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1 **MECHANICAL PROPERTIES OF C-S-H GLOBULES AND INTERFACES**
2 **BY MOLECULAR DYNAMICS SIMULATION**

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6
7 **ABSTRACT**

8 At meso-scale, Calcium Silicate Hydrate (C-S-H) can be considered as randomly
9 packed globules (about 4.2nm), which forms the basic unit cell, with water molecules
10 and voids. In this paper, the nanostructures for the globules are developed based on
11 some plausible atomic structures of C-S-H. The mechanical properties for the C-S-H
12 globules are determined through molecular dynamics simulation. Interfaces between
13 the C-S-H globules are also simulated with different amount of water molecules. Key
14 material parameters, e.g., Young's modulus, strength and fracture energy, are
15 obtained. It has been found that longer mean chain length of silicate tends to increase
16 the strength of C-S-H and change the fracture behavior from brittle to ductile failure,
17 in the chain length direction. In the other direction, however, silicate chains do not
18 play an important role while interlayer structure matters. Moreover, pores in the
19 C-S-H nanostructures can considerably reduce the strength of the globule structures in
20 the normal direction to silicate chain but the weakening effect becomes substantially
21 less in silicate chain direction. Further, it has been found that for all types of the
22 interfaces between C-S-H globules, the interface with no extra water molecules has
23 the greatest tensile/shear strength. The mechanical properties obtained in this paper
24 for C-S-H nanostructures and interfaces are necessary inputs to the meso-scale
25 modelling of C-S-H via either granular mechanics, i.e., DEM, or continuum
26 mechanics, i.e., FEM.

27 **KEYWORDS**

28 C-S-H; mechanical properties; molecular dynamics modeling; interfaces; colloidal
29 model; meso-scale.

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31 1. INTRODUCTION

32

33 Since the invention of modern cement, there has been considerable mass of research
34 carried out in improving cement characteristics in terms of toughness [1], strength [2,
35 3] and durability [4, 5]. Recently, there is a growing research interest in modeling the
36 atomic structure and investigating the nano/micro-scopic properties of cement [6-10].
37 In light of difficulties in conducting experimental tests at the nano/micro-scale level,
38 atomic modeling provides a unique view in understanding the fundamental behavior,
39 especially mechanical properties, of the cementitious materials.

40 Calcium Silicate Hydrates (C-S-H) gel is the main binding phase of the cement
41 hydration products, significantly contributing to the cohesion and strength of cement.
42 C-S-H gel is known as imperfect crystalline and a close analogue of Tobermorite and
43 Jennite minerals. In the past three decades, a number of crystalline models for C-S-H
44 structure were identified or developed, based on the well-known Tobermorite and/or
45 Jennite structures [11-17]. 14 Å Tobermorite and Jennite are the most common
46 crystalline phases presented, whereas the modelling of real imperfect crystalline
47 structure of the C-S-H gel is tremendously challenging. Generally, the C-S-H
48 structure can be characterized in terms of calcium/silicon (Ca/Si) ratio which
49 normally ranges from 0.6 to 2.3 [18]. 14 Å Torbermorite has a chemical formula
50 $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ and a density of 2.18g/cm^3 . Typical Jennite has a Ca/Si ratio of
51 1.5, a density of 2.27g/cm^3 and a formula $\text{Ca}_9\text{Si}_6\text{O}_{18}(\text{OH})_6 \cdot 8\text{H}_2\text{O}$ [19]. Accordingly,
52 Richardson [14] has developed Tobermorite/Jennite (T/J) model and
53 Tobermorite/Calcium Hydroxide (T/CH) model for C-S-H. The T/J model is a
54 combined Tobermorite and Jennite domains while the T/CH model contains
55 Tobermorite silicate chains sandwiching calcium hydroxide, providing higher Ca/Si
56 ratios. Another widely-cited C-S-H model is the so-called realistic molecular structure
57 of C-S-H, developed by Pellenq and his co-workers [20]. This model has defected
58 silicate chains, consisting of silicate monomers, dimers and pentamers. It has a Ca/Si

59 ratio of 1.65 which is close to the recent experimental findings, i.e.,
60 $(\text{CaO})_{1.7}(\text{SiO}_2)(\text{H}_2\text{O})_{1.80}$, by neutron scattering measurements [21]. They postulated
61 that the Ca/Si ratio remains the most important parameter in any model construction
62 of C-S-H. Moreover, Richardson [22] developed a series of models for C-S-H with
63 Ca/Si lower than 1.4 representing different mean chain lengths using crystal-chemical
64 and geometrical reasoning.

65 Based on the C-S-H models, atomic simulation, mainly through molecular dynamics
66 (MD) modeling, have been conducted in recent years to determine the mechanical
67 properties of C-S-H. Al-Ostaz, et al. [23] simulated the mechanical properties of the
68 14 Å Tobermorite, Jennite and calcium hydroxide. They have found that the force
69 field chosen and size of simulation box affected the results. For example, different
70 force fields resulted in different mechanical properties. Moreover, the C-S-H unit
71 needed to be duplicated 3×3×3 to match the experimental mechanical properties for
72 initial MD modeling as the mechanical properties of the original unit and 2×2×2
73 supercell were not very close to the experimental data. Moreover, Hou, et al. [24]
74 modeled the C-S-H structure based on the 11Å Tobermorite [25] with ClayFF force
75 field [26] and investigated the effects of the water layer, silicate chain, and Calcium
76 atoms in the interlayer on the mechanical properties of C-S-H. Other than elastic
77 properties, MD simulation can also be employed to study the fracture properties of
78 cement at the nanoscale. A similar structure as proposed in Pellenq, et al. [20] was
79 used and duplicated several times to form a cube with the size of 13.8 nm; direct
80 tension was then applied to investigate the Mode I fracture of C-S-H under CSHFF
81 force field [27]. It has been found that Ca-O and Si-O bonds were provided to
82 contribute the most cohesive force on xy plane, and weaker H- bonds bind the
83 structure on z plane. In addition, size effects have been shown as result of different
84 size of the central voids made by deleting different number of atoms, on weakening
85 stiffness and cohesive force of C-S-H. Further, fracture toughness of C-S-H were

86 evaluated by MD simulations, and the brittleness was discussed in comparison with
87 other brittle materials at the atomic scale [28].

88 When the structure of C-S-H evolves from nanoscale to mesoscale, it is much more
89 unclear. There are perhaps only two widely acknowledged models, namely, Colloidal
90 model [29, 30] and Feldman-Sereda model [31], to describe the mesostructure of
91 C-S-H. In Jennings's Colloidal model, a globule (about 4.2nm) forms the basic unit
92 cell which is a discrete nano particle; the globules are not linked together but packed
93 randomly with water molecules and voids. In Feldman-Sereda model, however, long
94 layers of C-S-H are well aligned and extend from one nanocrystalline region to
95 another. The 4.2nm unit cell (globule) of C-S-H in the Colloidal model has four or
96 five layers of silicate chains, sandwiching Calcium ions, water molecules and possibly
97 pores. The unit cell then discretely joins each other in different directions to form the
98 mesostructure of C-S-H. To simulate the mesoscale mechanical properties of C-S-H,
99 granular mechanics would be of much interest; however, the mechanical properties of
100 the globule itself and the interfaces on the joining surfaces of these nanostructure cells
101 would need to be obtained in advance. This paper attempts to determine the basic
102 mechanical properties of the globule of C-S-H and the interfaces of the globules in
103 terms of different water contents. The atomic structure of C-S-H in Richardson [14]
104 and the ReaxFF force field are employed in the molecular dynamics simulation. The
105 results in this study will provide important and necessary input for mesoscale
106 modeling of C-S-H by either discrete element modeling or finite element modeling.

107 **2. MODEL CONSTRUCTION**

108 The atomic structures of C-S-H used in this paper are chosen from Richardson [22],
109 i.e., T2_ac and T11_14sc. T2_ac is a double-chain Tobermorite-based monoclinic
110 structure, derived from Merlino, et al. [32] in which all the interlayer Ca atoms are in
111 octahedral coordination with oxygen atoms in silicate chains, as shown in Figure 1(a).
112 T11_14sc is also a Tobermorite-based monoclinic structure but the mean length of

113 silicate chains is 11 Å and the layer spacing is 14 Å, as presented in Figure 1(c).
114 Based on these two structures, two orthorhombic structures are generated (Figure 1(b)
115 and (d)). Moreover, in Jennings's Colloidal model intraglobular pores (IGP) may exist
116 in the unit cell of globule and the effects of IGP have not been addressed or simulated
117 yet. In this paper, a structure containing IGP is produced as shown in Figure 1(e). And
118 the characteristics of all five models is listed in Table 1. All structures are tested
119 under uniaxial tension along y and z axis. For T2_ac molecular structure with
120 chemical formula $\text{Ca}_4\text{H}_2(\text{Si}_2\text{O}_7)_2\text{Ca}_4\text{H}_2\text{O}$, the lattice parameters of $a = 11.35 \text{ \AA}$, $b = 7.3$
121 \AA , $c = 21.5 \text{ \AA}$ and $\beta = 98.4^\circ$ with space group C12/c1 are duplicated as $4 \times 6 \times 2$ along
122 x-, y-, z- directions, respectively, to generate Model I; the structure is then changed to
123 orthorhombic structure, where the volume, density, atom position and bonds
124 information are kept the same, as named Model II. For T11_14sc molecular structure
125 with chemical formula $\text{Ca}_9(\text{Si}_{11}\text{O}_{28}(\text{OH})_6)(\text{H}_2\text{O})_{7.25}$, the lattice parameters of $a = 11.35$
126 \AA , $b = 7.3 \text{ \AA}$, $c = 52.7 \text{ \AA}$ and $\beta = 95.5^\circ$ with space group C1 are duplicated as $4 \times 6 \times$
127 1 supercell along x-, y-, z- directions, respectively, to generate Model III; the structure
128 is then changed to orthorhombic, namely, Model IV. Model V is the IGP structure.
129 LAMMPS [33] is used to perform the MD simulations.

130

131 Model III and Model IV have advantages to be used as the basic structure to
132 investigate the effects of IGP [30] on the mechanical properties of C-S-H, since the
133 interlayer Calcium atoms have the occupancy lower than 1.0 which can be arranged in
134 MD simulation for a targeting structure. In this paper, Model IV is modified by
135 rearranging the first upper interlayer Calcium atoms in the unit with a number of
136 water molecules to maintain appropriate Ca-O coordination number [22], for a
137 porosity of 10.43%, shown as Model V in Figure 1(e). All simulation boxes, i.e.,
138 Models I – V, are relaxed for 50 ps in the isobaric-isothermal ensemble (NPT) and
139 coupled to zero external pressure in the x, y, z dimensions. The Nose-Hoover
140 thermostat is used to keep the temperature at 300 K, and the Nose-Hoover barostat is

141 used to maintain the pressure at $p = 0\text{Pa}$. After it reaches equilibrium, the system is
142 subjected to the tensile load along y- and z-direction with a constant strain rate at 0.08
143 $\text{\AA}/\text{ps}$. For the strain-stress relation along y direction, the pressures in the x and z
144 directions are kept at zero, and for the strain-stress relation along z direction, the
145 pressures in the x and y directions are kept at zero.

146

147 ReaxFF has been extensively used in simulating the molecular behavior of C-S-H
148 structures, e.g., [34, 35]. In general, ReaxFF can simulate the chemical and physical
149 interactions between Ca, Si, O, H atoms in the C-S-H gel and the interfaces. The
150 potential energy defined by the ReaxFF can be expressed as follows [36]:

$$\begin{aligned} 151 \quad E_{system} = & E_{bond} + E_{lp} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{coa} + E_{C2} + E_{tors} + E_{conj} + \\ 152 \quad & E_{H-bond} + E_{vdWaals} + E_{Coulomb} \end{aligned} \quad (1)$$

153 where E_{bond} is bond energy, E_{lp} is long pair energy, E_{over} is over coordination energy,
154 E_{under} is under coordination energy, E_{val} is valence angle energy, E_{pen} is penalty energy,
155 E_{coa} is three-body conjugation energy, E_{C2} is C=C correction, E_{tors} is torsion rotation
156 energy, E_{conj} is four-body conjugation energy, E_{H-bond} is hydrogen bond interaction
157 energy, $E_{vdWaals}$ is van der Waals interaction energy and $E_{Coulomb}$ is coulomb interaction
158 energy. The energy of per atom is calculated by defined potentials from neighbor
159 atoms. In the present study, not all of terms in Eq.(1) are considered necessary and
160 some of them are set to zero, which reduces terms of the energy expression as
161 follows:

$$162 \quad E_{system} = E_{bond} + E_{over} + E_{val} + E_{tors} + E_{vdWalls} + E_{Coulomb} \quad (2)$$

163

164 **Interfaces between the globules**

165 Jennings's Colloidal model (2008) sheds light on simulating the mesoscale
166 mechanical properties of C-S-H by using granular mechanics, i.e., discrete element
167 method, or continuum mechanics, i.e., finite element method. No matter which

168 method is used to simulate the meso system of C-S-H, the interfacial properties
169 between the unit globules should be known as a prior. To investigate the normal and
170 shear strengths at the interfaces in different directions, two supercells of Model IV are
171 connected to each other along (100), (010) and (001) planes. Five different
172 thicknesses of water layers are added in the interface to investigate the effect of water
173 content on the interfacial properties, 0.0, 0.5, 1.0, 1.5, 2.0 Å, respectively. The density
174 for water is 1 g/cm³ and the Water/Si ratio for each model is 0.66, 0.86, 1.04, 1.25 and
175 1.37, respectively. The simulation box is relaxed for 50 ps in the isobaric-isothermal
176 ensemble (NPT) and coupled to zero external pressure in the x, y, z dimensions. After
177 that, the boundaries are changed to non-periodic and shrink-wrapped in three
178 dimensions for the shear test and the microcanonical ensemble (NVE) is employed.
179 During each shear test, the bottom atoms are fixed and the top atoms are loaded to
180 move along the interface with a constant loading rate at 0.08 Å/ps. During each
181 tensile test, the bottom is fixed and the top is moved vertically to the interface with a
182 constant loading rate of 0.08 Å/ps.

183 **3. RESULTS AND DISCUSSION**

184 **3.1 Mechanical properties for C-S-H globules**

185 The complete tensile test simulations for the C-S-H globules along y- and z-
186 directions (along silicate chains and normal to silicate chains respectively) are shown
187 in Figure 2. In addition, the direct tensile stress-strain relationships obtained are
188 shown in Figure 3. In y-direction, all the five structures present linear increases in the
189 initial elastic stage while Model I and II have slightly lower elastic modulus than the
190 other three structures. Model I and II have very close tensile stress-strain relationship
191 which has the maximum stress about 9 GPa at the strain of 0.11. These two structures
192 are very brittle, since following the maximum value, the stress suddenly reduces to
193 4.5 GPa and keeps constant for the next 0.2 straining. It then gradually decreases until
194 the complete separation. For Models III, IV and V, the stresses develop in similar

195 trend and increase up to about 11 GPa. Different from Model I and II, these three
196 structures undergo a clear ductile development before they gradually decrease. Such a
197 ductile stage in the mechanical behavior is caused by the longer mean length of the
198 silica chains, which provide higher force carrying capability during tensile test along
199 the y-direction. Moreover, it is interesting to find that the Model V (i.e., IGP structure)
200 has some minor strength decrease at y-direction, compared with Models 3 and 4. This
201 means the intralayer pores can slightly affect the mechanical properties in the silicate
202 chain length direction. It makes sense as the y-direction mechanism is mainly
203 provided by the silicate chains which are not significantly affected by these pores. In
204 z-direction which is the direction vertical to the silica chain, Models I and II have
205 much higher strengths compared with Models III, IV and V. The stress-strain curves
206 for Models I and II in z-direction are close to those in y-direction except for the
207 softening pattern. However, the C-S-H structures of Models III – V have much lower
208 strengths in z-direction in comparison with those in y-direction. This is because the
209 interlayer Calcium and water interface in Models III – V provide a weaker connection
210 compared to Model I and II, where the Calcium atom is in octahedral coordination
211 with oxygen atoms resulting in much stronger interactions. Compared to Models III
212 and IV, Model V (IGP structure) has much lower strength, i.e, 1.15GPa, while the
213 Model III and IV go up to 1.9 GPa. It demonstrates that the existence of IGP can
214 significantly reduce the strength of the C-S-H globules in the z-direction (i.e., the
215 normal direction to the silicate chains).

216

217 The modulus of Elasticity calculated from the stress-strain curves and the maximum
218 stress of each structure of C-S-H are shown in Table 2. The Young's modulus of the
219 five structures along z-direction is in the range of 39 GPa to 54 GPa, which is
220 reasonable compared to the experimental data of cements in range of 38 GPa to 56 GPa
221 for wetted cement with low porosity and simulation data of tobermorite-like and
222 jennite-like structures in range of 35 GPa to 56 GPa [37, 38]. The strength of each

223 structure is also in the reasonable range compared to tobermorite-like structure at about 1.4 GPa
224 along z-direction and 9 GPa along y-direction [28, 39]. The Young's modulus in y direction
225 increases when the C-S-H gel changes to orthorhombic from monoclinic. By contrast,
226 the strengths in y and z directions and the Young's modulus in z direction reduce for
227 the orthorhombic structure. The change of crystal system has an impact on the
228 mechanical properties; although the difference is not significantly large, it needs to be
229 rigorous in establishing C-S-H structures. On the other hand, for some large scale
230 molecular system modelling or interfacial properties study, the structure will need to
231 be changed slightly under duplication or packing or fitting in simulation box.
232 Interestingly, Model V shows lower mechanical capacity, especially in z-direction,
233 with 28% and 40% reduction for modulus of Elasticity and strength compared to
234 Model III, respectively. Under loading the existence of IGP will cause rearrangement
235 of Calcium in the interlayer.

236

237 **3.2 Mechanical properties for the interfaces between C-S-H globules**

238 Figure 4 illustrates Model IV packed with 0 to 2 Å water layer interface on different
239 surfaces of the globules, and the structure with W0, W5, W10, W15, W20 stand for
240 the interface with a water layer of 0.0, 0.5, 1.0, 1.5, 2.0 Å added, respectively. The
241 force F_i exerted on atom i is given by $F_i = -\frac{\partial E_i}{\partial r_i}$, where E_i is the interaction
242 energy for atom i , and r_i is the position of atom i . The total shear force F on the
243 fixed atoms is calculated by $F = \sum F_i$. The tensile force F is considered as being
244 transferred to the interface between two C-S-H globules. The stress at the interface
245 can be calculated as follows:

$$246 \quad \sigma = \frac{F}{A} \quad (3)$$

247 where F is tensile force at the interface, and A is the force-resisting area. Due to the
248 tensile test, the area in Equation (3) is kept constant, the tendency of the

249 force-displacement and stress-strain curve is the same and only the stress-strain
250 curves are shown in Figure 5.

251

252 For all three types of interfaces, the interface with no extra water molecules has
253 greatest tensile strength compared to other structures with added water, because of the
254 destructive effect of water on the bond generation between two C-S-H globules. For
255 (001) interface, the stresses of other four structures with different amount of water
256 molecules added present similar properties and there is no significant difference
257 among the maximum value of stress, initial elastic stage and trend of curve. For (010)
258 and (100) interfaces, the slope of initial elastic stage and the maximum value of stress
259 both decrease with the increase of water content. The details of the tensile mechanical
260 properties calculated from Figure 5 are shown in Table 3.

261

262 Young's modulus is defined by the slope of the initial elastic stage. Compared to the
263 mechanism analysis of C-S-H globules during compressing test, the results in this
264 study cover different Young's modulus between C-S-H interfaces in range of 10 GPa
265 to 37 GPa in three elastic stage under compression [40]. The fracture energy G_F is
266 determined from the area under the stress-strain curves in Figure 5, multiplied by the
267 initial length of the simulation box. For (001) surface, with water molecules added,
268 the maximum stress, Young's modulus and fracture energy show no significant
269 difference among different water content. For (010) and (100) surfaces, the maximum
270 stress and Young's modulus decrease with the increase of water molecules. The
271 minimum values of the fracture energy in three interface types all show in the
272 structure with 2.0 Å and 1.5 Å water layer. It is interesting that the maximum value of
273 stress and Young's modulus of W0 structure in (010) interface are almost the same as
274 the value of Model III along y-direction in Table 2. This is because Reaxff allows
275 bond breakage and generation so that the interface reconnects as one C-S-H unit
276 during equilibrium to form the original structure. For further simulation such as FEM

277 and DEM, the results in (001) interface are recommended, because it is the natural
278 cleavage plane which is also the weakest layer in the C-S-H structure [41]. The tensile
279 properties are calculated by the average of four structures with extra water molecules
280 as: $\sigma_{\max} = 0.98 \pm 0.09$ Gpa ; Young's modulus $E = 29.92 \pm 3.55$ GPa ;
281 Fracture energy $G_F = 0.47 \pm 0.13$ J/m².

282

283 The shear properties for the interfaces of C-S-H globules with different water content
284 are also simulated and the shear force – displacement curves are shown in Figure 6.
285 The shear force F is directly related to the interfacial stress transfer and can be used
286 as the basis to derive the interfacial shear strength of the globule interfaces. Figures
287 6(a)-(c) show the relation between the shear force along moving direction F and the
288 shear displacement for different thickness of water layers for the three types of
289 interfaces. For 001 surface, all the five curves start to increase linearly. The maximum
290 force is achieved for the water layer 0 Å, which is $313.4 \text{ kcalmol}^{-1}\text{Å}^{-1}$ at 5.4 Å shear
291 displacement. After the maximum value of each curve, the shear force along x
292 direction gradually decreases with fluctuation. It can be found that the effect of water
293 layer is significant for 001 surface since the overall shear force of 0 Å water layer is
294 much higher than that of the other four interfaces. This indicates that the water
295 molecules interdict the intralayer Calcium-Oxygen bonding between the globules.
296 The shear force fluctuates over the displacement which is normal for molecular
297 dynamics simulation.

298

299 According to Amonton's law of adhesion [42], the friction force F is divided into two
300 parts: $F = \mu L + F_0$, the external normal force L multiplied by the friction
301 coefficient μ and the internal force F_0 impacted by the adhesion between the surface.
302 In this study, L continuously decreases due to the reduction of the contact surface in
303 the globules interface; the internal force F_0 should initially increase because of bond
304 stretching and then decrease due to bond breakage. During any fluctuation stage of F ,

305 the generation and breakage of bonds in the interface both happen. The shear force–
 306 displacement generally follows Amonton’s law for individual curves. The simulation
 307 of the interfacial shearing clearly shows both the chemical interaction (i.e. bonding)
 308 and the physical interaction occurring at the interface between two globules for three
 309 surfaces, as shown in Figure 4. The shear stress τ can be determined as follows:

$$310 \quad \tau = \frac{F}{A_{CSH-CSH}} = \frac{F}{a_0 \times (b_0 - \Delta b)} \quad (4)$$

311 where $A_{CSH-CSH}$ is the contact area between two C-S-H globules in the interface, a_0 is
 312 the length of C-S-H vertical to the shear direction, b_0 is the width of C-S-H along the
 313 shear direction and Δb is the shear distance of the moving C-S-H globule. For (001)
 314 surface, $a_0 = 43.43 \text{ \AA}$, $b_0 = 50.60 \text{ \AA}$, for (010) surface, $a_0 = 41.60 \text{ \AA}$, $b_0 =$
 315 32.43 \AA , and for (100) surface, $a_0 = 50.60 \text{ \AA}$, $b_0 = 41.60 \text{ \AA}$, respectively. By
 316 using Eq. (4) and the values of a_0 and b_0 above, the shear stress can be calculated as a
 317 function of the displacement for each surface. Figures 7 (a), (c) and (e) show the
 318 relationship between the shear stress and displacement and Figures 7 (b) (d) and (f)
 319 present the maximum shear stress, average shear stress and error bars. The average
 320 stress is calculated after the first peak stress. In the shear stress-strain curves for all
 321 three interfaces, stresses all increase first and then fluctuate over certain values. Such
 322 a shearing mechanism of the interfaces can be simplified to a linear increase, followed
 323 by a constant development over the strain; or it may be called bi-linear stress-strain
 324 curves which can be easily implemented in FEM or DEM modelling. This
 325 yielding-like shearing behaviour after its peak stress is not commonly seen in
 326 macroscale shear stress development in cementitious materials, where the shear stress
 327 usually drops after its strength. It can be found out that the shear strength, i.e., the
 328 maximum shear stress, for any type of interfaces of the C-S-H globules, has the
 329 highest value when no water layer exists. When water molecules are presented at the
 330 interfaces, however, the strength is reduced. Another interesting finding is the content
 331 of water molecules is not a very sensitive parameter. For example, the average
 332 stresses for W5, 10, 15 and 20 of all these interfaces are relatively the same, as shown

333 in Figures 7 (b), (d) and (f). The interfacial shear strength of C-S-H globules interface
334 is then calculated by the average value of the stress for (001) surface with 0.5 Å, 1.0
335 Å, 1.5 Å and 2.0 Å water layer thickness to be about 560.29 ± 135.44 MPa; for (010)
336 surface is about 780.63 ± 39.51 MPa; and for (100) surface, the shear strength is
337 about 564.53 ± 78.33 MPa.

338

339 The shear stress-displacement curves, often known as bond-slip relation, for the
340 C-S-H globule interfaces and the mechanical properties for C-S-H globules are
341 derived for C-S-H. These properties have been hardly seen in existing literature. It has
342 significant impact on multi-scale modeling (either FEM or DEM) in terms of
343 providing necessary inputs for the nanoscale C-S-H structures. These properties are
344 usually not available due to difficulties in conducting experiments. This is why trial
345 and error analysis is always applied for estimating the mechanical properties. The
346 mechanical properties derived in this paper can well be used for defining the
347 bond-slip behavior between the unit C-S-H globules as well as the constitutive
348 relation for the globule itself.

349 **4. CONCLUSIONS**

350 In this paper, the C-S-H globules and the interfaces between the C-S-H globules have
351 been modeled at the atomic scale and the complete mechanism has been studied
352 through MD simulations. Reaxff was used to provide the interactive potentials for the
353 whole molecular system. Key material parameters, e.g., Young's modulus, strength
354 and fracture energy, were determined for the globules and interfaces. It has been
355 found that the atomic structure significantly affects the mechanical performance of the
356 C-S-H structures. Longer mean chain lengths (i.e., Models III - V) tend to increase the
357 strength of C-S-H and, more importantly, change the fracture behavior from brittle
358 failure to ductile failure, along the silicate chains direction. In the direction normal to
359 silicate chains, however, silicate chains do not play an important role while interlayer

360 structure matters. Octahedral coordination of Calcium with oxygen atoms will result
361 in stronger interactions and higher mechanical strengths in the normal direction.
362 Moreover, pores (i.e., IGP) in the C-S-H globules can considerably reduce the
363 strength of the globule structures in normal to silicate chain direction but the
364 weakening effect becomes less significant in silicate chain direction. Further, the
365 effects of water content at the interfaces between globules were investigated and the
366 normal strength and the shear strength for the interfaces were determined. It has been
367 found that, for all types of the interfaces, the interface with no extra water molecules
368 has greatest tensile/shear strength, because of the destructive effect of water on the
369 bond generation between two C-S-H globules. However, it is interesting to find the
370 strength is not very sensitive to the amount of water since different water content at
371 the interfaces resulted in roughly similar mechanical performance. It can be
372 concluded that the mechanical properties obtained in this paper for C-S-H
373 nanostructures and interfaces are highly complementary to the meso-scale modelling
374 of C-S-H via granular mechanics, i.e., DEM, or continuum mechanics, i.e., FEM.

375

376

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512 **List of Tables**

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514 1. The characteristics of five models used for simulation

515 2. Simulated results for the mechanical properties of C-S-H nanostructures along y-
516 and z- directions

517 3. Simulated results for the mechanical properties of the C-S-H interfaces along x-,
518 y- and z- directions

519 Table 1 Characteristics of the five models used in the simulation

Model Name	Original structures from Richardson [22]	Supercell unit ($\text{\AA} \times \text{\AA} \times \text{\AA}$)	Crystalline Structure	Mean length of silicate chain	Bridging tetrahedral connection
Model I	T2_ac	45.4×43.8×43, $\beta = 98.4^\circ$	monoclinic	2 \AA	adjacent
Model II	T2_ac	45.4×43.8×43	orthorhombic	2 \AA	adjacent
Model III	T11_14sc	45.4×43.8×52.7, $\beta = 95.5^\circ$	monoclinic	11 \AA	staggered
Model IV	T11_14sc	45.4×43.8×52.7	orthorhombic	11 \AA	staggered
Model V	T11_14sc	45.4×43.8×52.7	orthorhombic	11 \AA	staggered

520

521 Table 2 Simulated results for the mechanical properties of C-S-H nanostructures
522 along y- and z- directions

	Modulus of Elasticity in y- direction (GPa)	Strength in y- direction (GPa)	Modulus of Elasticity in z- direction (GPa)	Strength in z- direction (GPa)
Model I	85.53	9.13	46.97	7.44
Model II	87.22	8.95	44.88	7.15
Model III	108.10	11.78	53.42	1.93
Model IV	112.71	11.17	51.29	1.92
Model V	116.8	10.94	38.39	1.15

523

524 Table 3 Simulated results for the mechanical properties of the C-S-H interfaces along
 525 x-, y- and z- directions, and W0, W5, W10, W15, W20 stand for the interface with a
 526 water layer of 0.0, 0.5, 1.0, 1.5, 2.0 Å added, respectively.

527

[001]	W0	W5	W10	W15	W20
Maximum Stress (GPa)	1.64	1.04	0.98	0.85	1.05
Young's modulus (GPa)	49.41	34.65	27.14	27.25	30.65
Fracture energy (J/m ²)	1.20	0.50	0.59	0.29	0.50
[010]					
Maximum Stress (GPa)	13.42	5.29	1.93	1.27	1.33
Young's modulus (GPa)	102.18	44.25	19.15	12.29	11.49
Fracture energy (J/m ²)	5.51	1.80	0.34	0.36	0.31
[100]					
Maximum Stress (GPa)	6.09	3.05	1.88	1.45	1.14
Young's modulus (GPa)	75.79	53.28	34.06	25.87	15.48
Fracture energy (J/m ²)	3.79	0.91	0.76	0.43	0.32

528

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- 539 maximum value and average value of stress for each curve in the interface.

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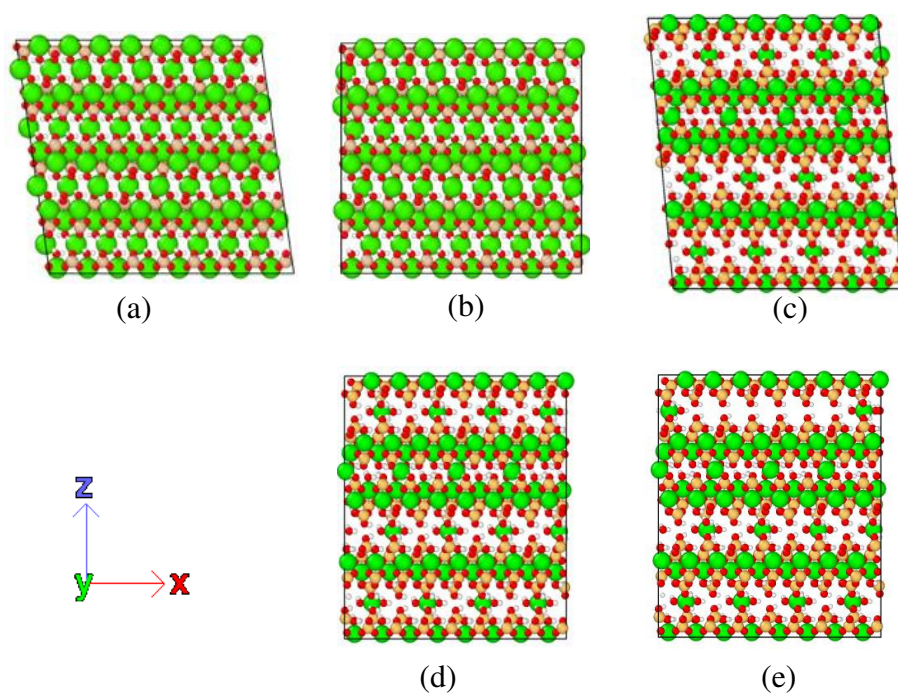


Figure 1 Molecular structures of (a) Model I, (010) surface of T2_ac in monoclinic structure (b) Model II, (010) surface of T2_ac in orthorhombic structure (c) Model II, (010) surface of T11_14sc in monoclinic structure (d) Model IV, (010) surface of T11_14sc in orthorhombic structure (e) Model V, (010) surface of T11_14sc with IGP in orthorhombic structure. Green atoms are Calcium, cantaloupe atoms are Silicon, red atoms are Oxygen and white atoms are Hydrogen in water molecules.

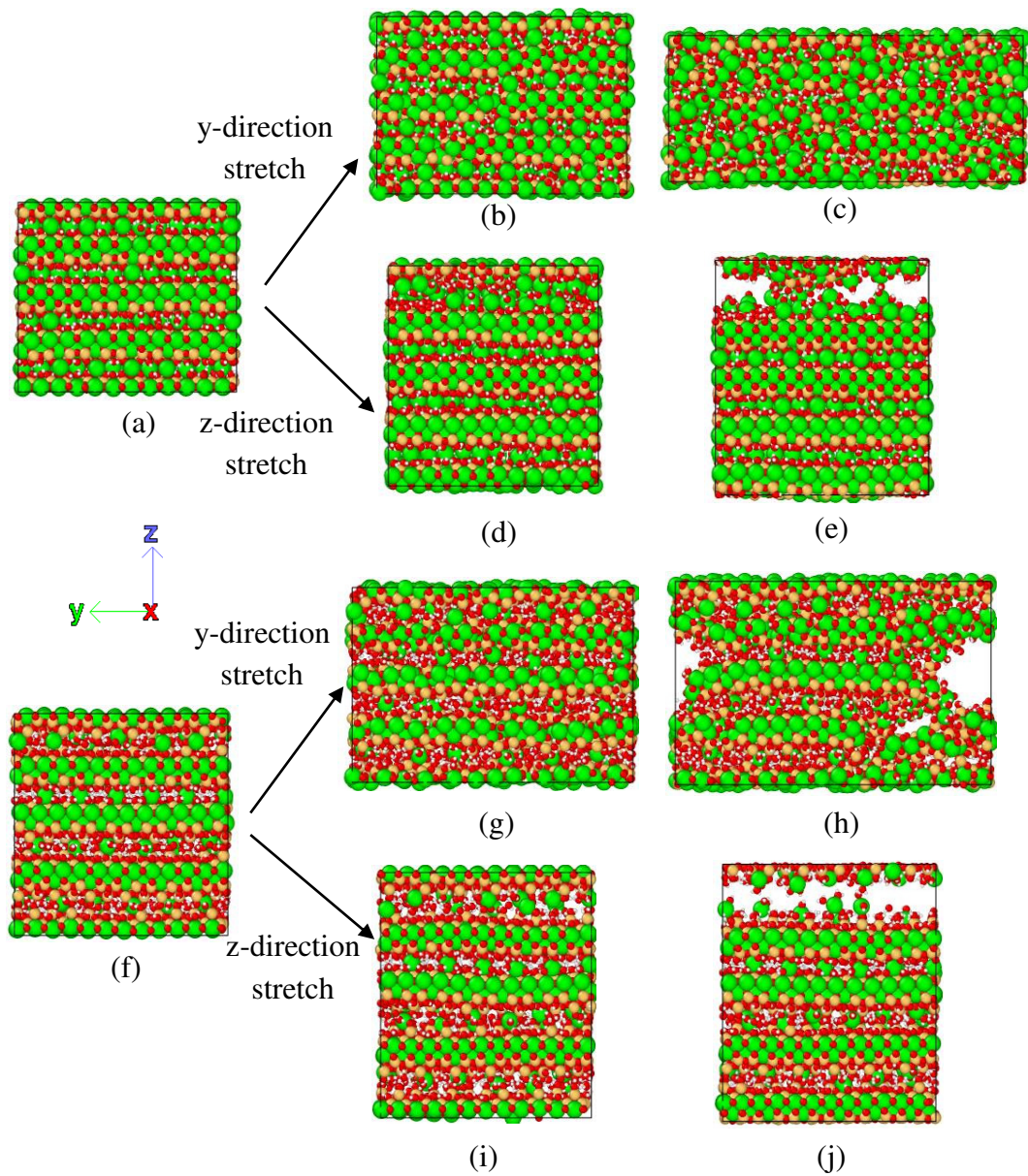
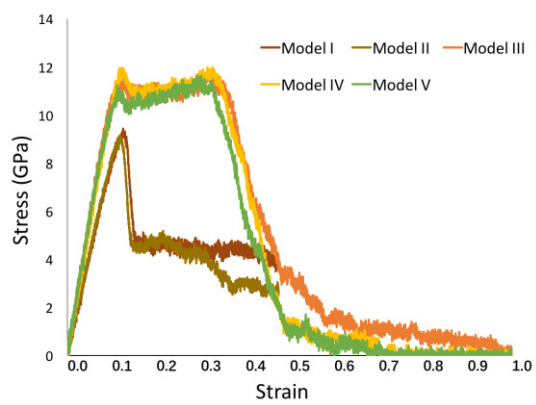
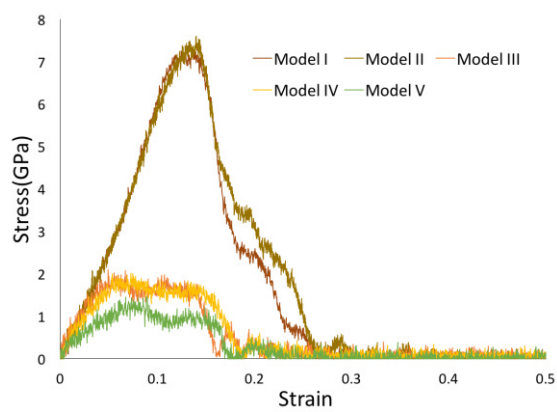


Figure 2 Tensile test simulation of Model I and Model III along z- and y- Directions. (a) Model I after equilibrium. (b) After the maximum value of the stress for Model I along y-direction. (c) The failure happens in Model I along y-direction. (d) After the maximum value of the stress for Model I along z-direction. (e) The failure happens in Model I along z-direction. (f) Model III after equilibrium. (g) Model III after the maximum value of the stress along y-direction. (h) The failure happens in Model I along y-direction, (i) After the maximum value of the stress for Model I in z-direction. (j) The failure happens in Model I along z-direction.



(a)



(b)

Figure 3 Stress-strain curves for five different C-S-H structures along (a) y-direction (b) z-direction

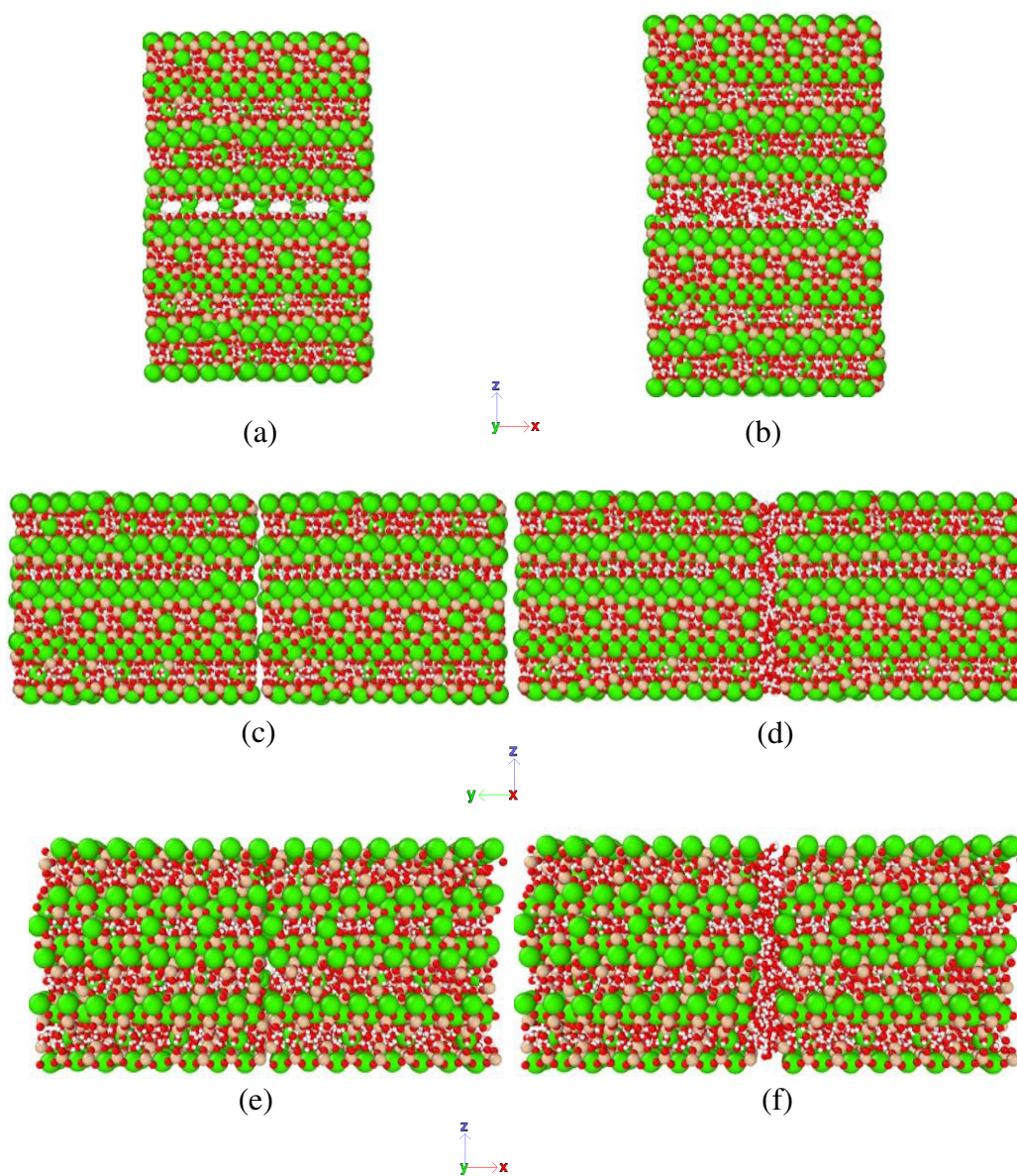
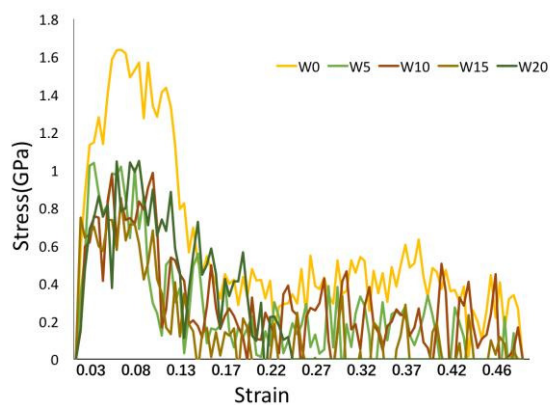
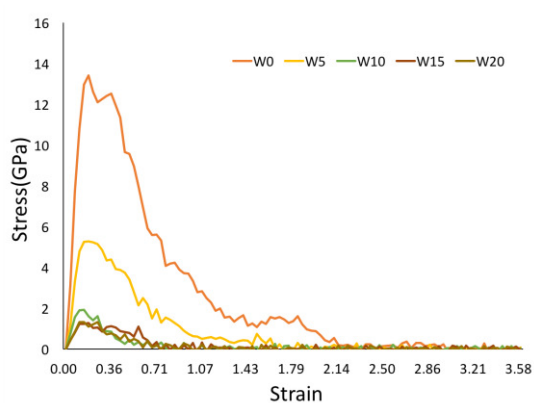


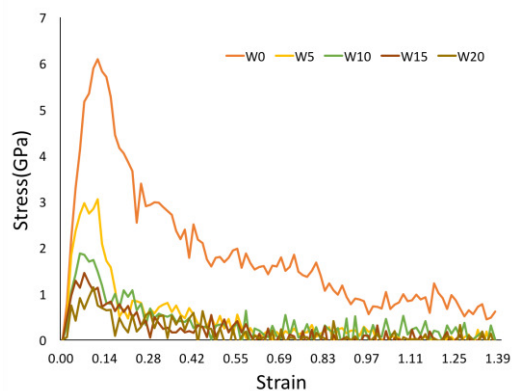
Figure 4 Molecular structure of (a) (001) surface with 0 Å water layer (b) (001) surface with 2.0 Å water layer (c) (010) surface with 0 Å water layer (d) (010) surface with 2.0 Å water layer (e) (100) surface with 0 Å water layer (f) (100) surface with 2.0 Å water layer



(a)

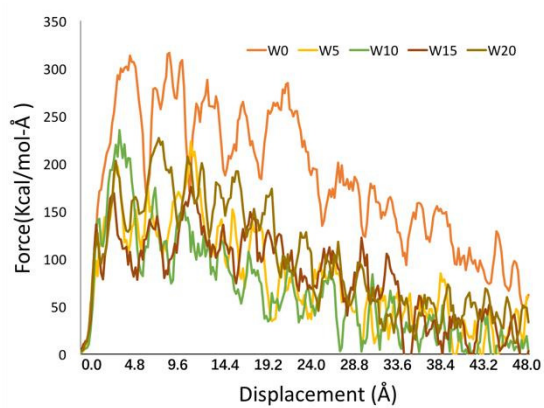


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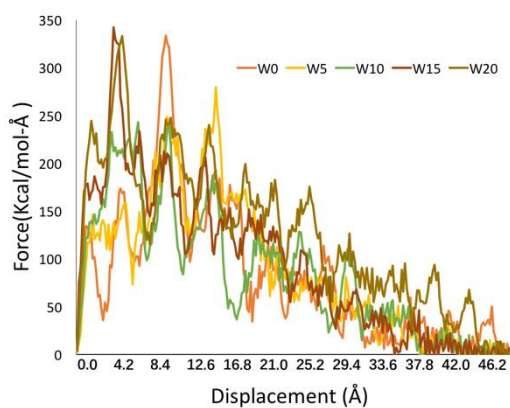


(c)

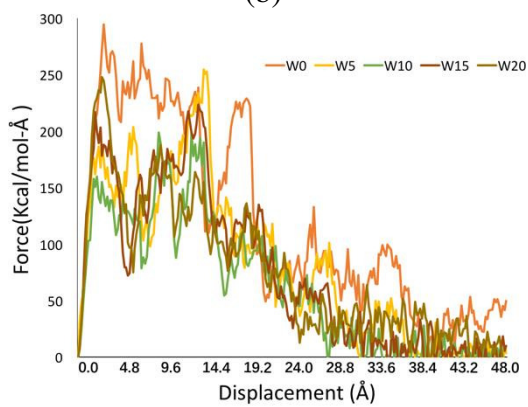
Figure 5 Tensile stress-strain curve for different water content in (a) (001) interface (b) (010) interface (c) (100) interface. W0, W5, W10, W15, W20 stand for the interface with a water layer of 0.0, 0.5, 1.0, 1.5, 2.0 Å added, respectively.



(a)



(b)



(c)

Figure 6 Shear force-displacement curve for different water content in (a) (001) interface (b) (010) interface (c) (100) interface

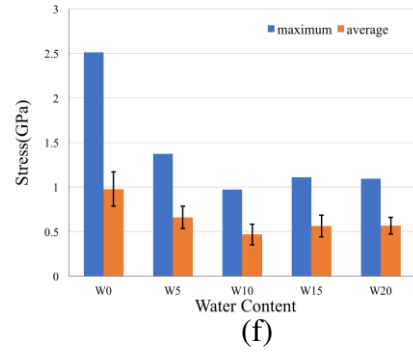
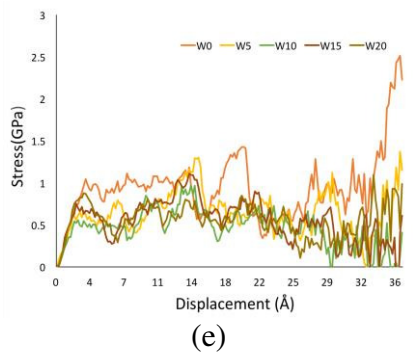
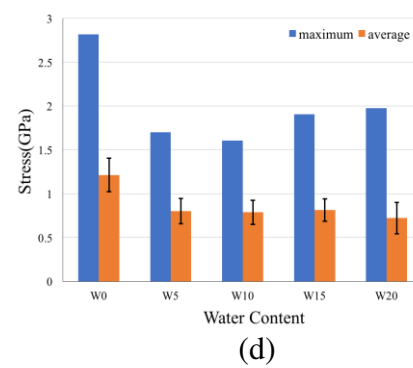
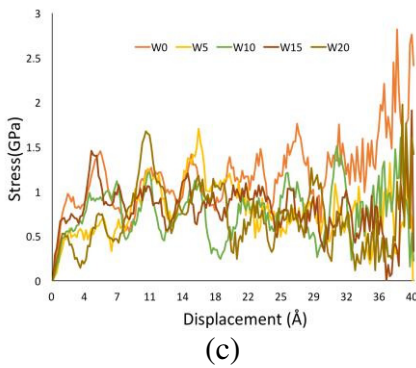
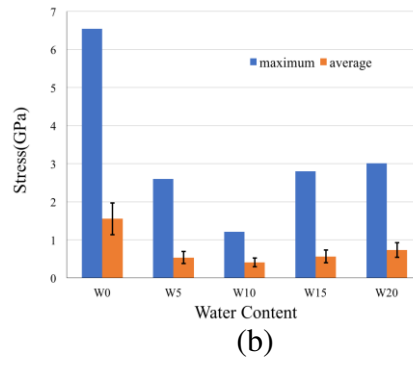
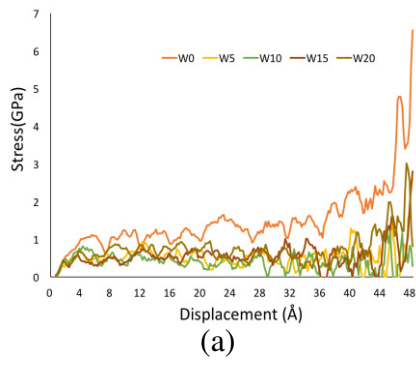


Figure 7 Stress-displacement curve for different water content in (a) (001) interface (c) (010) interface (e) (100) interface. Maximum value and average value of stress for each curve in (b) (001) interface (d) (010) interface (f) (100) interface.

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