

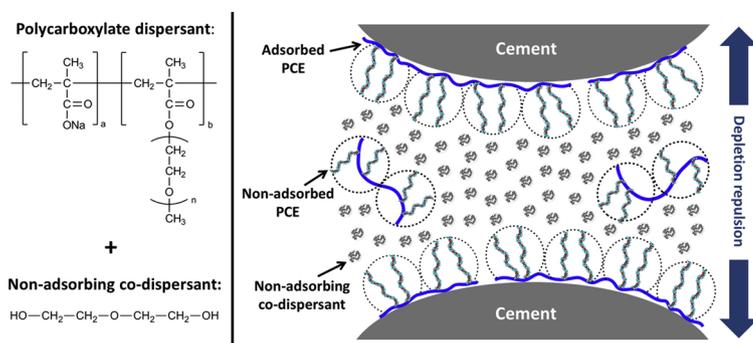
Non-adsorbing small molecules as auxiliary dispersants for polycarboxylate superplasticizers

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GRAPHICAL ABSTRACT



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ABSTRACT

The dispersing ability of polycarboxylate superplasticizers (PCEs) can be ascribed to the electrostatic and steric stabilization of cement suspensions. For this purpose, PCEs need to adsorb on the cement particle surface to become effective at all. In this study, it is demonstrated that at low water to cement ratios ≤ 0.30 , even non-ionic molecules like diethylene glycol or 2-methyl-2,4-pentanediol which do not adsorb on cement, but remain dissolved in the interstitial pore solution, can greatly enhance cement dispersion when combined with PCEs such as conventional methacrylate ester based comb co-polymers. Their effect as co-dispersant is particularly pronounced for PCEs possessing a low side chain density and long side chain length. Relative to the co-dispersants it was found that especially non-polar small molecules like neopentyl glycol greatly enhance the paste fluidity. These molecules significantly reduce the surface tension of the pore solution and thus increase the wettability of cement. Based on results from spread flow tests, adsorption measurements and pendant drop tensiometry it is concluded that in cementitious systems formulated at low w/c ratios, non-adsorbing molecules with a molecular weight of ≤ 1000 g/mol induce repulsive depletion forces which prevent cement particles from agglomeration. This way, such small molecules act as auxiliary or co-dispersant when combined with PCEs.

1. Introduction

Many chemical admixtures which are commonly applied in the construction industry achieve their properties via an adsorptive working

mechanism [1–3]. Typical examples are plasticizers and superplasticizers which are added to cement-based materials for dispersion of the solid particles. For this reason, all dispersing additives exhibit anionic groups (e.g. sulfonate, carboxylate, phosphonate or phosphate anchors) to

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facilitate the adsorption on positively charged surface sites through electrostatic attraction [4–7]. The adsorption is a multi-step process including diffusion, accumulation and reorganization of the polymer chains at the solid-liquid interface [8]. It is affected by the molecular properties and architecture of the polymer (e.g. anionic charge amount, chemical nature of anchor group, molecular weight, stereochemistry and conformation of the polymer, etc.), the ion concentration and pH value of the dispersing medium as well as the surface charge of the particles [9–12]. After the adsorption of the polymeric dispersants, attractive *van der Waals* forces are disrupted between the oppositely charged surfaces of the individual clinker and hydrate phases, thus leading to the disagglomeration of cement and to improved fluidity [13–15].

Polycarboxylate superplasticizers (PCEs) are among the most efficient cement dispersants. These comb-shaped (brush-like) polymers consist of a main chain holding anionic carboxylate groups and several linear side chains made up from polyethylene glycols or a mixture of polyethylene/polypropylene oxide units that are attached to the polymer backbone [16,17]. It is well established that the superior dispersing performance of PCEs originates from the electrostatic and steric stabilization of cement particles [4,18]. Due to adsorption of the PCEs, the cement particles become homogeneously negatively charged, thus provoking an electrostatic repulsion. Furthermore, the non-ionic side chains of the PCEs stretch out into the pore solution and create a steric barrier which prevents cement particles from reagglomeration [19]. Generally, the dispersing efficacy of PCEs correlates with the adsorbed amount of polymer, whereas the non-adsorbed portion present in the pore solution determines the time-dependent fluidity properties (“slump retention” behavior) [20–22]. Accordingly, PCEs which adsorb almost quantitatively on cement entail a rapid decrease of the initial flowability, since no free polymer is left for the dispersion of new hydrate phases. However, recent studies suggest that the portion of non-adsorbed PCE not only controls the slump loss behavior, but also can play an important role for the dispersion of concentrated cement suspensions [23]. This was first observed by *Sakai et al.*, who investigated the effect of methacrylic acid-co-polyethylene glycol methacrylate ester polymers (MPEG-PCEs) on the viscosity of belite-rich low heat Portland cement – silica fume blends at water to powder (w/p) ratios from 0.16 – 0.32. It was found that at low w/p ratios (i.e. 0.16), especially those PCEs were highly effective which only adsorbed in low quantities, while the major part remained in the pore solution. Consequently, in such case the high fluidity cannot be attributed only to the adsorbed amount, but originates more from the portion of non-adsorbed PCE. Further evidence for this effect was given by a follow-up study in which it was demonstrated that the apparent viscosity of cement pastes even decreased at PCE dosages above the saturated adsorption [24]. Moreover, recently *Sun et al.* demonstrated that besides non-adsorbed PCEs, also other components suspended in the pore solution like nano-sized ettringite and other fine matters < 200 nm can contribute to cement dispersion at low w/c ratios [25]. All these previous findings imply that non-adsorbing polymers and nano particles can be quite beneficial for the stabilization of highly particle loaded systems. This was further supported by additional studies showing that other non-ionic polymers such as polyethylene glycol (PEG) of low molecular weight [26,27], hydroxypropyl methyl cellulose [28] or the macromonomers used in the PCE synthesis [26] are capable of improving the dispersing efficacy of PCE superplasticizers. Conversely, polyethylene glycols with a high molecular weight ($M_n = 56,000\text{--}570,000$ g/mol) were found to increase the yield stress and viscosity of cement pastes when combined with a MPEG-type PCE, due to attractive depletion forces which considerably contribute to the flocculation of the particles [29].

Therefore, the question arises how non-ionic molecules with a molecular weight < 1000 g/mol behave and whether such small molecules can induce any dispersion. Thus, the aim of the present study was to investigate the effect of low molecular compounds, namely of glycol and diol derivatives, on the fluidity of cement pastes prepared at w/c ratios of 0.22 – 0.40, and to broaden the knowledge about the structure-performance relationship of non-adsorbing additives. Various small molecules

Table 1
Phase composition of the cement sample used in the study.

Phase	wt. %
C ₃ S	53.3
C ₂ S	25.7
C ₃ A _{cubic}	4.2
C ₃ A _{orthorhombic}	4.6
C ₄ AF	2.6
Free Lime (<i>Franke</i>)	0.1
Anhydrite	3.3
Hemihydrate*	0.7
Dihydrate*	0.1
Arcanite (K ₂ SO ₄)	0.5
Calcite	3.9
Quartz	1.0

* determined by thermogravimetry.

were combined with MPEG-PCEs possessing different anionic charge amounts and side chain lengths to identify those PCEs which benefit the most from such a co-dispersant. The effectiveness of the auxiliary dispersants was assessed via spread flow tests, and to elucidate their working mechanism adsorption measurements and pendant drop tensiometry were conducted. Generally, the main purpose of this study was to get a more profound understanding of the role of non-adsorbing molecules for the dispersion of concentrated cement suspensions.

2. Materials and methods

2.1. Cement

An ordinary Portland cement CEM I 52.5 N (Milke® classic from HeidelbergCement, Geseke plant, Germany) was used for the experiments. Its phase composition as quantified by X-ray diffraction (Bruker AXS D8 Advance, Karlsruhe, Germany) using *Rietveld* refinement is provided in Table 1. The amounts of hemihydrate (CaSO₄ · ½ H₂O) and gypsum (CaSO₄ · 2 H₂O) were determined by thermogravimetry (Netzsch STA 409 TG-MS, Selb, Germany) and the free lime was quantified according to the *Franke* method.

The average particle size (d_{50} value) of the cement was 13.45 μm (laser granulometry; CILAS 1064 instrument, Cilas, Marseille, France) and the density was 3.19 g/cm³ (helium pycnometry; Ultrapycometer 1000, Quantachrome Instruments, Boynton Beach, USA). For the specific surface area (*Blaine* fineness) a value of 3479 cm²/g was obtained. The particle size distribution of the cement is shown in Fig. 1.

2.2. Non-adsorbing additives

A broad range of glycol and diol derivatives was tested as non-adsorbing additives. These compounds were all designated as small molecules because of their low molecular weight between 100–150 g/mol.

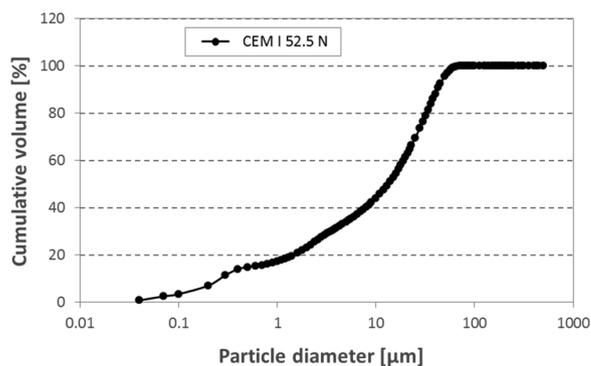
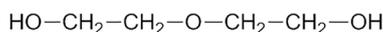
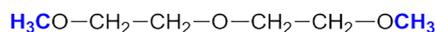


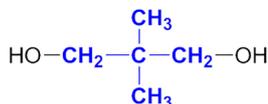
Fig. 1. Particle size distribution of the cement sample.



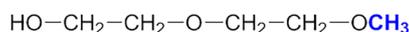
diethylene glycol (DEG)



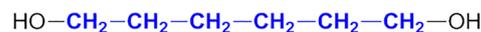
diethylene glycol dimethyl ether (DEGDME)



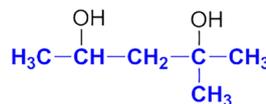
neopentyl glycol (NPG)



diethylene glycol monomethyl ether (DEGMME)



1,6-hexanediol (HD)



2-methyl-2,4-pentanediol (MPD)

Fig. 2. Chemical structures of the non-adsorbing small molecules tested in the study.

An overview of their chemical structures is presented in Fig. 2. From there it can be seen that the non-ionic co-dispersants comprise quite different amounts of non-polar and hydrophobic groups (shown in bold and blue color).

The non-ionic molecules diethylene glycol (DEG; purity $\geq 99\%$), diethylene glycol monomethyl ether (DEGMME; $\geq 99\%$) and diethylene glycol dimethyl ether (DEGDME; $\geq 99\%$) were provided by Clariant (Burgkirchen, Germany). 1,6-Hexanediol (HD; $\geq 97\%$) and neopentyl glycol (NPG; $\geq 98\%$) were purchased from Merck (Darmstadt, Germany), while 2-methyl-2,4-pentanediol (MPD; $\geq 98\%$) was obtained from Alfa Aesar (Karlsruhe, Germany). These molecules were used to investigate the structure-performance relationship of the non-ionic co-dispersants. In addition, polyethylene glycols with molar masses of 300 (PEG 300; $\geq 99\%$), 1000 (PEG 1000; $\geq 99\%$) and 3000 g/mol (PEG 3000; $\geq 99\%$) were tested to determine the impact of the molecular weight, respectively chain length on the spread flow enhancing capability. The non-ionic character of the co-dispersants was verified by charge titration (see chapter 2.3.2.) in synthetic cement pore solution (SCPS), hence no adsorption through electrostatic attraction was possible. Also note that the non-adsorbing additives do not provoke any fluidity when individually admixed into the cement paste.

2.3. MPEG-type PCE superplasticizers

2.3.1. Synthesis

The dispersing performance of the non-ionic additives was investigated in the presence of seven structurally different MPEG-PCEs. The polymers were synthesized via aqueous free radical copolymerization involving methacrylic acid ($> 99\%$; Sigma-Aldrich, Steinheim, Germany) and ω -methoxy polyethylene glycol methacrylates ($> 98\%$; Clariant, Burgkirchen, Germany) at varying molar ratios and side chain lengths of the macromonomer. Sodium persulfate ($\geq 99\%$; Merck) was used as initiator and 3-mercaptopropionic acid ($\geq 99\%$; Sigma-Aldrich) as chain transfer agent. A detailed description of the synthesis can be found in [16]. In contrast, PCE sample 7PC6 was obtained by grafting a methoxy-terminated polyethylene glycol (Polyglykol M350; $\geq 99\%$; Clariant) onto a polymethacrylic acid backbone with $M_n = 4700$ g/mol at 180°C under reduced pressure (~ 0.03 mbar) [30]. All synthesized PCEs were designated as xPCy, with x being the number of ethylene oxide (EO) units in the polyethylene glycol side chain ($n_{\text{EO}} = 7, 25, 45$ and 114) and y being the molar ratio of methacrylic acid to ω -methoxy polyethylene glycol

methacrylate (2–8 : 1). The synthesized polymer solutions exhibited a pH of ~ 2 –3 and were neutralized to pH = 7 with 30 wt.% NaOH to yield aqueous solutions with a solid content of ~ 30 wt.%. The chemical structure of the synthesized MPEG-PCEs is illustrated in Fig. 3.

2.3.2. Polymer characterization

Size exclusion chromatography (SEC) was performed to determine the molar masses and polydispersity (PDI) of the synthesized polymers. A Waters Alliance 2695 separation module coupled with a refractive index detector (2414 module from Waters, Eschborn, Germany) and a Dawn EOS 3 angle static light scattering detector (Wyatt Technology, Santa Barbara, CA) were used for the measurements. Solutions of the PCEs with a concentration of 10 g/L were prepared, filtered through a $0.2 \mu\text{m}$ syringe filter and injected on a precolumn and three Ultrahydrogel columns (150, 250, 500) for separation. The mobile phase was an aqueous 0.1 M NaNO_3 solution (adjusted with NaOH to a pH = 12) which was pumped at a flow rate of 1.0 mL/min. The molar masses were calculated based on the dn/dc value of polyethylene glycol (0.135 mL/g) [31].

The anionic charge of the MPEG-PCEs and the non-adsorbing molecules was quantified by polyelectrolyte titration employing a particle charge detector (PCD 03 pH; BTG Instruments, Weßling, Germany). Here, 10 mL of a 0.1 g/L solution of the analyte in synthetic cement

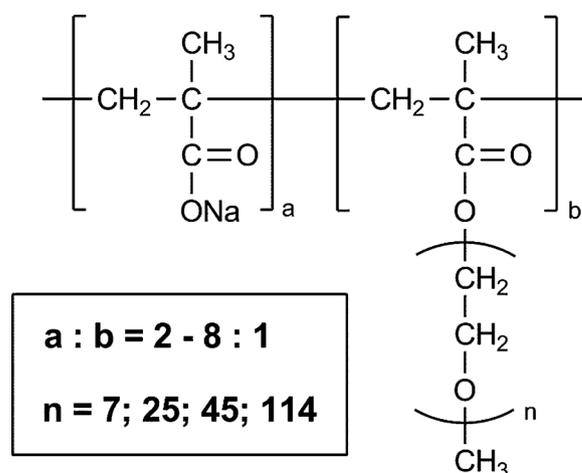


Fig. 3. Chemical composition of the MPEG-based superplasticizers.

pore solution (SCPS) were used and titrated against a cationic 0.001 M poly dimethyl ammonium chloride solution (polyDADMAC) until charge neutralization was achieved (isoelectric point). By means of the volume of consumed polyDADMAC solution, the anionic charge per gram of polymer was calculated. More information about the method and a detailed instruction of the experimental procedure are provided in [32]. The SCPS exhibited a pH of 12.8 and was composed of 1.720 g $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$, 6.959 g Na_2SO_4 , 4.757 g K_2SO_4 and 7.120 g KOH dissolved in 1 L of de-ionized (DI) water.

Dynamic light scattering measurements were carried out to ascertain the hydrodynamic radii (R_h) of the polymers. For this purpose, solutions of the PCE samples with a concentration of 10 g/L were prepared using SCPS as solvent, filtered through a 0.2 μm syringe filter into a cuvette and then analyzed with a Zetasizer Nano instrument (Malvern Instruments, Worcestershire, United Kingdom). After an equilibration time of 120 s at 25 °C, five independent measurement runs were performed. The hydrodynamic radii were reported as average values, with a standard deviation of ± 0.1 nm.

To understand the structural properties of the PCEs better, also the main and side chain lengths of the polymers were calculated. The length of one EO unit in the polyethylene glycol side chain was assumed to be 0.278 nm, while a value of 0.251 nm was adopted for the C–C–C bond in the polymer backbone [33]. Moreover, the solution conformations of the PCEs were established according to the model proposed by Gay and Raphaël [34]. Hence, the tested polymers are assigned to the stretched backbone worm (SBW), flexible backbone worm (FBW) and flexible backbone star (FBS) domain, respectively. An overview of the molecular properties of all synthesized MPEG-PCEs is given in Table 2.

2.4. Research methods

2.4.1. Cement dispersion

The effect of the non-adsorbing additives on the rheological properties of cement pastes was investigated by mini slump tests, following the specifications outlined in DIN EN 1015. The experiments were conducted at different w/c ratios ranging from 0.22 – 0.40. At first, the dosage of the PCE was determined to obtain a spread flow of 18 ± 0.5 cm at a given w/c ratio. This dosage was applied for the ensuing experiments, where the dispersing capability of the non-ionic additives was evaluated in the presence of different MPEG-PCEs. The co-dispersants were dissolved in the mixing water at dosages of 0.1 – 0.9 % by weight of cement (bwoc) together with the respective amount of the PCE superplasticizer (dosage of the PCE correlates to a spread flow of 18 cm). The amount of water introduced by the PCE solution was subtracted from the total volume of the mixing water to maintain a constant w/c ratio. The spread flow tests were conducted as follows: within 5 s 400 g cement were added to the mixing water containing the pre-dissolved PCE and non-ionic co-dispersant. The mixture was vigorously stirred for 4 min with a spoon and finally poured into a Vicat cone (height 40 mm, top diameter 70 mm, bottom diameter 80 mm) placed on a glass plate. After complete filling, the Vicat cone was immediately lifted upwards and retained for 5 s over the spreading cement

Table 2

Molecular properties of the synthesized PCE superplasticizers.

	45PC2	45PC4	45PC6	45PC8	7PC6	25PC6	114PC6
M_w (g/mol)	39,500	23,700	22,200	19,500	13,400	17,100	82,000
M_n (g/mol)	15,900	12,800	11,200	10,500	6,300	8,800	27,000
PDI (M_w/M_n)	2.5	1.9	2.0	1.9	2.1	1.9	3.0
Conversion of macromonomer (%)	93	94	96	93	93	90	98
Anionic charge in SCPS ($\mu\text{eq/g}$)	720	1610	2450	2850	4300	1820	1500
R_h (nm)	6.5	5.4	4.5	4.3	3.1	3.5	8.3
Main chain length (nm)	5.3	6.6	7.6	8.6	12.1	9.0	8.4
Side chain length (nm)	12.5	12.5	12.5	12.5	1.9	7.0	31.7
Solution conformation acc. to Gay	SBW	FBW	FBW	FBW	FBW	FBW	FBS

slurry. The diameter of the cement paste was measured twice with a caliper, the second measurement being in a 90° angle to the first one and averaged to give the spread flow value. All experiments were performed at a temperature of 20 ± 1 °C.

2.4.2. Kinematic and dynamic viscosity

The kinematic and dynamic viscosity of aqueous solutions of PCE sample 45PC6 and of different non-ionic polyethylene glycols in SCPS was measured with an Ubbelohde viscometer. The aim of these experiments was to investigate the impact of the non-ionic co-dispersants on the viscosity of the pore solution. To carry out these experiments under similar concentration conditions as prevailing in the cement paste, first the water loss caused by initial wetting and cement hydration was quantified. For this reason, a cement paste which was fluidized with 0.208 % bwoc of 45PC6 (dosage corresponds to a spread flow of 18 cm at w/c = 0.22) was filtrated using a hydraulic press [35] to determine the water volume that is not consumed in the initial cement hydration. This amount of water was considered in the preparation of the samples which were composed of 0.208 % bwoc of 45PC6 and varying dosages of different polyethylene glycols (i.e. 0.1 – 0.9 % bwoc) in SCPS. The polymer solution was filled into the reservoir of a glass capillary (type: 501 10/1 from Schott Instruments, Mainz, Germany), equilibrated to 25 °C in a water bath and then the flow time was measured which represents the time the liquid takes to pass a specific distance between two calibration marks. From the viscometer constant K, the flow time t and the flow time dependent Hagenbach-Couette correction term ζ , the kinematic viscosity ν was calculated:

$$\nu = K \cdot (t - \zeta) \quad (1)$$

Subsequently, the dynamic viscosity η_{dyn} can be obtained by multiplying the kinematic viscosity with the specific density ρ of the solution:

$$\eta_{\text{dyn}} = \nu \cdot \rho \quad (2)$$

2.4.3. Adsorption measurements

To gain a better understanding of the role of the non-ionic additives in cement dispersion, adsorption measurements were performed using the depletion method. Adsorption isotherms were developed for the individual PCEs, and also the effect of the co-dispersants on the adsorbed amounts of the PCEs was studied. In a typical experiment, 50 g cement, 13 mL DI water (w/c = 0.26) and the respective amount of the dispersants to be tested were added into a 50 mL centrifuge tube, homogenized for 4 min with a vortex mixer and centrifuged for 15 min at 8500 rpm. The supernatant that contains the non-adsorbed compounds was removed, filtered through a 0.2 μm syringe filter and diluted with a 0.1 M HCl to prevent carbonation. Thereafter, the total organic carbon (TOC) content of the solutions was quantified with a LiquiTOC-II instrument (Elementar Analysensysteme; Hanau, Germany). Every sample was measured twice and the received values were reduced by the organic carbon content of a blank cement paste to account for the presence of other organic components such as grinding aids. Finally, the adsorbed amount of the polymer was deduced from

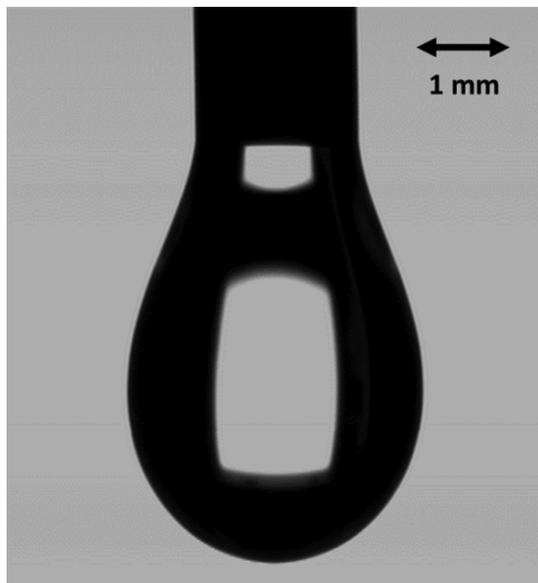


Fig. 4. Surface tension measurement using the pendent drop method.

$$Bo = \frac{\Delta\rho g R^2}{\sigma}$$

Bo = Bond number

$\Delta\rho$ = Density difference

g = Gravitational acceleration

R = Drop radius at the apex

σ = Surface tension

the difference of the TOC content of the initial polymer solution (= reference) and the supernatant extracted from the cement paste (= residual concentration of the polymers at equilibrium condition).

2.4.4. Pendant drop tensiometry

A drop shape analyzer (DSA100 from Krüss; Hamburg, Germany) was used to assess the impact of the non-ionic additives on the surface tension. In this method, a small droplet of a polymer solution is suspended from a steel needle (capillary tube) and a video image of the pendant drop is recorded with a camera (see Fig. 4). The surface tension can be derived from the fitted contour of the droplet by means of the Bond number Bo that presents the ratio of gravity forces to the surface tension forces which determines the drop shape [36,37].

Mixtures of the PCE polymer 45PC6 and the non-ionic small molecules were prepared in SCPS and filtered through a 0.2 μm syringe filter to remove dust particles. The concentration of the PCE was kept constant at 0.208 % bwoc, while for the co-dispersants different dosages were tested (0.1 – 0.9 % bwoc). Here again, the water consumption owed to the initial cement hydration was taken into account to achieve comparable concentrations of the additives like in the pore solution of the cement paste. For each sample, the surface tension was measured five times at 20 °C and reported as average.

3. Results and discussion

3.1. Relationship between molecular size and effectiveness of non-ionic additives

It has been reported previously that polyethylene glycols with a molecular weight of 2000 g/mol enhance the cement paste fluidity when combined with a MPEG-type PCE [26]. However, no information was provided about the dependence of the dispersing effectiveness from the molecular weight of the co-dispersants. Therefore, spread flow tests were conducted using various polyethylene glycols (PEGs) with molar masses in the range of 300 – 3000 g/mol. As those non-ionic additives do not produce any fluidity when admixed to cement, they always require a PCE superplasticizer to become effective. For this reason, combinations of 0.208 % of PCE sample 45PC6 and varying amounts of the polyethylene glycols were applied in the spread flow tests which were performed at a w/c ratio of 0.22. 45PC6 was used for these investigations as representative superplasticizer due to its median side chain density and side chain length of all synthesized polymers.

Throughout the study, the PCE was always dosed in such amounts to obtain a spread flow of 18 cm at a given w/c ratio when no co-dispersant was present. Fig. 5 illustrates the spread flow enhancing effect of the different PEGs as a function of their dosage.

From there it can be seen that the performance of PEG greatly depends on the molecular size. To be more specific, the highest paste fluidities were observed for PEG 300 which exhibits the lowest molecular weight and shortest chain length ($n_{EO} = 7$). For instance, PEG 300 enhanced the spread flow from 18 to 24 cm at a dosage of 0.5 %, while a smaller increase was attained by PEG 1000 ($n_{EO} = 23$). In contrast, PEG 3000 ($n_{EO} = 68$) only slightly improved the spread flow at dosages ≤ 0.5 % bwoc, and higher additions even decreased the fluidity. These results suggest that especially small molecules with a low molecular weight seem to be very powerful co-dispersants which are more suitable to augment the dispersing capability of PCE superplasticizers.

3.2. Effect of non-ionic additives on dynamic viscosity

To elucidate the reasons for the different behavior of the PEG samples in the spread flow tests, viscosity measurements were performed next. Here, the dynamic viscosity of solutions of 45PC6 combined with PEG samples in SCPS were ascertained with an *Ubbelohde* viscometer. To conduct these experiments at similar concentrations such as existing in the cement paste, the amount of water which is consumed by the cement within the first minutes of hydration was

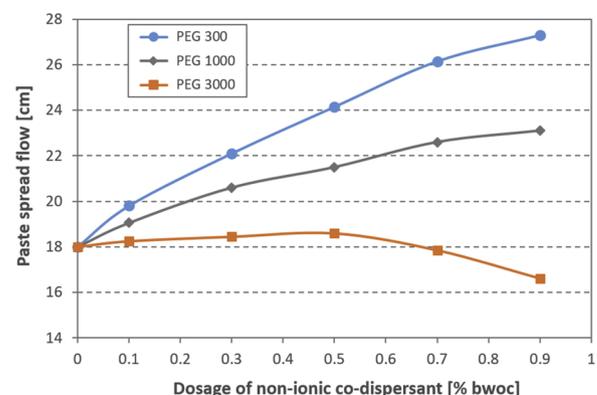


Fig. 5. Effect of the molecular weight of different polyethylene glycols on the dispersing efficacy of PCE 45PC6 in cement (w/c = 0.22).

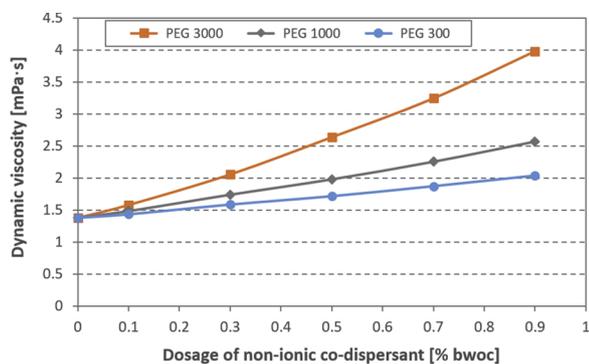


Fig. 6. Dynamic viscosity of synthetic cement pore solutions holding 0.208 % bwoc of PCE 45PC6 and different amounts of PEG samples.

considered in the sample preparation. It was found that at a w/c ratio of 0.22, most of the mixing water was already soaked up by the cement after 4 min and only 30 % could be regained by filtration. This already demonstrates that at such low w/c ratios the volume of the interstitial pore solution becomes very small. Fig. 6 shows the dynamic viscosities of the samples for ascending dosages of the non-ionic PEG samples.

As is obvious from the figure, much higher dynamic viscosities were recorded for PEG 3000 compared to the low molecular PEG species. A considerable increase of the dynamic viscosity was observed for PEG 3000 at dosages ≥ 0.5 % (e.g. an increase from 1.4 to 3.2 mPa·s at 0.7 %). Transferring these results to the cement paste it can be inferred that PEG 3000 exerts a thickening effect on the interstitial pore solution and hence increases cement paste viscosity. Since the volume of the interstitial pore solution is quite small at $w/c = 0.22$, chain entanglements between such long-chain PEG molecules might occur that could induce friction and thus impair fluidity. Such negative interaction would be less possible for PEGs of low molecular weight and with short chain length. Therefore, the highest spread flow values were obtained for PEG 300 which only slightly increased the pore solution viscosity due to its low molecular size.

3.3. Impact of w/c ratio on dispersing effectiveness of co-dispersants

Further mini slump tests were conducted to establish those w/c ratios at which the co-dispersants are most effective. Since the previous investigations have revealed that low molecular compounds are particularly beneficial, diethylene glycol (DEG; $M_n = 106$ g/mol) was applied as non-ionic additive. In the experiments, PCE sample 45PC6 was combined with different dosages of DEG at w/c ratios from 0.22 – 0.40. At first, the dosages of the PCE superplasticizer were ascertained to achieve a spread flow of 18 cm. This was attained by 0.041 % ($w/c = 0.40$), 0.11 % ($w/c = 0.30$), 0.18 % ($w/c = 0.26$) and 0.208 % ($w/c = 0.22$), respectively of this PCE. When lowering the w/c ratio, it was noticed that the cement pastes exhibited an increased “sticky” behavior, characterized by a low speed of flow. This was reported before in other studies and ascribed to a high plastic viscosity which originates from the low amount of water and the high solids content of the cement paste [30,38–40]. The above dosages of 45PC6 were then applied in the ensuing mini slump tests in which the spread flow enhancing effect of DEG was studied at different w/c ratios (see Fig. 7).

It can be seen that the dispersing performance of DEG was quite low at w/c ratios from 0.30 – 0.40. High dosages were required to achieve at least a minor increase of the paste fluidity from DEG addition. However, at low w/c ratios (0.22 – 0.26) much higher spread flow values were obtained. Furthermore, it was observed that in the presence of DEG the stickiness of the cement paste was reduced and a “softer” consistency (i.e. a less viscous cement paste) was achieved. Interestingly, at a w/c ratio of 0.22 DEG entailed a similar paste fluidity like PEG 300, thus indicating that a molecular weight between 100–300

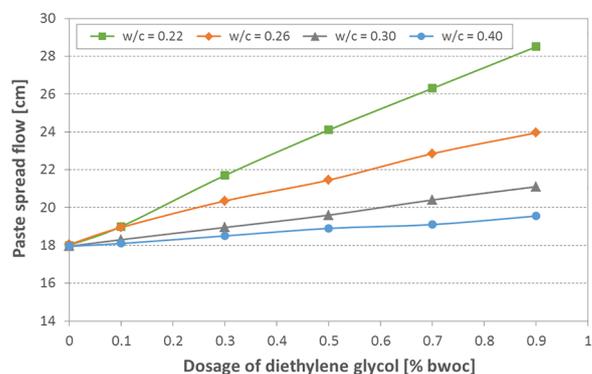


Fig. 7. Impact of the w/c ratio on the spread flow enhancing effect of diethylene glycol in combination with PCE 45PC6; results from cement paste.

g/mol appears to present an optimum for the auxiliary dispersant. These findings signify that the non-ionic co-dispersants become highly effective at low w/c ratios only, where the cement particles are more densely packed and the distance between the binder particles becomes relatively narrow.

3.4. Relationship between PCE molecular structure and spread flow improving effect of DEG

It is well known that the dispersing properties of PCEs are defined by the molecular architecture of the polymers. Depending on the side chain density or the length of the polyethylene glycol pendants, rather different behavior in application is observed [10,41]. Therefore, the question arises whether specific PCE structures can benefit more from the addition of non-ionic co-dispersants. For this purpose, a series of structurally different MPEG-PCEs was synthesized and tested in combination with DEG at $w/c = 0.22$. First, the spread flow enhancing effect of DEG was probed for PCEs possessing the same side chain length ($n_{EO} = 45$) but different side chain densities (45PCy polymers) (see Fig. 8). The dosages required from each PCE for a spread flow of 18 cm were found to be 0.49 % (45PC2), 0.193 % (45PC4), 0.208 % (45PC6) and 0.211 % (45PC8), respectively. As is obvious from the figure, not much difference was observed between the PCE samples at dosages ≤ 0.3 %. However, at higher dosages the dispersing efficacy was particularly improved for those PCEs which exhibit a low side chain density and a high anionicity.

Thereafter, spread flow tests were conducted using PCEs of different side chain lengths, but synthesized with the same molar ratio of methacrylic acid to the MPEG macromonomer (xPC6 series). The dosages applied of those PCEs were 0.46 % (7PC6), 0.211 % (25PC6) and 0.223 % (114PC6), respectively. According to Fig. 9, 114PC6 which holds the longest side chain profited most from the addition of DEG, followed by

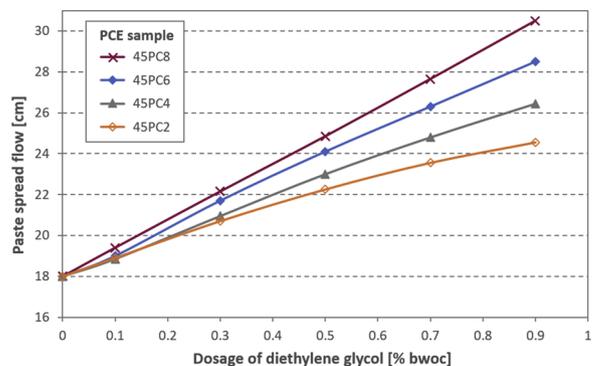


Fig. 8. Impact of side chain density of MPEG-PCE samples possessing the same side chain length ($n_{EO} = 45$), but different anionicity on the co-dispersing effect of DEG; results from cement paste ($w/c = 0.22$).

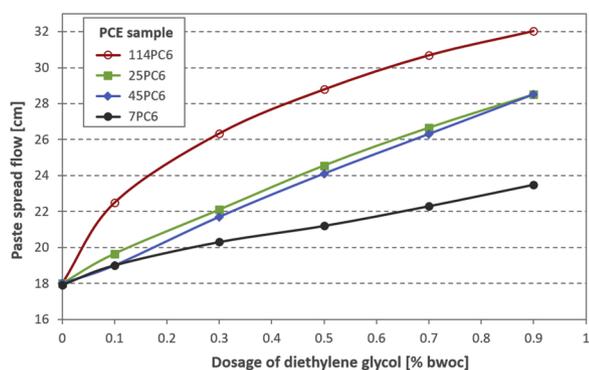


Fig. 9. Impact of the side chain length of different MPEG-PCE samples synthesized with the same molar ratio, on the spread flow enhancing effect of DEG; results from cement paste ($w/c = 0.22$).

45PC6 and 25PC6 with medium and short length side chains. The least increase in fluidity was recorded for the PCE exhibiting the shortest side chain (7PC6). It is remarkable that the performance of DEG was particularly weak in the presence of PCEs which required relatively high dosages to achieve the initial spread flow value (i.e. 45PC2 and 7PC6). Based on these findings it can be inferred that DEG is a very powerful co-dispersant for PCEs with a low side chain density and long side chains.

3.5. Adsorption measurements

To get more insight into the working mechanism of the non-ionic co-dispersants, adsorption measurements were performed. At first, adsorption isotherms for the individual MPEG-PCEs were developed. This was conducted at a slightly higher w/c ratio of 0.26, because at $w/c = 0.22$ no sufficient volume of pore solution could be extracted by centrifugation. Fig. 10 displays the Langmuir-type adsorption isotherms for all MPEG-PCEs tested. With rising dosages the adsorbed amounts increase up to a plateau value which represents the point of saturated adsorption where the surface sites are completely covered by the polymers.

As expected, the saturated adsorbed amounts increased with higher anionicity (= decreasing side chain density) of the 45PCy polymers (Fig. 10a). This is in agreement with the findings from previous studies [10,11]. For the xPC6 polymers, slightly higher plateau values were found for the PCEs exhibiting shorter side chains (Fig. 10b). Additionally, it was confirmed that diethylene glycol does not show any adsorption when individually admixed to the cement (Fig. 10a). Even negative adsorption values were observed for DEG which originate from the water loss through the cement hydration.

In the following, it was investigated whether DEG exerts any influence on the adsorption of the PCEs. For this purpose, the adsorbed amounts were measured for combinations of different PCEs at increasing dosages of DEG. The adsorption values of the individual PCEs at the dosages for a spread flow of 18 cm were used as reference (i.e. 0.215 % (45PC2); 0.18 % (45PC6); 0.316 % (7PC6); 0.166 % (114PC6)). As is evident from Fig. 11, DEG did not affect the adsorbed amounts of any PCE, regardless of the DEG dosage applied or the specific molecular structure of the PCE. This clearly suggests that DEG remains freely dissolved in the interstitial pore solution, where it contributes to the dispersion of the particles.

Still, the question remained why certain molecular structures of the PCE benefit more from the addition of DEG. This aspect was investigated by plotting the portion of non-adsorbed PCE as a function of the polymer dosage (see Fig. 12).

It can be seen that a much higher fraction remained non-adsorbed for those PCEs which exhibited a high side chain density (e.g. 74 % (45PC2) vs. 24 % (45PC8) at 0.2 %). This can be attributed to their low anionic character which provokes a low adsorption affinity (e.g. anionic charge amounts 720 $\mu\text{eq/g}$ (45PC2) vs. 2850 $\mu\text{eq/g}$ (45PC8)). Conversely, no big difference was found for the PCEs that were

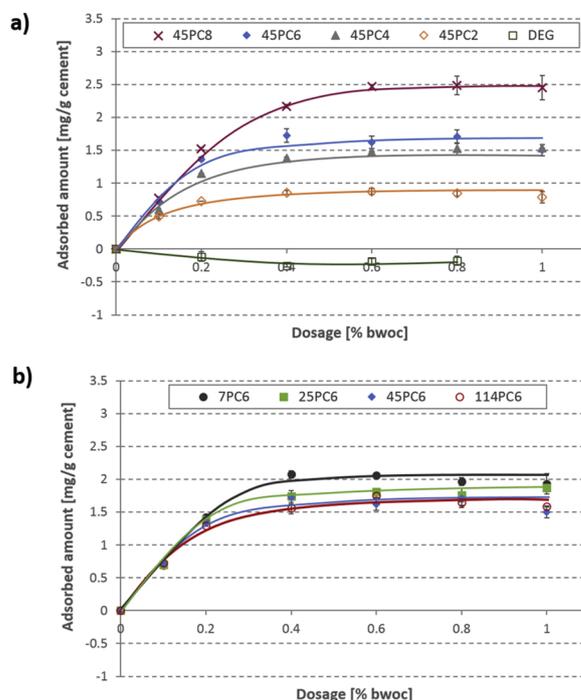


Fig. 10. Adsorption isotherms developed in cement paste at $w/c = 0.26$ for MPEG-PCEs possessing a) different side chain densities; b) varied side chain lengths.

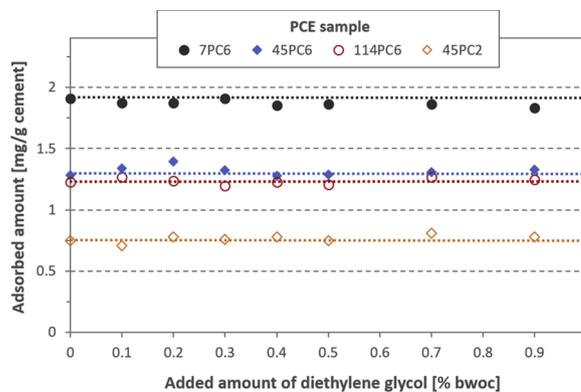


Fig. 11. Effect of different dosages of DEG on the adsorbed amounts of various PCE samples in cement paste ($w/c = 0.26$).

synthesized at the same molar ratio. Interconnecting these findings with the results from the spread flow tests (Figs. 8 and 9) it can be concluded that DEG especially enhances the fluidity of those PCEs which adsorb almost quantitatively and where only a small portion remains in the pore solution. In contrast, the effect of DEG is rather limited on PCEs which only adsorb in low amounts and thus entail a high residual concentration of non-adsorbed polymer. However, this is not the case for PCEs with varied side chain lengths (xPC6 series). All these PCEs show similar portions of non-adsorbed polymer. This suggests that DEG performs differently with PCEs exhibiting a different side chain length, with longer side chains providing a stronger effect than short ones.

3.6. Co-dispersing performance of structurally different non-ionic co-dispersants

In the next section, several glycol (DEGMME, DEGDME) and diol (HD, NPG, MPD) derivatives were tested as non-ionic co-dispersants (see Fig. 2) to probe whether the chemical composition also influences the effectiveness of such auxiliary dispersants. Here, 45PC6 was utilized as

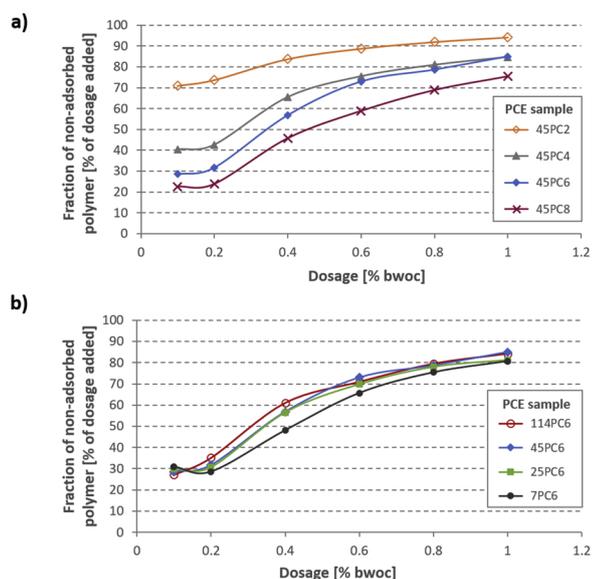


Fig. 12. Fraction of non-adsorbed PCE polymer as a function of the dosage for PCEs exhibiting a) different side chain densities or b) varied side chain lengths; results from cement paste ($w/c = 0.26$).

superplasticizer and combined with the non-adsorbing molecules at $w/c = 0.22$.

As evident from Fig. 13, different spread flow values were obtained, depending on the chemical structure of the small molecules. For instance, at a dosage of 0.1 %, MPD increased the spread flow from 18 to 23 cm, while DEGMME only provoked a slight increase to 19 cm. However, all co-dispersants tested produced higher paste fluidities compared to DEG. Most interestingly, the best performance was noticed for the diols MPD, NPG and HD which are commonly applied as shrinkage reducing agents. When taking a closer look at the chemical composition of the co-dispersants, it becomes apparent that especially those compounds with a higher amount of hydrophobic groups were more effective.

3.7. Effect of co-dispersants on surface tension of SCPS

To explain the different performance of the small molecules in the spread flow tests, surface tension measurements were performed using a drop shape analyzer. The aim of these experiments was to study the effect of the co-dispersants on the surface tension of aqueous solutions of superplasticizer 45PC6 in SCPS. Here again, the water loss through the initial cement hydration was taken into account.

At first, the surface tension of the pure SCPS was measured. A value

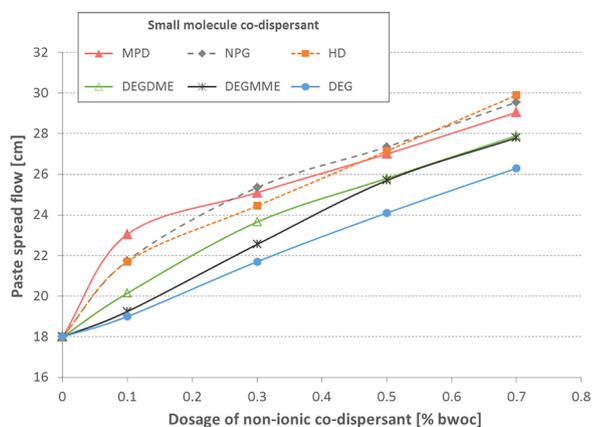


Fig. 13. Spread flow for structurally different co-dispersants, combined with PCE 45PC6; results from cement paste ($w/c = 0.22$).

of 71.1 mN/m was recorded which corresponds to the data in the literature [42]. Additionally, the surface tension of SCPS holding 0.208 % of 45PC6 was captured. The PCE decreased the surface tension from 71.1 to 52.4 mN/m. This can be attributed to the surfactancy of the PCE which comprises hydrophilic (e.g. carboxylates, PEG side chains) as well as hydrophobic groups (e.g. methylene bridge, methyl groups). Thereafter, the surface tension was determined for combinations of 45PC6 at different additions of the non-ionic co-dispersants.

From Fig. 14 it can be seen that DEG only caused a minor reduction of the surface tension. However, small molecules with more hydrophobic groups (e.g. methyl, alkyl substituents) than DEG induced a much higher decrease of the surface tension. For example, DEGDME which incorporates two additional methyl groups reduced the surface tension from 52.4 mN/m to 48.8 mN/m at 0.5 %, whereas for HD which possesses a hexyl chain even a lower value (46.3 mN/m) was ascertained. For MPD which represents the most effective co-dispersant, the strongest decline in the surface tension to 41.1 mN/m was observed.

Based on these results it can be concluded that less polar molecules with a higher proportion of hydrophobic groups reduce the surface tension of the pore solution more than molecules which mainly comprise hydrophilic moieties (e.g. hydroxyl, ether, oxyethylene groups). It is known from literature that by lowering the surface tension, the accessibility of water to the cement surface is enhanced which results in a higher fluidity [43–45]. This is in agreement with the observations from the spread flow tests where it was noticed that in systems which contained a less polar co-dispersant the cement paste became much faster fluid during the mixing. Due to the decreased surface tension of the pore solution, the solid-liquid interface energy is reduced which consequently improves the wetting behavior of the particles. It might be argued that the higher spread flow values may possibly originate from air bubbles which are introduced into the cement paste, as it is well known from surfactants that air bubbles induce a ball-bearing effect and hence improve the fluidity [46]. However, when mixing the cement paste no air-entrainment was observed at the dosages tested. Additionally, the same paste fluidities were obtained when a non-ionic, polyether siloxane based defoamer was applied to the cement paste. This suggests that the higher fluidity for the less polar co-dispersants mainly originates from an improved wettability.

3.8. Mechanistic model

Based on the findings achieved so far, a mechanistic model was developed to explain the underlying working mechanism of the co-dispersants (see Fig. 15).

Adsorption measurements have shown that the non-ionic additives do not adsorb on cement nor modify the adsorbed amounts of the PCEs. This indicates that they remain in the interstitial pore solution, where they can implement a spacer effect between the cement particles.

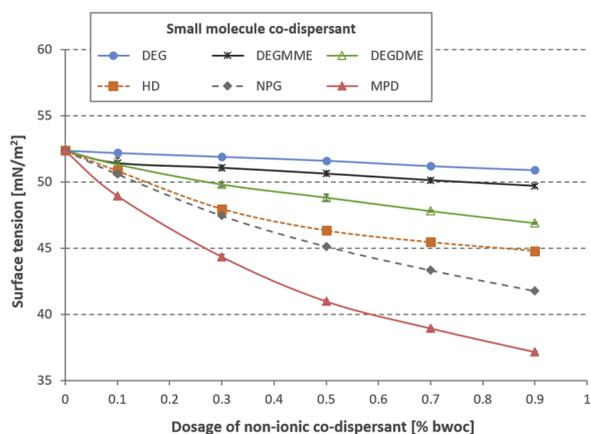


Fig. 14. Surface tension of solutions holding 0.208 % of PCE 45PC6 and different dosages of non-ionic co-dispersants, measured in SCPS.

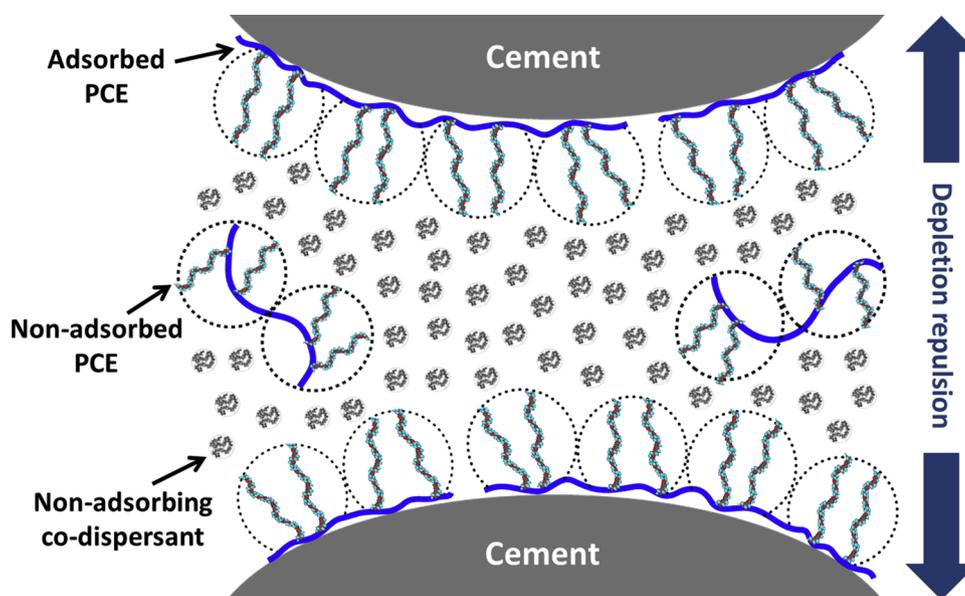


Fig. 15. Conceptual sketch illustrating the working mechanism of the non-adsorbing co-dispersants in cement at low w/c ratios.

According to the model on the solution conformation of comb copolymers from *Gay* and *Raphaël*, it is established that the side chains of PCEs align in form of blobs along the main polymer chain [34,47]. Therefore, we suppose that the co-dispersants exist between those blobs and hinder in this way the cement particles from approaching too close, as otherwise a local depletion of the small molecules would occur. Such condition is entropically unfavorable and therefore avoided through the formation of repulsive depletion forces [48–51]. These repulsive interactions contribute – in addition to the electrosteric stabilization provided by the adsorbed PCEs – also to cement dispersion and thus improve fluidity. However, this is only the case at low w/c ratios, where the cement particles are densely packed and the pore space becomes quite narrow. It was reported in previous studies that depletion repulsion is especially favored at high concentrations of the non-adsorbing polymers [27,52,53]. When we calculate the concentrations of the small molecules in the pore solution considering the water loss through the initial cement hydration at $w/c = 0.22$, we obtain concentrations in the range of 15–136 g/L for dosages from 0.1 – 0.9 %. This clearly demonstrates that the pore solution is very crowded at such low w/c values with the co-dispersants. Owing to those high concentrations, the small molecules cannot be pushed out very easily from the gap between approaching cement particles, thus creating depletion stabilization.

However, at high w/c ratios the spacer molecules are less or not at all effective due to the larger distance between the particles. Moreover, the spacer effect is less pronounced for PCEs which adsorb less and leave a significant residual concentration non-adsorbed in the pore solution. This implies that repulsive depletion forces also can be induced by non-adsorbed PCEs and explains why polymers that adsorb almost quantitatively benefit more from the addition of the co-dispersants. Furthermore, the depletion effect is particularly strong for PCEs with long side chains signifying that the range and magnitude of the repulsive depletion forces depend on the fraction of non-adsorbed PCE as well as on the specific molecular architecture of the polymer.

4. Conclusion

In this study it was demonstrated that non-ionic additives can be used to augment the dispersing performance of MPEG-PCEs at low w/c ratios. Glycol and diol derivatives with a molecular weight ≤ 300 g/mol were found to provide a superior effect over non-adsorbing polymers which were investigated in previous works. Moreover, spread flow tests showed that small molecules exhibiting a higher portion of

hydrophobic groups increased paste fluidity more effectively. These small molecules reduce the surface tension of the pore solution and thus improve the water wettability of cement.

Mechanistic investigations revealed that the non-ionic co-dispersants do not alter the adsorbed amounts of the PCEs, but remain dissolved in the pore solution. There, they provide a spacer effect whose range and magnitude depends on the molecular structure of the PCE and the concentration of the non-adsorbed constituents.

Our findings signify that at low w/c ratios other dispersing mechanisms come into play. Here, especially the portion of non-adsorbed compounds becomes crucial for the stabilization of the particles.

Most remarkably, it was observed that the non-ionic small molecules not only increased the spread flow, but also reduced the “sticky” behavior of the cement paste which typically occurs at low w/c values. This specific effect of the co-dispersants on the rheological parameters of cement-based materials will be discussed in another paper.

Author contribution statement

M. Ilg carried out the experiments and wrote the manuscript with support from J. Plank who supervised the project.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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