Effect of different macromonomer molecular size in polycarboxylate superplasticizer by molecular dynamics simulation

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Abstract. Molecular dynamics simulations were carried out to investigate the solution conformation of polycarboxylate superplasticizer (PCE) with different macromonomer molecular size. Simulation results showed that the larger size of macromonomer in the PCE make the molecules have greater intermolecular interactions. The probability of water molecules around the PCE molecules affected the water distribution in the systems. These results indicated that there were more water molecules around the main chain of PCE, while the macromonomer in PCE was larger. Knowledge of the interaction relationship between water molecules and PCE using molecular dynamics simulation opens the way for understanding the mechanism of superplasticizer in cement systems.

1. Introduction

In the past decades, chemical admixtures have attracted increasing attention in the cement industry. Superplasticizers are one kind of chemical admixtures that can be added to cement mixtures to improve the workability of cement and concrete. Polycarboxylate superplasticizer (PCE) is one of the superplasticizers that easy to be designed and synthesized for different functions [1]. PCEs usually composed of polymer backbone containing anionic groups and grafted side chains. The anionic groups adsorb onto the cement surface electrostatically and the side chains provide steric repulsion, resulting in an excellent cement-dispersing effect. The grafted side chains usually designed from different types and sizes of polyoxyethylene glycols (PEGs). The PEGs of different structures lead to different properties of the synthesized PCE and that affect the dispersing performance of PCE.

Generally, the PCE conformation is a key factor affecting the working properties in concrete systems. The solution conformation of PCE not only affects the adsorption ability but also affects the dispersion properties in cement. Shu et al. reported that PCE containing high backbone methyl group content exhibited a more extended polymer backbone in pore solution due to the hindered free rotation of polymer backbone and more carboxylic groups could be accessible for adsorption [2]. Ran et al. synthesized a series of PCEs with different side conformation to investigate the dispersing mechanism in terms of rheological behavior and dispersion in cement system [3]. These indicate that there is a relationship between solution conformation and performance of PCE.

Recently, molecular dynamics (MD) simulation has been widely used to study cement systems, especially in the chemical admixture. Hirata et al. used MD simulation to simulate the PCE polymers
adsorbed on the surface in pore solution [4]. Chuang et al. simulated PCE molecules with different side-chain length in aqueous solution [5]. However, more insights are needed to understand and control the properties of PCE at the microscopic scale.

The present study aims to understand the effect of macromonomer molecule size in PCE systems. Toward this propose, four kinds of PCE molecules with different macromonomer molecule size were designed in aqueous solution. MD simulation was carried out to investigate the solution conformation of PCE. The interaction between molecules in the PCE system is the main factor affecting the properties of PCE. The results facilitate to clarify the molecular interaction mechanism between PCE systems that help to develop structure-property relationship of PCE molecule.

2. Methods
MD simulations were used to study the solution conformation of PCE molecule with different molecule size of macromonomer in aqueous solution. The PCE molecules were composed by two kinds of monomer, acrylic acid (AA) sodium and isopentenyl polyethylene glycol (IPEG), with the ratio of AA:IPEG being 4:1. The macromonomer of IPEG had different size with molecular weight of 600, 1200, 2400, and 3000 which consistent with commonly used in the chemical admixture industry. These four kinds of PCE molecules with different macromonomer molecule size were called PCE1, PCE2, PCE3, and PCE4. The molecular weight of PCE was consistent with our synthesized PCE polymer, which had been widely used in the concrete industry.

The MD simulation was used all-atom molecular dynamics simulation with COMPASS forcefield [6]. The PCE, solvent molecules and sodium ions were randomly place in the systems with the periodic boundary conditions. The sodium ions were used to balance the system charge. The concentration of PCE in the all systems was 10%, which was also consistent with the product concentration. There were 5500, 9000, 15700, and 19000 water molecules with TIP3P water model in the system respectively. All MD simulation was carried out in the canonical ensemble (NVT) with the time step equal to 1.0 fs with the system temperature set at 298 K. The total simulation time was over 1000 ps and eventually reached thermal equilibrium. An extra MD simulation run of 100 ps was carried out for analysis.

3. Results and Discussion
In the MD simulation, we studied the solution conformation of four different structure PCE molecules (PCE1, PCE2, PCE3 and PCE4) with same concentration at PCE in aqueous solution. Figure 1 shows the snapshots of PCE1, PCE2, PCE3 and PCE4 systems. The black, rad, and white balls represent carbon, oxygen, and hydrogen atoms, respectively. The PCE molecules have different solution conformation in the different systems. The PCE molecules with small size macromonomer aggregate themselves, on the other hand, the PCE molecules with large size macromonomer are easily cross-linked with other PCE molecules. The macromonomer with larger size in PCE molecule has more intermolecular interaction with each other molecule. That increases the steric repulsion effect in PCE system resulting in influence the dispersion properties of cement.

Figure 1. The snapshots of (a) PCE1 (b) PCE2 (c) PCE3 and (d) PCE4 in aqueous systems.

In order to analyze the intermolecular interaction between molecules, radial distribution functions (RDFs) of molecule in the trajectory were calculated. RDF shows the local structure and understanding
the atomic distribution of substance, which obtains the effective intermolecular potentials and the probability between two objects. The intermolecular relationship between PCE molecules is shown in figure 2. Op is defined as the oxygen atom on the PCE molecule. In figure 2, the PCE molecule with larger size of macromonomer has more intermolecular interaction, while the smaller-sized macromonomer has small interaction. This result is consistent with the experiment that shows the long side chain of PCE increase the steric hindrance effect in cement systems [3].

![Figure 2. The radial distribution functions of $g_{Op-Op}(r)$ between PCE molecule in systems.](image)

In addition, the distribution of water molecules around the PCE molecules affect the hydration as well as dispersion cement in system [7]. Figure 3 shows the RDF between the main chain of PCE and water molecules. Om is defined as the oxygen atom on the main chain of PCE molecule; OH is defined as the oxygen atom on the water molecule. In figure 3, all the main chain of PCE molecules have obvious hydrogen bonds with the water molecules. The probability of water molecules in four systems are PCE4 > PCE3 > PCE2 > PCE1. The hydrogen bonds make PCE molecules easily soluble and disperse in water. The distribution of water molecules around the main chain of PCE affects the water density at the cement interface due to PCE adsorption structure.

![Figure 3. The radial distribution functions of $g_{Om-OH}(r)$ in systems.](image)

To further understand the distribution of water around the main chain, the number of water molecule was calculated. The main chain of PCE was selected and calculated the space within a radius of 5 Å. The water molecules were counted in this space as shown in figure 4. The number of water molecules around the main chain of PCE increases as the molecule size of the macromonomer increases. This phenomenon indicates that the more water molecules tend to gather near the main chain of PCE with the larger molecule size in PCE macromonomer. These results show the water molecules around the main chain of PCE depend on the molecules size of macromonomer. The trapped water molecules not only affect the hydration kinetics of cement but also affect the water reducing properties of PCE. These reasons influence the working performance of PCE in the cement systems.
Figure 4. The number of water molecules around the main chain of PCE molecules.

4. Conclusion
MD simulation was carried out to investigate different macromonomer molecule size of PCE molecules with the same concentration in aqueous solution. Our results showed that the steric hindrance properties of PCE depend on the macromonomer molecule size in PCE. The larger size of macromonomer in PCE molecule had larger intermolecular interaction. On the other hand, the distribution of water molecules was also affected by the macromonomer molecule size in PCE. The more water molecules surround the main chain of PCE because the PCE had a larger macromonomer. MD simulations provided molecular insight on superplasticizers in aqueous solution. Knowledge of the distribution of molecules in the PCE systems at the microscopic scale help to further understand the mechanism of PCE.

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