Reactive molecular dynamics simulation of the mechanical behavior of sodium aluminosilicate geopolymer and calcium silicate hydrate composites

Mohammad Rafat Sadat[a], Krishna Muralidharan[b], Lianyang Zhang[a],*

[a] Department of Civil Engineering and Engineering Mechanics, University of Arizona, Tucson, AZ 85721, USA
[b] Department of Materials Science and Engineering, University of Arizona, Tucson, AZ 85721, USA

ABSTRACT

This paper for the first time used reactive molecular dynamics (MD) simulation to study the mechanical behavior of geopolymer binder (GB) and calcium silicate hydrate (CSH) composites. Specifically, GB-CSH composites with different Ca/Si ratios for the CSH phase were constructed and their mechanical behavior in terms of ultimate tensile strength, fracture toughness and strain energy release rates were investigated. It was observed that the Ca/Si ratio of CSH greatly affects the mechanical response of the composite. Increasing the Ca/Si ratio from 1.2 to 1.65 created more disorder in the silica layers in CSH and decreased the mechanical properties of the composite. However, the completely glassy CSH at a Ca/Si ratio of 2.0 showed slight improvement of mechanical properties due to high three-dimensional (3D) tetrahedral network. A detailed analysis of bond evolution and bond angle distribution showed their direct correlation with the observed mechanical response. The failure of the GB-CSH composites were always governed by the breaking of Si−O bonds within the CSH, near the GB-CSH interface. Low Ca/Si ratio structures showed more Si−O bond breakage, while in high Ca/Si ratio structures, deformation mobilization was accompanied by significant change in bond angles within GB.

1. Introduction

Geopolymer cement has drawn great attention in recent times due to its remarkable physical and mechanical properties and low energy requirement for its production. Much experimental research has been conducted on the effect of source material types [1,2], source material composition [3–5], and curing condition [3,6] on the physical and mechanical properties of the final geopolymer products. It has been found that in the presence of Ca-rich precursors both geopolymer binder (GB) and calcium silicate hydrate (CSH) phases can be produced and the resulted GB-CSH composite can show enhanced physical and mechanical properties [2].

Yip et al. [7] used metakaolin (MK) and ground granulated blast furnace slags (GGBFS) to produce geopolymers, where the dual presence of GB and CSH gels was confirmed. Further, alkaline activation of only GGBFS was found to produce calcium alumino silicate hydrate (CASH) where the Si atoms in the silica chains are replaced by Al at the bridging sites of Si tetrahedra and the resulting negative charge is balanced by alkali cation (i.e. Na) between the silica sheets [8,9]. Depending on the synthesis conditions and the nature of source materials, geopolymerization in the presence of Ca-compounds can form calcium hydroxide (CH) [10], CSH gel [2,10,11] along with GB gel or form an

entirely different CASH gel phase [8,9]. The atomic scale structure of CASH gel has been studied previously using latest computational methods [12,13]. However, although widely observed in experimental studies, to the best knowledge of the authors, no previous work has been undertaken using computational methods to investigate the co-existence of GB and CSH as separate phases. At the atomic scale, the mechanism of the interfacial interaction between the two phases needs to be better understood for the optimum design of geopolymer in the presence of Ca. This kind of information cannot be obtained from physical experiments alone. In this regard, molecular dynamics (MD) simulation provides a good way to study the interfacial interaction between GB and CSH.

In this study, GB-CSH composites were constructed using ReaxFF MD simulation [14] and their structural, dynamical and mechanical properties were studied in detail, aiming to better understand geopolymer in the presence of Ca.

2. Background

2.1. ReaxFF MD simulation

ReaxFF was first developed by van Duin et al. [15] in 2001 using

bond order (or bond strength), in a fashion similar to the Tersoff [16] and Brenner [17] potentials. In these interatomic potentials, the bond order monotonically decreases with the coordination of an atom and that information is added as a parameter into the interatomic potential function. Since ReaxFF is based on the concept of bond order, it allows for dynamic formation and breaking of bonds and hence can simulate chemical reactions. Furthermore, when a deformation is applied, ReaxFF can dynamically adjust the charge of various species but in typical classical MD potentials, the charge of an atomic species is always fixed. Because of the aforementioned advantages, ReaxFF has gained remarkable acceptance among researchers and has been increasingly used for simulating a diverse array of materials including sodium silicate glass [18], CSH gel [19], silica-water interface [20], alumina-water reaction for hydrogen fuel extraction [21], sol-gel synthesis of bio-active glasses [22] and water dynamics in smectite clay-zeolite composites [23].

2.2. MD simulation of CSH and geopolymer

A great number of MD simulation studies have been undertaken to understand the CSH structure and find its mechanical properties from a bottom up fashion. Pellenq et al. [24] proposed a molecular model of CSH gel consistent with experimental determination using neutron scattering and Extended X-ray Absorption Fine Structure (EXAFS) measurements. Bauchy et al. [25] used ReaxFF potential for simulating CSH structure. Unlike the core shell parameters used in [24], the use of ReaxFF allowed the dissociation of water into −OH groups. Good agreement between the CSH simulation and experimental data was observed in terms of Si−O, Ca−O and Si−Si correlations from X-ray pair distribution function (PDF). The crystal structure of tobermorite with a Ca/Si ratio of 1 was also simulated to compare its PDF with that of CSH (Ca/Si = 1.65) structure. Manzano et al. [19] used MD to study the shear deformation behavior of CSH gel. It was emphasized by the authors that although the macroscopic mechanical behavior is the combined effect of multiple features emerging at different scales, in most cases the deformation within the CSH gel itself will play an important role. It was found that the water rich defective regions in the CSH gel are responsible for the development of deformations. It was also found that the development of deformation was less localized in tobermorite than in the CSH. Qomi et al. [26] studied the dynamics of nanoconfined water within the silicate layers of CSH using ReaxFF MD simulation. It was found that the composition of CSH gel has a significant effect on the structure of water. The dipole moment, Voronoi density and the number of hydrogen bonds per water molecule were found to increase with the Ca/Si ratio. The mobility of water was also found to be strongly composition dependent. The diffusivity of water increased with higher Ca/Si ratio by up to one order of magnitude. The diffusivity at all Ca/Si ratios was 1/1000th of that of bulk water. The self-diffusivity of water in the interlayer was found to be roughly ten times smaller than the one observed from experiments. It was explained by the authors that the experimental results can only look at the dynamics of water at the mesopores but cannot address the water dynamics inside the nano pores of CSH. Bauchy et al. [27], in a different study, determined the fracture toughness and critical energy release rates of CSH gel using ReaxFF MD simulation. The fracture toughness determined from MD was in good agreement with the experimental values. The CSH structure was found to be showing nano ductility due to the inherent flexibility of the CSH structure. It was suggested by the authors that the MD results cannot be directly compared with the experimental data due to the presence of various phases and different pore size in hardened cement paste. Hou et al. [12] introduced Al within the CSH to study its effect on the structure and mechanical properties of calcium aluminate silicate hydrate (CASH) using ReaxFF MD simulation. It was found that the addition of Al played a crucial role in connecting the defective silicate chains and transforming the CSH gel from a layered structure to a 3D network. The failure stresses obtained for the CASH were found to

be higher than that of the CSH gel. Using MD simulations, Manjano et al. [28] showed that introducing defects in crystalline CSH (e.g. tobermorite, Jennite) leads to lower mechanical properties, which is in good agreement with the experiments. Increasing only the Ca/Si ratio slightly lowers the mechanical properties of the crystalline CSH, but their magnitude is much higher compared to the experimental results without the presence of any defects. Zhou et al. [29] in a very recent MD simulation study showed that increasing the Ca/Si ratio enhances the chloride absorption in CSH gel. The Cl adsorption is facilitated by the generation of non-bridging oxygen sites and free Ca ions with the increment of Ca/Si ratio.

In contrast, very few MD simulation studies have been carried out on geopolymer binder (GB). Kupwade-Patil et al. [30] showed the effect of temperature and Si/Al ratio on the stability of GB using MD. In our recent work [31], MD simulations were used to understand the effect of nano confined molecular water on the structure and mechanical properties of GB. To the best of our knowledge, no previous studies have been conducted to understand the interfacial interaction between GB and CSH and correlate the interface structure with the mechanical properties of the GB-CSH composite. Therefore, this paper will make the first attempt to shed light on this problem. To do that, first the molecular models of GB and CSH are created separately and an interface between the two phases is formed. Then the effect of composition (i.e. Ca/Si ratio) in CSH on the mechanical properties of the GB-CSH composite is studied. For better understanding of the GB-CSH composite, a detailed characterization of the structure of the interface and the respective phases is also performed.

3. Methodology

3.1. Computational details

The total energy in ReaxFF is defined as below:

$$E_{system} = E_{bond} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{tors} + E_{conj} + E_{vdwals} + E_{Coulomb} \quad (1)$$

where E_{bond} is the bond energy which depends on the bond order (BO) of two atoms. BO depends on the interatomic distance between two atoms. E_{over} and E_{under} are the energy penalty for over- and under-coordination of atoms, respectively. E_{val}, E_{pen}, E_{tors}, E_{conj}, E_{vdwals} and $E_{coulomb}$ are the valence angle energy, penalty energy, torsion energy, conjugation energy, van der Walls energy and Coulombic energy, respectively [15].

The parameters of ReaxFF are discussed in detail in the original paper of ReaxFF for hydrocarbons [15] and will not be repeated here. ReaxFF corrects for the BO if an atom is over-coordinated. In ReaxFF, BO is associated with the interatomic distance by a simple equation with separate terms for sigma, first pi and second pi bonds. The BO and its corrections make ReaxFF inherently many-body. This causes ReaxFF to be computationally more expensive than traditional MD potentials. To account for Coulombic interactions, ReaxFF typically eschews Ewald summation (or any other long-range interaction based methods that account for charge-charge interactions), and instead uses direct real-space summations with shorter-range spatial cutoffs [15,32]. To calculate atomic charges, ReaxFF uses electronegativity equilibration method (EEM) [33], which is similar to the charge equilibration (qeq) scheme [34]. This is rather an attractive feature for simulating hydrated aluminosilicates like geopolymer which can have different neighboring environment due to the presence of water and alkali cations. The parallel codes reax/c and qeq/reax [35] available in LAMMPS package [36] were used for running all simulations in this paper. The ReaxFF parameters used in the current study were originally developed and used for Smectite clay-zeolite composites by Pitman et al. [14]. These parameters were also successfully used in predicting the structure of sodium silicate glass [18]. The full interatomic potential parameters can