The Optimal Design on the Molecular Structure of a Fluid Transport Inhibitor Applied to Reinforced Concrete Structures

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ABSTRACT: Inhibiting the penetration of water molecules and aggressive ions is of considerable significance in improving the durability of reinforced concrete structures. In this work, molecular dynamics (MD) is employed to design a high-efficiency organic fluid transport inhibitor. MD results indicate that there is mutual complementation between the hydrophilic and hydrophobic functional groups in the chemical structure of this polymer. One end with the carboxyl groups can stably adsorb on the surface of the cementitious matrix due to the strong attraction from calcium ions. Simultaneously, the rest of the hydrophobic part of the polymer can stand up to maximize the repelling effect on the penetration of fluids. Furthermore, for high cost-effectiveness performance, the minimum number and the optimum position of the carboxyl groups of one polymer inhibitor have been determined. As the molecular structure contains two hydrophilic groups, only if located at the same end, the polymer chain can display the most preferable adsorption morphology.

1. INTRODUCTION

The transport process of water and ions is vital to the overall performance of a porous matrix. Especially for concrete, the most widely used building material, the penetration of fluids throughout its hierarchical pore structure highly affects the mechanical properties, durability, and volume stability of this porous material, for example. The rapid transport of water and chloride ions may decrease the frost and corrosion resistance of concrete, respectively, as subjected to the cold and marine environment. Therefore, it is of great significance to improve the impermeability of the cementitious matrix.

Numerous pieces of literature show that organic coatings, polymer cement coatings, or internal polymer modification can enhance the impermeability of concrete. In addition, glass powder, metakaolin, slag, and other mineral admixtures can reduce the permeability of chloride ions throughout concrete. Incorporation of nanosilica, self-healing microcapsules, polypropylene fibers, expanded polystyrene, and other substances can also inhibit the rapid transport of aggressive ions by reducing the size and number of macropores. A new type of self-compacting antiseepage and anticracking concrete was developed by using an expansion agent instead of equivalent cement. However, although the measures above can effectively eliminate the macropores and heal the macrocracks, few contributions have been made to address the transport of fluids into nanochannels within calcium silicate hydrates (C-S-H), which is believed to largely determine the overall impermeability of concrete.

Calcium silicate hydrate gels, as the main hydration products of ordinary Portland cement, contribute large numbers of small gel pores and capillary pores to the concrete matrix. Recently, several kinds of nanomaterials and polymers have been added into the cementitious matrix to block the C-S-H gel pores. Since 1978 in the United States, polymer emulsion-modified concrete has been the main protection system for bridge decks, reducing the intrusion of harmful media. Li Luan et al. found that multiwalled carbon nanotubes (MWCNTs) enhance the impermeability of cement-based composites. The Ohama model points out that the cement-hydrated cementitious material is connected to the polymer, which changes the internal structure of the concrete. Small molecules will gradually connect and fill the internal structure of concrete. Su et al. found that the polymer will adhere to the cement paste or even the surface of the aggregate. The polymer film restricts the development of pores and greatly improves impermeability. So far, some nanohydrophobic agents, made from low-molecular-weight polymers with the functional groups of silane or carboxyl, have been invented to limit the transport of fluids through these nanochannels. It is reported that these agents can stably

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adsorb on the surface of nanopores by covalent or ionic connections, which block the effective transport path of fluids. However, direct evidence on this nanoscale mechanism is still missing due to the resolution limitations of laboratory equipment.

Molecular dynamics (MD), a numerical computation method based on force fields, can serve as a bridge between macroscale experimental outcomes and the nanoscale theoretical mechanisms. The transport of fluids, the configuration of polymer chains, and interfacial interaction details can be unraveled by MD simulations. It has been widely used in the fields of computational chemistry, materials science, and biophysics. Yang et al. used molecular simulation to study the transport mechanism of water and chloride ions within C-S-H nanopores and declared that C-S-H exhibits a hydrophilic surface. Zhou et al. studied a polymer-based C-S-H nanopores and declared that C-S-H exhibits a hydrophilic surface.

In this work, molecular dynamics was utilized to optimize the chemical structure of polymers, as such to design a highly cost-effective fluid transport inhibitor. The transport process of sodium chloride aqueous solution throughout a nanometer-sized C-S-H channel was simulated, while chain polymers were placed into the channel to investigate the inhibiting effect of organic agents. Moreover, the influence of the number and position of the −COO⁻ group on the inhibiting efficiency of the chain polymers was also taken into consideration. The interaction mechanisms among fluids, the C-S-H surface, and the polymers during the transport process were unraveled by a comprehensive analysis of the atomistic trajectories from MD simulations.

2. RESULTS AND DISCUSSION

2.1. The Transport Process of Water and Ions in Nanopores. The transport screenshots of water and ions in the C-S-H/polymer composite nanogel pores at 100, 500, 800, and 1200 ps are shown in Figure 1. The gray parts in Figure 1 are the polymers incorporated in the gel pore. In the first 100 ps transmission process, few differences occur among each model, but in the subsequent period, the transmission process of the model with the premixed polymer in the channel slows down. The P1 model lags slightly behind the blank control group, while for the three groups of P2–P4 models, it can be observed that the transmissions significantly lag behind the control group after introducing polymers. Since the polymer is not fixed on the surface of the gel pores in advance, the polymer also moves with the fluid when the fluid penetrates the end of the pore due to capillary adsorption. At 1200 ps, the fluid in the blank control group has arrived at the end of the pores, while that in the P1–P4 model does not fill the entire pore, and the filling rates of the P2–P4 pores are all around 64%. According to the transport screenshots of the fluid in the channel, when there are two or more −COO⁻ groups, it shows a preferable water-blocking performance.

Figure 2 shows the changes in the penetration depth of water molecules, Na⁺ ions, and Cl⁻ ions over time under the five groups of models. Using the penetration depth curve can better reveal the differences of fluid transmission in each gel pore. The penetration depth was calculated by counting the positions of frontier molecules. In order to eliminate random effects, the Y coordinates of the first 10 water molecules and the Y coordinates of the first three ions in the simulation process were respectively counted, and the average values were taken as the penetration depth of water and ions. As shown in Figure 2, at the same time, the blank control group has the largest penetration depth value followed by the P1 model, the three groups P2–P4 have the smallest penetration value, and the three are in a similar range. At 1500 ps, the fluid in the blank control group has passed over the end of the channel faster than the other groups. From the penetration curves, it can be seen that the penetration depth of each model is similar in the first 100 ps. In the subsequent simulation period, the relationship of penetration depth is none > P1 > P2 (P3 and P4). The penetration rate of the model doped with a polymer is significantly affected. The interaction between polymers, ions, and the surface during the transport process will be further described later.

2.2. Structure of the Polymer Confined in the Pores of the C-S-H Gel. The water-blocking effect of P2 and P4 is not much different, but P4 has more hydrophilic groups. Here, we have made an investigation on the morphology of the two in the gel pores. In the process of transport simulation, the adsorption state of the P2 and P4 polymers in the channel is shown in Figure 3. Among them, the gray chains represent polymer chains in the pores, and cyan rods represent water molecules. Combining the Y−Z plane and X−Z plane views of various polymer models, the polymers mostly adhere to the surface of the substrate in the form of unfolded chains near the C-S-H surface. From the gray polymer chains in Figure 3a, it can be observed that when the number of the −COO⁻ group is two, as it can be stably adsorbed on the surface for a long time, it has a good hydrophobic form and may be stable for a while. We observed that a small part of the chain was folded because the polymer chain itself was relatively soft, but from the X−Z direction view, it can be observed that the hydrophobic area did not decrease significantly. From part of the gray polymer chains in Figure 3, from their Y−Z plane view, it can be seen that near the liquid surface where the fluid invades, the whole polymer chains tend to extend to the middle of the channel and stand upright in the gel channel to hinder the advancement of the fluid to the greatest extent. When the polymer is in this state, it exerts the most significant effect and prevents the capillary adsorption and intrusion of water. Meanwhile, Figure 1 shows that the polymer will move synchronously with the fluid. As a result of this synchronous movement, there are a few polymers that are in an
amorphous state instead of the abovementioned optimal water-blocking state in Figure 3.

In order to study the interaction between the polymer and the C-S-H surface, the radial distribution function (RDF) of the oxygen (Op) in the $-\text{COO}^-$ groups and the matrix surface calcium (Caw) was calculated. Figure 4a shows the Caw–Op RDF curve. The first peak of the RDF is at 2.65 Å, which represents the length of the chemical bond of calcium–oxygen. The Caw ions on the surface are connected to the silicon chains in C-S-H through Ca–O (nonconnected oxygen in the matrix), so the polymer and the matrix are chemically bonded through O–Ca–Op. As shown in Figure 4b, the gray chain is the P2 polymer near the surface of the C-S-H matrix, the green balls are surficial calcium ions, and the yellow-red sticks are the C-S-H matrix. The polymer is adsorbed on the surface of the matrix by bonding with calcium ions, this is the visual interpretation of Figure 4a. In addition, it can be observed from Figure 4a that as the number of $-\text{COO}^-$ increases, the interaction with the interface weakens to a certain extent. This is because the $-\text{COO}^-$ groups are more likely to interact with water molecules in the solution to form hydrogen bonds. We will discuss this in detail in the following content.

From Figures 1 and 2, they point out that when the number of $-\text{COO}^-$ groups of the incorporated polymer is 1, it has a certain blocking effect on the penetration of water molecules and chloride ions into the nanopores, but it is inconspicuous. Further, the blocking effect on fluids gets promoted significantly, as the number of $-\text{COO}^-$ groups increases to 2. Interestingly, the blocking effect does not improve again, although the $-\text{COO}^-$ group continues to increase. As shown in Figure 4a, for the P4 polymer, Caw and Op also exist in the first sharp peak near 2.65 Å and show preferable spatial correlation, at the situation of four $-\text{COO}^-$ groups, which can contribute to the increase in polar groups. Nevertheless, Figure 5a shows the RDF curves of the oxygen atom in the $-\text{COO}^-$ group and the hydrogen atom (Hw) in the water molecules. The RDF curves of Hw–Op have a peak at 1.85 Å, which indicates that the $-\text{COO}^-$ group in the polymer chain can form a hydrogen bond with water molecules. Moreover, from P1 to P4, the peak value gradually increased, indicating that with the increase in the number of $-\text{COO}^-$, the possibility of bonding between Op and Hw gradually increased. More Op appears around Hw that is, polymer molecules are more inclined to interact with the aqueous solution so that a more ideal inhibitory effect is not obtained. It can be seen from Figure 5b,c that the hydrophilic end and the hydrophobic end are uncoordinated. Due to the short length of the hydrophobic end, it is difficult to extend itself to achieve a strong water-blocking effect, more likely to be scattered in the solution. Figure 5d shows the specific minute structure diagram of the P4 polymer and water molecules. The polymer in the gel pore sometimes adsorbs and interacts with the matrix and sometimes desorbs and interacts with water molecules. Although it is equipped with much high-polarity $-\text{COO}^-$ groups, it cannot achieve a more ideal water-blocking effect. Thus, it can be seen

![Figure 2. Penetration depth of (a) H$_2$O, (b) Cl$^-$, and (c) Na$^+$ changing with time.](image)
that the polymer with two polar groups has a good coordination
effect. This is sufficient to inhibit fluid intrusion to a great extent,
and more $-\text{COO}^-$ groups have little effect.

In order to study the interaction between surface atoms and
ions in the solution after incorporating a polymer, the RDFs of
nonconnected oxygen atoms $O_s$ in the matrix and the $\text{Na}^+$ in
the solution and the chloride ions (Cl) and sodium ions (Na) are
drawn, as shown in Figure 6. The RDF can be described as the
ratio of the local density to the average density of the system.
The largest peak of the RDF of $O_s$–$\text{Na}$ in Figure 6a appears near
2.35 Å. The corresponding peak value of the P1–P4 model is
lower than that of the blank control model (none), as the
incorporation of a polymer slows down the intrusion of fluids
and reduces the local density. Meanwhile, the RDF of Cl–Na in
Figure 6b also exhibits similar characteristics. Due to the
incorporation of a polymer, the water intrusion is delayed, and
the local density of the atom is relatively reduced.

The interaction energy between the polymer and interface
structure atoms, as well as between the polymer and solution
water molecules, can reflect the state of inhibitor molecules of
different structures in the simulation system. As shown in Table
1, in the four simulation systems P1–P4, as the number of
$-\text{COO}^-$ increases, the interaction energy between the polymer
and the interface structure atoms and the solution water
molecules increases, which is attributed to the strong polarity of
$-\text{COO}^-$. As the number of $-\text{COO}^-$ groups increases, the
interaction energy of P/water is gradually higher than that of P/
C-S-H. This is consistent with the results obtained in Figures 4a
and 5a. The connection between the polymer and C-S-H is
weakened, and it tends to interact with water instead. Therefore,
when the number of $-\text{COO}^-$ increases, the suppression
efficiency has not been further improved.

2.3. The Dynamic Properties of Fluid Transport in the
C-S-H Channels. It can be observed from the above analysis
that the incorporation of polymers can hinder the intrusion of
fluids, thereby weakening the connection between ions and
the interface to a certain extent. The time correlation function
(TCF) can be used to evaluate the stability of the bond between
the positions of the atoms vary from moment to moment. Mean square displacement (MSD) is one tool to monitor the migration of various atoms in the system. Figure 8 displays the mean square displacement (MSD) of water molecules (water molecules represented by O_w in water), chloride ions, and sodium ions in the control group and each experimental group. In the first 200 ps, the MSD of each atom almost overlaps. After 200 ps, the MSD value of each atom begins to differ, and a significant change occurs until 500 ps. In Figure 8, no matter what kind of element, all satisfy MSD (none) > MSD (P1) > MSD (P2) ≈ MSD (P3) ≈ MSD (P4). The slope of the MSD curve is directly proportional to the diffusion coefficient D, and the slope of the mean square displacement versus time curve is 6D. The greater the MSD value, the greater the slope of the curve, indicating its movement, and the faster the diffusion rate. The velocity of the fluid slows down with the incorporated polymer, especially the experimental groups containing two or more −COO− groups in the polymer chain. The increase in the MSD value of various atoms slows down, which indicates that the movement of the fluid is significantly inhibited. As shown in Figure 8, no matter what kind of element, in each system, the MSD values increase proportionally with time, that is, there is no obvious fluctuation in the slope, indicating that the migration process is relatively stable. This shows that the introduction of the polymer weakens the diffusion rate of the fluid and limits the capillary transport of the fluid in the gel pores. The P3 and P4 models show similar characteristics to the P2 model. Their MSD curves almost overlap, but they are always lower than the none and P1 models.

2.4. Evaluation of Polymer-Based Nanomaterials. For the results of the above simulation, nanomaterials based on the molecular configuration of P1 and P2 were synthesized. The composition of the cement paste is relatively simple, and the water absorption experiment in the paste system can better reflect the role of synthetic polymer-based nanomaterials. Therefore, through the water absorption experiment under the pure slurry system, the effect of inhibiting water transmission was evaluated. As shown in Figure 9, in the system after adding P1 and P2, the water absorption rate of cement is greatly reduced, satisfying none > P1 > P2. The initial water absorption in the P1 system is about 1.5%, which is higher than 0.8% in the P2 system. As the immersion time increases, the water absorption rate of the P2 system always remains very low and finally stabilizes at about 2.8%, which is far lower than 13.8% in none. This confirms that the incorporation of polymer-based nanomaterials with the P2 molecular configuration effectively inhibits the transmission of water molecules in cement-based nanopores, and it is superior to nanomaterials synthesized based on the P1 molecular configuration.

3. CONCLUSIONS
In this work, several polymer chains with different chemical structures were designed, and MD was employed to evaluate their fluid transport inhibiting efficiency in the nanopore of a C-S-H matrix. Moreover, it was demonstrated through experiments. The following conclusions can be obtained:

(1) The incorporation of polymers in the nanopore can hinder the intrusion of water to a certain extent and delay the dynamic migration of fluids. It is attributed to the hydrophilic and hydrophobic groups grafted on the polymer. The deprotonated carboxyl groups can tightly adsorb on the C-S-H surface based on the O_w−Caw

Figure 4. (a) Radial distribution function of the calcium atoms on the C-S-H surface and the oxygen atoms in the deprotonated carboxyl groups in the polymer and (b) snapshot of the interface between the P2 and the C-S-H surface.
connections on the interface, which limits the free movements of polymers. Meanwhile, the hydrophobic end with the alkyl group extends outward and stands perpendicularly to the interface plane, which maximizes the water-blocking effect.

(2) The influence of the number of hydrophilic groups for each polymer on the fluid transport inhibiting efficiency is
evaluated, which obeys the following order: none < P1 < P2 ≈ (P3/P4). The inhibiting efficiency will increase with the increase in the number of contained hydrophilic groups due to a stronger adsorption configuration. However, the increment approaches 0 once the number is over 2. Since the total length of the polymer chain is fixed, more carboxyl groups will lead to the decrease in effective hydrophobic groups, which weaken the fluid’s transport inhibiting effect. Therefore, the optimal number of hydrophilic groups for each polymer is determined to be 2 when considering the synthesis cost. Furthermore, in the presence of the P2 polymer, the atom pairs of sodium and chloride ions both in the solution and the interface become unstable due to the attracting effect on the cations from polar functional groups of polymers.

The interaction mechanisms among polymers, the C-S-H matrix, and fluids, interpreted in this work, may help design a highly cost-effective agent, which can substantially inhibit the transport of water and aggressive ions throughout the nanopores of C-S-H gels and therefore considerably improve the durability of reinforced concrete structures.

4. METHODOLOGY

4.1. Model Construction. To study the transport process of water and ions in the gel pores when polymers exist in concrete, a transport model was established based on the literature. The initial unit cell of C-S-H with a Ca/Si of 1.7 was used as a cement matrix to construct ideal gel pores. As shown in Figure 10a, to produce a channel with a width of about 5.8 nm and a length of about 8.9 nm, the initial C-S-H model was subjected to supercell expansion treatment and cut along the (001) direction. The surface of the gel pores was handled to balance the charge of the entire system. Then, the liquid phase was created with the composition of 1 mol/L NaCl aqueous solution (6592 water molecules, 118 chloride ions, and 118 sodium ions). The size of

| interacting part | interaction energy (kcal/mol) |
|------------------|------------------------------|
| P1/C-S-H         | −125.085                     |
| P2/C-S-H         | −163.710                     |
| P3/C-S-H         | −253.543                     |
| P4/C-S-H         | −307.104                     |
| P1/water         | −112.277                     |
| P2/water         | −172.106                     |
| P3/water         | −257.473                     |
| P4/water         | −316.087                     |
the liquid phase was 21.6 Å × 100 Å × 91.26 Å, and the density was about 1.04 g/cm³. The liquid phase was placed below the substrate in light of Figure 10a. The polymer models were used to study the influence of the number of −COO⁻ groups on the efficiency of blocking the fluid. As shown in Figure 10b, the four polymers (P1–P4) contained 1–4 −COO⁻ groups, respectively. The clusters were all located at one end of the entire polymer chain, and the chain lengths of the four polymers were the same. Four strings of each polymer were placed in the gel pore and unconnected to the surface; in this case, the polymer concentration was about 0.04 mol/L, which accounted for about 1.7% of the mass of C-S-H. The simulations of the influence of the number of −COO⁻ groups included five groups of models, namely, the blank control group and the experimental groups mixed with four polymers of P1–P4. In order to prevent the atoms from flying out, a sufficient vacuum layer was set at the end of the gel hole along the Y direction, and the final model size was 21.6 Å × 252.08 Å × 91.26 Å.

4.2. Force Field and MD Procedures. In the following research, the whole system was an organic–inorganic hybrid system. The ClayFF force field was adopted to characterize the interaction between the C-S-H matrix and the atoms in the NaCl solution, while the CVFF force field was used to describe the polymer.45–49 The whole simulation process was carried out in LAMMPS.50 Before the simulation started, the energy of the entire system was minimized to eliminate the influence of an unreasonable configuration. The entire simulation was carried out in the NVT ensemble at a temperature of 300 K. The simulation process was as follows. First, a water film of about 2 Å along the Y direction at the entrance of the gel hole was fixed. One 500 ps kinetic simulation was done to make the matrix and solution reach a thermodynamic equilibrium state. Subse-

Figure 8. MSD of (a) water molecules, (b) Cl⁻, and (c) Na⁺ in the nanopores under different models.

Figure 9. Changes in the water absorption rate of the cement paste over time.
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was 0.7% (the mass ratio of the unit cement). The solidified size of the cement paste was 40 mm × 40 mm × 160 mm. After curing for one day, it would be demolded and cured for 27 days under the conditions of 20 ± 2 °C and humidity exceeding 95%. After the curing was completed, a water absorption experiment was carried out.

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