Insights on the Interfacial Strengthening Mechanisms of Calcium-Silicate-Hydrates/Polymer Nanocomposites

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Abstract

Mechanical properties of organic/inorganic composites can be highly dependent on the interfacial interactions. In this work, with organic polymers intercalated into the interlayer of inorganic calcium silicate hydrates (C-S-H), the primary binding phase of Portland cement, great ductility improvement is obtained for the nanocomposites. Employing reactive molecular dynamics, the simulation results indicate strong interfacial interactions between polymers and the substrate contribute greatly to strengthening materials, when C-S-H/poly ethylene glycol (PEG), C-S-H/poly acrylic acid (PAA), C-S-H/poly vinyl alcohol (PVA) were subject to uniaxial tension along different lattice directions. In the x and z direction tensile process, the Si – O...Ca bonds of C-S-H gel, which were elongated broken to form Si-OH and Ca-OH, play a critical role in loading resistance, while the incorporation of polymers bridged the neighboring silicate sheets, and activated more those hydrolytic reactions in the interfaces to avoid strain localization, thus increasing the tensile strength and postponing the fracture. On the other hand, Si-O-Si bonds of C-S-H mainly take the loading when tension along y direction were applied. During the post-yield stage, the rearrangements of silicate tetrahedra occurred to prevent the rapid damage. The polymer intercalation further elongates this post-yield period by forming interfacial Si-O-C bonds, which promote rearrangements and heal the connectivity of defective silicate morphology, significantly improving the ductility. Among the polymers, PEG exhibits the strongest interaction with C-S-H, and thus C-S-H/PEG possesses the highest ductility. We expect the molecular-scale mechanisms interpreted here shed new light on the stress-activated chemical interaction in the organic/inorganic interfaces, and help eliminate the brittleness of cement-based materials from the genetic level.

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1 Introduction

Nature has shown the combination of organic and inorganic materials can equip the composites with advantages from both sides, giving birth to extraordinary mechanical properties. Bones and teeth are perfect examples with great strength and ductility. Ubiquitously, the structural robustness and resilience of organic/inorganic composites under (static or dynamic) mechanical loading has raised diverse applications in all walks of engineering fields, such as gas adsorption, chemical sensing and piezoelectric devices, catalytic process, and medical scaffolds.¹⁻⁸ In terms of nanocomposites, the interfacial interactions between organic and inorganic phases become dominant in determining the mechanical properties, due to the length scales involved.⁹⁻¹¹ Therefore, in order to achieve a better bottom-up understanding and more effective performance control of nanocomposites, deeper insights on the interfacial interactions between phases at nanoscale, and knowledge of their correlations with overall material properties are needed.

As the most commonly used building materials world widely, nearly 30 billion tonnes of concrete are consumed per year, the manufacturing of which is responsible for 8-9% anthropogenic CO₂ emission.¹² One strategy to reduce this environmental footprint is to improve the mechanical performance of concrete, especially its ductility, so that less concrete is required to satisfy the same civil engineering demand.¹³⁻¹⁶ The toughness enhancement of inorganic cements, mortars and concretes, can be achieved by the incorporation of organic polymers, as described in many recent studies.¹⁷⁻²² For instance, poly vinyl alcohol (PVA) has been utilized widely as additives in cementitious materials, and can increase the toughness dramatically.^{18,19,23} The addition of poly ethylene glycol (PEG) or poly acrylic acid (PAA) was also proved to affect the fracture energy of ordinary Portland cement (PC)²⁰ and polyalkenoate cement paste²², respectively. However, most of these results focus on the qualitative characterization at macro-scale. There is still little knowledge of the molecular-scale interaction in the interfaces between polymers and the cementitious matrix, as well as the strengthening mechanism.

On the other hand, calcium silicate hydrate (C-S-H), which is the basic constituent unit of PC concrete, essentially governs the durability, strength, and ductility when cement-based materials are mixed with polymers.^{15,24-28} Hence, it is of great interest and values to investigate the interactions between C-S-H and polymers. The obvious shift of basal peak position in XRD diffractograms of synthesized samples has implied the intercalation of polymers into the interlayer of C-S-H nanocrystals²⁹⁻³¹, where the two phases interact deeply, and modify the structure and properties of the nanocomposites.³²⁻³⁵ As for the mechanical properties of C-S-H/polymer nanocomposites, several researchers reported higher modulus in their nanoindentation measurements compared with pure C-S-H samples^{28,36}. Unfortunately, how the ductility was affected is still remain unrevealed, due to the experimental difficulties to access smaller length scale.

Molecular dynamics (MD) can provide complementary understanding on the experimental finding, help interpret the interaction mechanisms in the

organic/inorganic interfaces, and give molecular insights into the composition, structure and mechanical properties of the nanocomposites.^{37–39} Pellenq et al⁴⁰ proposed the “realistic model” of C-S-H with calcium to silicon molar (C/S) ratio of 1.7, which perfectly reproduced the structure experimentally characterized by small-angle neutron and X-ray scattering measurements⁴¹, and precisely predicted the elasticity and strength properties^{42,43}. The mechanical properties of C-S-H with various C/S ratios, and its structural analogues jennite and tobermorite, calculated from other researchers’ molecular dynamics simulation, also reached a good agreement with experiment results.^{44–49} Moreover, by molecular dynamics, Geng et al^{50,51} explained the interlayer stiffening mechanism in the z direction when C-S-H/C-A-S-H samples were subject to hydrostatic pressure, while Hou et al^{44,45,52} illustrated the damage process and hydrolytic reactions of C-S-H with different C/S ratios and saturation degrees during the uniaxial tensile process along x, y, and z directions, and suggested the high plasticity of C-S-H in the y direction may be attributed to the rearrangements of silicate tetrahedra. As concluded in many MD studies, C-S-H features a relative ductile behavior at nanoscale,^{53–55} and the strengthening and toughening mechanisms on introducing either impurities (i.e. carbon nanotubes, calcium hydroxides), or lattice defects (i.e. dislocations, voids) to C-S-H have been further elucidated.^{56–58} However, for C-S-H/polymer nanocomposites, the simulation of mechanical behaviors and mechanism interpretation is still missing, with only the interfacial connections and interactions between organic and inorganic phases reported.³⁸

Therefore, in the present work we aim to investigate, for the first time, the mechanical response and constitutive relations of C-S-H/polymer nanocomposites that are subjected to uniaxial tension, evaluate the influence of polymer intercalation, strain rate, and tensile direction on the ductility and other mechanical properties, and explore the interfacial interaction mechanisms by molecular dynamics. Three types of polymer molecules, i.e. PVA, PAA, and PEG, with hydroxyl, carboxyl and C-O-C functional groups respectively, are selected as the intercalation guests into C-S-H interlayer, due to their wide application and excellent performance in both ductility enhancement at macroscale and structure modification at nanoscale.

2 Simulation Methods

2.1 Reactive Force Fields

The reactive force field (ReaxFF) was employed in this work for both the composite model construction and the uniaxial loading testing process. ReaxFF has been successfully applied in the organic^{59,60} or inorganic⁶¹ systems, and the good compatibility in the organic/inorganic interfaces was also proved⁶². Instead of predefining the connectivity at a fixed state (e.g. ClayFF or CSHFF force fields), ReaxFF utilizes a bond order – bond length scheme, which depicts the smooth energy evolution so that the breakage and formation process of chemical bonds can be captured. In this way, we are able to obtain the reactive features and mechanisms of significant reactions in the silica/water interfaces, such as the water dissociation and silicate

polymerization^{55,63,64}, which can be coupled with the mechanical response of the materials when subjected to large deformation. The fitting of quantum chemical calculations defined the parameters of ReaxFF, the specific values of which can be referred to the previous published papers^{59–61,65,66}. In this work, we merged the sets of Ca/Si/H/O and C/O/H parameters from Ref. [62] and [56], respectively. The combined ReaxFF force field was proven to show a good performance in modeling the interfacial interactions between C-S-H and organic phases, and the mechanical response when nanocomposites were subjected to uniaxial tensile process.⁶²

2.2 Models

According to the previous experimental research, there is strong evidence that PAA³¹ and PEG³³ can be intercalated into the interlayer of C-S-H. The possibility of the intercalation of PVA is also considerable when low molecular weight polymers were mixed with C-S-H samples.³⁵ Therefore, to be consistent with the experiment description, we constructed three nanocomposite models, with PEG, PVA, and PAA polymers placed in the interlayer region of C-S-H, respectively.

The first step is to establish a proper host structure of C-S-H. The C/S ratio of the structure is determined to be 1.3, because this value was commonly used in C-S-H/polymer research and considered as the optimal value for polymer intercalation.^{29–31} Matsuyama suggested the intercalation amount of polymers reached a maximum when the host C-S-H had a C/S=1.3. Although previous studies proved different C/S composition would lead to substantially distinct mechanical responses and interaction mechanisms^{44,45}, they are not in the consideration of this work in order for an optimal intercalation effect. Afterwards, structures of polymer chains (PAA, PEG, and PVA) are added. To be consistent with the experiment research³³ (the molecular weight of PEG used was around 300), each polymer chain is composed of 8 monomers. For each specie, four polymer chains are intercalated into the C-S-H, with a dosage of 0.2-0.25g polymer/g Ca, which is also in the range of the experimental data^{30,31,35}. Below is the detailed manipulation.

An anhydrous C-S-H model was initialized from the 11Å tobermorite crystal structure⁶⁷ containing no water molecules. To modify the C/S to 1.3, proper amount of bridging site silicate tetrahedra and calcium ions were removed and added respectively. After the operation, the silicate chain linkage information (Q species distribution) of the model satisfied the experimental results probed by ²⁹Si nuclear magnetic resonance tests (NMR)^{68,69}. Subsequently, polymers of PAA, PVA, and PEG, each as an unfolded chain shape composed of 8 monomers (see Fig.1), were respectively intercalated into the interlayer regions of the anhydrous C-S-H. Finally, we perform a Grand Canonical Monte Carlo (GCMC) simulation with water chemical potential fixed to a value that corresponds to the bulk liquid phase with 1g/cm³ density at 298K, in order to make both pure C-S-H and C-S-H/polymer models reach a saturated state.⁷⁰ An equal number of attempts for translation, rotation, creation or destruction of water molecules are performed in GCMC simulation, with the runs of at least 10⁸ steps to reach system equilibrium, and then production run of 2×10⁸ steps.

Each of the models has a dimension of around 40×40×40 Å³ along x, y, and z

directions, with total 7200-7300 atoms. As shown in Fig.1, the sheets of calcium and silicate tetrahedra lie in the xy plane, where along the y direction the defective silicates line up. Along the z direction, the interlayer and intralayer regions are alternately arranged. Reactive force field molecular dynamics simulations were then carried out in an isothermal-isobaric (NPT) ensemble for the structural analysis, with the equilibrium time 100ps and production time 300ps.

2.3 Uniaxial Tension Tests

We applied a uniaxial tensile loading process to both the pure C-S-H and three C-S-H/polymer models, at a fixed strain rate of 0.08ps^{-1} . In the beginning, the models were relaxed at 298K until the zero external pressure was reached in x, y, and z directions. Subsequently, the uniaxial loading started along one direction, during when the pressure normal to tension direction was always kept zero for the purpose of anisotropic relaxation with no restrictions. The artificial deformation constraint can be removed by this manipulation. The stress-strain curves were plotted by recording the pressure development along the tensile direction as the internal stress as a function of applied strain. Considering the large number of atoms involved in each model, the reliable statistics and constitutive relations can be obtained for mechanisms analysis. To further explore the effect of strain rate on the mechanical responses of models, a much slower loading rate 0.008ps^{-1} was applied on both pure C-S-H and C-S-H/PEG nanocomposite.

Fig.1 Structures of polymers, PEG($\text{C}_{16}\text{O}_8\text{H}_{34}$), PVA($\text{C}_{16}\text{O}_8\text{H}_{34}$), PAA($\text{C}_{23}\text{O}_{16}\text{H}_{32}$) and panorama of the simulation system: red, green, yellow, white and grey spheres represent oxygen, calcium, silicon, hydrogen and carbon atoms, respectively; the chain model of polymers are enlarged in the panorama picture for viewing convenience.

3 Results and Discussions

3.1 Structures

Ahead of the loading tests, the equilibrium structures of the pure C-S-H and three C-S-H/polymer nanocomposites are presented here, in order to briefly introduce the basic features of C-S-H and the effects of polymer intercalation, as a foreshadowing of the mechanism interpretation in Section 3.3.

3.1.1 Calcium Silicate Hydrates

The layered structure of the pure calcium silicate hydrates can be clearly observed in Fig.2. The calcium-oxygen polyhedral sheets are constructed by the calcium ions Ca_s attracting the surrounding oxygen atoms O_s , on which the defective silicate tetrahedral chains are grafted. Between the neighboring calcium silicate sheets, the interlayer calcium Ca_w and water molecule are present. The structure of C-S-H generated here resembles what illustrated in Ref.¹⁵. Q species of Si can be defined by the number of bridging oxygen atoms connected to itself. As shown in Fig.3a, the middle silicon is considered as Q_2 due to the two bridging oxygen atoms connected, and those in both ends are defined Q_1 . Q_1 and Q_2 are the only existing Q species in the molecular structure of C-S-H, as exhibited in Fig.3b, the proportions of which are still consistent with NMR results⁶⁸ ($\text{Q}_1/(\text{Q}_1+\text{Q}_2)\approx 0.6$) after the equilibrium is reached.

Besides the covalent bonds of silicon and oxygen atoms, the ionic bonds formed between calcium and oxygen is responsible for the cohesion of C-S-H structure as well. To deal with the Ca-O spatial correlations, the radial distribution function (RDF) is employed, which is defined as the probability of finding an atom B located at a distance

r from an atom A ($g_{AB}(r)$), as the formula shows: $g_{AB}(r) = \frac{\langle N_{AB}(r) \rangle}{\rho dV(r)}$, where $\langle N_{AB}(r) \rangle$

denotes the ensemble average number of atoms B located at a distance between r and $r + dr$ away from the given atom A, ρ denotes the atomic density of atoms B, $dV(r)$ is the corresponding volume of the shell between r and $r+dr$. According to the RDF calculation, the bond length of Ca-O is around 2-3Å (see the first peak position in Fig.4a). The coordination O of calcium ions can be further decomposed into O_s (from calcium silicate sheets), and O_w (from water molecules) according to their chemical environments. As presented in Fig.4b, one calcium ion can be coordinated by about 3.6 O_s and 2.5 O_w atoms on average. Moreover, the reaction of water dissociation takes place due to the high reactivity of non-bridging oxygen and calcium ions, which are able to attract the -H and -OH from water respectively, to form the hydroxyl groups, Si-OH and Ca-OH, as illustrated in Fig.5. It should be noted that this reaction can be regarded as an indicator of the structure changes in the tensile process, which will be explained in Section 3.3.

Fig.2 Structure of calcium silicate hydrates without polymers (green balls are calcium ions, red and yellow sticks are silicate tetrahedra, white and red lines are water molecules).

Fig.3 (a) The definition of Q species; (b) distribution of Q species in model of pure C-S-H.

Fig.4 (a) Radial distribution function between Ca and O_s from silicate tetrahedra, O_w from water molecules. (b) Coordination number of calcium.

Fig.5 Dissociation of water molecules.

3.1.2 Calcium Silicate Hydrates with Polymers Intercalated

After the complete relaxation and equilibrium process, the intercalated PVA, PAA, PEG exhibit different behaviors in the interlayer regions of C-S-H. The chains of PVA and PAA remain relatively intact, while the PEG chains were strongly attacked and broken into short ones (see Fig.6a-c). Quantitatively, as calculated in Fig.6d, the mean chain length of PVA and PAA is almost half of the original length. In contrast, for PEG, the mean chain length is only one tenth of the original one, indicating PEG interacted strongly with the C-S-H substrate. As illustrated in Fig.7a-c, the local structure rearrangements occurred in the interfaces between C-S-H and polymers in all three nanocomposites. For PAA and PVA, the C-C bonds (C denotes carbon atom, different from that in “C-S-H”) were broken and the C-O-Si bonds were formed. It seems both C-C and C-O bonds in the chemical structure of PEG were attacked, and the isolated –CH alkyl groups were produced to act as a bridging part of two neighboring calcium silicate sheets (see Fig.7c). It should be noted that the formation of strong C-O-Si bonds has been verified by first principles calculation in some similar organic/inorganic systems, e.g. carbon nanotube/silica oxide interface.^{71,72}

The influence of polymer intercalation on the distribution of Q species in the C-S-H structure were calculated and shown in Table 1. Compared with the silicate connectivity of pure C-S-H, the intercalation of PVA almost has no effect on the substrate structure while PEG influences C-S-H relatively heavily. In the C-S-H/PVA nanocomposites, the new Q₃ structure, corresponding to the branch structure is produced. It means not only the Ca-O coordination described above, but also the covalent bonds contribute to the interlayer connections of the nanocomposites. Besides Q₃, Q₀ is also included in the structure of C-S-H/PAA nanocomposites, showing a few dimers were depolymerized to isolated monomers. In C-S-H/PEG nanocomposites, the percentages of both Q₀ and Q₃ are larger than those of PAA and PVA. Furthermore, the Q₄, an indicator of network structure, emerges as a result of the strong interaction between PEG and C-S-H substrate.

In the light of the radial distribution function (RDF) patterns in Fig.8a, the pronounced Ca-O_p (oxygen from polymers PAA, PVA, and PEG) peaks indicate the calcium ions from C-S-H are also able to attract the components of polymers. The bond strength between calcium and different oxygen species can be distinguished according

to the peak position in RDF. Ca-O_s and Ca-O_w pairs are closer compared with Ca-O_p, on the basis of the first peak position. Therefore the Ca-O_p bond is weaker and less stable. The average number of coordination oxygen atoms of each calcium ion were calculated and shown in Fig.8b (the cutoff distance is 3 Å). Obviously, in all three C-S-H/polymer nanocomposites, calcium can be coordinated by O_s, O_w, and O_p. In terms of the total number of oxygen coordination (O_t), Ca in C-S-H/PVA is coordinated by the least oxygen and Ca in C-S-H/PEG the most.

Fig.6 Overall view of calcium silicate hydrates with polymers intercalated. (a) PVA (b) PAA (c) PEG (d) residual chain length /original chain length for three polymers (green balls are calcium ions, red and yellow sticks are silicate tetrahedra, white and red lines are water molecules, balls of other colors are for the polymer atoms: grey for carbon, white for hydrogen, and red for oxygen).

Fig.7 Local snapshots after structure rearrangements: (a) PVA (b) PAA (c) PEG (red and yellow sticks are silicate tetrahedra, white and red lines are water molecules, balls of other colors are for the polymer atoms: grey for carbon, white for hydrogen, and red for oxygen).

Table 1 Q species distribution after the structure rearrangements.

structure	Q0 (%)	Q1 (%)	Q2 (%)	Q3 (%)	Q4 (%)
Pure C-S-H	0	43.24	56.76	0	0
C-S-H/PVA	0	42.91	56.98	0.11	0
C-S-H/PAA	0.11	43.58	56.08	0.22	0
C-S-H/PEG	0.55	44.82	53.15	1.35	0.11

(a)

(b)

Fig.8 Coordination of calcium after rearrangements: (a) Radial distribution function of Ca and O species from polymers; (b) coordination number of Ca for different polymers.

3.2 Mechanical Properties

The stress-strain curves are capable to capture the mechanical response of pure C-S-H and its nanocomposites when they are subjected to tensile loading, which may give insights into the constitutive relations of materials at the atomic scale. As shown in Fig.9a, pure C-S-H shows different mechanical behaviors when subjected to tension at a fixed strain rate 0.08ps^{-1} along x, y, and z directions. It seems the z direction of C-S-H structure is the weakest. When tension along z direction are exerted, initially in the elastic stage, stress goes up proportionally to the strain and then slowly reaches the maximum value, around 4.5GPa. Afterwards, the stress decreases continuously to 0 at a strain of around $0.32 \text{ \AA}/\text{\AA}$. There is also a protruding parabola curve for the stress-strain relation in the x direction, except for the higher values both for maximum stress and failure strain. It indicates that the failure mechanism of C-S-H should be similar, in terms of the evolution of composition, structure and dynamics during the tensile process along x and z direction, which will be further discussed in Section 3.3.1. However, the stress-strain relation during the y direction tensile process is distinguished with much higher plasticity. After the stress reaches the maximum point, it experienced discontinuous decrease, which can be categorized into several stages. In the beginning, it falls down by around 1.5GPa and then arrives at a plateau from $0.2 \text{ \AA}/\text{\AA}$ to $0.3 \text{ \AA}/\text{\AA}$. Subsequently, it keeps going down until another plateau occurs from $0.45 \text{ \AA}/\text{\AA}$ to $0.5 \text{ \AA}/\text{\AA}$, the duration of which is shorter than the previous one. Finally, the stress resumes to decrease until the failure. The multiple stages of reduction on stress imply the occurrence of structural rearrangements in pure C-S-H when subjected to tension along y direction so that the rapid decrease of stress is prevented and the higher plasticity is resulted. Furthermore, based on the performance in the elastic stage, the tensile strength and Young's modulus were calculated and shown in Fig.10. Pure C-S-H owns the highest tensile strength and Young's modulus in y direction, and the lowest values in z direction. The high pressure XRD experiments of pure synthetic C-S-H achieved a similar result, which indicates the z direction of C-S-H is of the smallest stiffness.⁵¹

As shown in Fig. 9b-d, the intercalation of polymers has significant influence on the mechanical response of C-S-H when subjected to exterior tension loading, significantly increasing the ductility in all three directions. In the elastic stage, no obvious difference is observed between the pure C-S-H and the polymer intercalated nanocomposites in both x and y directions. All the stress-strain curves almost overlap with each other (see $0-0.15 \text{ \AA}/\text{\AA}$ in Fig.9b-c), thus approximately the same values are achieved either in tensile strength or in Young's modulus for those two directions (see Fig.9d). As an exception, in the z direction, the maximum stress of polymer intercalated nanocomposites are higher than that of pure C-S-H in spite of the similar slope before reaching the maximum. Therefore, it indicates models with polymers have higher

tensile strength, while the Young's modulus of all structures are at the same level, as shown in Fig.9d. More importantly, four models of nanocomposites behave quite different in the post-yield stage in all three directions. Compared with the pure C-S-H, the intercalation of all three polymer species, PEG, PAA, and PVA, makes stress decrease more slowly after the elastic stage, postponing the fracture. Among them, PEG tends to increase the ductility most remarkably in x, y, and z directions. From this perspective, the simulation results presented here comply with the macroscopic experiments, in which the incorporation of these three types of polymers improved the fracture energies and toughness of cement pastes or mortars.^{20,22,23}

Fig.9 Tensile stress-strain curves for pure C-S-H and nanocomposites: (a) pure C-S-H along all three directions; (b) pure C-S-H and nanocomposites along x direction; (c) pure C-S-H and nanocomposites along y direction; (d) pure C-S-H and nanocomposites along z direction.

Fig.10 Mechanical properties for pure C-S-H and nanocomposites: (a) Tensile strength; (b) Young's modulus.

3.3 Mechanisms

3.3.1 Influence of Tensile Direction

As introduced by Hou⁴⁵ and Zhu⁷³, thermodynamically in the pure C-S-H model, two types of hydrolytic reactions should take place, as a result of the activation energy reduction during the tensile process. The two hydrolytic reactions can be expressed in chemical Formula 1 and 2, respectively. In Formula 1, the ionic bonds between Ca and Si-O groups are elongated until broken, forming the same amount of Ca-OH and Si-OH in the presence of water molecules. In Formula 2, during tensile process, a stable covalent Si-O-Si bond is stretched longer till broken, and the remained Si-O and Si would immediately react with water to form 2 Si-OH.

As the products of hydrolytic reactions, the number evolution of Ca-OH and Si-OH for pure C-S-H in tensile process was recorded as indicators of mechanisms. Fig.11a shows the evolution in all three directions, while Table 2 presents the initial, final, and generated numbers of Ca-OH and Si-OH for pure C-S-H during the whole process. Obviously, Formula 1 will produce the same amount of Ca-OH and Si-OH, while Formula 2 only produces Si-OH. Along x and z direction, Ca-OH and Si-OH experience synchronous growth (see Fig.11a) with the exact same increase number in the end (see Table 2), implying only the reaction 1 occurs. In addition, no changes in the number of Q species along these two directions are observed (see Fig.11b, 11d), which also indicates silicate chains were not affected. Therefore, the stretching and breakage of $Si - O \cdots Ca$ bonds are believed to be responsible for the strain evolution.

Along y direction, synchronous growth of Ca-OH and Si-OH is also observed before strain reaches 0.2 Å/Å. Then a rapid increase of Si-OH makes it differentiate with the growth of Ca-OH when the strain goes beyond around 0.25 Å/Å. In the meanwhile, the number of Q₂ starts to drop with the increase of Q₀ and Q₁ (Fig.11c), which supports the dissociation of Si-O-Si bonds. The total generated number of Ca-OH and Si-OH is 106 and 163 respectively, indicating the occurrence of both reactions listed in Formula 1 and 2. The breakages of stronger Si-O-Si bonds also contribute to the strain development, which requires higher stress and energy^{44,46}. This means the y direction of C-S-H is stronger and stiffer than the other two directions, in favor of the results in Fig.10. It should be noted that, when the strain is over 0.4 Å/Å, the trends for Q₀, Q₁, and Q₂ are all reversed. The increase of Q₂ and the decrease of Q₀ and Q₁ indicate the re-polymerization and rearrangements of silicate chains took place at the post-yield stage, to prevent rapid stress decrease and postpone the final failure, which can account for the plateau illustrated in Fig.9b.

As a conclusion, for the pure C-S-H model, the failure mechanism is similar for tensile process along x and z directions, during which only the ionic bonds between Ca and Si-O groups were stretched broken. In the y direction tensile process, both of the two hydrolytic reactions occurred, in which the participation, breakages and rearrangements of Si-O-Si bonds explain the higher tensile strength, Young's modulus, and ductility in this direction.

Fig.11 (a) Number evolution of Ca-OH, Si-OH and number evolution of Q species for pure C-S-H as a function of strain in the tensile process of (b) x, (c) y, (d) z directions.

Table 2 Generated number of Ca-OH and Si-OH for pure C-S-H during the tensile process in x, y, and z directions.

	Ca-OH				Si-OH			
	Starting number	Ending number	Generated number	Generated proportion	Starting number	Ending number	Generated number	Generated proportion
x		505	37	7.91%		361	37	11.42%
y	468	574	106	22.65%	324	487	163	50.31%
z		488	20	4.27%		344	20	6.17%

3.3.2 Influence of Polymer Intercalation

The mechanisms on the mechanical responses with respect to the influence of polymer intercalation will be interpreted in the tensile process along z and y direction respectively. Description on mechanisms along the x direction is skipped due to the similarity as z direction.

For preliminary qualitative description of the tensile damage process along the z direction, the configurations of pure C-S-H and C-S-H/PEG nanocomposites at strain levels of 0, 0.1, 0.2, 0.35, 0.5 Å/Å are compared in panels, as shown in Fig.12. At the beginning, although the two models have the similar interlayer spacing (see 0 Å/Å in Fig.12a), the intercalated PEG molecules can connect the neighboring silicate layers by the formation of Si-O-C bonds (see Fig.7c for better vision). In pure C-S-H, since there is no such strong covalent connection along z direction, the relatively weaker interlayer

region is rapidly stretched open, and major gaps can be observed when strain reaches $0.2 \text{ \AA/\AA}$. Meanwhile, the C-S-H/PEG model still looks intact, with lower expansion rate of the interlayer region. It should be noted that the PEG chains are gradually aligned along z direction. As the strain proceeds to $0.35 \text{ \AA/\AA}$, the C-S-H model is completely fractured, while the polymer bridge across the interlayer region still makes C-S-H/PEG integrated in spite of the appearances of some major cracks. Once the PEG chains are attacked broken when strain reaches about $0.5 \text{ \AA/\AA}$, the overall model comes to a fracture. Therefore, the intercalation of PEG bridges the neighboring silicate tetrahedral layers by the formation of Si-O-C bonds, which contributes to the increase in tensile strength and failure strain. It is worth mentioning that in the MD study of carbon nanotubes (CNT) reinforced C-S-H, the similar phenomenon of CNT bridging adjacent silicate layers, as well as the corresponding strengthening and toughening effects of CNT on the matrix were also observed, when the nanocomposite was subject to tensile process.⁵⁸

Furthermore, the difference in the number revolution of Ca-OH and Si-OH can reveal another enhancement mechanism due to the intercalation of polymers. In Fig.13a, the rise of the Ca-OH/Si-OH number within C-S-H/PEG initializes earlier than that for pure C-S-H, suggesting PEG can effectively reduce the energy barrier of this hydrolytic reaction. And the occurrence of this reaction is observed to have multiple stages, since there are several upwards slopes in the curves of the Ca-OH/Si-OH number for C-S-H/PEG ($0-0.1 \text{ \AA/\AA}$, $0.2-0.25 \text{ \AA/\AA}$, $0.28-0.4 \text{ \AA/\AA}$). It should be related to the different coordination environment of calcium ions, as represented in Fig.4b and 8b. The coordination of O from PEG may make calcium ions vulnerable to divorce from the Si-O groups, forming the Ca-OH and Si-OH. The hydrolytic reaction of calcium ions only coordinated by O from water molecules or silicate tetrahedra may occur later due to the higher activation energy, as the case in the pure C-S-H model. As Fig.13b shows, it seems the generated number of Ca-OH/Si-OH during the tensile process can reflect the ductility of the models. In all models, the number of Ca-OH is equal to the number of Si-OH, meaning only Formula 1 tool place. The most ductile C-S-H/PEG has the highest hydroxyl numbers, while the most brittle C-S-H owns the lowest numbers. The intercalation of PAA and PVA also makes the matrix ductile, with intermediate numbers. More Ca-OH/Si-OH being generated means more $\text{Si}-\text{O}\cdots\text{Ca}$ bonds dissociate to undertake the strain, thus the stress can be distributed more evenly, and failure caused by strain localization can be avoided. In addition, these $\text{Si}-\text{O}\cdots\text{Ca}$ can be regarded as sacrificial bonds to dissipate energy when materials are subjected to tensile loading, as described in Ref.⁷⁴.

$0 \text{ \AA/\AA}$

Fig.12 Snapshots of (a) pure C-S-H and (b) C-S-H/PEG nanocomposites in z direction tensile process (green balls are calcium ions, red and yellow sticks are silicate tetrahedra, white and red lines are water molecules, balls of other colors are for the polymer atoms: grey for carbon, white for hydrogen, and red for oxygen).

Fig.13 (a) Number evolution of Ca-OH and Si-OH in C-S-H and C-S-H/PEG composites during z direction tensile process; (b) generated number of Ca-OH and Si-OH during z direction tensile process for all models.

As for the y direction, mechanisms differ at elastic, yield, and post-yield stages, which are defined by the stress-strain relations. Fig.14 and Table 3 provide the number evolution and total generated number of Ca-OH/Si-OH at each stage during the y direction tensile process, respectively. At the elastic stage (around 0-0.15 $\text{\AA}/\text{\AA}$), the number of generated Ca-OH and Si-OH keeps agreeing with each other, showing only Formula 1 occurred to undertake the strain. As described earlier, the intercalation of PEG dramatically decreases the activation energy of calcium as a result of the coordination condition changes, thus leads to the largest number of Ca-OH in all four models. The intercalation of PVA and PAA also has a similar effect. At the yield stage (around 0.15-0.3 $\text{\AA}/\text{\AA}$), the number of generated Si-OH is slightly greater than that of Ca-OH in all cases, meaning Formula 2 initializes. At the former two stages, the reaction mechanisms of the four models are qualitatively similar, hence their stress-strain curves almost overlap with each other. At the last stage, Formula 2 becomes predominated as is suggested by the obvious inequality in the number of Si-OH and Ca-OH. During this stage four models exhibit different mechanical behaviors. However, it seems there is no direct correlation between the reaction number of Ca-OH/Si-OH and ductility in this direction. Therefore, more attention should be paid to the structural rearrangements discussed in Section 3.3.1, as it causes the high failure strain in the y direction of pure C-S-H.

Fig.14 Number of (a) Ca-OH (b) Si-OH evolution during y direction tensile process.

Table 3 Generated number of Ca-OH and Si-OH in three stages during the tensile process in y direction.

	Elastic stage (0-0.15Å/Å)		Yield stage (0.15-0.3Å/Å)		Post-yield stage (0.3-0.8 Å/Å)	
	Generated	Generated	Generated	Generated	Generated	Generated
	Ca-OH	Si-OH	Ca-OH	Si-OH	Ca-OH	Si-OH
C-S-H	14	14	41	47	51	102
C-S-H/PEG	40	40	43	51	46	129
C-S-H/PAA	22	22	39	41	46	128
C-S-H/PVA	20	20	38	44	46	103

Fig.15 describes the detailed configurations of pure C-S-H and C-S-H/PEG nanocomposites at strain levels of 0, 0.2, 0.4, 0.8 Å/Å during y direction tensile process. As the strain goes up, the layer structure of C-S-H is disturbed and become less organized, which implies the increasing breakages and rearrangements of silicate tetrahedra. For the C-S-H/PEG nanocomposites, the intercalated PEG molecules are always evenly distributed in the interlayer region at any strain levels. It indicates the PEG chains are also elongated, broken and rearranged, accompanying synchronously with the C-S-H substrate during the tensile process. When the strain reaches 0.8 Å/Å, the pure C-S-H is completely fractured, while the C-S-H/PEG nanocomposite is still integral, with PEG chains broken into pieces to fill in the cracks.

Fig.16 gives Q species distribution for all four models during the y direction tensile process. The overall trends are the same for pure C-S-H and three polymer intercalated nanocomposites (see Fig.16a-d). After the strain reaches slightly lower than 0.2 Å/Å, quantities of Q₁ and Q₀ begin to increase as a result of the dissociation of Q₂. Subsequently when strain is over 0.4 Å/Å, there comes the opposite trend, proving the occurrence of rearrangements. Considering the strain value of 0.4 Å/Å is also the turning point where the overlapping curves begin to differ in the stress-strain curves (see Fig.9c), the process of arrangements is supposed to cause the plasticity difference in four models. It should be noted Q₃ or even Q₄ plays a significant role in the arrangements process, since previous ab initio research⁴⁶ confirmed these high connectivity silicate chains can strongly improve the stiffness of tobermorite by the hinge effect⁷⁵. It can be seen from Fig.16e, as strain increases from 0.4 to 0.8 Å/Å, there is an upwards tend for the number of Q₃ in all four models, during when the oscillations are attributed to the simultaneous breakages and formations of Q₃ structure. Overall, C-S-H/PEG always has the largest number of Q₃, while numbers of C-S-H/PAA and C-S-H/PVA become higher than that of pure C-S-H during the later period. For Q₄, which is a symbol of network structure of ultra-high connectivity, only C-S-H/PEG model possesses a small fraction.

Furthermore, we compare the parameters which describe the rearrangement capacity and connectivity of the four structures at the post-yield stage. The maximum numbers of Q₃/Q₄, as well as broken C-C/C-O and generated Si-O-C bonds are listed in Table 4. The Si-O-C bonds, which bridge the silicate and polymer chains, can significantly improve the system connectivity. For the case of C-S-H/PEG nanocomposites (as

shown in Fig.17), during the tensile process, the -C-C-O groups were stretched open, with each of the carbon atom grafted into the non-bridging oxygen atoms, turning both Q₂ silicates into Q₃. Among the polymers, the most C-C/C-O bond breakages are observed in PEG chains, and these broken PEG short groups reacted with the silicate tetrahedra, forming the largest amount of Si-O-C bonds, contributing to the greatest number of Q₃/Q₄. These reactions highly promoted the rearrangements and dramatically increased the connectivity of the whole system, therefore it can explain the substantial ductility improvement at the post-yield stage when C-S-H/PEG was subject to y direction tension. The intercalation of PAA and PVA can also give birth to certain amount of Si-O-C bonds, whilst only silicate chains are responsible for the connectivity in pure C-S-H. Therefore, C-S-H/PAA and C-S-H/PVA are more ductile than pure C-S-H.

In conclusion, along the y direction tensile process, it is the rearrangement capacity and connectivity of the whole system at the post-yield stage that determine the mechanical response of materials.

0Å/Å

0.2Å/Å

0.4Å/Å

Fig.15 Snapshots of (a) pure C-S-H and (b) C-S-H/PEG nanocomposites in y direction tensile process (green balls are calcium ions, red and yellow sticks are silicate tetrahedra, white and red lines are water molecules, balls of other colors are for the polymer atoms: grey for carbon, white for hydrogen, and red for oxygen).

(e)

Fig.16 Q species evolution during the y direction tensile: (a) pure C-S-H; (b) C-S-H/PEG; (c) C-S-H/PAA; (d) C-S-H/PVA; (e) comparison of Q₃ and Q₄ in all structures for better view.

Table 4 Comparison of the rearrangement capability and connectivity of pure C-S-H and three polymer nanocomposites during post-yield stage.

	Maximum number of Q species during the post-yield stage		Maximum number during the post-yield stage	
	Q3	Q4	Broken C-C or C-O bonds	Generated Si-O-C bonds
C-S-H	11	0	0	0
C-S-H/PEG	20	2	37	26
C-S-H/PAA	16	0	20	20
C-S-H/PVA	13	0	20	17

Fig.17 Snapshot for rearrangement between inorganic silicate and organic chains in C-S-H/PEG nanocomposites.

3.3.3 Influence of Strain Rate

The effect of loading rate on the mechanical response of C-S-H and C-S-H/polymer nanocomposite along z direction is illustrated in Fig.18a-b. In both cases, when subjected to different loading rates, the models exhibit a similar stress-strain relation, except for a lower tensile strength and failure strain at lower strain rate 0.008ps^{-1} . As described in Section 3.3.1, along z direction tensile process only formula 1 took place to undertake the strain, and the reaction indicators, number evolutions of Ca-OH/Si-OH, are recorded in Fig.19a-b. In the pure C-S-H model, when loading was applied at a lower strain rate of 0.008ps^{-1} , the number of hydroxyls rises faster than that at 0.08ps^{-1} , after strain reaches $0.1\text{\AA}/\text{\AA}$ (see Fig.19a), which is approximately corresponding to the tensile strength point in Fig.18a. It means slower loading was able to cause more bond breakages and structural damage after the elastic stage, so lower tensile strength

is observed. Finally, when the model of pure C-S-H was completely fracture, the numbers of Ca-OH/Si-OH at two strain rates are almost the same. For C-S-H/PEG nanocomposite, the difference in the number evolution of hydroxyls between 0.008ps^{-1} and 0.08ps^{-1} is similar as that for pure C-S-H. Therefore, it can be concluded that along z direction tensile process, the loading rate has the same effect on the mechanical response of pure C-S-H and C-S-H/PEG nanocomposite.

However, for the uniaxial tensile process along y direction, pure C-S-H and C-S-H/PEG model show distinguished changing modes in the stress-strain relations when subjected to a slower loading test. As shown in Fig.18c, in spite of a lower tensile strength at 0.008ps^{-1} , C-S-H behaves more ductile than the case of 0.08ps^{-1} after the elastic stage. On the contrary, it seems lower loading rate is not able to improve the ductility of C-S-H/PEG composite (see Fig.18d). The linkage information of silicate chains as a function of strain at 0.008ps^{-1} for both pure C-S-H and C-S-H/PEG is illustrated in Fig.19c-d, and the comparison of the final Q species number between two strain rates is given in Table 5. Overall, for both models, as the strain goes up, either at a faster or slower rate, Q2 structures broke down to form Q0 or Q1 structures. At the post-yield stage, the number of Q2 became stable, and Q3 (even Q4) structures were formed due to the rearrangements. Finally, for C-S-H, there are more Q0, Q1, and Q3 but fewer Q2 at 0.008ps^{-1} . It means when loading was applied more slowly, more Si-O-Si bond breakages and rearrangements took place, which contributes to the more ductile behavior. Nevertheless, it is more complicated for C-S-H/PEG composite. On the one hand, there is an opposite changing trend in the number of Q0, Q1, and Q2, indicating that lower strain rate made less Q2 dissociation occur. On the other hand, more high stiffness structures Q3 and Q4 emerged, which represented more arrangements took place. The PEG polymers contribute to these extra arrangements. As described in Section 3.3.2, during the tensile process along y direction, polymers could be stretched broken and connected with the defective silicate chains. At 0.008ps^{-1} , in the whole system 44 C-C or C-O bonds were broken in PEG, and instead, 33 Si-O-C bonds were generated. Compared with the numbers calculated at 0.08ps^{-1} (shown in Table 4), polymers contributed more in the rearrangements of the system.

Fig.18 Tensile stress-strain curves for C-S-H reference and C-S-H/PEG composites at different strain rates: (a) C-S-H along z direction; (b) C-S-H/PEG composites along z direction; (c) C-S-H along y direction; C-S-H/PEG composites along y direction.

Fig.19 Number of Ca-OH and Si-OH evolution at different strain rates: (a) C-S-H along z direction tensile process; (b) C-S-H/PEG composites along z direction tensile process; Q species evolution during the y direction tensile at strain rate 0.008ps^{-1} : (c) pure C-S-H; (d) C-S-H/PEG.

Table 5 Comparison of the final Q species number between the strain rate of 0.08ps^{-1} and 0.008ps^{-1} for the pure C-S-H and C-S-H/PEG model, respectively.

	Q0	Q1	Q2	Q3	Q4
C-S-H at 0.08ps^{-1}	7	487	385	9	0
C-S-H at 0.008ps^{-1}	24	528	318	18	0
C-S-H/PEG at 0.08ps^{-1}	59	534	274	20	1

In summary, the one order of magnitude slower loading rate has the same influence on both C-S-H and C-S-H/PEG along z direction, while along y direction the two models possess different susceptibilities to the strain rate. Given the fact that the strain rate used in real laboratory measurements is normally around 10 orders of the magnitude smaller than the molecular simulated ones described here, some findings in this work cannot be directly applied into the similar cases at macroscale. There are always huge gaps between the experimental and calculated values due to the different scales involved. In terms of C-S-H samples with the same C/S of 1.3, Geng et al⁵¹ reported the bulk modulus of 83.4 GPa from high pressure XRD measurements, while Manzano et al⁴⁷ obtained only around 25 GPa from the molecular simulation. The intrinsic features of materials, which greatly depend on the length scale, govern the mechanical responses of both C-S-H and C-S-H/polymer composite. Therefore, the mechanical behaviors and mechanisms interpreted here may only take effect at the atomistic scale, and further upscaling studies are still necessary.

4 Conclusions

In this work, PEG, PAA, and PVA were respectively intercalated into the interlayer of C-S-H model, where the backbones of polymers interacted with silicate tetrahedra and calcium ions in the interfaces, modifying the local structure and forming the organic/inorganic nanocomposites. Molecular dynamics based on reactive force field was employed to unravel the mechanical behaviors and stress-strain relations of the nanocomposites during the uniaxial tensile process along x, y, and z directions. The results indicate that, except for a slight increase in the tensile strength along y direction, the intercalation of polymers has no obvious effects on the mechanical properties in the elastic stage, neither the Young's modulus nor the tensile strength. However, there is a significant increase in the ductility of all C-S-H/polymer nanocomposites in all directions.

The interfacial strengthening mechanisms are describe as follows. For the tensile process along x and z directions, the stretching and dissociation of Si – O ... Ca ionic bonds contributed mainly to the strain development. The incorporation of polymers strengthened the interlayer regions in two ways. On the one hand, polymers were able to bridge the neighboring silicate sheets by the formation of Si-O-C bonds, which dramatically strengthened the interlayer and prevented its rapid broadening. On the other hand, the coordinated oxygen atoms from polymers could decrease the activation energy of Si – O ... Ca bonds, causing more hydrolytic reactions. This can avoid the strain localization and dissipate more energy, and thus improve the ductility. Nevertheless, during the y direction tensile process the mechanisms were quite different. At the elastic and yield stages, the hydrolytic reactions mentioned above were still predominated. While at the post-yield stage, the breakages and formations of stronger Si-O-Si bonds took over, and the rearrangements of silicate tetrahedral chains determined the stress-strain relations. The Q₃ structure occurring in the rearrangements

of silicate chains stiffened the materials and postponed the fracture. Intercalation of polymers could highly promote the rearrangements by the formation Si-O-C bonds, which created more Q₃ and even Q₄ silicates and rise the overall connectivity of the whole system. In the meanwhile, the short broken polymer chains could act as fillers for the cracks.

Among the selected the polymers, PEG interacted with the matrix the most strongly, where the largest numbers of C-C or C-O bonds were broken to connect with the silicates, and thus C-S-H/PEG nanocomposite is the most ductile in all three directions. PVA and PAA have lower impacts, but still make materials less brittle when intercalated into the interlayer of C-S-H. Moreover, a much slower loading rate has the same influence on both C-S-H and C-S-H/PEG along z direction, decreasing the tensile strength and failure strain, while along y direction the two models possess different susceptibilities to the strain rate.

This work sheds new light on the stress-activated chemical interaction between organic and inorganic materials, and will be of broad interest to the scientists and engineers working in the fabrication of high mechanical performance composites. The results and mechanisms presented here can provide solutions to removing the brittleness of concrete from the genetic level. In this way, much less cement shall be consumed in the construction industrials, which significantly contributes to the low carbon economy and sustainable development. However, limitations still remain, which needs further investigations. On the one hand, this work only addresses the C-S-H with C/S=1.3, while various compositions exist in the real cement-based materials, which tend to cause significantly different mechanical responses and interfacial mechanisms. On the other hand, further work at larger length scales should be complemented due to the unrealistic strain rate employed in this simulation.

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