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Atomic-scale dynamics and mechanical response of geopolymer binder under nanoindentation

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ABSTRACT

Using molecular dynamics simulations, the mechanical response of amorphous geopolymer binder (GB) under spherical nanoindentation was examined as a function of GB composition (Si/Al ratio), indenter size (radius of indenter) and loading rates. The observed hardness values were strongly dependent on the indenter size and loading rates. Specifically, the GB hardness increased with decreasing indenter size and increasing loading-rate. The indenter size effect and the effect of loading rate were related to the ease of rotation of the underlying Si and Al tetrahedra in conjunction with the breaking of bridging Si—O and Al—O bonds. Further, for a given indenter size, increasing the Si/Al ratio increased the hardness and Young's modulus of the GB, which was correlated to higher strength of Si—O bonds as compared to Al—O bonds present in the GB.

1. Introduction

Solid-state materials are known to exhibit size-dependent mechanical properties. At very small scales, typically at the nanoscale, they show extraordinary strength, fatigue resistance, hardness and toughness that can measure orders of magnitude higher than those at macroscales [1–5]. Of particular importance and relevance is the hardness of materials; in particular, microindentation (MI) and nanoindentation (NI) tests are widely used to characterize the mechanical properties of materials at their respective distinct spatial scales. Both MI and NI tests provide an accurate measure of the intrinsic mechanical properties of materials. However, indentation size effects (ISE) are typical of such tests, with the size effects being especially dominant during NI. Specifically, ISE is correlated to increase in material hardness at smaller indentation depth for a typical pyramidal or Berkovich indenter [6–10] or for a spherical indenter with decreasing sphere radius [7,11,12]. ISE is very common in crystalline materials and is attributed mainly to geometrically necessary dislocations (GND) beneath the indenter during nanoindentation [7,13–15].

Characterization of the mechanical response of materials under NI can be obtained either via experiments or via computer simulations. In particular, computer simulations offer an attractive method of probing the size-/scale-dependent indentation effects, without resorting to time-consuming and typically expensive experiments. In this regard, using molecular dynamics (MD), we have undertaken a bottom-up approach to predict the elastic and plastic response of *geopolymer binder (GB) under NI*. Specifically, in this work we examine the response of GB as a function of composition (Si/Al ratio) when undergoing nanoindentation with spherical indenters of different radius and at different loading rates. The choice of geopolymers is chiefly motivated by the fact that they are beginning to gain prominence as an important, environmentally friendly industrial and engineering material. Further, GB is amorphous, and thus identifying the extent as well as the mechanisms that underlie ISE will provide new insights into NI of amorphous materials, which, to the best of our knowledge, has not been studied extensively. It is worth noting that MD is particularly suited to study ISE, given the atomic-scale and nano-scale resolution that it offers. Further, MD software packages like LAMMPS [16] are especially optimized to carry out large scale simulations in order to characterize the mechanical response of materials, especially under NI [17–19]. In a very recent study [20], ISE has been observed in the MD simulation of amorphous polyethylene for conical indenters as a function of indentation depth. However, in the present study we have used spherical indenters to study ISE in geopolymers, where the ISE was observed with the change of indenter radius. Further, the structure of geopolymer is distinct from traditional polymers containing individual chains

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and molecules. Hence, a clear picture of the atomic scale mechanism of geopolymer is very important to properly understand ISE in this material.

2. Background and motivation

The term 'geopolymer' was first coined by Davidovits [21] in 1989 based on an underlying 'geosynthesis' condensation reaction step [22] leading to the 'polymerization' of individual silicate and aluminate monomers and oligomers (dimers, trimers, etc.) [23,24]. Geopolymer is formed by the alkali activation of aluminosilicate source materials such as fly ash, metakaolin, blast furnace slag, and mine tailings and is considered a potential sustainable alternative to ordinary Portland cement (OPC). At the atomic-scale, it is similar to aluminosilicate glass, though the processing does not involve high temperature steps [25]. At the microstructural level, geopolymer consists of unreacted precursor crystals and a fully reacted amorphous aluminosilicate gel binder phase (called geopolymer binder or GB) connecting the unreacted particles. Geopolymers have various industrial applications and possess superior mechanical properties as well as high temperature withstanding capacity with respect to OPC [24]. In this context, in addition to studying the macroscale properties of geopolymers, MI and NI have been used to probe the intrinsic mechanical response of geopolymer constituents [26–28]. It was shown that GB is weaker/more compliant than the unreacted crystal phases. The results of previous NI investigations on the weaker GB phases are given in Table 1. As seen in Table 1, there is variation in the reported values of hardness and elastic modulus of GB. Němeček et al. [26] have pointed out that the mechanical properties of GB are independent of the source-material and processing conditions, *implying that the variation in the reported GB properties is possibly due to the ISE associated with indentation experiments*.

MD has been used to conduct NI on thin films [31], single crystals [32–34], amorphous materials [35–37] and ceramics [19,38]. Although NI in MD is typically performed at high loading rates and smaller indentation depths compared with experimental studies, it can still provide valuable information about the atomic scale mechanisms that dictate the mechanical response of materials [39]. For example, Lodes et al. [19] have used MD to study the ISE and pop-in (deviation from elastic behavior) in CaF_2 single crystals and found good agreement with experimental observations. Zhang and Tanaka [32] have shown that the inelastic deformation of Si monocrystal is caused by amorphous phase transformation during NI. Knap and Ortiz [40] used the MD based quasicontinuum method to understand the effect of indenter size on the load displacement behavior of Au (0 0 1) and it was found that use of larger indenter increased the slope of load displacement curve during loading and a drop in load was not observed for a given penetration depth for larger indenters. While MD simulations have also been used to perform NI on amorphous materials such as borosilicate glasses [36,37], to the best of our knowledge, no previous attempt has been made using MD to study the deformation mechanisms of geopolymers during NI.

3. MD simulations: Methodology and implementation procedure

In NI experiments, different types of indenters can be used, including spherical, conical, Vickers (square pyramid), and Berkovich (three sided pyramid). However, in MD simulations, considering simulation convenience and straightforward interpretation of the loading curves, a spherical indenter is typically implemented. This can be achieved by selecting a virtual rigid spherical indenter as outlined by Kelchner et al. [41], where the interaction between the indenter and the substrate is chosen to be purely repulsive [39,40,42]. Details on the indenter-substrate interactions as well as the interatomic interactions between the constituent atoms of GB are given in the following section.

3.1. Interatomic potential

A non-bonded Buckingham potential was used to define the M—O_s bonds (M = Si/Al/Na), where O_s is the oxygen of the tetrahedral AlO_4 and SiO_4 units:

$$V(r) = A\exp(-r/\rho) - C/r^6 \tag{1}$$

where the first part is the Born-Meyer repulsion term and the second part is the attractive term. The details of the interatomic potential have been described in our previous work [43] and will not be repeated here. The hydroxyl oxygens are designated here as O_h and the M—O_h interactions are also defined by the Buckingham potential. The M—O_h parameters are given in Table 2.

For the interaction between the O_h and H atoms of the –OH group, a Morse function is used:

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

where D_{ij}, a_{ij}, r_o and C are the parameters as listed in Table 2.

To perform nanoindentation, a rigid spherical indenter is simulated by using a repulsive potential that forces the atoms to stay outside of the indenter:

$$U^{ext} = \sum_{\alpha=1}^{N_A} F(r^\alpha) \tag{3}$$

where r^α is the distance between atom α and the center of the indenter, and

$$F(r) = \begin{cases} K(r-R)^2 & \text{for } r < R, \\ 0 & \text{for } r \geqslant R \end{cases} \tag{4}$$

where R is the indenter radius. The radius chosen in this work is in accordance with previous MD simulations of nanoindentation [35,38]. The constant K in Eq. (4) is related to the effective stiffness of the indenter and defines the 'softness' of the indenter surface [42]. In this work, based on previous MD simulations of NI [19,42], K was chosen as 7.62 eV/Å^3 which corresponds to an indenter elastic modulus of 1220 GPa (the same as that of diamond). This value is much higher than the substrate indentation modulus observed in this study.

Table 1
Nano indentation test results of geopolymer binder.

Ref.	Type of indenter	Source material	E (GPa)	H (GPa)	Max load (mN)/penetration depth (nm)	Loading type
Němeček et al. [26]	Berkovich	Fly ash and metakaolin	17–18	1.25[a]	2.0/305.9	Fixed load (30 s)
Belena et al. [28]	Berkovich	Metakaolin	14	0.5	–	Fixed load (30 s)
Skvara et al. [29]	Berkovich	Fly ash	36.1 ± 5.1	1.13 ± 0.3	30/1200	Fixed load (200 s)
Allison et al. [27]	Berkovich (20 nm tip radius)	Fly ash	–	3.86[a]	2.0/213.65	–
Das et al. [30]	Berkovich	Fly ash	15–20	0.58[a]	2.97/534.0	–

[a] Not explicitly reported in the respective references, but was calculated by current authors based on data given in reference.