

Molecular Dynamics Study of The Structural and Mechanical Properties of Polymer Insertion In Calcium Silicate Hydrate

Abstract

Adding organic polymers is an important means to change the properties of inorganic materials. Calcium silicate hydrate (C-S-H), as the main component of cement-based materials, is particularly important to enhance the mechanical properties. Due to the limitations of experiments, molecular dynamics simulations is used in the study of the structural changes of materials at the atomic level. In this paper, by using molecular dynamics simulation, the hexadecane, octadecane, phenolic resin, and ibuprofen are added to C-S-H respectively, and the changes of structure, dynamic system, and mechanical properties between the polymers and C-S-H were explored at the atomic level. The results showed that all the four polymers interacted with the calcium silicate layer structure inside C-S-H and successfully entered into the internal pores. The four polymers added increased the flexibility and compressive strength of C-S-H. In addition, the ibuprofen added can effectively enhance the ductility of the material. The study in this paper on nanoscale mechanical properties of C-S-H/ polymer composites plays an important role in the modification and design of this material.

1. Introduction

Portland cement is the most widely used building material today, which is used in railway, electric power, road, bridge, military and other fields [1-5]. However, cement-based concrete has poor ductility and is prone to brittle failure under tension and bending. Calcium silicate hydrate is the most important product of Portland cement after hydration, and its content is up to 60-70% [6]. In order to improve the sustainable development and the structure durability of cement materials, it is especially important to study the microstructure and mechanical properties of calcium silicate hydrate.

In order to increase the fracture resistance and durability of cement-based materials, organic polymers have been widely used to modify the property of concrete materials [7-11]. The experimental results show that adding polymer can effectively improve the mechanical strength, tensile strength and corrosion resistance of modified concrete. Hamoush et al. enhanced the mechanical properties and durability of concrete by adding polyvinyl alcohol fiber to concrete [12]. Singh et al. greatly improved the mechanical properties, ductility and plasticity of concrete by adding PEG to it, in which the PEG exists in concrete in flocculation and peeling state [13]. In recent years, adding polymer to C-S-H to modify the property of concrete has received a lot of attention, because it combined the high elasticity and flexibility of the polymer and the heat resistance and hardness of C-S-H. Matsuyama et al. first studied C-S-H/ polymer composites and found that polymers can be inserted between C-S-H layers [14]. Beaudoin et al. studied the effects of adding HDTMA, MB, PEG, PVA, and PAA respectively in C-S-H layers on the silicon polymerization of C-S-H by using ^{29}Si MAS NMR, and effectively improved the volume stability, mechanical properties, and corrosion resistance of C-S-H [15]. Ha et al. performed similar studies by scanning transmission X-ray and microscopy [16]. The experiment shows that the oxygen atom and some functional groups in the polymer form Ca-O bond and hydrogen bond with the silicate, water molecule and calcium ion in C-S-H. The added polymers enhance the hydrogen bond strength in the interface region and can restore the defect of the C-S-H silicate chain [17]. This can

effectively restrain the propagation of crack under tensile load, and improve the bond strength and ductility of C-S-H gel. Due to the amorphous characteristics of C-S-H gel, adding polymer to it increases the complexity of its structure, leading to the structure can't be accurately observed by experimental method [18]. Therefore, the modification of C-S-H gel at atomic level plays an important role, and the modification at atomic level can fundamentally provide a solution.

Molecular dynamics simulations have been applied to the study of interaction of materials at atomic level, as well as the study of organic and inorganic composites [19-23]. The adsorption of some polymers on the C-S-H surface has also been studied using molecular dynamics simulations. Hou et al. studied the effects of surface functional groups on the stability of C-S-H [24]. Zeng et al. studied the conformation and density distribution of clay with polymer inserted [25]. Zhou et al. studied the effects of interlayer polymers on the ductility and mechanical strength of C-S-H under strain and tension in Reaxff [26]. Alkanes are important polymers for energy storage. The intercalation of alkanes into C-S-H has great application values. Some drugs also act as intercalated polymers. C-S-H can act as carriers for drugs, and can also be used in drug transfer and release. Resin polymers have strong adhesion and high insulation, and could potentially enhance these properties for C-S-H. Therefore, simulation of the insertion of alkanes, resins and some drugs in C-S-H and their effects on its properties are particularly important.

In this paper, by means of molecular dynamics simulation, hexadecane, octadecane, phenolic resin and ibuprofen were inserted into the C-S-H layers respectively to study the relationship between structural evolution and mechanical properties. Uniaxial tensile test is used to test the mechanical properties of the system such as Young modulus and volume modulus. In addition, the stress-strain relationship of C-S-H/ polymer system and the effect of polymer on C-S-H at nanoscale are also studied. The study of nanoscale mechanical properties of C-S-H/ polymer composites plays an important role in the modification and design of the material.

2 . Simulation Method

2.1 Selection of force field

In this paper, Materials Studios was used for molecular modeling and dynamic simulation of C-S-H/ polymer composites [27]. In this simulation, Clayff force field was used to simulate C-S-H gel [28]. Clayff force field is widely used in the study of cement-based systems, and can be successfully applied to the simulation of calcium hydroxide, Tobermorite and other calcium silicon systems [29-33]. PCFF force field is used for the study of interlayer polymers, which is widely used in the simulation of organic matter and protein, as well as the simulation of low molecular organic crystals [34-35]. In addition to calculating the interatomic potential energy, the force field parameters can also express the calculation methods of bond length, bond Angle and torsion Angle.

2.2 Modeling

In this paper, the 11A Tobermorite crystal structure proposed by Hamid was used as the original model of molecular dynamics simulation, and 4,2,1 supercells were established in X, Y and Z axes

[36]. Subsequently, the Ca/Si ratio was adjusted from 1 to 1.5, and the silicon chain Q structure distribution consistent with the NMR test was obtained by deleting the silicate chain, which was Q0 ~ 13%, Q1 ~ 67%, and Q2 ~ 20% in turn [37]. After the C-S-H model was established, hexadecane, octadecane, ibuprofen, and phenolic resins were added into the interlayer region of anhydrous dry cells respectively. Subsequently, the Metropolis calculation method of Monte Carlo method was used for the calculation of water absorption of the C-S-H gel and four C-S-H/ polymer composite models [38]. Monte Carlo method is widely used in the calculation of water absorption of microporous and mesoporous materials [39-43]. In this process, water molecules are randomly added, subtracted, moved, and rotated, and are added to the C-S-H model through Metropolis's repeat sampling method to minimize the energy. The molecular formula of C-S-H gel model after water absorption is $(\text{CaO})_{1.5}(\text{SiO}_2)_{1.66}\text{H}_2\text{O}$, which is close to $(\text{CaO})_{1.7}(\text{SiO}_2)_{1.8}\text{H}_2\text{O}$ obtained in SANS test [44]. Finally, the energy minimization calculation of the C-S-H gel and C-S-H/ polymer composite model system was carried out using the NVT ensemble (fixed volume, temperature, and number of particles) of dynamic simulation.

2.3 Calculation of mechanical properties

In this paper, the GULP module was used to optimize the system of C-S-H gel and C-S-H/ polymer composite model, and the Forcite module was used to test the change of mechanical properties. Firstly, relax the C-S-H model by using the NVT ensemble of dynamics simulation in Gulp module, in a step size of 1fs and a total duration of 1000ps. Set the temperature to 298K, and use the Nose-Hoover thermostat to monitor and adjust the temperature, pressure, energy, etc., to maintain system stability. And calculate the static electricity with Ewald method and calculate the VDW force with the atom-based method. Then, calculate the mechanical properties of C-S-H model with Forcite module, by the method of gradually elongating the model along X, Y and Z axes for uniaxial tension, to obtain the stress-strain curves. Meanwhile, measure the Young's modulus, volume modulus and shear modulus of the model along different axial directions to reflect the bonding strength between atoms.

3.1 Model verification

Figure 1 shows the C-S-H crystal model established in this paper and the model with polymer added. In order to verify the authenticity and rationality of the model in the experimental test, XRD was used to test the characterization of the model structure, and to compare with the actual pdf card. Figure 2 (a) shows the XRD spectrum of the C-S-H model established in this paper, and its characteristic peak values in the interval of 0° to 45° are roughly 5.9° , 18.6° , 23° , 29° , 30° , 31.8° , 33° and 39° . Zhou et al. measured the XRD spectrum of C-S-H gel in different Ca/Si ratios through experiments, as shown in Figure 2 (b) [45]. The Ca/Si ratio of the C-S-H model established in this paper is 1.5, which is consistent with the XRD spectrum measured in the experiment (blue curve). It can be seen that the C-S-H model established in this paper is consistent with the C-S-H molecular structure of the synthesis experiment.

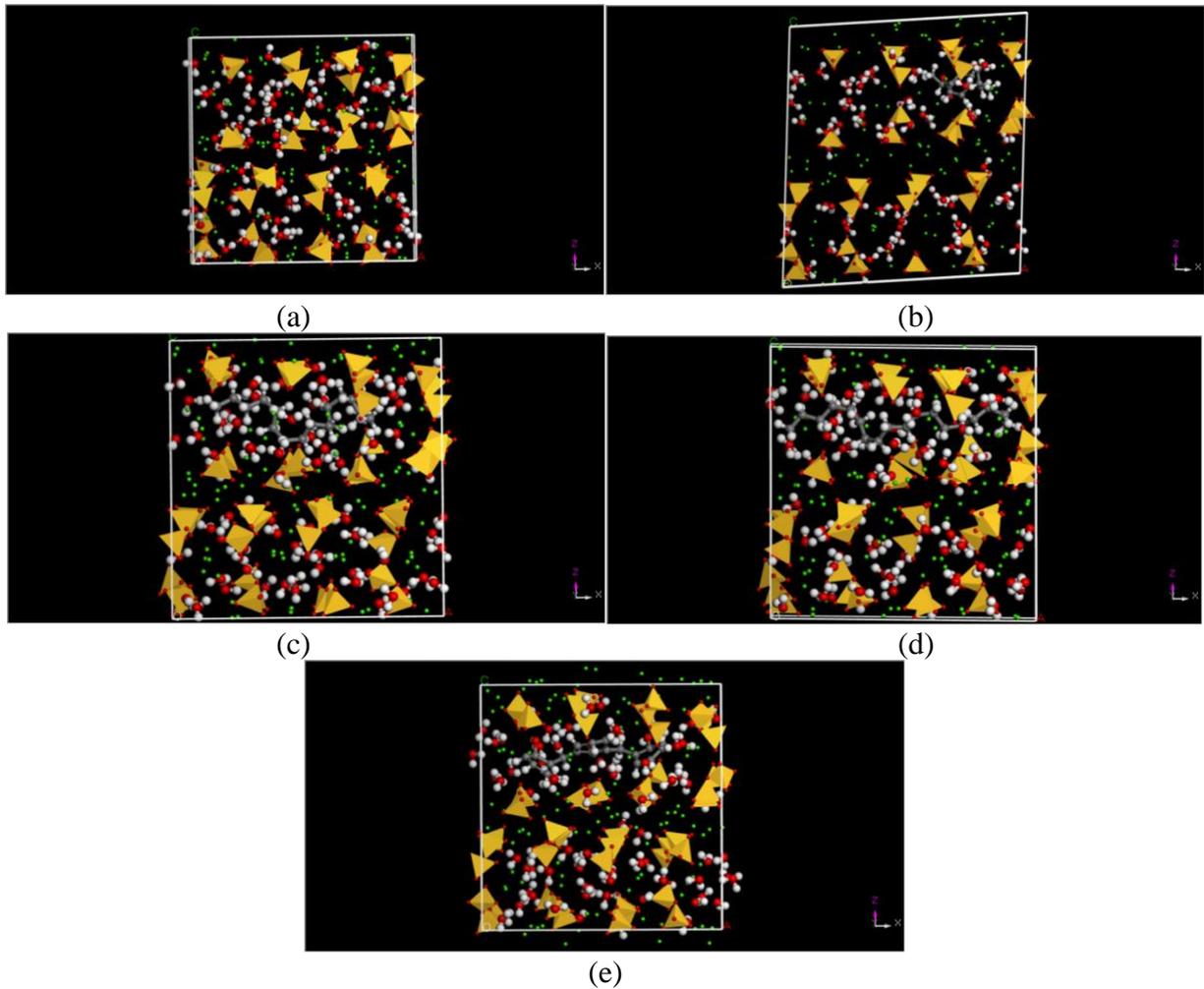


Figure 1. Structure Models of C-S-H and Interlayer Polymer Inserted: (a) Pure C-S-H crystals (b) C-S-H/ ibuprofen (c) C-S-H/ hexadecane (d) C-S-H/ octodecane (e) C-S-H/ phenolic resin. In which, the grey balls are carbon, the red balls are oxygen, the white balls are hydrogen, the green balls are calcium, and the yellow polygons are silicon oxygen tetrahedron.

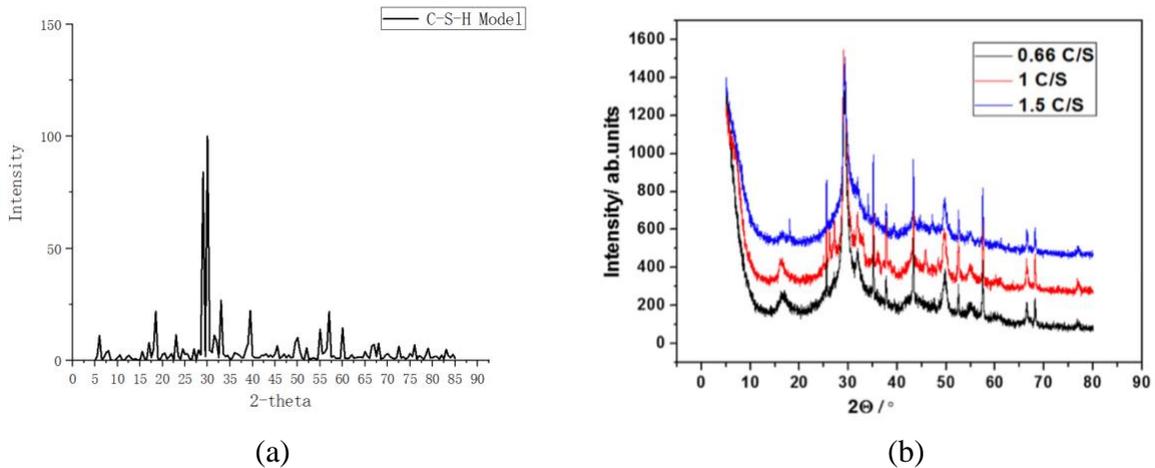


Figure 2. XRD Comparison (a) Pure C-S-H XRD spectrum established in this paper with a Ca-Si ratio of 1.5 (b) XRD spectrum obtained in the experiment with a Ca-Si ratio of 1.5 (blue curve)

3.2 Evolution of model structure

3.2.1 C-S-H sandwich structure

Figure 3 shows the intensity distribution of different atoms perpendicular to the bottom plane along the (0 0 1) direction. Figure 3 (a) shows the atomic distribution of pure C-S-H, where the density distribution of calcium and silicon atoms presents a relatively ordered sandwich-like structure, indicating the arrangement of calcium silicate layers. The calcium atoms in C-S-H can be divided into the calcium atoms in the calcium silicate layer and the calcium atoms between the layers. It can be seen from the figure that the interlayer calcium atoms and the calcium silicate layers are distributed alternately. In the interlayer region in Figure 3(a), a high intensity of interlayer calcium atoms can be seen. After the addition of the polymer, the ordered structure of pure C-S-H was disturbed. Figure 3(b) shows the atomic distribution of C-S-H with interlayer hexadecane added. It can be seen from the figure that the intensity of the polymer is distributed between 13A and 19A, while the interlayer distribution of C-S-H is between 14A and 18A, indicating that the polymer partially entered the pore defect of C-S-H and interacts with the calcium silicate layers in it. In addition, it can be seen that the distribution of calcium and silicon atoms in the calcium silicate layer changed from sharp to wide, and the peak of strength also decreased. This means that with the addition of the polymer, the ordered structure of the calcium silicate layers in C-S-H is disturbed to a certain extent. As the polymer enters the internal defect of C-S-H, it forms chemical bonds with water molecules and calcium atoms, leading to structural changes in the calcium silicate layers. Figure 3(c), 3(d), and 3(e) show the strength distribution of atoms of C-S-H with octadecane, phenolic resin, and ibuprofen added respectively. It is worth mentioning that in Figure 3(e), the position of calcium silicate layers of C-S-H changed from the original 14A - 18A to 19A - 23A. This suggests that the addition of ibuprofen causes a change in the whole lattice size of C-S-H. Figure 4 shows the length of lattice of pure C-S-H and C-S-H with polymer added along the Z-axis. It can be concluded that the addition of ibuprofen did increase the length of lattice along the Z-axis, while the addition of other polymers did not change the size of the C-S-H lattice.

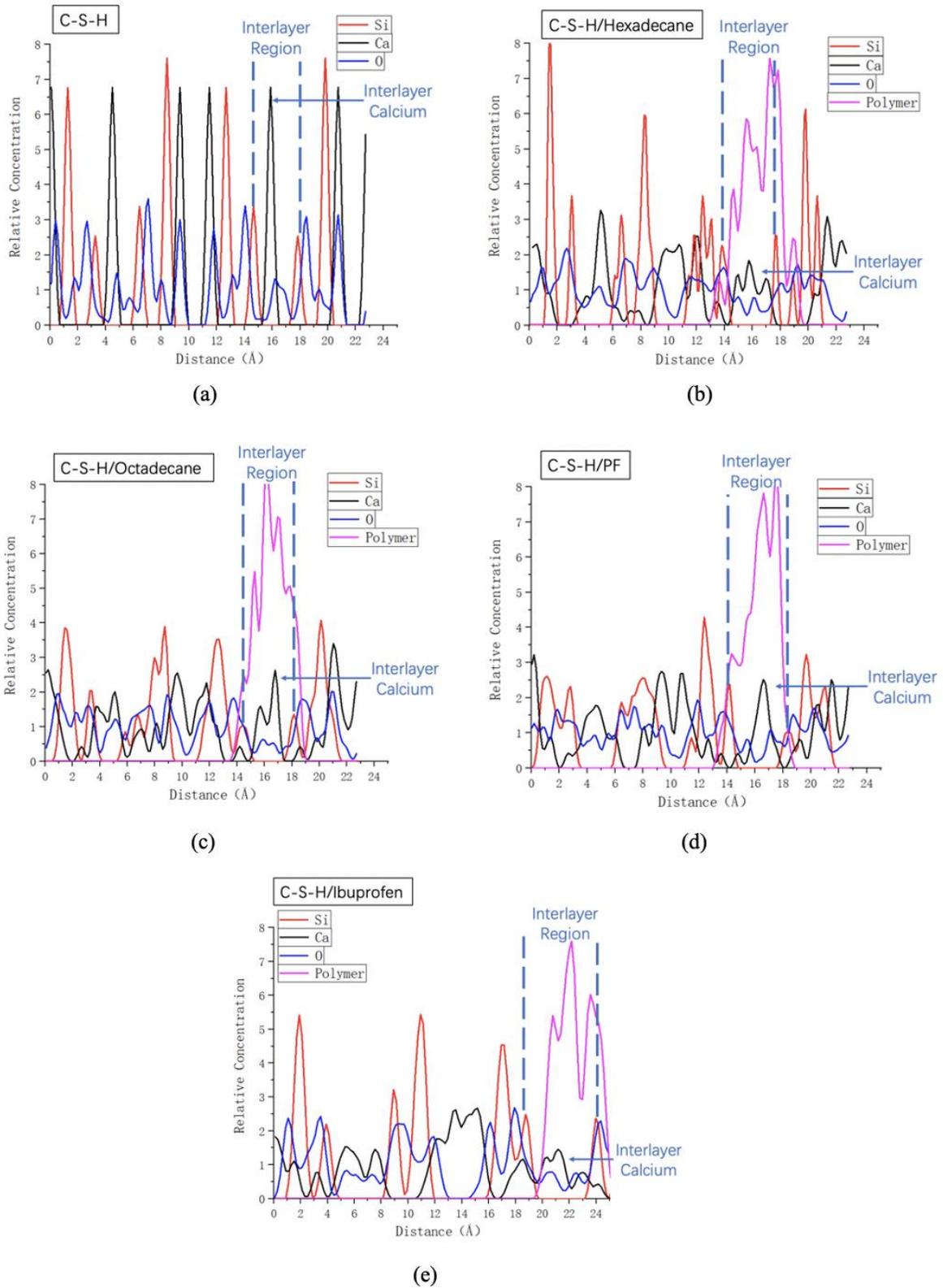


Figure 3. Density Distribution of Silicon, Calcium, Oxygen, and Polymers (a) Pure C-S-H crystals (b) C-S-H/ hexadecane (c) C-S-H/ octadecane (d) C-S-H/ phenolic resin (e) C-S-H/

ibuprofen.

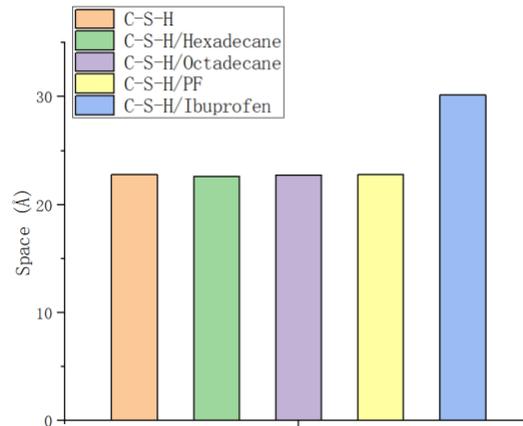


Figure 4. Lattice Length of Pure C-S-H and C-S-H Polymer Composites Along the Z-Axis

3.2.2 Interactions between polymers and C-S-H

The interactions between polymer and C-S-H can be indicated by the radial distribution function. Figure 5 shows the comparison of radial distribution functions of C-S-H and its different polymer composites. According to the figure, the RDF function peaks of C-S-H are 1.05 Å, 1.55 Å, and 2.55 Å, while the RDF peaks of C-S-H/ polymer composite are 0.95 Å, 1.55 Å, and 2.85 Å. The deviation of the peak value indicates that the polymer added between the layers interacts with the calcium atoms inside C-S-H. As shown by Figures 6(a), 6(b), 6(c), and 6(d), the C-S-H interacts with the interlayer hexadecane, octadecane, phenolic resin, and ibuprofen added respectively. According to Figure 6(a), 6(b), 6(c), and 6(d), the interaction between C-S-H and the interlayer hexadecane, octadecane, and phenolic resin added is dominated by the VDW force between the polymer and a large number of calcium atoms and a small amount of silicate. In addition, alkanes could not form hydrogen bonds, while phenolic resins did form weak hydrogen bonds with water molecules in C-S-H. Compared with other groups, C-S-H interacts less with ibuprofen, and the water molecules do not form stable hydrogen bonds with ibuprofen.

In the four different C-S-H/ polymer composite systems, the polymers can interact with the calcium atoms in the interlayer calcium atoms and the calcium silicate layer. This also confirms the phenomenon shown in Figure 3 that the interlayer polymers enter the internal pores and defects of C-S-H, and interact with calcium atoms, leading to the disruption to the ordered structure. In the four groups of models, the interactions are ranked as octadecane > phenolic resin > hexadecane > ibuprofen from the largest to the smallest. The main reason may be that the octadecane has larger molecular weight which leads to the larger dispersion force, so it has a greater interaction with the adjacent silicate and calcium atoms. Phenolic resin can also form hydrogen bonds with neighboring water molecules while featuring higher molecular weight. In comparison, ibuprofen lacks these features, so its interaction with C-S-H is impacted.

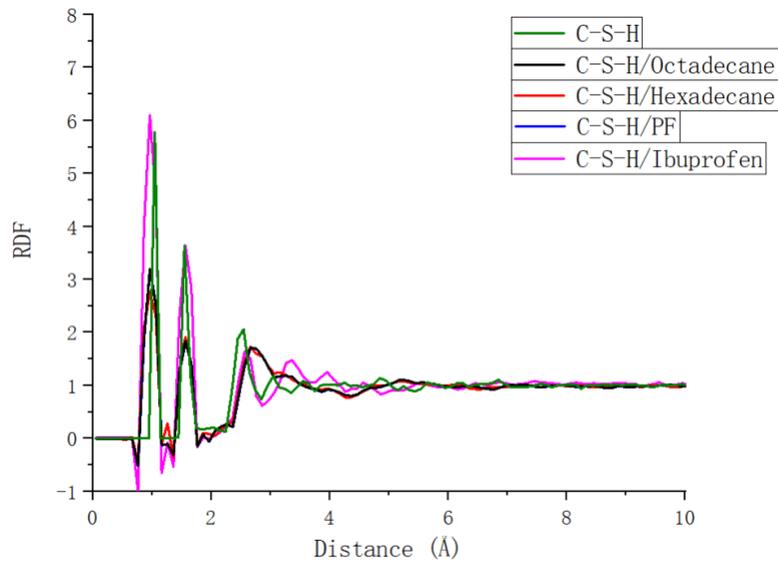


Figure 5. Radial Distribution Curve of Pure C-S-H and Its Polymer *Composites*

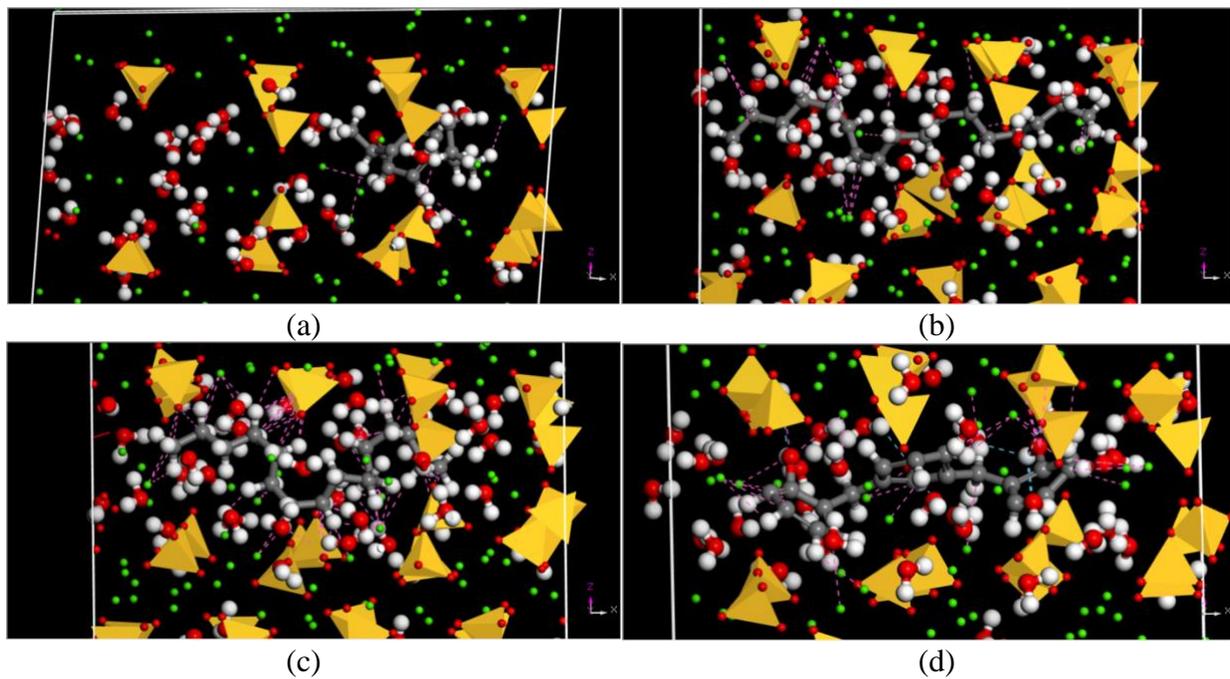


Figure 6. Interactions between polymers and C-S-H (a) C-S-H / ibuprofen (b) C-S-H / octadecane (c) C-S-H / hexadecane (d) C-S-H / phenolic resin. In the figure, the gray ball represents carbon, the red ball represents oxygen, the white ball represents hydrogen, the green ball represents calcium, and the yellow polygon represents silicon oxygen tetrahedron.

3.2.3 Dynamic system change

In this paper, the mean square displacement is used to describe the dynamic variation of the system, and the intermolecular motion can also indicate the stability of the chemical bonds between molecules. Figure 7 shows the mean square displacement curve of C-S-H/ polymer

system. Figure 7(a) shows the changes of calcium, silicon, oxygen in water molecules and polymer MSD as the time increases in C-S-H/ phenolic resin system. It can be seen from the figure that the changes of MSD of silicon atom are very small, indicating the relatively stable skeleton structure of C-S-H. The changes of MSD of calcium atoms and water molecules are great, indicating that they are subject to larger dynamic effect after the addition of polymer. Fig. 7(b) shows the MSD curves of different C-S-H/ polymer systems. As shown in the figure, the liquidity of C-S-H/ ibuprofen system is very high, while the liquidity of the other three systems is similar. This is related to the weaker interaction between C-S-H and ibuprofen discussed in the previous section. In comparison, hexadecane, octadecane, and phenolic resins interact strongly with C-S-H, which limits their fluidity.

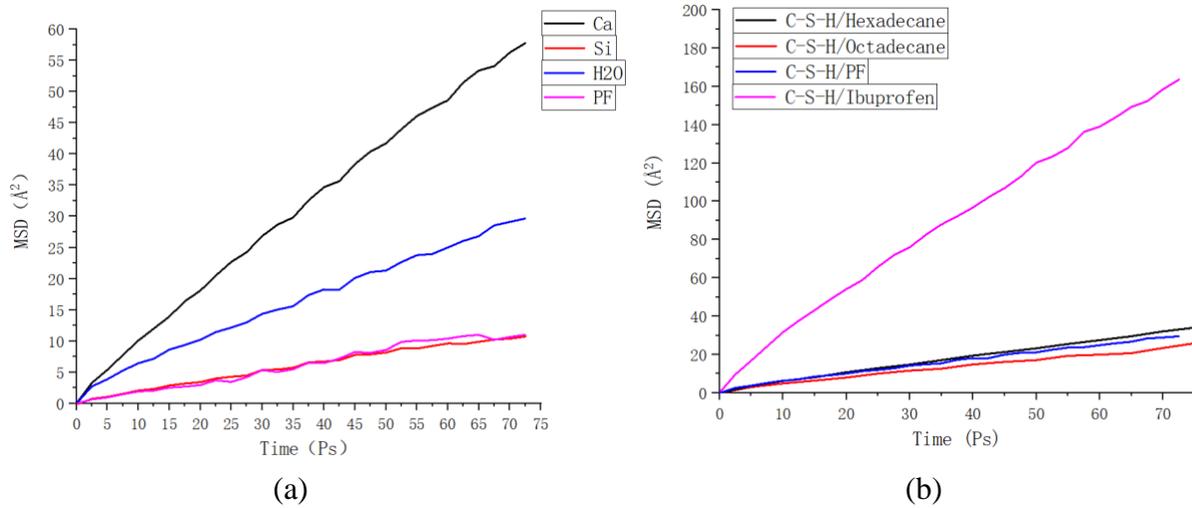


Figure 7. MSD evolution (a) calcium, silicon, water, and polymers in C-S-H/ phenolic resin system (b) Different C-S-H / polymer systems

3.3 Mechanical property test

3.3.1 Stress-strain test

In order to test the mechanical properties of C-S-H, the stress-strain of C-S-H/ polymer composites is measured by uniaxial tensile test. Due to the anisotropic crystal structure of C-S-H, the tension in different axial directions will have different effects on the structure. According to previous studies, C-S-H is most vulnerable to structural damage under tension due to its weak chemical bond along the Z-axis [46]. Therefore, this paper studies the mechanical properties of C-S-H under the tension in Z-axis. Figure 8 shows the stress-strain curves of pure C-S-H and different C-S-H/ polymer systems under the tension along the Z-axis. As shown in the figure, the curve of pure C-S-H under tension can be divided into three stages, that is, the stress rapidly rises to 2.5GPa under the strain from 0 to 0.05, the stress slowly drops to 1.5 GPa under the strain from 0.05 to 0.1, and finally the stress rapidly drops under the strain from 0.1 to 0.12. It can be seen from the figure that adding ibuprofen to C-S-H can effectively prolong the second and third stages of the tension process. In conclusion, adding ibuprofen can effectively improve the ductility of C-S-H. However, the stress-strain curves of other C-S-H/ polymer systems did not change significantly.

3.3.2 Test of Young modulus, volume modulus, and shear modulus

In order to better characterize the mechanical properties of the model, Table 1 shows the Young modulus, volume modulus, and shear modulus of pure C-S-H and C-S-H/ polymer composites. It can be seen from the table that adding hexadecane, octadecane, phenolic resin, and ibuprofen to C-S-H can reduce the Young modulus of the system, and increase the flexibility and reduce the brittleness of C-S-H. And all the additives increased the bulk modulus of the system and effectively improved the compressive strength of C-S-H. In addition, except for octadecane, all other polymers affected and reduced the shear modulus, and enhanced the flexibility of C-S-H. Adding octadecane to C-S-H increased the shear modulus, rigidity and hardness of C-S-H. According to the above mechanical property tests, adding interlayer resins, alkanes and ibuprofen drugs to C-S-H can increase the flexibility and compressive strength of the material, and adding ibuprofen can effectively improve the ductility of the material.

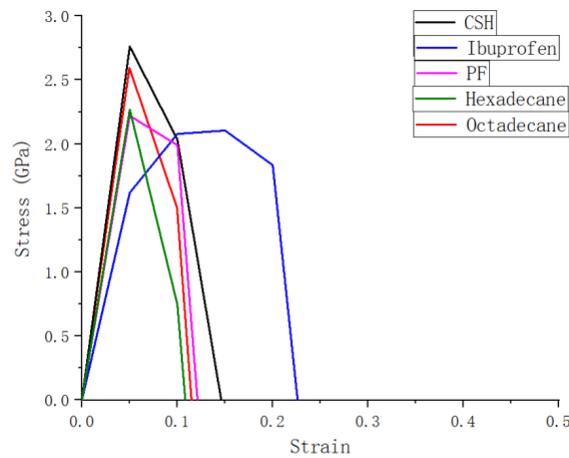


Fig. 8. Stress-strain Curves of Pure C-S-H and Its Polymer Composites Under Tension Along Z Axis.

	Young's Modulus (GPa)- z	Bulk Modulus (GPa)	Shear Modulus (GPa)
C-S-H	29.28	2.16	6.42
C-S-H/Hexadecane	6.58	4.14	3.20
C-S-H/Octadecane	24.15	41.16	8.26
C-S-H/PF	18.23	20.86	5.61
C-S-H/Ibuprofen	19.03	3.64	1.99

Table 1. Young Modulus, Volume Modulus, and Shear Modulus of Pure C-S-H and Its Polymer Composites Measured Under Tension Along Z Axis.

3.4 Discussion on mechanism

Adding polymers to C-S-H is closely related to the modification of C-S-H structure and the change of the microstructure. As mentioned in the previous section, the added polymers can affect the ordered interlayer structure of C-S-H and can form an interaction force with the interlayer calcium silicate layers and water molecules. In order to better study the influence of the interaction force between polymers and C-S-H on the mechanical properties of the material, the study was conducted from the atomic level. Figure 9(a) and 9(b) show the atomic structures of pure C-S-H

and C-S-H/ ibuprofen composites at low and high strain levels respectively. As shown in Figure 9(a), under strain, the pure C-S-H gradually lost the order interlayer arrangement, and finally the calcium silicate layer structure collapsed. The C-S-H/ ibuprofen composite system also has a great change in the layer structure under strain, but the layer structure can remain relatively intact. Under a small strain, the initial chemical bond between the polymer and C-S-H was broken and microcracks between the layers began to occur. The interlayer cracks expand under higher strains. It can be seen from the figure that the polymer can still form chemical bonds with the internal system of C-S-H, even if the structure of the composite system has dramatic changes under the strain. And it can be observed that the polymer undergoes rotation and torsion under this action. This indicates that the polymer can have a certain adhesion effect on C-S-H under tension, and its bond strength can effectively increase the ductility of C-S-H.

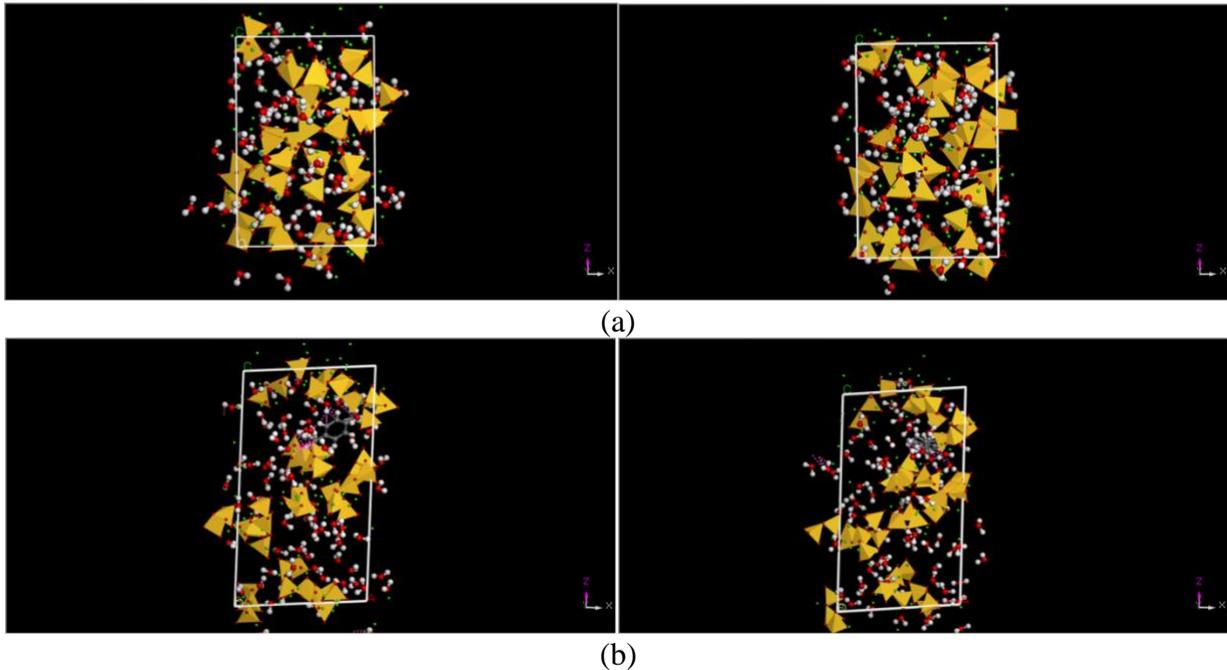


Figure 9. Structure evolution of C-S-H/ polymer systems under the tension along Z-axis (a) Pure C-S-H (b) C-S-H / ibuprofen. Among them, the gray ball represents carbon, the red ball represents oxygen, the white ball represents hydrogen, the green ball represents calcium, and the yellow polygon ball represents silicon oxygen tetrahedron.

4. Conclusion

In this paper, by using molecular dynamics simulation, the hexadecane, octadecane, phenolic resin, and ibuprofen were added into C-S-H respectively, and the effect of adding polymer on the internal structure and dynamics of C-S-H was studied. Then, the effect of the interaction between the polymers and C-S-H on the mechanical properties of composites was studied. The conclusions are as follows:

Hexadecane, octadecane, phenolic resin, and ibuprofen can be added into C-S-H, and the added polymers can interact with the calcium silicate system and interlayer calcium atoms in C-S-H, so as to disorder the C-S-H structure and enter the C-S-H defect.

The interaction force between polymer and C-S-H is mainly VDW force. In addition, phenolic resin can also form hydrogen bonds with the water molecules inside C-S-H. In the four groups of models, the interaction force between C-S-H and the polymers was in the order of octadecane > phenolic resin > hexadecane > ibuprofen, and the main reason was related to the relative molecular weight of the polymers.

The addition of hexadecane, octadecane, phenolic resin, and ibuprofen can effectively change the mechanical properties of C-S-H. The addition of the four polymers all reduced the Young's modulus in Z-axis, which resulted in the increase of the flexibility and the decrease of the brittleness of C-S-H. In addition, ibuprofen can effectively improve the ductility of C-S-H. The addition of alkanes, resins, as well as drugs in C-S-H all have great application values. Insertion of alkanes serves as an energy storage pathway. The intercalation of resins improves the insulation of C-S-H under high or low temperatures. C-S-H is also used in drug release and loading, and thus the insertion of drugs is also an important topic of study.

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