Atomistic dynamics simulation to solve conformation of model PCE superplasticisers in water and cement pore solution

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The working mechanism of polycarboxylate ether (PCE) type superplasticisers in concrete was studied from the point of view of conformational changes of the polymer simulated by molecular dynamics in pure water and cement pore solution. Three typical types of PCEs, namely a methoxy polyethyleneglycol monomethacrylate–sodium methacrylate copolymer (PCEM), a polyethyleneglycol mono allyl ether–sodium maleate copolymer (PCEA) and a polyethyleneglycol mono (3-methyl-3-butenyl) ether–sodium acrylate copolymer (PCEI) were investigated using large-scale atomistic molecular dynamics simulations. It was observed that the PCE polymers which possess negatively charged backbones were stretched in water due to electrostatic repulsion. However, they were found to be significantly shrunken and distorted in synthetic cement pore solution, depending on the polyethylene glycol (PEG) density along the backbone, resulting in the aggregation of PEG side chains due to the salting-out effect.

Notation

$D_{\text{end-end}}$	end-to-end distance
dn/dc	refraction index increment
M_n	number average molecular weight
M_w	absolute weight average molecular weight
R_g	radius of gyration
R_h	hydrodynamic radius

Introduction

Polycarboxylate-based superplasticisers (PCEs) with polyethylene glycol (PEG) pendants can fluidise concrete with an extremely small amount of water and maintain the fluidity much longer than the conventional naphthalene sulfonate-type superplasticisers; this is because of their excellent dispersing force (Jeknavorian *et al.*, 1997; Shonaka *et al.*, 1997; Tsubakimoto *et al.*, 1981). Hence, PCEs play an important role today in providing high-durability concrete, such as ultra-high strength concrete (Kinoshita *et al.*, 1997) and self-compacting concrete (Okamura and Ouchi, 2003).

Polycarboxylate-based superplasticisers adsorb onto the cement surface with their negatively charged carboxyl groups present in the polymer backbone, while the PEG side chains

stretch toward the water phase. It is believed that the excellent dispersion capability of PCEs is due to the steric repulsion of these PEG side chains. However, the correlation of PCE backbone structures with their dispersion performance is not well understood.

Many researchers have demonstrated that the steric repulsion of PCEs increases with increasing PEG side chain length or the adsorbed layer thickness (Houst *et al.*, 2008; Kauppi *et al.*, 2005; Kleshchanok and Lang, 2007; Nawa, 2006; Sakai and Daimon, 1997; Uchikawa *et al.*, 1997; Yoshioka *et al.*, 1997) and that the performance of PCE is affected by the extent of surface coverage as well (Flatt and Bowen, 2006).

Gay and Raphaël (2001) were the first to classify comb-shaped copolymers according to their grafting density and the relative lengths of the main and side chains. Later, based on a scaling law approach extracted from Gay and Raphaël's model, Borget *et al.* (2005) described the effects of salt-containing solutions on the microstructure and behaviour of polymethacrylate-g-polyethylene oxide (PEO) comb polymers. Recently Flatt *et al.* (2009) elaborated on the adsorbed conformation of PCEs, which they regarded as non-ionic comb-like polymers.

Based on the blob model they predicted the polymer conformation in aqueous solution and when adsorbed on the surface of a substrate. The calculated properties – that is, polymer radius of gyration, adsorbed layer thickness, surface coverage and steric repulsion force – were in good agreement with experimental results measured by atomic force microscope on a flat calcium-silicate-hydrate (C-S-H) substrate in calcium hydroxide ($\text{Ca}(\text{OH})_2$) solution.

These early studies provided very useful insights; nevertheless, they need to be further extended to advance the understanding of superplasticisers. For instance, the PCE polymer structures considered in the studies were limited. The charges and interactions were absent in the models. The aggregation of PEG side chains was also not considered.

In this paper, atomistic molecular dynamics (MD) simulations have been used to study polymer conformations in various environments and the conformational changes can be characterised in detail by analysing the time evolution of the systems provided by the simulation trajectory. MD simulations have been applied in studies of the conformation of PEO and polypropylene oxide (PPO) in various solvents. Recently, MD simulations have been applied to concrete. Mohan *et al.* (2014) showed that the addition of 1~2% PCE superplasticiser has no effect on the mechanical properties of C-S-H. Mishra *et al.* (2012) studied the adsorption of PCE oligomers on dry and hydroxylated tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$ or C_3S) surfaces and found out that PCEs have higher adsorption energy on dry C_3S compared to on a hydroxylated C_3S surface. Shu *et al.* (2016) investigated the influence of backbone stiffness on the polymer conformation. However, to the best of the present authors' knowledge, there is no MD simulation study which reports on the conformation of PCEs in cement pore solution.

Here, the conformations of three common types of PCEs in water and synthetic cement pore solution are reported based on results of large-scale atomistic MD simulations. The PCEs used in this work were a methacrylate type, an allyl ether type and an isoprenyl ether type, with ethylene oxide (EO) unit numbers in the side chain of 25, 34 and 25, respectively. They are denoted as PCEM-25, PCEA-34 and PCEI-25. These PCEs have different monomer composition ratios and absolute molar masses (M_w). However, they showed the same flow value in the mini-slump test at different dosages. PCEA-34 is an alternating copolymer with ABAB sequence, whereas PCEM-25 is a random copolymer (Pickelmann *et al.*, 2015), where A and B refer to the monomer units containing the carboxylic group and PEG side chain, respectively. PCEI-25 is considered as a block copolymer with ABA, ABAA and AA blocks, as evidenced by ^{13}C nuclear magnetic resonance (NMR) spectroscopy (Plank *et al.*, 2016). This is consistent with experiments showing that the isoprenyloxy polyethylene glycol (IPEG) macromonomers hardly polymerise with each other.

To understand the effect of the monomer sequence, two kinds of PCEI-25 were constructed with the same monomer molar ratio (grafting ratio) and the same M_w . The first is a random copolymer and is denoted as PCEI-25-I. The second is an alternating copolymer denoted as PCEI-25-II.

Various conformational properties, such as radius of gyration ($R_{g(\text{MD})}$), hydrodynamic radius ($R_{h(\text{MD})}$) and end-to-end distance ($D_{\text{end-end}(\text{MD})}$), were calculated during MD simulations and compared with experimental results.

Lastly, the conformational change of the multi-branch PEG with different degrees of branching was studied in solutions to observe the congestion effect of PEG chains on the aggregation.

Materials

Cement

The cement used in this study was an ordinary Portland cement (CEM I 52.5 N Milke®classic from Heidelberg Cement, Geseke plant, Germany). Its phase composition as determined by quantitative X-ray diffraction (Bruker D8 advance instrument, software Topas 4.0) is presented in Table 1. The specific surface area of $3299\text{ cm}^2/\text{g}$ was measured using a Blaine instrument (Toni Technik, Berlin, Germany). An average particle size (d_{50} value) of $12.02\text{ }\mu\text{m}$ was determined by way of laser granulometry Cilas 1064 (Cilas, Marseille, France), and the density was 3.16 g/cm^3 as measured by a Helium pycnometer (Quantachrome, Odelzhausen, Germany).

PCE copolymers

The chemical structures of the PCE samples studied, PCEM-25, PCEI-25 and PCEA-34, are shown in Figure 1. Their individual synthesis methods have been described previously (Hirata *et al.*, 2000; Lange *et al.*, 2012; Yamamoto

Table 1. Phase composition of CEM I 52.5 N sample^a

Phase	wt%
C_3S , m	70.1
C_2S , m	11.0
C_3A , c	5.1
C_3A , o	2.1
C_4AF , o	2.5
Free lime (Franke)	0.9
Periclase (MgO)	0.0
Anhydrite	2.5
Hemihydrate ^b	0.3
Dihydrate ^b	0.4
Calcite	3.3
Quartz	0.7

^aDetermined by Q-X-ray diffraction analysis using Rietveld refinement

^bDetermined by thermogravimetry

Figure 1. Chemical structures of the PCE samples studied: (a) PCEM-25; (b) PCEI-25; (c) PCEA-34

et al., 2004). The properties of the synthesised polymers are summarised in Table 2.

The M_w , the polymer content (monomer conversion) and the polydispersity index (PDI) were determined by size exclusion chromatography (SEC; Waters Alliance 2695 from Waters, Eschborn, Germany) equipped with refractive index (RI) detector 2414 (Waters, Eschborn, Germany) and a three-angle dynamic light-scattering detector (mini Dawn from Wyatt Technologies, Santa Barbara, CA, USA): prior to application on the columns, the polymer solutions were filtered through a 0.2 μ m filter. The polymers were separated on an Ultrahydrogel precolumn and three Ultrahydrogel (120, 250 and 500) columns (Waters, Eschborn, Germany) using 0.1 M aqueous sodium nitrate (NaNO₃) solution (adjusted to pH 12.0 with sodium hydroxide (NaOH)) as an eluent at

a flow rate of 1.0 ml/min. The value of refraction index increment (dn/dc) used to calculate M_w and M_n for all polymers is 0.135 ml/g (value for PEO) (Teresa *et al.*, 2001).

The SEC spectra of the PCE samples are displayed in Figure 2. The polymer content (percentage of monomers converted to polymer) was determined by the area (%) of the polymer profile in the RI diagram.

It has to be noted that polymer PCEM-25 showed extremely strong scattering intensity at very high M_w (elution volume $\sim$ 15 ml), which may result from a crosslinked PCE caused by PEG di-methacrylate present in the macromonomer, or by peroxide on PEG chains during polymerisation (Hirata *et al.*, 2000; Paas *et al.*, 2015). However, it is negligible in the simulation because of a quite low content of 0.7 wt%. Furthermore, PCE sample PCEA-34 contains a noticeable amount of non-reacted allyl ether macromonomer, but is simulated as an alternating copolymer.

Figure 3 illustrates the initial structure of the PCEs before geometric optimisation. All polymer models are constructed by way of the polymer builder function of the Materials Studio package. In PCEA the side chains line up much more densely along the backbone than in PCEM and PCEI because of an alternating copolymer.

In all three PCE samples of PCEM-25, PCEI-25 and PCEA-34, the weight ratio of PEG macromonomer/carboxylic monomer was optimised for best dispersion. For example, the weight ratio of the monomers in PCEM-25 was 75/25 (PEG monomer/acid monomer), which is in good agreement with the value that has been suggested by Winnefeld *et al.* (2007) as well. In this paper, the dosages applied in the cement paste tests were all converted to the values for the pure polymers without residual monomers to compare the effects of the polymers themselves.

The $R_{h(MD)}$ were verified by the hydrodynamic radius of $R_{h(VIS)}$ measured. The $R_{h(VIS)}$ were determined by a Viscotek

Table 2. Monomer composition and analytical data of the PCE samples

PCE-P ^a	M_w^b	τ^c : mol %	Composition: wt% ^d		Polymer content ^b : %	Polydispersity index, PDI (M_w/M_n)
			PEG	Carboxylic		
			Monomer	Monomer		
PCEM-25	68 800	21	75	25	96.1	2.2
PCEI-25	93 800	31	85	15	92.2	2.6
PCEA-34	63 100	50	91	9	70.4	2.8

^aP: number of ethylene oxide (EO) units

^bDetermined by SEC

^cGrafting molar ratio

^dWeight ratio of monomers used in the polymerisation process

Figure 2. SEC spectra of the PCE samples: (a) PCEM-25; (b) PCEI-25; (c) PCEA-34

Figure 3. Initial structures of the PCE samples before geometric optimisation, with specific bond angles and interatomic distances which are inherent in each atom: (a) PCEM-25 with 9921 atoms; (b) PCEI-25-I with 13 999 atoms; (c) PCEI-25-II with 13 999 atoms; (d) PCEA-34 with 9816 atoms

GPC Max VE 2001 (Malvern Instruments Ltd, UK) equipped with a triple detector array (TDA 302, Malvern Instruments Ltd, UK) – that is an RI detector, a viscometer and two

light-scattering detectors (low angle and right angle, 670 nm). The $R_{h(VIS)}$ were calculated by the Einstein equation defining the relationship between the polymer viscosity and M_w using

Figure 4. Initial structures of (a) PEG-100, (b) TMP-150 and (c) Sorbitol-300. All hydrogen atoms are hidden for clarity

statistical light scattering. The PCE samples were separated on a TSK guard column α and three TSK gel (α -5000, α -4000 and α -3000) columns (Tosoh Corporation, Tokyo, Japan). As the mobile phase, a mixed solvent of acetonitrile and water ($\text{CH}_3\text{CN}/\text{H}_2\text{O} = 80/20$ wt ratio) containing 0.10 M boric acid (H_3BO_3)/0.05 M sodium hydroxide (NaOH) was used at 40°C and a flow rate of 0.8 ml/min. Prior to application on the columns, the polymer solutions were filtered through a 0.2 μm filter. The value of dn/dc used to calculate M_w for all polymers is 0.135 ml/g (value for polyethylene oxide) (Teresa *et al.*, 2001).

Multi-branch PEG

To understand the aggregation of PEG side chains in cement pore solution, three types of multi-branch PEGs were built up and their conformational changes in synthetic cement pore solution were simulated. The PEG compounds used were PEG-100, TMP-150 and sorbitol-300, where PEG-100 is a linear polymer with 100 EO units, TMP-150 is a trimethylol propane EO adduct having three PEG branches each, with 50 EO units linking to the end carbon of propane through an ether bond, and sorbitol-300 is a sorbitol EO adduct containing six PEG branches each with 50 EO units linking to each backbone carbon atom of sorbitol through an ether bond. The initial structures are shown in Figure 4.

The simulation results of $R_{h(\text{MD})}$ were verified by measuring the hydrodynamic radius of $R_{h(\text{DLS})}$ obtained by dynamic

light-scattering (DLS) measurements. The $R_{h(\text{DLS})}$ values were determined by Zetasizer Nano ZSP (Malvern Instruments Ltd, UK), which utilises the Stokes–Einstein equation that defines the relationship between the hydrodynamic radius of a sample and its speed due to Brownian motion using DLS. The polymer concentration was 0.5 wt% in solution and the temperature was 25°C.

The PEG compounds were synthesised by EO addition to the corresponding alcohols using potassium hydroxide (KOH) as a catalyst.

Experimental and simulation procedures

Performance test with cement using ‘mini slump’ test

For the determination of the paste flow, a ‘mini slump’ test was utilised and carried out as follows. First, a constant water-to-cement (w/c) ratio of 0.3 was chosen. At this w/c ratio, the dosages of the polymers required to reach a spread of 26 ± 0.5 cm were determined. Generally, the polymer was dissolved in the required amount of mixing water placed in a porcelain cup. The amount of water contained in the polymer solution was subtracted from the amount of mixing water. Next, within 5 s, 350 g of cement were added to the mixing water and agitated manually for 1 min, then rested for 1 min without stirring. This was followed by intensive stirring for another 2 min. The cement paste was immediately poured into a Vicat cone (height 40 mm, top diameter 70 mm, bottom diameter 80 mm) placed on a glass plate and the cone was

vertically lifted. The resulting spread of the paste was measured twice, the second measurement being at a 90° angle to the first, and averaged to give the spread value. All tests were carried out at 22°C.

Molecular dynamics simulations

The synthetic cement pore solution used in the simulations was generated using the following amount of salts: 1.72 g/l gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), 6.959 g/l sodium sulfate (Na_2SO_4), 4.757 g/l potassium sulfate (K_2SO_4) and 7.12 g/l potassium hydroxide (KOH) (pH = 13.1). The salts are assumed to be completely dissociated in water. Based on this assumption the exact molar concentrations of Ca^{2+} , SO_4^{2-} , Na^+ , K^+ and OH^- are calculated to be: Ca^{2+} : 0.010 M, Na^+ : 0.098 M, K^+ : 0.181 M, SO_4^{2-} : 0.086 M and OH^- : 0.127 M. For simulation purposes, the molar concentrations are converted to volumetric concentrations: Ca^{2+} : $6.087 \times 10^{-3}/\text{nm}^3$, Na^+ : $5.901 \times 10^{-2}/\text{nm}^3$, K^+ : $0.109/\text{nm}^3$, SO_4^{2-} : $5.203 \times 10^{-2}/\text{nm}^3$ and OH^- : $7.642 \times 10^{-2}/\text{nm}^3$.

The time evolution of the conformations of the polymers were obtained by classical MD simulations using the Gromacs package (Berendsen *et al.*, 1995; Hess *et al.*, 2008; Lindahl *et al.*, 2001; Spoel *et al.*, 2005). Simulations were performed using the *NVT* ensemble (constant temperature, volume and number of atoms) at room temperature (300 K) with a time step of 2 fs. The Lincs algorithm (Hess *et al.*, 1997) and its parallel version P-Lincs (Hess, 2008) are applied to constrain bonds involving light atoms such as hydrogen. Prior to each run, energy minimisation and a 5 ns dynamics relaxation under the grand canonical ensemble *NPT* with pressure $P = 1$ bar and temperature (300 K) was applied, followed by about 200 ~ 350 ns *NVT* runs. The visual molecular dynamics (VMD) visualisation package (Humphrey *et al.*, 1996) was used to analyse various properties such as radius of gyration (whole polymer), end-to-end distance (backbone and side chains) and hydrodynamic radius for the whole polymer based on MD trajectories was saved every 10 000 steps (20 ps) and averaged in the last 30 ns of the simulations. The ‘optimised potentials for liquid simulations’ (OPLS) all atom (Jorgensen *et al.*, 1996) force field was applied for all polymers and ions, except for OH^- and SO_4^{2-} . Force field parameters for OH^- and SO_4^{2-} ions were taken from the ‘chemistry at Harvard macromolecular mechanics’ (Charmm) force field.

Results and discussion

Dispersing performance of PCEs

To obtain an initial cement paste flow of 26 ± 0.5 cm, the PCE dosages measured were 0.14 wt% (PCEM-25), 0.10 wt% (PCEI-25) and 0.14 wt% (PCEA-34). This result signifies that the PCE polymer PCEI-25 possesses the highest dispersing ability of all these samples tested.

Polymer conformation in pure water and in synthetic cement pore solution

The typical time evolution of various conformation properties in water and synthetic cement pore solution for PCEM-25, PCEI-25-I, PCEI-25-II and PCEA-34 oscillate around a certain value in the range of about 200 ~ 300 ns, indicating the system has reached a steady state and is well equilibrated.

The various conformation properties obtained are listed in Table 3. The radii of gyration ($R_{g(\text{mf})}$) predicted by the mean-field model (Flatt *et al.*, 2009; Gay and Raphaël, 2001) and the hydrodynamic radii of $R_{h(\text{VIS})}$ measured are also listed for comparison. The snapshots of the last frame for all PCEs are shown in Figure 5.

First, it can be seen from Figure 5 that all the polymer molecules have become shrunken and distorted in the synthetic cement pore solution. Comparing PCEI-25-I (random copolymer) and PCEI-25-II (alternating-like copolymer), it can be seen how the aggregation of the adjacent PEGs affects the conformation of the backbone in synthetic cement pore solution. Namely, the backbone of PCEI-25-I is surprisingly shrunken and distorted by the strong aggregation of adjacent PEGs, as well as the salting-out effect of the backbone, whereas PCEI-25-II is shrunken probably because of the salting-out effect on the backbone. Bailey and Callard (1959) showed that the solubility of PEO in water should be lowered by the presence of salts and is drastically reduced by a pH level beyond 12. These salting-out effects are reflected by an increase of PEG hydrophobicity in solution, resulting in a high degree of entanglement of the polymer chains. Certainly, for all PCEs, the end-to-end distances for the PEG side chains ($D_{\text{end-end(MD)}}^{\text{sidechains}}$) are a bit smaller in cement pore solution than in water due to the salting-out effect (Table 3).

Early reports also showed that PEG molecules easily aggregate with each other by hydrogen bonds (Begum and Matsuura, 1997; Linegar *et al.*, 2010) and PEG side chains would entangle due to close proximity (de Gennes, 1987; Flatt and Bowen, 2006). The magnitude of the aggregation of PEG side chains is found to follow the trend: PCEA-34 (proximity distance, 0.54 nm) > PCEM-25 (0.58 nm) $\approx$ PCEI-25-I (0.59 nm) > PCEI-25-II (0.72 nm). Here, the proximity distances were determined from the initial polymer structure, as shown in Figure 3. In addition, the relevant PEG radii of gyration of 1.31 ± 0.28 nm ($P = 25$) and 1.56 ± 0.35 nm ($P = 34$), as calculated by the relational expression with the molecular weight in water according to Devanand and Selser (1991), are much longer than half of the proximity distances, thus strongly suggesting the possibility of an interaction between PEG side chains.

Comparing the end-to-end distances of the polymer backbones ($D_{\text{end-end(MD)}}^{\text{backbone}}$), those of all PCEs in water are larger than those in synthetic cement pore solution (Table 3). This indicates that in water the PCE backbones are considerably

Figure 5. Conformations of PCEs in water and synthetic cement pore solution. (a), (b), (c) and (d) show PCEM-25, PCEI-25-I, PCEI-25-II and PCEA-34 in water, respectively. (e), (f), (g) and (h) show PCEM-25, PCEI-25-I, PCEI-25-II and PCEA-34 in synthetic cement pore solution, respectively

Table 3. Polymer properties in water and synthetic cement pore solutions calculated from molecular dynamics simulations

Polymer type	$D_{\text{end-end(MD)}}^{\text{backbone}}$: nm	$D_{\text{end-end(MD)}}^{\text{sidechains}}$: nm ^a	$R_{\text{g(MD)}}$: nm	$R_{\text{g(mf)}}^{\text{b}}$: nm	$R_{\text{h(MD)}}$: nm	$R_{\text{h(VIS)}}^{\text{c}}$: nm
PCEM-25 (water)	28.2	2.64 ± 0.30	9.1	9.8	5.8	—
PCEI-25-I (water)	34.0	2.63 ± 0.37	10.4	11.8	6.3	—
PCEI-25-II (water)	31.0	2.62 ± 0.37	10.0	11.8	6.4	—
PCEA-34 (water)	9.0	3.20 ± 0.50	3.9	8.5	3.8	—
PCEM-25 (cement)	16.3	2.44 ± 0.27	6.3	—	4.0	5.5
PCEI-25-I (cement)	10.7	2.60 ± 0.45	4.6	—	3.7	—
PCEI-25-II (cement)	23.0	2.60 ± 0.22	7.5	—	5.7	7.9
PCEA-34 (cement)	8.2	3.16 ± 0.35	3.8	—	3.7	2.9

^aAveraged over all side chains in a PCE chain

^bRadius of gyration predicted by mean-field model

^cHydrodynamic radius measured by a Viscotek GPC Max VE 2001 (Malvern Instruments Ltd, UK) in a mixed solvent of acetonitrile and water containing 0.10 M boric acid (H₃BO₃)/0.05 M sodium hydroxide (NaOH)

stretched (rigid) due to the electrostatic repulsion between the negatively charged carboxylic acid groups. Contrastingly, in synthetic cement pore solution the backbones are significantly

distorted and shrunken (flexible). Interestingly, in water the $D_{\text{end-end(MD)}}^{\text{backbone}}$ for PCEI-25-I is slightly larger than that of PCEI-25-II. However, it is significantly smaller than that in

Figure 6. Conformations of multi-branched PEGs in synthetic cement pore solution: (a) PEG-100; (b) TMP-150; (c) sorbitol-300

synthetic cement pore solution, indicating that the congestion of the PEG side chains adjacent along the PCE backbone significantly affects the conformation of the PCEs as well.

Bailey *et al.* (1964) also demonstrated that PEO would form molecular association complexes with poly(acrylic acid) or poly(methacrylic acid) in an aqueous solution due to hydrogen bonding between ether oxygens and carboxyl groups at a low pH level of 4 to 10 and an ion–dipole interaction at higher pH. However, the ion–dipole interaction disappears at pH levels greater than 7 in the presence of salts, such as sodium chloride (NaCl). Therefore, formation of molecular associative complexes between PEG side chains and carboxylic groups can be ruled out here.

Next, the values of $R_{g(MD)}$ and $R_{h(MD)}$ obtained from simulations were compared with $R_{g(mf)}$ and $R_{h(VIS)}$, respectively. The $R_{g(MD)}$ values for PCEM-25 and PCEI-25 are slightly smaller than $R_{g(mf)}$ in water, whereas $R_{g(MD)}$ of PCEA-34 is much smaller than $R_{g(mf)}$. Arguably, the reason for that is that the mean-field model disregards the aggregation of PEG side chains, which, however, the simulation has shown is significant in PCEA-34.

In synthetic cement pore solution, the $R_{h(MD)}$ values of the PCEs are a bit smaller than the experimental values of $R_{h(VIS)}$ except for that of PCEA-34. This effect is probably caused by salting-out resulting from the higher ionic strength

($I \approx 210$ mM and 150 mM in synthetic cement pore solution and in the mobile phase used in the measurements, respectively) and higher pH value (pH = 13.1 and 12.0, respectively). However, as for PCEA-34, it is suggested that the denser PEG side chains present in PCEA-34 interact with each other even in water, producing a highly coiled polymer.

Lastly, the MD simulation of three types of multi-branch PEGs in synthetic cement pore solution showed that strong aggregation of the PEG branches is only observed for sorbitol-300, which has six PEG branches linking to each –OH group in the sorbitol backbone, confirming that many PEG chains which are closely located are aggregated (Figure 6). In contrast, the PEG side chains in PEG-100 and TMP-150 do not aggregate and adopt stretched conformations. Table 4 lists $R_{h(MD)}$ and $R_{h(DLS)}$ in solutions. It suggests that in synthetic

Table 4. Hydrodynamic radius (nm) calculated by MD simulations and measured by DLS

	PEG-100	TMP-150	SB-300
In water			
$R_{h(DLS)}^a$	2.25	2.32	2.58
In synthetic cement pore solution			
$R_{h(MD)}$	1.60	1.95	1.50
$R_{h(DLS)}^a$	1.69	1.98	2.57

^aPolymer concentration is 0.5 wt. %

cement pore solution PEG-100 and TMP-150 shrink, and the $R_{h(MD)}$ values agree quite well with $R_{h(DLS)}$; however, sorbitol-300 molecules are probably associated by intermolecular interaction during DLS measurement.

Therefore, the shrinking of the PCE backbone in synthetic cement pore solution is probably accelerated by the aggregation of the PEG side chains as well as the salting-out effect of the backbone itself.

Subsequently, the adsorbed conformation and the relationship with the cement-dispersing effect will be studied and reported in another paper. The authors expect that these simulations at the molecular level will shed light on the structure–property relationship and will be useful in the design of an even more effective next generation of PCE type superplasticisers.

Conclusions

The solution behaviour of three types of common PCE concrete superplasticisers (PCEM, PCEA and PCEI) in pure water and in synthetic cement pore solution was studied by atomistic MD simulations. The backbones of those PCEs are considerably stretched (rigid) in water due to the electrostatic repulsion between negatively charged carboxylic acid groups, whereas in synthetic cement pore solution the backbones are significantly distorted and shrunken (flexible) due to the aggregation of the hydrophobic PEGs as well as the salting-out effect on the backbone.

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