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An atomistic characterization of the interplay between composition, structure and mechanical properties of amorphous geopolymer binders

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ABSTRACT

The amorphous geopolymer binder-phase is the primary adhesive constituent within a geopolymer and consists of completely polymerized glassy networks of (SiO_4) and $(AlO_4)^-$ tetrahedra as well as interstitial charge-balancing alkali cations. In this context, the mechanical properties of the geopolymer binder-phase were examined as a function of the underlying silicon to aluminum ratio using molecular dynamics (MD) simulations. Detailed structural analysis reveals that the presence of edge-sharing $(AlO_4)^-$ tetrahedra, nanoscale voids as well as non-bridging oxygen and penta coordinated aluminum atoms significantly impact the ensuing elastic moduli, ultimate tensile strength and the nature of failure of the geopolymer binder-phase. In particular, the simulations indicate that there is an optimal silicon to aluminum ratio (~2–3) that results in enhanced mechanical properties. This study provides, for the first time, valuable insight into the structural mechanisms that are responsible for the strength and mechanical properties of the geopolymer binder-phase.

1. Introduction

Growing demand for environment friendly, low cost cementitious materials has led to efforts for developing viable alternatives to ordinary Portland cement (OPC). Davidovits [1] pioneered the development of such an alternative named geopolymer, which is a product formed through the alkali activation of metakaolin. Later, geopolymers were also synthesized from other aluminosilicate source materials such as fly ash [2–4], blast furnace slag [5–7], mine tailings [8–10] and red mud [11,12]. Typically, the activation of a source material results in the formation of a biphasic "composite", which consists of unreacted source-material particles bonded by an amorphous geopolymer binder-phase (GBP) [13]. Specifically, the GBP consists of a completely polymerized network of (SiO_4) and $(AlO_4)^-$ tetrahedra, with alkali cations residing in the interstices of the GBP network for charge balance [13]. In addition to the unreacted source-material particles and GBP, the geopolymer composite also contains a wide distribution of voids in which residual water is present [14,15].

The mechanical properties of geopolymer composites (referred to as geopolymers herein) have been widely investigated experimentally [12,14,16,17], due to their importance as a new structural material. The experimental studies indicate that the Si/Al and Na/Al ratios play a crucial role in determining the mechanical strength of geopolymers. The strength of geopolymers increases with increasing Si/Al or Na/Al ratio up to a certain level and then starts to decrease, meaning that there is an optimum value for both the Si/Al and Na/Al ratios. Table 1 summarizes the optimum Si/Al and Na/Al ratios at the maximum unconfined compressive strength for geopolymers studied by different research groups. It is noted that these ratios are for the source materials and may be quite different from the corresponding ratios in the GBP due to the fact that some of the Si, Al and/or Na in the source materials may not take part in the geopolymerization process. The experimental studies also indicate that the degree of geopolymerization or the amount of GBP has a great impact on the mechanical properties of geopolymers. However, to the best of our knowledge, there has been no systematic effort in examining the mechanical properties of GBP as well as their effect on the ensuing mechanical response of geopolymers. Towards this end, as an important first step, we examine the structure–composition–mechanical property relations of GBP using an atomistic computational technique namely molecular dynamics (MD). While this work focuses on atomic scale mechanisms that govern the mechanical properties of GBP as a function of GBP composition, the success of this work will spur the development of hierarchical models that accurately represent the multiscale mechanical response of geopolymers.

It is well known that there are striking similarities between geopolymers and sodium aluminosilicate (NAS) glasses. In particular, both are amorphous as seen from X-ray diffraction (XRD) [18,19], and their respective NMR spectra show a predominance of four folded Si and Al tetrahedral connectivity [19–21], although the geopolymers show an additional NMR feature corresponding to the six-fold coordinated Al characteristic of the minority unreacted source material such

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Table 1
Optimal Si/Al and Na/Al ratios leading to maximizing mechanical strength as identified in literature (modified from [25]).

No.	Source material	Optimum Si/Al	Optimum Na/Al	Reference
1	Metakaolin	1.9		[14]
2	Copper mine tailings and fly ash	1.89		[10]
3	Metakaolin and blast furnace slag	1.58–1.73		[6]
4	Metakaolin	1.75–1.90	1.2	[26]
5	Fly ash	1.95	1.0	[27]
6	Metakaolin	1.7–1.9	0.8–1.0	[28]
7	Municipal solid waste incinerator fly ash	2.0		[29]
8	Metakaolin	2.5	1.3	[30]
9	Metakaolin	2.5	1.25	[31]
10	Kaolinite and fly ash	2.0		[32]
11	Kaolinite, albite and fly ash	2.1		[32]
12	Metakaolin	2.0	1.0	[33]
13	Metakaolin	2.75	1.0	[34]
14	Metakaolin	1.55	1.15	[35]
15	Kaolin	1.64	1.09	[36]

as metakaolin [22]. The dominant tetrahedral peak, which is consistent with four-fold Al atoms, can be ascribed to the polymerized GBP [22], and thus a direct correlation between the GBP and the NAS glass structures at the atomic- and nano-scales can be expected. In this context, in this work, using NAS glass structures as proxies, MD simulations of GBP with varying Si/Al ratios (1:1 to 4:1), while fixing the Al/Na ratio at 1 to ensure charge neutrality, will be carried to explore and characterize the interplay between the composition and mechanical properties of GBP. It is also worth pointing out that transmission electron microscopy (TEM) has revealed that the GBP is similar to porous amorphous aluminum silicate structures [14,23], with the overall density dependent on the processing conditions [13]. Specifically, high temperatures, high dilution rates and low silicon concentrations can lead to densification of the GBP [13]. In this regard, the MD simulations will be carried out on systems that correspond to dense, compacted GBP structures (the compacted density is also referred to as skeletal density [14,24]). An equally important aspect of this work is that the obtained results will also have important implications in furthering the understanding of NAS glasses in terms of the relations that characterize their composition and mechanical properties.

2. Background

MD is an atomistic simulation technique capable of modeling the thermodynamic, mechanical and transport properties of materials. The accuracy of classical MD simulations is governed by the choice of the underlying interatomic potential used for describing the interaction between constituent atoms (and molecules). While interatomic potentials are typically parameterized to replicate materials' thermodynamic properties that are either derived from first-principles or from experiment, they can provide valuable insight into the atomic-scale mechanisms that govern the mechanical response of materials to external stimuli [37–40]. Although MD simulations tend to systematically overestimate yield and failure stress/strain when compared to experimental data, the proper choice of the interatomic potentials still enables the ability to capture the trends that describe the composition (and temperature) dependent variation in materials' properties. The overestimation can be attributed to the fact that the size of MD simulation cells are at best, 100s of nanometers (with or without periodic boundaries), thereby precluding the incorporation of large defects (voids, pores). Further, MD simulations can only be carried out at high strain rates (as compared to experimentally achievable rates) due to computational constraints, and this serves as another reason for the systematic deviations from experiments while comparing MD and experimentally derived yield and fracture stresses/strains.

MD has been previously employed to understand the structure and mechanical response of NAS glass. Using MD, Zirl and Garofalini [41] studied the structure of NAS by varying the Al/Na ratio (0.25 to 2.0) in conjunction with the corresponding Si/Al ratio (4 to 1.2). A substantial amount (~25%) of non-bridging oxygen (NBO) was seen at low Al/Na ratios leading to an open network structure and high diffusivity of the alkali ion.

In a more recent study by Xiang et al. [42], the structure and mechanical properties of NAS glass as a function of different Al/Na ratios was studied using two-body potentials. In contrast to [41], the authors eschewed the usage of three-body terms in the potential form, noting that the three-body terms might have constrained the formation of non-tetrahedrally coordinated Al. Thus using simpler two-body terms, larger simulation systems consisting of around 3000 atoms were studied to get a better representation of the NAS glass structure. For Al/Na ratios less than 1, Al was mainly four-fold coordinated and formed an integral part of the network NAS glass structure; at Al/Na > 1, oxygen triclusters as well as some non-tetrahedrally coordinated (3–5) Al were seen and their concentration increased with increasing Al/Na ratio, with a consequent effect on the resulting elastic modulus of the NAS glasses.

In the current work, we expand upon earlier investigations of NAS glass structures by focusing on NAS glasses (which are GBP proxies) with a fixed Na/Al ratio equal to 1 while allowing the Si/Al ratio to vary between 1:1 and 4:1. We study the effect of the Si/Al ratio on the structure and mechanical properties of the NAS glasses under uniaxial strain. We conducted all our simulations at a uniaxial strain rate equaling $10^9\ \mathrm{s}^{-1}$ (0.001/ps) and temperature equaling 300 K. Due care was taken to ensure that the predicted trends were independent of the applied MD strain rate. Detailed structural analysis was carried out to comprehensively characterize the interplay between the composition, structure and mechanical properties (moduli, strength, fracture) of the NAS glasses.

3. Simulation procedure

A pairwise partial ionic charge model in tandem with a Morse potential [43] was used for representing interatomic interactions. The form of the potential is given below:

$$U(r) = \frac{z_i z_j e^2}{r} + D_{ij}\left[\left\{1 - e^{-a_{ij*}(r-r_o)}\right\}^2 - 1\right] + \frac{C_{ij}}{r^{12}} \tag{1}$$

where the first term represents the long range Columbic energy, in which z_i and z_j are the charges of atoms i and j, e is the elementary charge, and r is the interatomic bond distance; the second term is the short-range Morse function, in which D_{ij} is the bond dissociation energy, a_{ij} is a function of the slope of the potential energy well, and r_o is the equilibrium bond distance; and the third term is the repulsive contribution. The values of these parameters for different types of interactions are listed in Table 2. For long range Coulombic interactions, the particle–particle particle–mesh (PPPM) solver was used with a cutoff of 15 Å to enable accurate and efficient convergence of the real space and reciprocal space terms. In addition, a similar cutoff was also used for the short range interactions too.

Table 2
Potential parameters of Eq. (1) [43].

Interaction type (superscripts show the charges)	D_{ij} (eV)	a_{ij} (Å^{-2})	r_o (Å)	C_{ij} (eV Å^{12})
$\mathrm{Na}^{0.6}$–$\mathrm{O}^{-1.2}$	0.023363	1.763867	3.006315	5.0
$\mathrm{Al}^{1.8}$–$\mathrm{O}^{-1.2}$	0.361581	1.900442	2.164818	0.9
$\mathrm{Si}^{2.4}$–$\mathrm{O}^{-1.2}$	0.340554	2.006700	2.100000	1.0
$\mathrm{O}^{-1.2}$–$\mathrm{O}^{-1.2}$	0.042395	1.379316	3.618701	22.0