, a ‘mini slump’ test as described in DIN EN 1015 standard was employed [26]. At first, the water-to-cement (w/c) ratio of the paste without polymer to achieve a spread of 18 ± 0.5 cm (7.1 ± 0.2 in) was determined. At this w/c ratio, the dosage for 52IPEG2 sample to reach a spread flow of 26 ± 0.5 cm (10.2 ± 0.2 in) was determined. All remaining superplasticizers were then tested at this dosage.



Adsorbed layer thickness

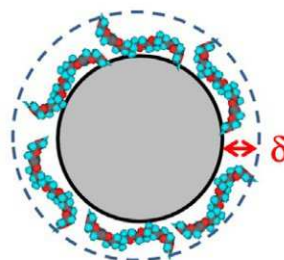


Fig. 5 – SEM image of monodisperse cationic polystyrene nanoparticles [d ~77 nm (3.0×10^{-6} in)] used as adsorbents (left) and principle of ALT measurement via increase of particle size captured by dynamic light scattering (DLS) technique; from [27] with permission.

The test was carried out as follows: in a porcelain cup the polymer with dosage of 0.06 % by weight of cement was mixed with DI water, whereby the water contained in the polymer solution was subtracted from the amount of mixing water. Then 300 g (10.5 oz) of OPC were added to the mixing water with w/c of 0.49 within 1 minute, the mixture remained at rest for 1 minute followed by 2 minutes of manual stirring. Thereafter, the cement paste was poured into a Vicat cone [height 40 mm (1.6 in), top diameter 70 mm (2.8 in), bottom diameter 80 mm (3.1 in)] placed on a glass plate and the cone was quickly lifted vertically. Once the cement paste had stopped flowing, the spread flow was measured twice at two angles perpendicular to each other. The averaged spread flow of these two values was recorded as the final spread flow value.

EXPERIMENTAL RESULTS AND DISCUSSION

ALT of polycondensate superplasticizers

The concentration-dependent adsorbed layer thickness for the BNS and AFS dispersants determined in a model cement pore solution of high alkalinity (pH $\sim$ 13) and Ca^{2+} concentration via DLS measurements from the increase of the polystyrene particle diameter $d_{H(z)}$ are displayed in **Fig. 6(a, b)**.

There, it is observed that the layer thicknesses at first increase gradually until they reach a plateau which signifies the point of maximum surface coverage attainable (also corresponding to saturated adsorption). This point is reached at a concentration of $\sim$ 20 mg/L (11.5 oz/in³) of polycondensate. There, extremely low values for the ALT of BNS [$\sim$ 0.3 nm (1.2×10^{-8} in)] and AFS [$\sim$ 0.6 nm (2.4×10^{-8} in)] are recorded. In fact, these values were even lower than expected, albeit both BNS and AFS present linear, non-branched polymers. The results signify that BNS (presumably because of its very rigid polyaromatic backbone) deposits itself in a particularly flat conformation onto the particle's surface whereas the AFS molecule possesses more conformational flexibility and hence can attach with more loops, thus leading to an expanded polymer layer. Second, the low values for the ALTs of both polycondensates suggest that with respect to their dispersing mechanism, apart from the strong electrostatic repulsion effect induced by them, the contribution from steric hindrance is almost negligible.

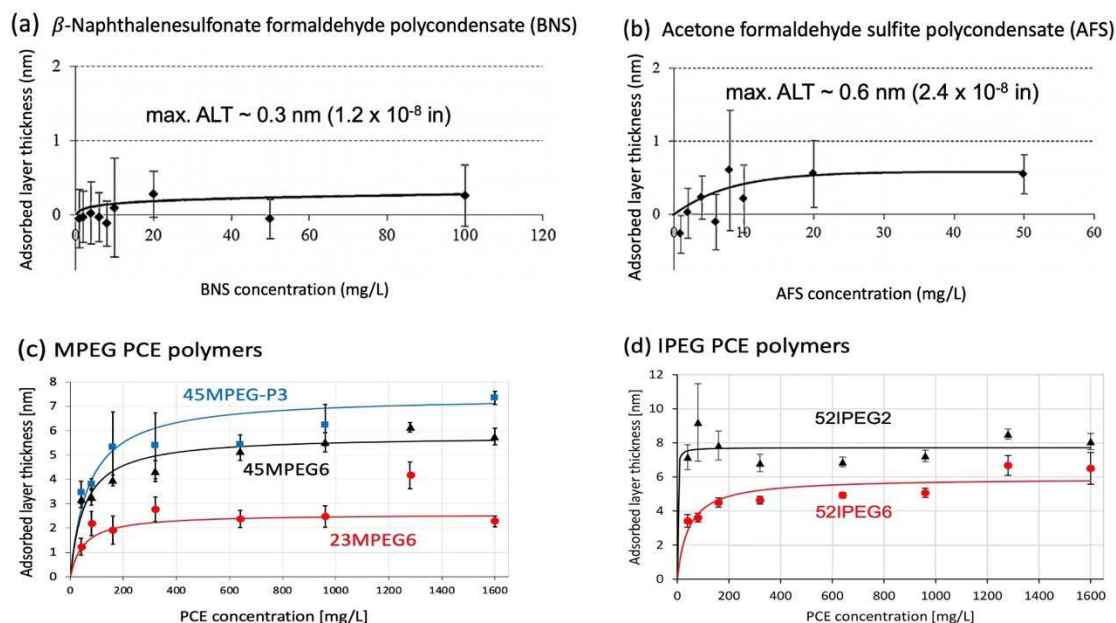


Fig. 6 – Dosage-dependent adsorbed layer thicknesses of various superplasticizers on cationic polystyrene nanoparticles, as determined via DLS measurements in a model cement pore solution; (a) BNS; (b) AFS, modified and with permission [27]; (c) MPEG PCE polymers; (d) IPEG PCE polymers; adapted with permission from [28]. (1 nm = 3.9×10^{-8} in, 1 mg/L = 0.57 oz/in³)

ALT of PCE polymers

In the next part, The ALTs of PCE comb polymers bearing side chains were determined. The results are presented in **Fig. 6(c, d)**. At first, the impact of different side chain lengths of MPEG PCEs prepared at the same molar ratio of acid: pendant group was probed. For this purpose, the ALTs of 23MPEG6 and 45MPEG6 were compared. Interestingly, for both polymers the ALTs initially increased rapidly with concentration, but then took significant additional dosages

to reach to point of maximum ALT. This signifies that at higher additions, those extra polymers fill the gaps still existing between individual already adsorbed PCEs which occupy the space in the form of truncated cones (see **Fig. 1**). As more and more PCE molecules are introduced, the truncated cones contract and become more narrowly packed, thus opening up additional interstitial space to facilitate the adsorption of more PCE molecules and producing an ALT of maximum density with respect to surface occupancy.

From the data presented in **Fig. 6(c)** it is evident that the value for ALT is strongly influenced by the side chain length. At maximum surface occupancy, the ALT of the PCE sample exhibiting a side chain made up of 23 EO units (23MPEG6) produced an ALT of 2.6 nm (1.0×10^{-7} in) whereas the polymer of the same molar composition, but holding longer pendant groups (45MPEG6) developed a layer of ~ 5.5 nm (2.1×10^{-7} in). This value is roughly twice of that of the PCE with shorter side chains, hence a direct, linear correlation appears to exist between the length of EO side chains and the ALT. Furthermore, it is also worth to note that the polymer layer produced by PCE comb polymers are one order of magnitude larger than those recorded for the polycondensate superplasticizers, thus highlighting the prominent role of the steric hindrance effect for these comb polymers with respect to cement dispersing efficacy.

Next, the impact of the grafting density (number of side chains per carboxylate group) was investigated by employing two IPEG PCEs, one synthesized at a molar ratio of acid: pendant group of 6:1 (= low grafting density; 52IPEG6) and another one exhibiting an acid : side chain ratio of 2:1 (= high grafting density; 52IPEG2). As can be seen from **Fig. 6(d)**, the grafting density impacts the ALT in two ways. First, a higher side chain density leads to a higher ALT. As such, 52IPEG2 develops a layer thickness of ~ 7.8 nm (3.0×10^{-7} in) as compared to ~ 5.9 nm (2.3×10^{-7} in) for the less densely grafted polymer 52IPEG6. Moreover, a high grafting ratio as in 52IPEG2 leads to a rapid increase of the ALT with dosage, and the maximum thickness of the adsorbed layer is reached at particularly low dosages. This behavior infers that a significant portion of this polymer remains unadsorbed in solution, as a relatively low amount occupies the entire surface which is available. The non-adsorbed portion of the PCE can then adsorb gradually on newly formed cement hydrates and thus provide the slump retention effect which is characteristic for these PCEs showing high side chain density. Opposite to this, the ALT of PCE polymer 52IPEG6 exhibiting a low grafting density increases only gradually with dosage and reaches the point of maximum surface occupancy at much higher polymer additions. This behavior which was also observed before for the two MPEG PCEs of same grafting density [23MPEG6 and 45MPEG6; see **Fig. 6(c)**] signifies that such PCE polymers initially spread out on the adsorption sites and occupy a relatively large area whereas when more polymer is dosed in, they attain a more compressed adsorbed conformation, thus giving way for additional polymers to fill the interstitial surface area.

ALT of phosphate superplasticizer

Finally, the layer thickness of the phosphate comb polymer 45MPEG-P3 was determined. This polymer was synthesized at a molar ratio of 3 : 1 of phosphate: pendant groups, hence it is characterized by a relatively high grafting density (for its chemical structure refer to the **Fig. 4**).

According to the **Fig. 6(c)** it develops a thick adsorbed layer faster than its less densely grafted counterparts 45MPEG6 and 23MPEG6, respectively. Additionally, because of its higher grafting density it also develops a thicker ALT of ~ 7 nm (2.7×10^{-7} in) which is close to that of 52IPEG2 exhibiting an even higher side chain density and a maximum ALT of ~ 7.9 nm (3.1×10^{-7} in).

Relationship between ALT and dispersing performance

According to the theoretical concepts in colloid science the ALT plays a pivotal role with regard to the steric hindrance effect between two particles, as is expressed by the Ottewill-Walker equation (see **INTRODUCTION** part). For this reason, the dispersing efficacy of the superplasticizer samples was assessed in cement paste, and the correlation between the spread flow values and the ALTs was investigated. The results are tabulated in **Table 4**.

First, the results suggest that the steric hindrance effect stemming from the polyethylene glycol side chains in the comb polymers is clearly visible and significant. All PCEs produce much higher spread flow values as compared to the linear polycondensate polymers. Second, it is observed that for PCEs of same molar ratio, but different side chain length the sample exhibiting a longer side chain – and hence a higher ALT – possesses a much-enhanced dispersing capacity over the product with a shorter side chain. This pinpoints the well-known superior effectiveness of PCEs exhibiting longer side chains – apparently, this feature is owed to a much-increased thickness of their adsorbed layer.

Table 4: Correlation between adsorbed layer thickness (ALT) and spread flow in cement paste (CEM I 42.5 R, w/c = 0.49), as determined by mini slump tests; superplasticizer dosage 0.06 % by weight of cement for all samples.

Superplasticizer sample	max. ALT [nm (10^{-8} in)]	Paste spread flow [cm (in)]
BNS	~ 0.3 (1.2)	21.5 (8.4)
AFS	~ 0.6 (2.3)	21.7 (8.5)
23MPEG6	~ 2.6 (10.1)	23.5 (9.2)
45MPEG6	~ 5.5 (21.5)	24.5 (9.6)
52IPEG2	~ 7.8 (30.4)	26.0 (10.1)
52IPEG6	~ 5.9 (23.0)	24.9 (9.7)
45MPEG-P3	~ 7.0 (27.3)	25.1 (9.8)

Another interesting observation from the data in **Table 4** is that polymers of high grafting density which produce particularly thick adsorbed layers do not disperse better than their less densely grafted counterparts. This effect can be attributed to the more pronounced electrostatic repulsion which is instigated by these polymers of low side chain density. It reveals that for PCEs, not only the steric hindrance effect is important relative to performance, but also their anionic charge amount and the resulting electrostatic repulsion. Apparently, this contribution is not as insignificant as is thought and often is underestimated when PCEs are looked at.

SUMMARY AND CONCLUSIONS

This study for the first time provides experimental data on the layer thickness of superplasticizers adsorbed on cationic nanoparticles suspended in a model cement pore solution at the point of maximum surface occupancy (= saturated adsorption). For polycondensate superplasticizers (BNS and AFS), extremely low ALT values of < 1.0 nm (3.9×10^{-8} in) were recorded whereas for the PCE comb polymers, much higher thicknesses of between ~ 2.5 and ~ 8 nm (9.8 and 31×10^{-8} in) were measured, thus emphasizing the important contribution of the PCE side chains to the steric hindrance effect. Those values are slightly higher as compared to those determined in AFM measurements indicating partial polymer compression when using this method, and significantly higher than from XPS experiments which is attributed to the drying process applied there. With regard to PCE molecular architecture it became evident that the side chain length impacts the adsorbed layer thickness much more than the grafting density. Furthermore, stronger anchor groups such as phosphate instead of carboxylate translate into a thicker adsorbed layer, and hence improved dispersing ability, probably resulting from a combination of increased electrostatic repulsion and steric hindrance. Relative to cement dispersion it was evidenced that the presence of pendant groups which provide the steric hindrance effect greatly increase cement fluidity, and that the impact of anionicity (= molar ratio between carboxylate and side chains) in a PCE molecule is less than the influence of the side chain length.

FURTHER RESEARCH

Our study provides insights into the significance of the adsorbed layer thickness of concrete superplasticizers and might stimulate future concepts for improved molecular design of PCE macromolecules. In particular, a comparison between PCE polymers possessing highly flexible and coiled or more rigid and stretched pendant groups would be interesting, as the latter might form even thicker adsorbed layers and hence show superior dispersing performance.

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BIOGRAPHY

Johann Plank is full Professor for Construction Chemistry at Technische Universität München, Germany. His research interests include cement chemistry, chemistry of lowcarbon binders, chemical admixtures, organic-inorganic composites and nano materials, latex dispersions, concrete, dry-mix mortars and oil well cementing. Prof. Plank authored 450 scientific papers, holds 40 patents and in 2015 received the prestigious Alois Aignesberger award from CANMET/ACI in honor of his profound work and inventions in the field of superplasticizers and other admixtures.

Johannes Stecher acquired a Bachelor and a Master degree in chemistry from the faculty of chemistry at Technische Universität München. In his Ph.D. study he investigated the synthesis, dispersing performance and interaction of phosphate MPEG comb polymers with cement and cationic nanoparticles. His work was published in several scientific journals and conference papers. After successfully finishing his Ph.D. in 2020, he joined a company producing instrumentation for the characterization of polymers.

Constantin Tiemeyer studied chemistry at Technische Universität München. After acquiring a Master degree he started his Ph.D. study with a focus on chemical admixtures for oil and gas well cementing including dispersants. He has authored several scientific papers on this subject. After his academic study he took a position in an industrial enterprise which - among other - produces additives for dry-mix mortars.

Tixotropic and chemical structural build-up of cement pastes with superplasticizer under different storage conditions

Kun Zhang, Alexander Mezhev, Wolfram Schmidt

Synopsis: The paper presents the results of a study on the influence of agitation on the structural build-up of fresh cement pastes using a penetration test. It first presents results about the influence of the penetrating shape's geometry on the influence on the cement paste specimen. Then, results are shown for the load-deflection curves depending upon time and agitation before testing. Based on the observation of the force required to penetrate the sample, conclusions on the structural build-up can be made. The observations were made over the course of time with samples that were left at rest and partly agitated before testing at different time steps. The setup allows to identify the contribution of the chemical reaction to the structural build-up process. The presence of superplasticizer obviously reduces the load that cement paste can withstand, while the loss of thixotropy is found notably lower than that of neat cement pastes.

Keywords: thixotropy, superplasticizer, structural build-up, texture analyzer, penetration test.

INTRODUCTION

Currently, there is a raising attention to the investigation of the structural build-up of fresh cement-based materials [1]. After deposition, cement-based materials quickly build up a structure, that is mainly thixotropic in nature [2-4]. Thixotropic structuration occurs during the dormant period of hydration, i.e. it cannot be captured using isothermal calorimetry. During this period, the structural build-up is described using a linear model [5]. Later, the onset of the acceleration period of hydration is accompanied with fast development of mechanical properties and heat evolution. During the acceleration period of hydration the structural build-up can be described using exponential model [6]. Yet, the hydration of cement-based material onsets immediately after the first contact with water [7], even though there is no heat emission observed. However, due to overlapping of chemical hydration and physical thixotropic structuration, it is hard to distinguish the influence of each component on the structural build-up. Furthermore, the presence of concrete admixtures, which are inevitable component of modern concrete, could drastically change the structural build-up [8] and prolong the dormant period of hydration [9].

The structural build-up process is expressed through the evolution of the elastic modulus and the static yield stress. The static yield stress originates from the colloidal interaction between particles and interparticle bridges occurring during the formation of hydration products [10]. Structural build-up is measured using the small amplitude oscillatory shear test (SAOS) [11] or the constant shear rate test (CSR) [12]. However, more and more researchers use alternative methods to observe the structural build-up process, e.g., the penetration test [13-16]. Penetration test employs various techniques for quantitative measurements of the properties of a given material [17]. Its specific strength is the ability to determine mechanical properties directly from indentation load and displacement measurements [18]. The conventional penetration test used to determine the setting times of cement-based materials is Vicat needle test (EN 196-3). However, due to the lack of sensitivity during the first hours of hydration the Vicat test could not be recommended to examine the structural build-up [19,20]. The sensitivity of penetration test might be increased by using different geometries of the penetration body, having larger contact area [21]. Additionally, the penetration test could be performed using different penetration speed, i.e. fast [22] and slow [16] penetration. Fast penetration exhibits result directly after the penetration and corresponds to the time of the measurement, while the slow penetration allow to observe the structural build-up over the course of time. The current paper aims to evaluate the impact of the thixotropic component of the structural build-up during the dormant and acceleration period of hydration using fast penetration method.

RESEARCH SIGNIFICANCE

The structural build-up of cementitious materials originates from the physical and chemical reactions that occur when the materials get in contact with water. To separate the influence of these processes on the structural build-up, the texture properties of cement pastes subject to intensive agitation after different resting times were compared to that of the cement paste hydrated at rest without any additional agitation. Tests were conducted with and without superplasticizer. Our results indicate that the presence of superplasticizer retains the thixotropic structuration of the cement paste longer. This article aims to illustrate the advantages and possibilities of the penetration method in evaluating the structural build-up in industrial casting processes, such as 3D printed concrete (3DPC).

EXPERIMENTAL INVESTIGATION

Materials

The cement used for the study was an ordinary portland cement (OPC), provided by CEMEX (CEM I 42.5 R), complying with EN 196. The Blaine value, compressive strength at 28 days, initial setting time are 3320 cm²/g, 61.8 MPa and 155 min, respectively. The particle size distribution of OPC is shown in Fig.1. The chemical and mineral constituents of the cements for the experiment is given in Table 1. Deionized water was used in all mixes. A commercial spray-dried polycarboxylate-based powder-type superplasticizer (SP) provided by BASF was used.

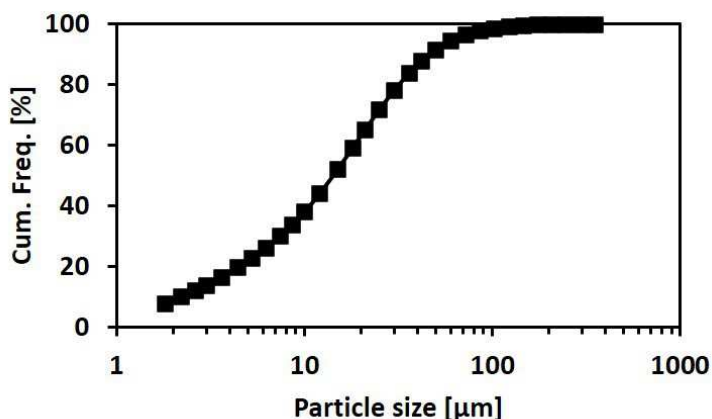


Fig. 1—Particle size distribution of OPC

Table 1—Chemical and mineral constituents of the cement powders for the experiment

Chemical components (%)							Mineral components (%)			
CaO	SiO ₂	Al ₂ O ₃	MgO	Fe ₂ O ₃	SO ₃	Na ₂ Oeq	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
62.97	19.97	4.30	2.35	2.91	3.45	0.33	56.0	18.0	8.0	8.5

Preparation of cement paste and test samples

Two different formulations were considered in this experiment: one was pure cement paste (CP) and another was cement paste with SP. The SP was added at 0.05% by the mass of cement. Cement pastes were prepared with deionized water at the fixed solid volume fraction of 0.45. Cement and SP were first added into a Kenwood kitchen mixer (for penetration test) and IKA STARVISC 200-2.5 mixer (for calorimetric investigations), then pre-mixed at low speed (200 rpm) for 30 s to fully homogenize the SP and cement, followed by adding water during the next 15 s. Then, the paste was mixed at low speed (200 rpm) for 2 min, and then the mixer was stopped for 60 s to manually homogenize the cement paste. This was followed by mixing at high speed (400 rpm) for 3 min and then the paste was transferred to beakers (50 mL) for the penetration test. All the mixing and testing processes were carried out at controlled room temperature ca. 22 °C ± 1 °C.

Penetration test

A texture analyzer is an instrument that can test the resistance of a material to penetration. The penetration velocity can be adjusted, and the respective force is measured. Here, a texture analyzer model CT3 (Brookfield Engineering Laboratories) with a 4.5-kg load cell was used for the texture investigations. To identify the best possible geometry, first measurements were conducted with different penetration probes: a ball probe (Fig. 2a), and a cylinder probe (Fig. 2b), and a cone probe (Fig. 2c). The parameters of these probes are shown in Table 2.



Fig. 2—The type of probe used in the experiment.

For the observation of the structural build-up under resting and agitation conditions the cone probe was used. Samples were tested 10 minutes after initial mixing and recorded as CP (cement paste) or CP_SP (cement paste with SP). In the next 4 hours, the samples were tested under resting and agitation conditions, with an interval of 1 h, recorded as CP_Xh (cement paste resting X hours) or CP_SP_AgXh (cement paste resting X h and agitated 1 min), where X was 1 to 4 h.

Table 2—Parameters of the probes

Shape	Abbreviation	Name	Diameter/angle	Penetration distance
Assessment of the geometry of the penetration body				
Cone	Co	A2-1000	30 mm, 60°	12 mm
Ball	Ba	TA18	12.7 mm	
Cylinder	Cy	TA44	4 mm	
Assessment of the structural build-up without and after agitation				
Cone	Co	A2-1000	30 mm, 60°	15 mm

The following experimental protocol was employed to collect the data:

Test type: compression; test speed: 0.2 mm/s; target type: distance; target value: 12/15 mm; trigger force: 0.5 g. For the penetration tests that were conducted to observe the influence of the probe, a penetration depth of 12 mm was chosen. For the test series where the role of agitation was observed over the course of time, only the cone probe was used, and the penetration depth was adjusted to 15 mm. A high number of penetration depths can be observed for the discussion. Here, the force at 12 mm penetration depth was selected for discussion. To ensure the repeatability of the experiments, all samples were repeated three times.

Calorimetric test

A TAM Air thermal activity micro-calorimeter was used to measure the hydration heat of cement pastes. The samples were prepared with an IKA STARVISC 200-2.5 mixer at solid volume fraction 0.45. For the reference samples CP and CP_SP, 15 grams of cement paste were placed in a plastic cup and then into the calorimeter at 20 °C. For the samples that were agitated at specific times, the sample was kept in an oven at 20 °C before agitation until the specified time was reached. Then the sample was agitated for 1 min after which then 15 g were taken and placed into the calorimeter. All tests were repeated one time.

Agitation of samples

In this experiment, an IKA STARVISC 200-2.5 mixer was used to agitate the sample. After the specified resting time, the sample was re-mixed at a speed of 200 rpm for 1 min. After mixing, the penetration force test and the calorimetric measurement were performed according to the above steps.

EXPERIMENTAL RESULTS AND DISCUSSION

Influence of the probe shape on the resistance to penetration of cement paste

To better understand the effects of the cement hydration and thixotropy on the structural build-up process, investigations using a texture analyzer with different probes for penetration tests of samples were performed.

The penetration force measured during the penetration of a probe to a constant depth of 12 mm ($F_{p, 12mm}$) as a function of time for a cement paste prepared with or without SP using different probes is presented in Fig. 3. The penetration force measured with all probes increases with the resting time. Regardless of the geometry of the probe, the $F_{p, 12mm}$ obtained with CP after resting for 2 h and the CP_SP after the resting for 3 h, was negligible and close to zero. Yet, after 3 h, the $F_{p, 12mm}$ obtained with the ball (Ba) and cone (Co) probe increases significantly. The cylindrical probe (Cy) showed only a slight increase after 3 h of hydration. The penetration force depends not only on the test surface area of the probe but also on the rigid network structure formed by cement hydration. The introduction of SP still showed a lower $F_{p, 12mm}$ after 2 h of hydration compared to CP, regardless of which probe was used. Since the SP is adsorbed on the surface of cement particles and hydrates it slows down the formation of rigid networks between particles and hydrates. It also can be seen in the Fig. 3 that the ball probe achieves the maximum force after 4 hours regardless of the presence of SP (Fig. 3).

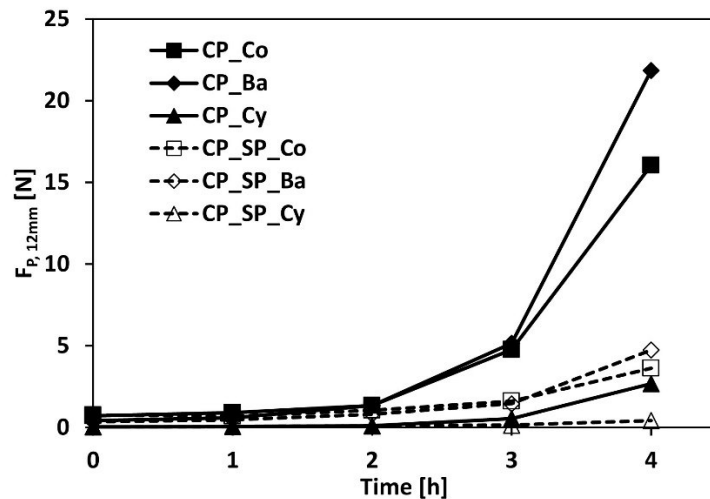


Fig. 3—Penetration force as a function of time for cement paste with or without SP at different probes.

Fig. 4 shows the development of penetration force normalized to the reference versus resting time after the preparation of samples. The reference is relative to the penetration force at t_0 (initial test without rest). All probes show similar penetration force development.

As shown in Fig. 4, the cone probe has the highest normalized force values when related to the reference as the rest time increases, and the smallest signal could be found with the cylinder probe. Thus, the cone probe was considered as the most suitable tool for the texture measurements, and the following experiments were all conducted using the cone probe.

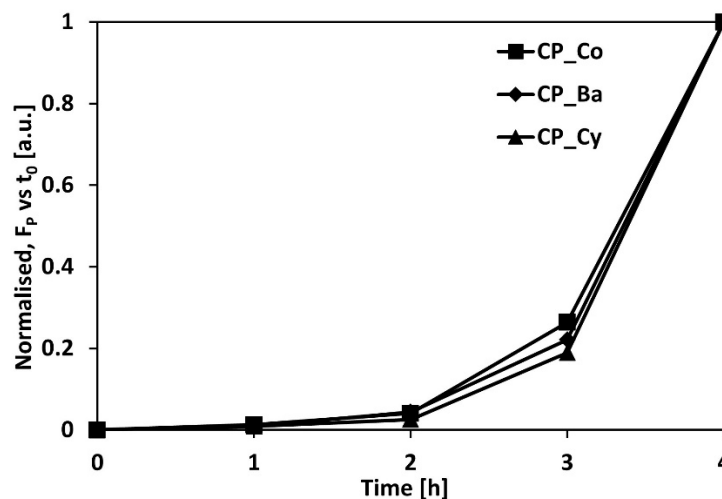


Fig. 4—The normalized value of the relative penetration force versus resting time.

Influence of supplementary agitation on the resistance to penetration of cement paste

Fig. 5 summarizes the penetration force (F_p) as a function of penetration depth for CP and CP_SP at different state. The results show that the F_p is related to penetration depth and increase with penetration depth. However, if the specific application requires a lower penetration force of cement paste, addition of SP is favorable (Fig. 5 b)). It was reported that the resistance to penetration is well correlated with the yield stress, as the yield stress is proportional to the penetration depth [23]. Rheological properties of cement paste, such as the yield stress, depend on the strength of particle-particle interactions and the aggregation and dispersion behavior of particles in a suspension, and reflect changes in the microstructure of cement hydration [24,25]. In addition, the hydration of cement promotes the growth of cohesive contact points between cement particles, thus, increasing the attractive interparticle strength. It was also observed in Fig. 5 that the F_p was clearly lower after agitation compared to F_p of the rested samples. Evidently, agitation disrupts the existing structure of hydration products, thus destroying the physical and chemical structure inside the cement paste.

The results in Fig. 5 a) shows that the F_p of the sample that was agitated before the test drops sharply compared to the one that was left at rest. The result after the introduction of SP is shown in Fig. 5 b), the penetration force of the agitated sample is reduced to a certain extent but not sharply, compared to the reference sample.

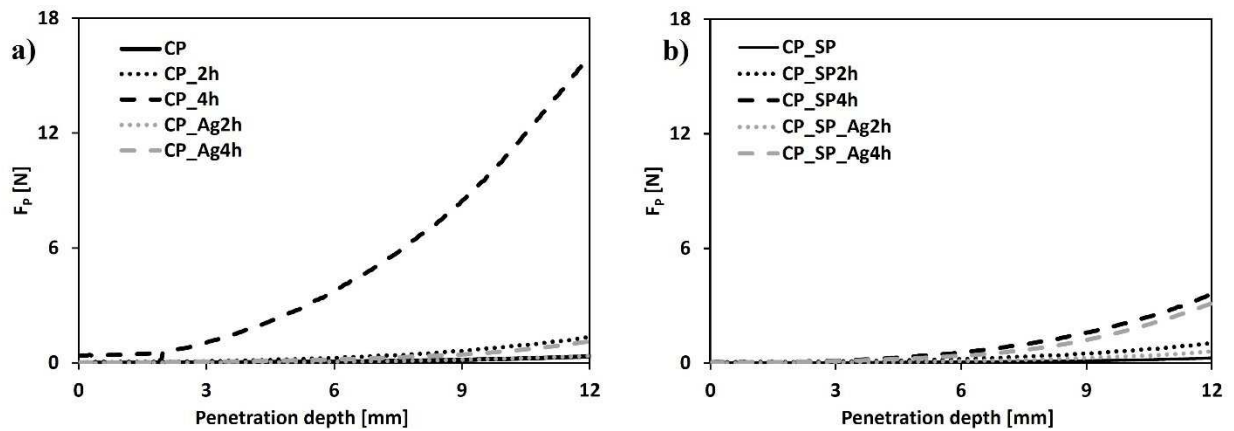


Fig. 5—Penetration force as a function of depth for cement paste at different state. a) without SP, b) with SP.

Results of the penetration force measurements ($F_{p, 12mm}$) as a function of resting time for cement paste prepared with or without SP at different state are shown in Fig. 6. Regardless of the presence or absence of SP, the $F_{p, 12mm}$ after being left to rest is greater than after being agitated again before testing. For the sample without SP the difference between the $F_{p, 12mm}$ for the non-agitated and the agitated cement paste is significantly increasing, while for the CP_SP this effect cannot be observed. Up to 3 h, regardless of the presence of SP the agitated samples nearly follow the same curve. Only after 4 h significant changes can be observed. While the CP shows a significant increase of the penetration force, the force of the corresponding CP_Ag remains very low. Both samples with SP shows the lower $F_{p, 12mm}$, of which the value is very similar regardless of whether it was left at rest or agitated. After the hydration for 4 h without of SP, a rigid structure is formed. However, obviously it can be fully broken by agitation. In return, the CP_SP shows a stronger rigidity of a structure than the agitated cement paste without SP. Apparently, this phenomenon can be related to the dispersion effect of SP on cement particles, which allows hydrate to be more stable between cement particles [26,27]. It is possible that the hydration products in solution are not too strongly affected by the agitation, and thus the structure provided by the dispersed hydration products in solution is stronger after agitation than that of the paste without superplasticizers, where hydration takes place more on particle surfaces, which then are sheared off by agitation. This can explain, why a more rigid structure with higher elasticity than the neat cement paste is retained with SP.

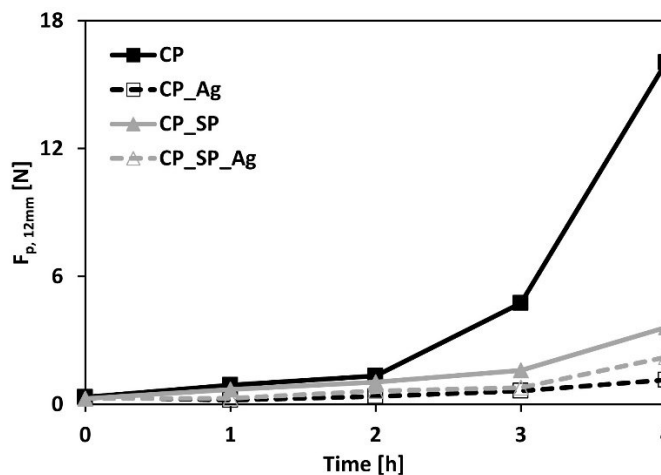


Fig. 6—Penetration force as a function of resting time for cement paste with or without SP at different state.

We defined a ratio between the penetration force of agitated samples and the penetration force samples tested without agitation. This ratio describes how strongly agitation reduces the structural strength at each given time step. The loss

can be considered as purely thixotropic (fully irreversible) loss at each time step as shown in Fig. 7 and was calculated according to (1):

$$A_{thix\ loss} = 1 - \frac{F_{agitated}}{F_{rest}} \quad (1)$$

where, F_{rest} is a penetration force tested after the sampling being at rest, $F_{agitated}$ is a penetration force tested after the sampling was agitated after being at rest. It can be seen from Fig. 7 that the value of CP_SP is always lower than CP and shows that the structure of CP_SP is less affected by the agitation than that of CP. This, however, is in relation to a generally lower penetration resistance of mixtures with SP. Thus, it can be considered that the thixotropic loss of CP_SP is lower than that of CP. In addition, this thixotropic component of the structural build-up of CP becomes smaller over the course of hydration, while it tends to increase for CP_SP. This indicates that the agitation without SP can effectively break the structure, while without agitation the build-up occurs very pronounced. In return, in systems with SP the hydration is generally slowed down also without agitation, so that the performance difference at rest and with agitation becomes less significant. The penetration force of the cement paste decreases with the introduction of SP, since the SP weakens the interaction between particles and increases the distance between cement particles (Fig. 5). At the same time the percentage of thixotropic structural build-up is always greater for the system with SP. This phenomenon becomes very interesting, as it suggests that the thixotropic part of the structural build-up of cement paste is higher when SP is introduced.

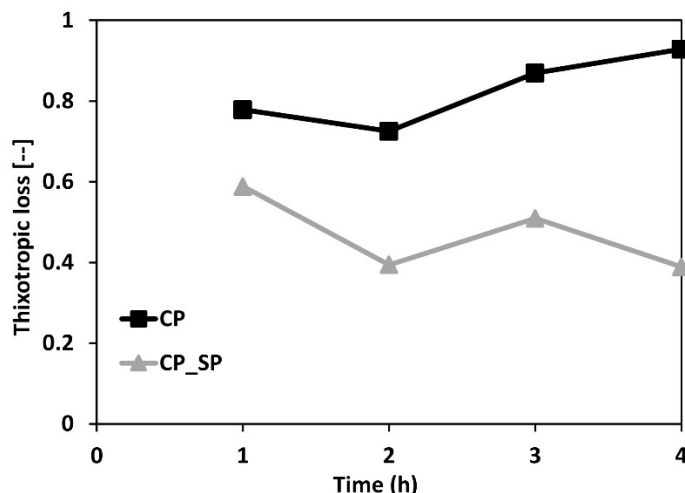


Fig. 7—Evolution of the thixotropic loss of cement pastes prepared with and without SP.

Influence of the supplementary agitation on the hydration kinetics

After the addition of water, the cement starts to dissolve in the water and the early hydration products such as AFT, C-S-H and portlandite begin to grow on the surface of cement particles and in the aqueous phase [28,29]. The slow formation of early cement hydrates after the initial reaction makes the heat release during the induction period very low. Fig. 8 shows the heat flow curves of cement paste with or without SP and cement pastes agitated after resting for 4 h. The heat rate of the agitated sample rises directly after reaching equilibrium with increasing hydration time. It is well known that a large amount of heat is generated immediately after the initial contact of cement with water, which shows the highest hydration peak at 0 h in calorimetric experiments. However, the presence of the high peak at the heat flow chart for agitated samples appeared due to opening of the calorimeter and introduction of samples. The accelerated hydration path overall becomes less steep for the CP_Ag4h, which could indicate more homogenous hydration due to the better-dispersed hydrates after agitation.

The introduction of SP into cement paste significantly retards the overall hydration. This retardation of hydration also accounts for the significantly lower penetration forces that could be observed (Fig. 5 and 6). The adsorption of SP makes the cement particles better dispersed, which changes the morphology and growth kinetics of cement hydration products. In addition, the adsorption of SP on the surface of cement particles hinders the diffusion of hydrated ions at the cement-solution interface, and the carboxyl groups in SP molecules may be complex with Ca^{2+} in the cement suspension, thereby inhibiting the nucleation and precipitation of hydrated products. As mentioned above, cement particles with better dispersibility exist stably in the cement suspension, and additional agitation cannot destroy the hydration products already formed between the cement particles due to the larger cement particle spacing.

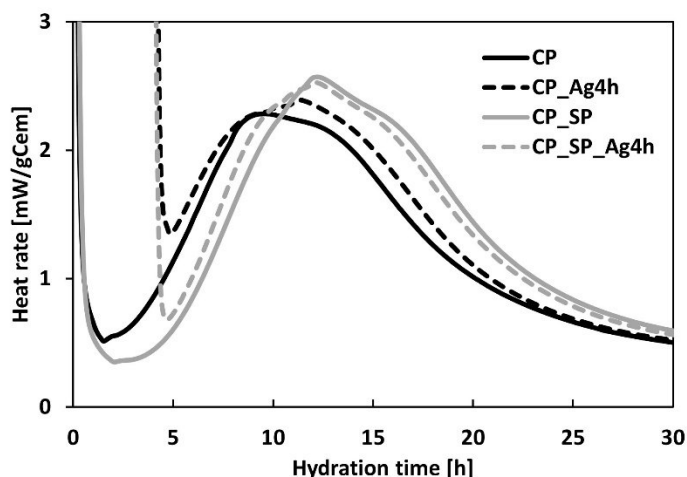


Fig. 8—Heat flow for cement pastes at different test conditions.

The rate of structural build-up of cement paste can be controlled by physical or chemical means. To show the influence of the agitation on the subsequent heat flow evolution the heat rate of the cement hydration was calculated. In this experiment, the slope of the heat rate curve during the acceleration period of hydration represents the hydration rate of cement, which is recorded as S_a . Fig. 9 shows the relationship between S_a and the hydration time. It can be seen from Fig. 9 that the S_a of the CP_Ag shows a linear behavior and in general the S_a of CP_Ag1h is higher than that of CP, since the additional agitation promotes the dissolution of C_3S at the sample that were at rest for 1 hour, which is still in the dissolution stage. In this induction period of cement hydration, the reaction is mainly controlled by the dissolution of C_3S , which in turn promotes the nucleation and growth of C-S-H in the acceleration period [28]. It is shown that the S_a of CP with additional agitation decreases linearly. After SP was introduced into the cement paste, the S_a is significantly increased in comparison to that of the neat cement paste, although it was still in the induction period. For CP_SP_Ag, the additional agitation delayed the emergence of the main exothermic peak, although it cannot destroy the hydration products generated between the cement particles with better dispersion during the induction period. It shows that the S_a of CP_SP_Ag is not related to the rest time of the sample.

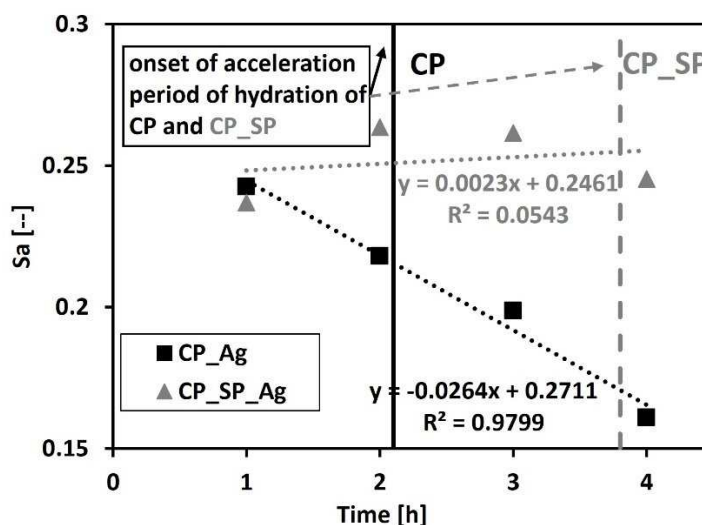


Fig. 9—Relationship between S_a and the hydration time, (S_a is the slope of the heat flow curve during the acceleration period of hydration, which is indicate the growth rate of the heat evolution)

The relationship between penetration force and hydration of cement pastes at different storage states

Fig. 10 depicts the relationship between penetration force and cement hydration. It can be seen from Fig. 10 a) that regardless of the presence of SP, the increase of the penetration force matches in time with the beginning of the acceleration period of hydration. Fig. 10 b) summarizes the relationship between the thixotropic loss and the S_a ratio

(Divide the S_a of the agitated sample by the S_a of the reference sample.). It can be seen from the figure that the thixotropic loss of CP decreases with the increase of S_a , while CP_SP shows more scatter. After agitation, it can be assumed that the linked structure formed between particles and hydrates breaks into smaller lumps, eventually reaching or getting close to an equilibrium state. Due to the thixotropic nature of cement pastes, the broken lumps begin to rebuild the network structure when the agitation stops. It shows that the thixotropic structural build-up of cement paste is related to the rate of network structure rebuild. The S_a of the CP_SP is greater than that of the CP (Fig. 9), and the thixotropic loss after agitation is lower than that of the CP (Fig. 7). This is because cement particles are more dispersed and stable in the cement paste with SP due to their adsorption on the surface of particles and hydrates. Applying additional agitation to CP_SP cannot destroy the rigid network structure formed between cement particles, and thus, these mixtures show a higher thixotropic structural build-up.

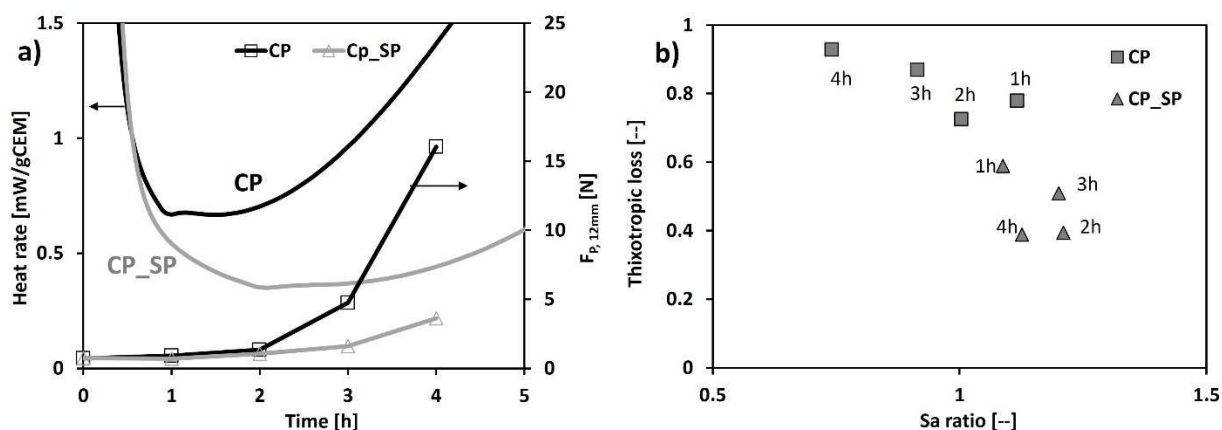


Fig. 10—Relationship between penetration force and cement hydration. a) is the evolution of penetration force is measured on samples placed at different times using penetration tests vs. hydration of cement paste. b) is the relationship between the thixotropic component and the growth rate of the hydrate.

SUMMARY AND CONCLUSIONS

Based on result obtained in this study the following conclusions can be drawn:

1. Different penetration probes cause different material responses. However, if this is normalized to the initial penetration force the influence of the probe geometry becomes insignificant.
2. After agitation, significantly smaller penetration forces could be measured without and in the presence of superplasticizer. However, the penetration force after agitation increased with time, indicating that a significant part of the structural build-up process is reversible, thus, is thixotropic.
3. A purely reversible component of the thixotropy structural build-up could be quantified by thixotropic loss. The thixotropic loss in cement pastes with SP is significantly lower than in samples without SP. This shows that the introduction of superplasticizer increases the thixotropic structure build-up of cement paste.
4. The penetration force of the cement paste increases with the increase of the heat flow of cement hydration during acceleration period. When agitation is applied at different times, the hydration reaction is slightly less retarded than in rest samples.

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BIOGRAPHY

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Effect of the PCE side chain length and grafting density on the plastic viscosity of cement paste

David Nicia and Dirk Lowke

Synopsis: Molecular parameters of polycarboxylate polymers (PCEs) affect important rheological properties of cement-based suspensions such as viscosity. As the viscosity has a significant influence on the form filling ability and segregation resistance, understanding and predicting the effect of the side chain length and grafting density on viscosity is of considerable importance. To investigate the effect of tailored PCEs with systematically varying side chain length and grafting density on the plastic viscosity of cement paste, parallel-plate rheometry, TOC analysis and spread flow measurements were performed. The results indicate that with decreasing side chain length as well as increasing grafting density, the plastic viscosity of cement paste with constant dynamic yield stress is reduced, with a dominating impact of the side chains. Furthermore, decreasing viscosity correlates with less non-adsorbed PCE. This finding could be related to the reduced viscosity of the interstitial aqueous phase, as less residual PCE and shorter side chains that protrude into the aqueous phase could reduce it. Hence, the macroscopic viscosity would decrease as well.

Keywords: Rheology of cement-based suspensions; Plastic viscosity; Polycarboxylate ether (PCE); PCE molecular structure; parallel-plate rheometry; PCE adsorption; Cement paste; stickiness

INTRODUCTION

PCE are widely used dispersants in concrete technology as they increase the workability in a dosage-efficient way and additionally allow for a flexible adaptation of their molecular structure to the requirements [1-3]. PCEs typically consist of a negatively charged backbone of carboxylate groups paired with PEG side chains. The charged backbone is responsible for adsorption while the side chains lead to steric repulsion and thus particle separation. The copolymer structure of PCE can be simplified using the parameters C/E, P and n (**Fig. 1**) [4]. C/E is the grafting density and reflects the charge density of the PCE, P represents the number of PEG units in the side chain while n expresses the number of repeat units containing one side chain in the whole polymer.

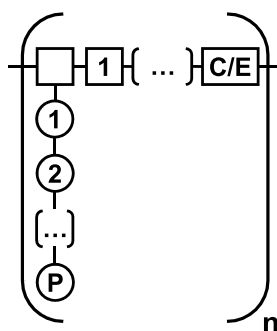


Fig. 1—Simplified schematization of comb-shaped PCE, redrawn based on [4]

In addition to yield stress and thixotropy, the viscosity of fresh concrete is one of the most important rheological parameters for predicting workability. The viscosity determines the macroscopic stickiness and is of decisive importance for the form filling ability [5,6] and segregation resistance [7,8]. These processing operations of cement-based suspensions occur in low shear rate intervals, so the plastic viscosity of the Bingham model is commonly applicable for modelling [7,9,10].

The addition of PCE typically reduces yield stress as well as viscosity with increasing dosage at w/b values down to approx. 0.20 [11-13]. In the case of very low w/b values from 0.16 to 0.20, a higher PCE dosage could lead to an increase in viscosity likely being attributed to an increase in the viscosity of the interstitial aqueous phase [11,14] or to non-compensatable interparticle friction due to a thin lubricating layer around the particles [15]. For cement-based suspensions with a constant yield stress, the viscosity may differ [1], among numerous parameters due to the PCE molecular structure. Winnefeld et al. [16] have shown that with increasing PCE charge density, the viscosity in mortars decreased, while the side chain length and molecular weight were less decisive in influencing viscosity. Furthermore, the authors stated that the copolymers leading to lower viscosities adsorbed largely at constant dosage so that adsorption seems to be of high importance as in the case of yield stress. Other studies suggest that a lower PCE side chain length can also lead to lower viscosity of the suspension due to a higher degree of adsorption when synthesized in a targeted manner [12,17,18]. Hot et al. [14] and Reiter et al. [19] have shown that besides the amount of adsorbed PCE, the density of the polymers in the liquid phase between the cement particles is likely to affect the viscosity. They suggest that the macroscopic viscosity could result from either more non-adsorbed polymers or a higher density/ longer side chains between adjacent particles.

In addition to PCE charge density and side chain length, studies by Lange and Plank [6,20] indicated that lower viscosity and correspondingly higher flow velocities could be obtained with increasing amounts of hydrophilic components in the PCE. The hydrophilic character increases with longer side chains, as the proportion of hydrophobic methyl groups in the copolymer decreases.

RESEARCH SIGNIFICANCE

The variety of PCE design options provides great potential for the tailored control and prediction of the rheological properties that are crucial for fresh concrete workability. Accordingly, the effect of different molecular structures on plastic viscosity has already been studied in various ways, but not sufficiently in practice-oriented concepts and with tailor-made PCE polymers. For this reason, we investigated ordinary Portland cement (OPC) pastes at constant workability (i.e. dynamic yield stress) as a function of systematically varying grafting density and side chain length using rotational rheometry and the TOC analysis.

EXPERIMENTAL INVESTIGATIONS

Concept of investigations

In this contribution, we address the question of how individual molecular structural parameters of PCE polymers (side chain length P and grafting density C/E) and their interaction with ordinary Portland cement (OPC), qualitatively affect the plastic viscosity of pastes at constant dynamic yield stress. Since fresh concrete is usually produced for a predefined consistency, i.e. dynamic yield stress, the question arises whether the viscosity can be controlled independently of the yield stress and hence optimized for its application (**Fig. 2**).

Throughout the experimental investigations, the dynamic yield stress was kept constant individually adapting the PCE dosage for a spread flow of 270 ± 5 mm (i.e. $\tau_{0D} = 9.3$ Pa acc. To [21,22]). The experimental investigations pursued the following main objectives:

- (1) Investigation of the qualitative effect of the PCE side chain length on the plastic viscosity considering the adsorption behaviour, and
- (2) Investigation of the qualitative effect of the PCE grafting density on the plastic viscosity considering the adsorption behaviour.

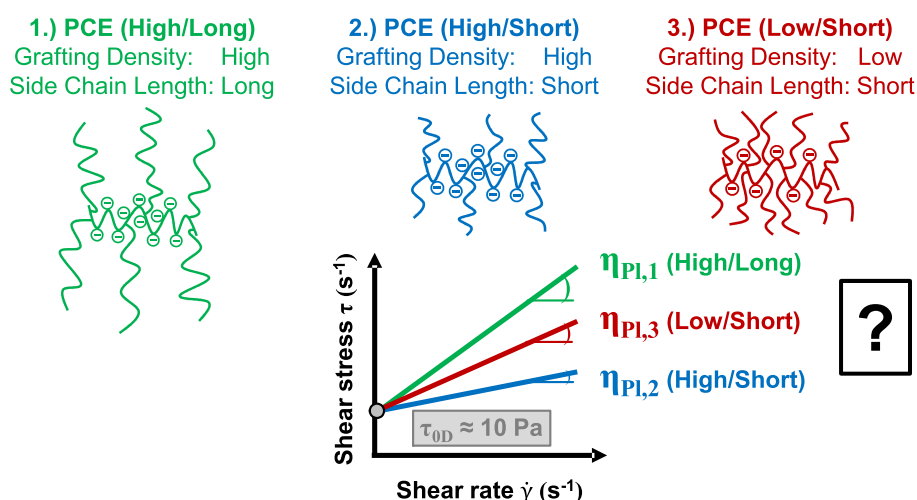


Fig. 2—Schematic representation of the effect of the PCE side chain length and grafting density on plastic viscosity at constant yield stress

Materials

Cement – A commercial Portland cement (OPC, CEM I 42.5 R) was used at a w/c ratio of 0.29 (**Table 1**). The mineralogical and chemical composition is summarized in **Table 2**. The value for loss on ignition is 2.5 wt.-% and the characteristic, volumetric particle sizes are $x_{3,10} = 3.32 \pm 0.23 \mu\text{m}$, $x_{3,50} = 17.24 \pm 1.84 \mu\text{m}$ and $x_{3,90} = 42.34 \pm 3.38 \mu\text{m}$ ($n=8$, from laser diffraction).

Table 1—OPC paste proportions of the investigated samples

CEM I [dm ³ /m ³]	Water, distilled [dm ³ /m ³]	w/c	V _w /V _c	Solid volume fraction Φ	Temperature after mixing [°C]
526	474	0.29	0.90	0.53	20 ± 1

Table 2—Mineralogical and chemical compositions of the cement

Phase	wt. %	Oxide	wt. %
Alite	65.4	CaO	62.9
Belite	11.3	SiO ₂	20.3
C ₃ A _{cubic}	3.3	Al ₂ O ₃	5.0
C ₃ A _{orth.}	1.7	Fe ₂ O ₃	2.9
C ₄ AF	10.1	MgO	1.3
Anhydrite	3.1	Na ₂ O	0.2
Bassanite	2.0	K ₂ O	0.7
Gypsum	0.5	SO ₃	3.5
Calcite	1.4	TiO ₂	0.2
Quartz	0.3		
Periclase	0.3		
Arcanite	0.2		

PCE – We examined seven VPEG-type PCE polymers, for which the qualitative information is summarized in **Table 3**. The PCE designation is based on the qualitative information on the side chain length: short (S), medium (M) and long (L) as well as grafting density low (Lo), medium (Me) and high (Hi)

Table 3—Qualitative information of the investigated VPEG PCEs including their solution conformation acc. to Gay and Raphael [23] as well as the average PCE dosage required for adjusting the target spread flow of 270 ± 5 mm

PCE	Side chain length	Grafting density	Solution conformation	PCE dosage mDos _{270mm} [mg _{PCE} /g _{CEM}]
S.Hi	Short	High	FBW*	2.17 ± 0.06
S.Me	Short	Medium	FBW*	1.77 ± 0.00
S.Lo	Short	Low	FBW*	1.14 ± 0.00
M.Hi	Medium	High	FBW*	1.00 ± 0.03
M.Me	Medium	Medium	SBW*	0.95 ± 0.01
M.Lo	Medium	Low	SBW*	1.21 ± 0.01
L.Hi	Long	High	SBW*	1.12 ± 0.01

* Flexible backbone worm (FBW) ** Stretched backbone worm (SBW)

Methods

Cement paste preparation – Before each cement paste production, 25 kg of bagged cement were homogenized in a bucket by tipping and rolling. The volume of cement paste was 1 dm³, which was produced in an EN 196-1 standard mixer. We used the direct addition mode, directly applying PCE into the mixing water and stirring it gently with a glass rod before adding the cement. The mixing process took 4 minutes and consisted of the following intervals:

- 1.) Mixing stage 1 (70 rpm) for 60 s, immediately after adding the cement
- 2.) Mixing stage 2 (140 rpm) for 90 s
- 3.) Mixing pause for 30 s
- 4.) Mixing stage 2 (140 rpm) for 60 s

Immediately after mixing, the temperature of the cement paste was measured to ensure the target interval of 20 ± 1 °C controlled by tempered distilled water. The container was covered with an acrylic glass plate until the preshearing step.

Spread flow test and dynamic yield stress calculation – Prior to the spread flow test and parallel plate rheometry, the cement paste was pre-sheared to reduce the impact of the varying thixotropic structural build-up at rest depending on the PCE molecular structure [24]. Therefore, the first preshear step was implemented 11 minutes after water-cement contact using a 4 bladed propeller stirring attachment fixed on a screwdriver for 30 seconds. After the

first preshear step, a sample was taken for parallel-plate rheometry and the container was covered again to prevent possible evaporation. 14 minutes after water-cement contact, we again presheared the paste for 30 s using the 4 bladed propeller. We started the spread flow experiment on a dry glass plate 15 minutes after water-cement contact by raising the cone and determined the diameter two times in perpendicular directions after the flow stopped. Based on the mean spread flow diameter, the dynamic yield stress according to Roussel [21,22] was calculated:

$$\tau_0 = \frac{225 \cdot \rho \cdot g \cdot V^2}{128 \cdot \pi^2 \cdot R^2} \quad (1)$$

where ρ is the bulk density of the sample, g being the gravity, V represents the volume of the tested sample and R the spread flow radius.

Parallel-plate rheometry – The plastic viscosity of the cement paste was determined using a parallel-plate rheometer with a sandpaper surface ($d_{\text{plate}} = 50$ mm, Gap = 1 mm, Sandpaper Grit P600 with average roughness 25.8 ± 1 μm). We selected this type of sandpaper to achieve an optimum between wall slip prevention and correct zero-gap determination as both phenomena affect the viscosity measurement [25,26]. Furthermore, a Peltier element was used for temperature stabilization (20 ± 1 $^{\circ}\text{C}$), as well as a temperature hood to minimize evaporation during the experiment. Owing to the non-Newtonian behaviour of cement-based suspensions, the shear rate was calculated with a decisive shear rate of $3/4R$ [27–29]. The sample is placed and trimmed in the rheometer 11 minutes after water-cement contact. Subsequently, the rheometer shear profile starts at 14 minutes (**Fig. 3 left**). After a 30 s preshearing period, a downward ramp profile with constant shear rate intervals of $\Delta t = 6$ s is used. The cement paste is subjected to shear rates from 90.33 s^{-1} down to 0.02 s^{-1} , with only the shear rate intervals between 33.88 s^{-1} to 1.41 s^{-1} being evaluated. The data points for the Bingham modelling were generated by averaging the parameters within the last 2 s of the evaluated shear rate intervals (**Fig. 3 right**).

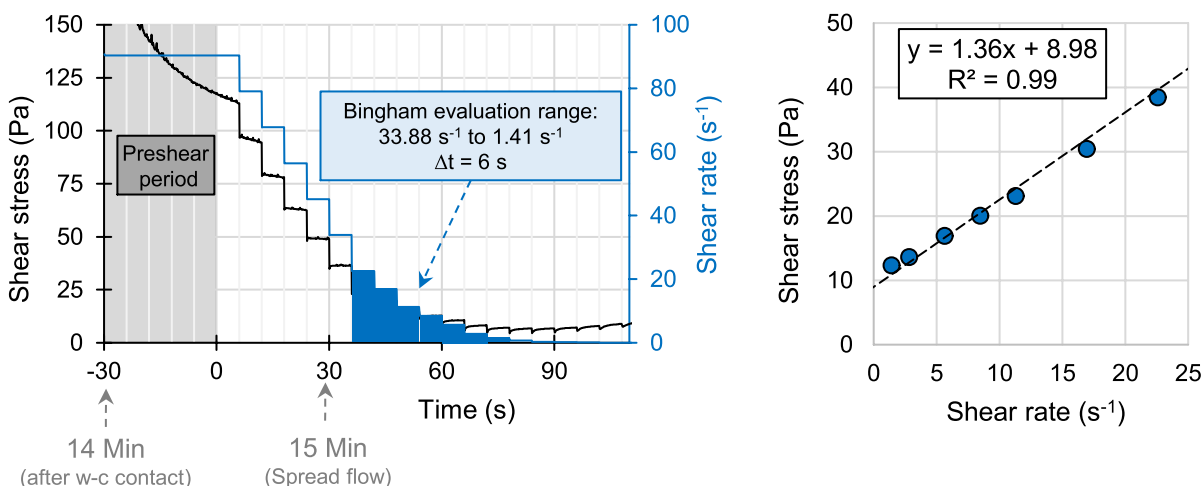


Fig. 3—Preshearing and downward ramp shear profile using an exemplary PCE superplasticized cement paste (left) and Bingham modelling in the defined evaluation range (right)

TOC analysis – TOC analysis was used to quantify the residual PCE amount in the aqueous phase of the rheologically characterized cement pastes. Using this method, we can determine the portion of non-adsorbed polymers that is important for evaluating the effect of individual molecular parameters on viscosity.

Sampling for pressure filtration was carried out in the case of a spread flow within the target interval of 270 ± 5 mm 16 minutes after water-cement contact. To isolate the aqueous phase, approx. 200 ml were filled into a pressure filtration cartridge and subjected to a pressure of 8 bar. The slightly turbid solution was passed through a syringe filter with a pore size of 0.20 μm . The filtrate was diluted at 1:20 to reach the calibration range of the TOC analyser. Also, the solution was mildly acidified with hydrochloric acid before the TOC measurement to stabilize against precipitation [30]. Organic carbon was determined as NPOC at 680 $^{\circ}\text{C}$ by high-temperature oxidation. The NPOC of the same cement paste without PCE was subtracted to account for other organic components.

EXPERIMENTAL RESULTS AND DISCUSSION

Effect of PCE side chain length on plastic viscosity at constant dynamic yield stress and adsorption behaviour

Fig. 4 left illustrates the effect of side chain length on plastic viscosity at constant dynamic yield stress of approximately 9.3 Pa. Overall, the viscosities of all PCE polymers studied are in the range of 0.72 Pa·s to 1.31 Pa·s. The plot illustrates that the plastic viscosity increases significantly with increasing side chain length. This observation is indicated for all grafting densities. The correlation between longer side chain length and a higher plastic viscosity may be attributed to a reduced adsorption ability, i.e. a higher amount of non-adsorbed polymers in the liquid phase. An alternative explanation could be chain end interactions, where the PCE adsorbs on adjacent cement particles, which could bridge the cement grains, forming a loose network similar to the working mechanism of viscosity modifying agents [32]. It is also worth noting that other researchers have found a viscosity-reducing effect due to non-adsorbed polymers through a lubricant effect [33] or by reducing the surface tension [34].

Fig. 4 right shows the amount of non-adsorbed PCE as a function of side chain length. The results reveal that the non-adsorbed quantity increases with increasing side chain length. This effect is caused by a pronounced charge shielding in the PCE backbone resulting from longer side chains [30]. Consequently, as the length of the side chains increases, more PCE polymers remain in the aqueous phase, increasing the density and viscosity of the interstitial aqueous phase and, as a result, the macroscopic plastic viscosity of the cement paste.

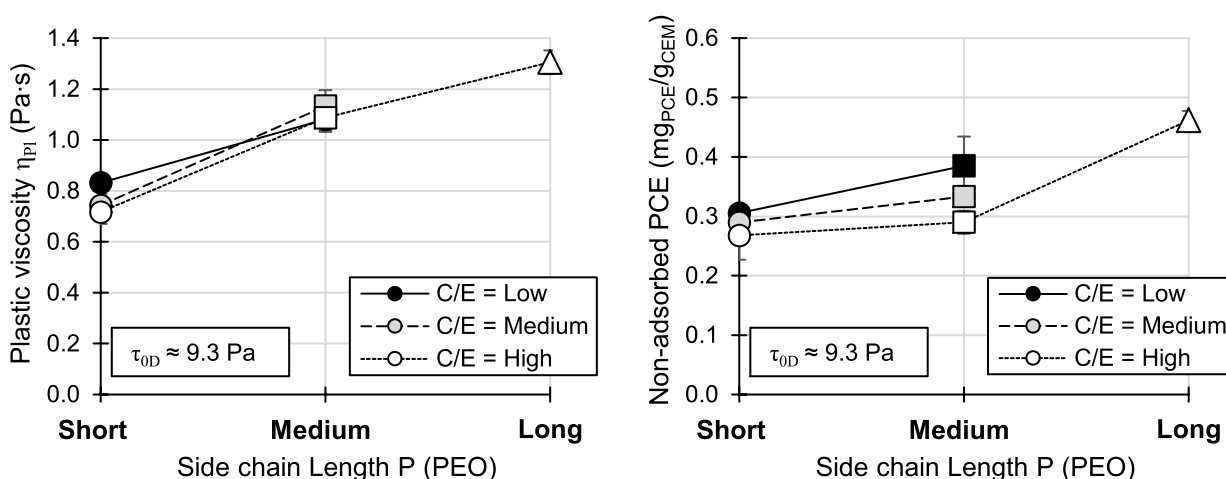


Fig. 4– Effect of PCE side chain length P on the plastic viscosity at constant dynamic yield stress of 9.3 Pa (left) corresponding quantity of non-adsorbed PCE (right)

Effect of PCE grafting density on plastic viscosity at constant dynamic yield stress and adsorption behaviour

In **Fig. 5 left** we show the effect of PCE grafting density on plastic viscosity at constant dynamic yield stress of approximately 9.3 Pa. There is a very slight reduction in plastic viscosity with increasing grafting density for PCEs with short side chains. At the same time, a slight decrease in the amount of non-adsorbed polymers in the liquid phase can be observed, **Fig. 5 right**. This may be explained by the fact that adsorption affinity rises with increasing grafting density [35]. As a result, less PCE would remain in the solution, resulting in lower interstitial fluid viscosity and, therefore, a lower macroscopic plastic viscosity. This basically confirms the previously described mechanism of decreasing viscosity as a result of decreasing amounts of non-adsorbed polymers.

In comparison, at medium side chain length, the plastic viscosity remains almost constant, **Fig. 5 left**. However, along with this, we observe a decrease in the amount of non-adsorbed PCE polymers. Thus, considering exclusively polymers with medium side chain length, plastic viscosity does not strictly correlate with the amount of the non-adsorbed PCE. This observation indicates that the effect of molecular structure, like protruding side chains of the adsorbed PCE, may superimpose effects from non-adsorbed polymers. Thus, further research is needed to address this question.

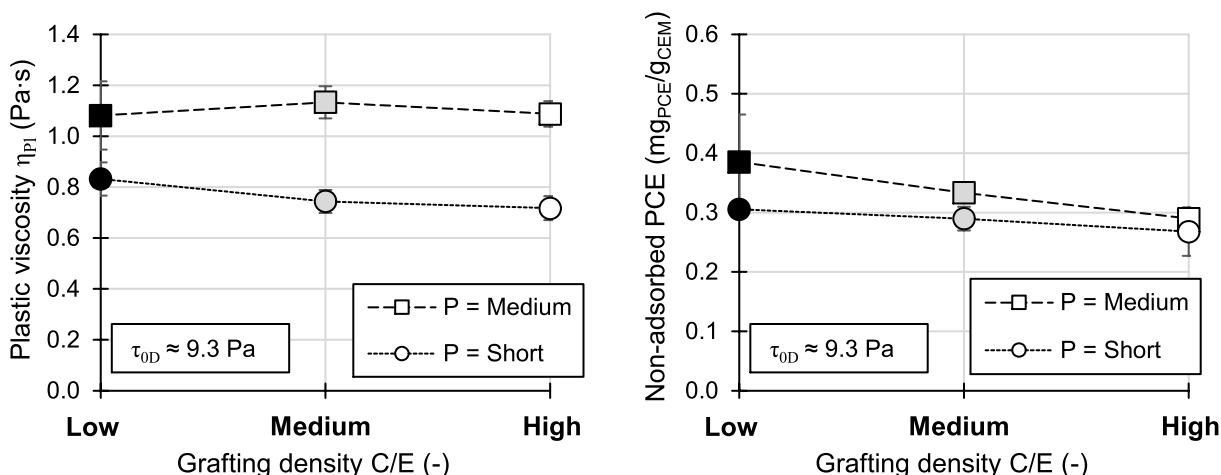


Fig. 5— Effect of PCE grafting density C/E on the plastic viscosity at constant dynamic yield stress of 9.3 Pa (left) and the corresponding quantity of non-adsorbed PCE (right); both rearranged from Fig. 4 to highlight the effect of the grafting density for a given side chain length P

The interaction of PCE molecular structure, amount of non-adsorbed PCE and plastic viscosity

Finally, to establish a link between the non-adsorbed quantity of the different PCE molecular structures and the plastic viscosity at constant dynamic yield stress, we present this correlation for the investigated polymers in **Fig. 6**. Overall, a linear correlation can be derived between plastic viscosity at constant dynamic yield stress and the amount of non-adsorbed PCE. The higher the amount of non-adsorbed polymers, the higher the viscosity. The explanation may be that more PCE in the aqueous phase increases the density and viscosity of the liquid, finally, resulting in a significant increase in macroscopic viscosity of the cement paste.

However, it is important to note here, that the amount of non-adsorbed polymers is affected by both side chain length and grafting density while viscosity is primarily correlating with a variation of the side chain length (**Fig. 6**). This is indicated by the fact that PCEs with medium side chain length have a constant viscosity despite a different adsorption behaviour as a function of the grafting density (**Fig. 6**, squared symbols). This points out further effects, e.g. by side chains of the adsorbed polymers, can superimpose the effects of the amount of non-adsorbed polymers. Finally, we conclude that the side chain length appears to be the dominant parameter affecting the plastic viscosity compared to the grafting density.

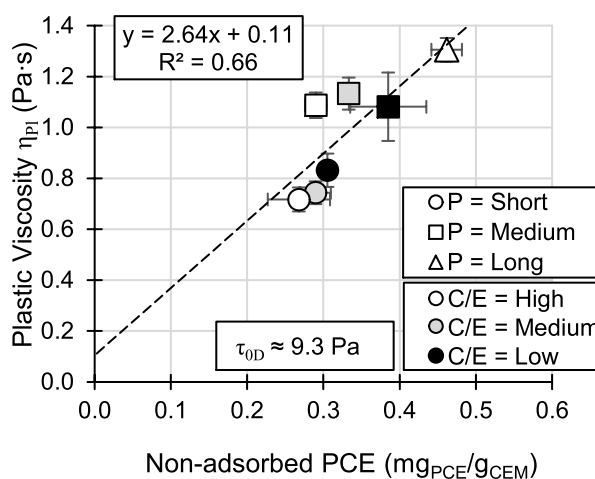


Fig. 6— Effect of the non-adsorbed amount of the investigated PCEs on the plastic viscosity at constant dynamic yield stress of 9.3 Pa (C/E - grafting density, P - side chain length)

CONCLUSIONS

This paper deals with the effect of PCE side chain length and grafting density on the plastic viscosity of cement paste at constant dynamic yield stress. Based on the experimental investigations, the following conclusions can be drawn on the main objectives:

(1) Side chain length appears to be the dominant parameter affecting the plastic viscosity. The investigations of all PCEs show that plastic viscosity at constant dynamic yield stress significantly increases with longer side chains. This can be attributed to an increased interstitial liquid viscosity caused by a higher amount of non-adsorbed PCE for PCE with longer side chains. This relationship is most likely due to an increased shielding of the backbone charges by longer side chains, leading to less adsorption.

(2) The effect of PCE grafting density on plastic viscosity tends to be less significant, as only short side chains demonstrated a slight reduction in plastic viscosity as grafting density increased. This decrease correlates with the amount of non-adsorbed PCE.

However, for medium side chains, there is no significant difference in plastic viscosity as a function of grafting density, although a decrease in the amount of non-adsorbed PCE was detected. This shows, that the effect of the amount of non-adsorbed polymers may be superimposed by other effects, e.g. caused by the side chain length of the adsorbed polymers.

ACKNOWLEDGMENTS

The project is funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation), Project Number 387118319, within the priority program SPP 2005 OPUS FLUIDUM FUTURUM—Rheology of reactive, multiscale, multiphase construction materials. The authors gratefully acknowledge the funding by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation). The rheometer at Technische Universität Braunschweig is funded by the European funding for the regions in Lower Saxony (EFRE)/NBank within the project “Rheo Struc 3D Lab” (85023242).

In addition, the authors would like to extend special thanks to BASF for synthesising, characterising and providing the PCE polymers for this research. Thanks go to HeidelbergCement AG for supplying the cement. Finally, the authors would like to thank Rolf Epperlein and Dominik Bergmann for their valuable help during the experimental part of this paper.

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BIOGRAPHY

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Novel hybrid additive for low-carbon concrete

Gilberto Artioli, Anna Bravo, Alberto Brocchi, Fabio Castiglioni, Maria Chiara Dalconi, Mikaela Decio, Giorgio Ferrari, Marco Mazzetti, Davide Salvioni, Luca Torelli, Luca Valentini

Synopsis: Supplementary Cementitious Materials (SCMs) can be effective levers to reduce the environmental impact of concrete. One of the major limitations for high substitution of clinker by SCMs in Portland cement is the loss of strength of the resulting concrete, particularly at early age, compared with similar concrete made with equivalent dosage of pure clinker Portland cement. Furthermore, the possibility to use larger fractions of SCMs requires strongly alkaline activators which pose environmental and safety problems and are not compatible with commercial PCE superplasticizers.

A new hybrid additive was synthesized which works, at the same time, as seed for the clinker phase and as an activator for alkali-activated binders. The new product consists of an alkaline suspension of micro-sized particles containing nano-structured CSH seeds, amorphous portlandite and AFm phases embedded in a polymeric matrix. The structure and the mechanism of action of the new product on slag cements have been investigated by Environmental Scanning Electron Microscopy, X-ray Powder Diffraction, Thermal Analysis and Isothermal Calorimetry.

The new product is fully compatible with PCE superplasticizers and can be used to produce alkali-activated concretes characterized by low-carbon impact.

Keywords: alkali activated materials; blended cements; ground granulated blast furnace slag; nanocomposites; polycarboxylate superplasticizers; seed catalysis; supplementary cementitious materials.

INTRODUCTION

Every year, more than 10 billion cubic meters of concrete are used, which makes it the second-most consumed material on Earth. The reasons for this success lie in its versatility, resilience, ease of production, low cost and durability. Furthermore, its high thermal mass and low air infiltration help reducing the energy required to heat and cool buildings. Besides these advantages, the production of concrete poses alarming environmental concerns for the massive CO₂ emissions associated with its production, which are mainly ascribed to Portland cement, the key input contributing for about 6 to 8 per cent of annual global CO₂ emissions [1]. The substitution of clinker by Supplementary Cementitious Materials (SCMs) such as fly ash, Ground Granulated Blast-Furnace Slag (GGBFS), pozzolanas, limestone and calcined clays in Portland cement represents a powerful lever for lowering the clinker to cement ratio and to reduce the CO₂ emissions. In some cases, particularly with GGBFS, the substitution levels in Portland cements can be up to 80 per cent, as for example in cement CEM III/B according to European Norm EN 197-1, which contains from 66 to 80 per cent of GGBFS as clinker substitute [2].

One of the most important limitations to high substitution levels of clinker by SCMs in Portland cement is the loss of strength of the resulting concrete, particularly at early age, compared with similar concrete made with the same dosage of Portland cement. Indeed, SCMs react slower than clinker and develop C-S-H only at a later time through the reaction with portlandite originated from clinker hydration. For these reasons, the actual global average clinker-to-cement ratio of commercial cements remains stationary around 0.71, still far from the ambitious target of 0.60 that is necessary to reach by 2050 to comply with 2-degree Celsius (°C) Scenario 2DS [3].

Alternative cement binding materials have been developed to further mitigate the environmental impact of CO₂ emissions of the cement industry [4]. Among these, Alkali Activated Materials (AAMs) received much attention from both academy and industry as potential substitutes of Portland cement. They are produced by the reaction of an aluminosilicate (the precursor) with alkali hydroxide and/or silicate solution. Many SCMs, such as GGBFS, fly ash, metakaolin and calcined clays, can be used as precursors for AAMs. Besides the potential advantages of AAMs in terms of CO₂ and energy savings compared to Portland cement, concern exists from both environmental and safety points of view for the high dosage of the strong alkaline reagents necessary for the activation of AAMs. Furthermore, existing polycarboxylate ethers PCEs are ineffective as superplasticizers in AAMs systems, mainly for their chemical instability and poor solubility in the extremely high pH environment that characterizes such mixtures [5].

In this paper the characteristics of a Novel Hybrid Additive (NHA) for the early strength enhancement of blended cements is presented, working at the same time as alkali activator for SCMs and as seed catalyst for the clinker fraction.

RESEARCH SIGNIFICANCE

The achievement of the target clinker-to-cement ratio of 0.60 by 2050 requires intense research efforts not only for the development of new SCMs and fillers but also for the research of new additives capable of promoting and enhancing the strength development of blended cements and Alkali Activated Materials, without altering the other properties of fresh and hardened concrete. The novel hybrid additive NHA of the present work represents the first example of a new class of admixtures combining different mechanisms of action which could play an important role for the development of low-carbon concrete.

EXPERIMENTAL INVESTIGATION

The novel hybrid additive NHA was synthesized in the laboratory and fully characterized by several analytical techniques, including elemental analysis ICP-OES, X-Ray Powder Diffraction (XRPD), thermal analysis TGA/DTA, particle size laser granulometry, Environmental Scanning Electron Microscope analysis (ESEM), Energy Dispersive X-Ray analysis (EDX), Liquid Chromatography (LC), Size Exclusion Chromatography (SEC). The novel additive was evaluated in mortar tests using two different slag cements, CEM III/A and CEM III/B according to EN 197-1 norm and one sample of GGBFS. The compressive strength at different curing times and the retention of the workability were measured in comparison with a reference mortar without the NHA. Isothermal calorimetry tests were performed on cement pastes to evaluate the heat development in the first hours of hydration. To demonstrate the effectiveness of NHA for the production of AAMs, Self-Compacting Concrete (SCC) was produced with GGBFS as a binder and NHA as activator and the flow characteristics and compressive strength development were measured and its environmental impact was calculated by LCA methodology.

Materials

Novel Hybrid Additive (NHA) – NHA was produced in the laboratory by mixing ordinary Portland cement type CEM I 52.5R according to EN 197-1 norm with water in excess (water-to-cement ratio $w/c = 6.0$) in the presence of a PCE superplasticizer until the residual content of C_3S/C_2S was less than 5 per cent of the initial concentration, as measured by XRD diffraction. The PCE was a 45 per cent solution of sodium salt of a copolymer of methacrylic acid with methoxy-polyethyleneglycolmethacrylate with side chain length of 5000 Da and average weight molecular weight M_w of about 90000 Da, as measured by SEC. The dosage of the PCE was 19 per cent by weight of cement. The final pH was regulated at about $pH = 13$ with sodium carbonate. The final product was a light brown stable aqueous suspension with a total solids content around 25 per cent by weight. The composition of the CEM I 52.5R Portland cement used and the characteristics of NHA are reported in Table 1 and in Table 2, respectively.

Table 1– Phase composition and physical characteristics of cement CEMI 52.5R used for the synthesis of NHA

Phase	%
C_3S	67.4
C_2S	6.7
C_3A	10.8
C_4AF	2.5
CaO	0.4
Portlandite	1.3
Gypsum	3.7
Bassanite	2.4
Calcite	4.2
Dolomite	1.1

Physical characteristics	u.m.	Value
Mean particle size d_{10}	μm	1.513
Mean particle size d_{50}	μm	8.002
Mean particle size d_{90}	μm	21.180
Blaine	cm^2/g	4900
L.O.I.	%	< 5

Table 2– Physical and chemical characteristics of NHA

Parameter	Units	Value
Total solids	%	25.0
pH	pH units	13.1
Density	g/cm^3 (lb/in ³)	1.25 (0.045)
Average Number Particle Size (Dv_{50})	μm	9.8
Viscosity	mPa.s	500
$Ca(OH)_2$	%	2.0
$CaCO_3$	%	7.7
$Na_2O_{eq.}$	%	3.0
SO_3	%	0.6
Organics	%	2.0
C_3S/C_2S	%	0.9
Monosulphate Ms	%	0.5
Monocarbonate+Hemicarbonate Mc+Hc	%	0.3
Amorphous-unknown (including CSH)	%	8.0

Binders – Two different slag cements, one CEM III/A with 58 per cent slag and one CEM III/B with about 76 per cent slag in substitution of clinker, and one GGBFS sample were used to evaluate the performance of NHA. The phases' composition and the classification of the different cements according to EN 197-1 are reported in Table 3 and the composition of the amorphous GGBFS is shown in Table 4.

Table 3 – Classification of the blended cements used in the present work according to EN 197-1 and measured phases' composition.

Composition range according EN-197-1	CEM III/A	CEM III/B
Clinker (%)	35-64	20-34
Slag (%)	36-65	66-80
Gypsum (%)	0-5	0-5
Phase composition		
C ₃ S + C ₂ S	28.9	18.4
C ₃ A	1.9	1.1
C ₄ AF	4.3	2.8
Anhydrite	1.7	1.8
Gypsum	0.2	< DL
Calcite	3.8	< DL
Dolomite	1.2	< DL
Amorphous+Unknown	58	76

DL = Detection Limit

Table 4 – Composition and mean particle size of GGBFS

Oxides composition (%)	GGBFS
CaO	41.8
SiO ₂	38.6
Al ₂ O ₃	10.1
MgO	6.6
TiO ₂	0.6
Fe ₂ O ₃	0.5
K ₂ O	0.5
MnO	0.3
SrO	0.1
Na ₂ O	0.4
SO ₃	0.5
Mean particle size (µm)	17.67

Analytical investigation

The composition of the different cements and GGBFS were determined by XRD, ICP-OES and LC techniques according to standard methods.

The techniques which were applied to investigate the composition and the structure of NHA are described in more detail in this section.

X-ray Powder Diffraction XRPD – Samples of NHA were collected at different times of reaction, treated with ethyl alcohol in excess to quench the hydration reaction and filtered. After washing with ethyl alcohol, samples were dried at 50 °C and analyzed. XRPD measurements were performed using a Panalytical X'Pert Pro diffractometer in reflection geometry, equipped with a Co anode X-ray tube (40 kV, 40 mA), Bragg-Brentano-HD optical module and X'Celerator detector. Diffraction patterns were collected in the 5 ° - 85 ° 2θ range, with 0.017° 2θ virtual step size, counting an equivalent time of 100 s per step. Dried powders were back-loaded on sample holder with a diameter of 37 mm. A known amount of zincite (ZnO - Baker) was added to the sample in order to indirectly quantify the