Molecular dynamics study of interfacial stress transfer in graphene-oxide cementitious composites

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ABSTRACT

Graphene oxide has been recently used to create cementitious nanocomposites with enhanced mechanical properties and durability. To examine the improvement on the mechanical properties of cement by adding graphene oxide, the understanding of the interfacial stress transfer is a key. In this work, pull-out tests were carried out using molecular dynamics simulations, incorporating cement and graphene oxide, to determine the shearing mechanism at the interface. For the first time, the shear stress-displacement curve, which represents the bond-slip relation has been calculated for a graphene oxide/cement nanocomposite at the molecular scale. This relation is significant and essential in multi-scale numerical modeling as it defines the mechanical properties for the interface elements. A yielding-like phase is found prior to the shear strength and a roughly bilinear softening phase (i.e. fracture/damage). Furthermore, the shear strength has been found in the range of 647.58 ± 91.18 MPa, based on different repeated simulations, which indicates strong interfacial bonding strength in graphene oxide cement.

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1. Introduction

Cementitious material, which is composed of mainly cement and possibly a mixture of fly ash, slag, limestone fines, silica fume, etc., is the most used construction material in the world. Since the invention of modern cement, there has been considerable research to improve its characteristics in terms of toughness [1], strength [2,3], and durability [4,5]. Other than the direct improvement of cement itself, a variety of fibers have been added to cement to enhance the properties of the cementitious materials. More recently, thanks to the rapid development of nanotechnology, a new dimension of research has been initiated in cementitious nanocomposites, investigating the properties of cement containing nanomaterials such as nanoparticles composed of metal oxide or silica [6], nanofibers [7], and nanotubes [8]. It has been shown that these nano-inclusions can significantly improve the compressive strength, flexural strength, Youngs modulus and other material properties of cement. Since the first successful isolation of the individual graphene sheet [9], graphene has been considered as an ideal nano-inclusion in numerous materials including cement [10]; however, the direct application of graphene in forming cementitious nanocomposites is currently limited due to dispersion issues.

Graphene oxide (GO), the oxidized form of graphene, has started to become accepted as a suitable inclusion in cement for its combined advantages of enhancement in mechanical properties, durability, and dispersibility [11–13]. For example, GO cement at 28 days with 0.06 wt% of GO content can increase compressive strength by 72.7%, and 0.04 wt% of GO content can increase the flexural strength by 67.1% [12]. As a 2-D structure, GO has a large aspect ratio, which could lead to reduced permeability and chloride ingress for optimal durability of the composite cementitious materials [13]. This shows that GO has significant potential in enhancing a variety of properties of cement. Scanning electron microscopy (SEM), X-ray diffraction (XRD), atomic force microscopy (AFM) has been used by Alkhateb and co-workers [10] to obtain the physical and chemical properties and resonant ultrasound spectroscopy (RUS) for certain mechanical properties of GO cement. Lv and co-workers [14] examined the effects of graphene oxide on the cement hydration process in terms of the crystals shapes and their formation with different dosages of GO inclusions. They found that cement formed flower-like structures on the surface when the dosages of GO ranged from 0.01% to 0.04%; however, it formed polyhedral structures from rod-like crystals on the surface when the dosages of GO exceeded 0.05%. Moreover, XRD tests showed [14] the GO sheets generate more

crystalline phases such as calcium hydroxide, ettringite, and mono-sulfoaluminate in cement.

Despite the promising future of incorporating GO in forming cementitious nanocomposites for optimal engineering properties, the current research of GO cement is still at a very early stage. To investigate the massive increase in the mechanical properties of GO cement, it is necessary to study the interfacial stress transferring mechanisms between the cement and the GO. The stress transferring mechanisms and effectiveness at the interfaces controls the global mechanical performance of the GO cement. Molecular dynamics (MD) provides unique insight into the mechanical performance of cementitious materials and nanocomposites at the nanoscale. MD can be used to calculate the deformation, the stress, and various molecular properties of cement systems [15–17]. A molecular approach to determining the mechanical properties of cementitious materials is extremely helpful when physical nanoscale experiments are not widely available. In GO cement, the GO is mixed and reacted with the main binding phase of cement — a calcium-silicate-hydrate (C-S-H) gel. Alkhateb et al. [10] has investigated the interfacial stress transfer for GO cement. In their study, a cell containing C-S-H with a layer of GO in the middle was constructed, and the COMPASS force field was applied. A pull-out test was conducted, and the interfacial strengths were calculated. However, the structure of C-S-H was not clear, and the full stress-strain curve, which represents the complete stress transferring behavior, was not shown. Li and co-workers [18] simulated the pull-out test of carbon nanotube polymer with MD and produced the full shear stress and displacement relation at the interface between the carbon nanotube and the polymer. Ding et al. [19] investigated the effects of GO sheets in poly(vinyl alcohol)/GO composites by using MD and found that the degree of oxidation of the GO sheet influenced the strength of interfacial binding characteristics between GO and the polymer. Liu et al. [20] examined the interfacial mechanical properties of wrinkled GO/polyethylene and GO/PMMA composites by pull-out tests with MD; it has been found that the pull-out velocity of the wrinkled GO sheet has a great impact on the interfacial stress transfer capacity for both types of composites and the wrinkled shape of GO can also enhance the interfacial mechanical properties. To the best knowledge of the authors, however, there is very little research in modelling the interfacial mechanical properties of GO/cement composite and none in deriving the complete interfacial shear stress/displacement relation with MD.

This paper attempts to model the interfacial stress transferring mechanism in GO reinforced cement using MD and derive the full shearing stress displacement curve by the pull-out test. The C-S-H structure used is based on 11 Å tobermorite, and the Lerf-Klinowski model for the GO structure is employed with random distribution of the functional groups. ReaxFF is used to represent the interatomic interactions in the MD simulation. The GO sheet is pulled out of the C-S-H and the full stress displacement curve is obtained based on which the complete stress transferring mechanism is discussed. The sensitivity of the pulling rate on the results is investigated and for each pulling rate, three tests/simulations are carried out to ensure repeatability and reliability. The interfacial shear stress is then calculated as a function of pull-out displacement. A yielding-like stage, between the linear stress increase and the stress softening, is identified. The elastic-plastic-fracture phenomenon has been first observed at nanoscale for GO cement composite and will have significant impact on engineering mechanical properties. The energies of the interface between GO and C-S-H, and the carbon atoms from the GO sheet are also calculated and discussed. The results from this model are highly complementary to finite element multi-scale modelling on GO cement composites. In order to accurately simulate the mechanical behavior of the GO cement, especially at the meso- and micro-scale, the interfacial properties between GO and cement are necessary. However, such properties are extremely difficult to determine from experimental tests. This has motivated the work in this paper.

The remainder of this paper is structured as follows. In Section 2, we present the formulation of the model which covers the molecular structure of the composite, the interatomic force field, and the loading protocol for determining the interfacial mechanical properties. In Section 3, we present results of the load-displacement relationship for different loading rates, as well as the energies for both the interface and the carbon atoms. We then analyze the interfacial mechanism and calculate the shear stress development over the pull-out displacement. Finally, the conclusions of this work are summarized in Section 4.

2. Model construction

The structure of C-S-H analyzed in this paper is constructed based on the 11 Å tobermorite structure reported in [21]. The structure of C-S-H is considered very similar to that of 11 Å tobermorite [22] with two main differences: the calcium/silicon ratio and the silicate chain length. Researchers have been trying to determine the molecular structure for C-S-H materials based on 11 Å or 14 Å Tobermorite, but there are still few widely acknowledged models. Pellenq et al. [23] have derived perhaps the first realistic molecular model for C-S-H with MD, which represented the first-step forward towards modelling the mechanical properties of C-S-H. However, the several shortcomings of the model have been pointed out, such as a few aspects of the structure do not match with the general observations on crystalline calcium silicate hydrates (e.g., the coordination of Ca—O) [24]. In this paper, the well-understood 11 Å tobermorite structure is used as the structure of C-S-H, which is believed reasonable, since the interface between the C-S-H and GO is the focus of the research.

The GO structure in this paper is based on the Lerf-Klinowski GO model [25] with the distortions neglected and the carbon plane structurally unaffected, as shown in Fig. 1. In this model, the functional groups, including epoxy and hydroxyl, are distributed randomly [26] to avoid the energy reduction of GO sheet due to the gathering of the functional groups [27]. Generally, the range of oxidation varies from a C/O ratio of 4:1–2:1 [28]. In this model, the ratio of C/O is set to 3.2:1. The distribution of oxygen atoms is derived by Dyer et al. [29], which was based on the density functional theory (DFT) analysis performed by Yan and Chou [27]. An epoxy functional group is a single oxygen atom bonded with two neighboring carbon atoms in the carbon plane. The C—O bond length at relaxation is found 1.44 Å. The C—C bond is stretched to 1.51 Å and the two carbon atoms move out of the plane by 0.34 Å. Therefore, the oxygen atom in an epoxy group is deduced at a perpendicular distance of from the carbon basal plane. The hydroxyl functional group is constructed as the OH group bonds to certain carbon atoms. The O—H bond length is found to be 0.98 Å, and the angle of C—O—H bond is 107.9°. The attached carbon atom is distorted out of the plane by 0.37 Å. The hydrogen and oxygen atoms are placed at the same plane perpendicular to the basal plane for simplicity. Therefore, the oxygen atoms in hydroxyl groups stay at perpendicular distance of $1.44 \sin 107.9° + 0.37 = 1.74$ Å from the basal plane. The average of the distance between the carbon sheet and oxygen atoms can be simply calculated as $(1.57 + 1.74)/2$ Å.

The interface between the GO sheet and the C-S-H matrix is difficult to model, due to the lack of data for the material composition near the interface. Fig. 2 illustrates the nanostructure of GO C-S-H and especially the interface between the GO and the C-S-H [30]. The functional groups of the GO sheet, mainly, oxygen atoms, react with the calcium atoms from the C-S-H and form a strong interface. To determine the distance between the calcium ion and the oxygen