The study on polycarboxylate superplasticizer with polyamine side chain using molecular dynamics simulation

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Abstract. A new type of water-reducing agent, which contains polyamine side chains, has been theoretically studied utilizing molecular dynamics simulation (MD) in this research. The models of three types of water reducers in an aqueous solution, including SNF, PCE, and PCA, have been constructed, simulated, and analyzed. The results indicate that compared to the linear structure of SNF, the traditional PCE water-reducing agent has a stronger interaction with water molecules, so it has a better water-reducing effect. This stronger interaction is mainly provided by the side chain of PCE. PCA further enhances the hydrophilicity of its side chain based on PCE structure, leading to a stronger interaction on water molecules than traditional PCE molecules. The migration ability of water-reducing agents and other molecules in the system has been further explored. The diffusion coefficient of three water reducer molecules decreases in the following order: PCE>SNF>PCA. This is due to the interaction between molecules, especially the incompatible strength and quantity of hydrogen bonding.

1. Introduction
Polycarboxylate ether (PCE) water-reducing agent, considered the 3rd gen concrete additive, has been widely used in different concrete production industries to satisfy different kinds of requirements. PCE molecules are generally comb-shaped or dendritic. Its structure can be flexibly designed by adjusting a series of conformational parameters, including the length of backbone and side-chain of PCE, the density of side chain, the density of charged, which makes it possible to meet the requirements of high performance and multi-function.

Molecular dynamics (MD) simulation, a computational chemistry method, is particularly suitable for chemical investigation at the molecular level. It is good to use it in conformation studies for polymers, like comb-shaped water-reducing agents. So far, computational chemistry has been applied to studying the molecular structure and mechanism of polycarboxylate ether for a while. For example, Hirata et al. used molecular dynamics simulation methods to calculate and simulate the adsorption conformation and adsorption behavior of different superplasticizer molecules in a similar real pore solution environment; In the research of Chuang et al. the different lengths of polycarboxylate ether side chains and their aqueous solution conformations are simulated. In addition, there are many examples to prove the practicability and sufficient reliability of computational chemistry methods, especially molecular dynamics simulation in the field of polycarboxylate ether molecular research.

For traditional PCE water reducers, the polyether side chains take large portions of the overall volume and surface area of the molecule. These side chains significantly contribute to its hydrophilicity and steric hindrance effect, leading to better dispersion in the concrete system. We proposed to replace the polyether side chain on the PCE molecule with polyamine that has better
hydrophilicity than polyether. This new type of “PCE” is expected to have a better dispersion ability in a concrete system. Herein, molecular dynamic simulation was used to study the conformation of polycarboxylate ether with nitrogen-containing side chains. Specifically, this study is two-fold. First, by simulating the conformation of the polyamine water-reducing agent (Polycarboxylate Amine-based Superplasticizer, PCA) solution, the structural characteristics and behavior of the PCA water-reducing agent are studied from the molecular level. Then, by comparing it with the solution conformation of the naphthalene-based water-reducing agent (Sodium Naphthalene Formaldehyde Superplasticizer, SNF) and the traditional polycarboxylate ether water-reducing agent (Polycarboxylate Ether-based Superplasticizer, PCE), the influence of the polyamine side-chain structure on the performance of the water-reducing agent was explored.

2. Method
All-atom molecular dynamics simulation was performed using to investigate PCA conformations in the explicit water environment. The conformational properties and behaviors of PCA were considered in this study, and then it was also compared to the conformations of SNF and PCE. The conformations of SNF, PCE, and PCA are shown in Figure 1 below, respectively.

![Figure 1. The conformation of (a) SNF, (2) PCE, (3) PCA](image)

The conformations of PCE and SNF were first constructed. The SNF molecule is designed to be polymerized from 53 monomers, and the resulting total molecular weight is about 11,600. The total molecular weight of the molecules mentioned above is close to the molecular weight of the corresponding molecules obtained in the synthesis experiment, which is in line with the actual situation. The polyether macromonomer used in the superplasticizer molecule is isopentenyl polyethylene glycol (IPEG), with a molecular weight of about 2400, containing 53 polyether repeating units and the same combination as acrylic acid. The monomer combination forms a polycarboxylate ether according to the monomer molar ratio of 4:1, and the resulting molecule has 10 side chains, and the resulting total molecular weight is about 27,000. Basically, the PCA structure was designed based on PCE. The oxygen atoms on the polyether macromonomer of the PCE molecule are replaced with aminyl groups, while other parts, like backbones, remain unchanged. Then, the constructed water-reducing agent molecule was randomly distributed in boxes with periodic boundary conditions, and 3000 water molecules were added to each system to simulate the true concentration of the synthesis experiment. At the same time, it is necessary to add appropriate sodium ions to balance the system charge.

All-atom molecular dynamics simulation was conducted using COMPASS forcefield and Forcite module in Materials studio 6.0 software package. COMPASS is one of the most used forcefields with good adaptability to the various molecular systems, including catalysts, polymer, solid, and liquid interfaces. The simulations were carried out in the canonical ensemble (NVT). The temperature of the system was set to be 298K, and the time step of the integration was set to be 1.0 fs.
3. Result and discussion

3.1. The conformation properties
When the system reaches thermodynamic equilibrium, the conformations of different superplasticizers were first observed in the snapshot of each of the three systems, shown in Figure 2.

![Figure 2. Solution conformation of (a) SNF, (b) PCE, (c) PCA](image)

The black, red, blue, and white ball represents carbon, oxygen, nitrogen, and hydrogen atoms, respectively. In general, it is easy to know that the initial conformations of these three water reducers were different, leading to various conformational properties. Figure 2(a) presents the conformation diagram of the naphthalene-based superplasticizer in solution. Since it has no side chains and the structure is a long straight chain, the molecules will be distorted in the solution environment; Figure 2(b) and 2(c) shows the conformations of PCA and PCE. Compared to SNF, the conformation of PCA and PCE are similar. Both of them have gathering side chains in the solution.

To further describe the different conformation in the solution, the radius of gyration, \( R_g \), for backbone and the side chain of the molecules were examined. The results are shown in Figure 3.

![Figure 3. The radius of gyration of different water reducers in solution](image)

As shown, the PCA molecule presents the highest \( R_g \) value, while the SNF has the lowest. The PCA conformation is stretched and loose in the solution compared to PCE and SNF, which is good for the steric hindrance between superplasticizers molecules. The difference of these conformations results from the hydrophilicity of different side chains. Compared to those side chains containing oxygen atoms, the side chain of PCA, which contains nitrogen, presents better hydrophilicity and, therefore, presents a stronger interaction between PCA and \( \text{H}_2\text{O} \) molecules. Besides, the conformations of the superplasticizer are associated with the thickness of the adsorption layer. Usually, a large \( R_g \) value would correspond to a large adsorption thickness, which means PCA molecules are expected to have a larger adsorption layer thickness than common SNF and PCE.

3.2. The intermolecular interactions between molecules
To further explore the behavior of water reducers in the aqueous solution, radial distribution function (RDF) was calculated as an index to characterize the relationship between the molecules in this system.
The RDFs of carbon atoms in water reducer molecules are shown in Figure 4, presenting the interaction between water reducer molecules.

![Image of RDFs of water reducer-water reducer in solution](image)

Figure 4. RDFs of water reducer-water reducer in solution

Note that $C_p$ in the diagram represents the carbon atom in the water reducers. It is known from the figure that there is no obvious intermolecular interaction between SNF molecules. In contrast, PCE molecules and PCA molecules do have a certain degree of intermolecular interaction, and the interaction between PCA molecules is stronger than that of PCE. These results are mainly caused by the steric hindrance effect from the side chains of water reducer molecules. The long side chain has an obvious steric hindrance effect. For SNF molecules, its long-chain structure has a long backbone but no side chain, leading to a very small interaction between water reducer molecules; in contrast, PCE molecules and PCA molecules have side chain structures, which are easy to interact with other water reducer molecules in the solution. In addition, it can be seen from Figure 3 that the radius of gyration of the PCA molecules in the solution is also larger than that of the PCE molecules, which causes the PCA molecules to be more stretched in the solution and easy to interact with other water reducer molecules. It shows that the PCA molecule has a larger steric hindrance effect than the other two water reducers.

To further understand the behavior of water reducer molecules and $H_2O$ molecules in the solution, a series of RDFs were calculated to investigate the interaction between water reducer and water molecules. The results are shown in Figure 5.

Specifically, Figure 5(a) presented the interaction between $H_2O$ molecule and nitrogen atom on the side chain of water reducer molecules, while the interaction between a water molecule and oxygen atom in the backbone of water reducer was shown in Figure 5(b).

Figure 5(a) shows that the curves representing SNF, PCE, and PCA have a similar trend. Three peaks of this diagram were generated at about 1.5 angstrom, which indicates that hydrogen bonds were formed between oxygen/nitrogen atoms from water reducers and oxygen atoms from $H_2O$. Furthermore, it can be seen from the signal that the peak of the SNF molecule is smaller than other water reducer signals. The backbone of PCA and PCE has a stronger interaction with a water molecule than SNF, which has a straight backbone but no side chain. Figure 5 (b) is the diagram for RDF between nitrogen/oxygen atoms in the side chain of water reducer molecules and oxygen atoms from water molecules, representing the mutual interaction between water reducer and water molecules. It can be seen from the figure that the corresponding curves of the three water reducers have obvious differences: SNF, the water reducer molecule without side chain, has no signal; the side chains of PCE molecules have intermolecular forces with water molecules, but they are not as stronger as the force between PCA molecules and water molecules. Since the side chain of PCA has a stronger interaction with a water molecule, it can be inferred that polyamine side chains are more hydrophilic than polyether side chains.
3.3. The behavior of molecules in the system

The analysis of the molecule trajectory in solution is also worth to be considered. In this study, the mean square displacement (MSD) of the molecules was introduced to characterize the migration ability of different water reducing agents and water molecules in the solution.

Figure 6(a) presents the mean square displacement of SNF, PCE, and PCA molecules in the aqueous solution. In general, the migration ability of different water reducing agent molecules varies greatly and decreases in the following order: PCE>SNF>PCA. The good migration ability of PCE molecules is attributed to their ridge backbone and flexible side chain. In contrast, SNF molecules have only rigid backbone parts, so their migration ability in the system is poor. PCA molecules also have a rigid backbone and flexible side chain part, but due to the greater interaction between the side chain and water molecules, the movement of molecules is restricted by water molecules, making it difficult for PCA molecules to migrate in the system.

The MSD values in Figure 6(b) indicate the migration of H$_2$O molecules in different systems. The results show that the H$_2$O molecules present comparable migration abilities, while the H$_2$O migration ability in PCA is relatively weak. The reason is the same as that in Figure 6(a). The strong intermolecular force between water molecules and PCA molecules makes the motion behavior of water molecules restricted by PCA molecules and reduces the diffusion behavior of water molecules in the system. The mobility of water molecules in the system can be described as the fluidity of the system, which is experimentally related to the rheological properties of the solution, and the rheological properties of the water-reducing agent greatly affect the material properties of the water-reducing agent. From a microscopic point of view, to understand the interaction between molecules, we can further understand the properties of materials.
4. Conclusion
In this study, molecular dynamics simulation was used to explore various conformations of SNF, PCE, and PCA water-reducing agents in solution. The results indicate that replacing the polyether side chain with polyamine could significantly increase the hydrophilicity of the water reducers, which means more hydrogen bonds would form between their side chain and water molecules. That makes the water reducer easier to dissolve in water, enlarges the conformation distribution of polymers in an aqueous solution, and increases the corresponding steric hindrance effect. Through the comparison of SNF and PCE systems, it can be found that their backbones present induce similar interaction with the water molecules. However, PCE exhibits a stronger interaction with water molecules because PCE has side chains that SNF linear molecules do not have. This increase is mainly due to the steric hindrance and the additional interaction with water provided by the side-chain conformation. Based on the conformational properties of PCE, PCA improves the hydrophilicity of the side chain of the water reducer by introducing polyamine side chains. Therefore, compared to traditional PCE water-reducing agents, PCA molecules show stronger interaction with water molecules.

The diffusion behavior of molecules in the system will also be affected by the interaction between molecules, and this effect will also cause different rheological properties of the solution. From this study, it is easy to know that the diffusion coefficient of polycarboxylate ether in solution is the largest, followed by the naphthalene-based water reducing agent. The smallest is the polyamine water reducing agent. PCA moves slowly in an aqueous solution due to more hydrogen bonds between water-reducing agents and water molecules. The intermolecular interactions, like H-bond, limit the migration of PCA. From another perspective, water molecules in the system are also trapped by PCA. As mentioned above, PCA has the strongest interaction with water molecules among the three water reducing agent molecules studied, so the migration of water molecules in the PCA system is also the most difficult.

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