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Investigation of the effects of graphene and graphene oxide nanoplatelets on the micro- and macro-properties of cementitious materials

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HIGHLIGHTS

- Durability related properties of GNPs- and GONPs-reinforced concrete are investigated.
- Micro-characterization is used to quantify the effects of GNPs and GONPs on the microstructure of cement paste.
- Atomistic modeling qualitatively demonstrates the different mechanisms of GNPs and GONPs on freeze-and-thaw performance.

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ABSTRACT

Recent research results discover that graphene nanoplatelets (GNPs) and graphene oxide nanoplatelets (GONPs) are capable of enhancing the smartness as well as improving the strength of cementitious materials by utilizing their unique mechanical, thermal and electrical properties. Although the graphene-reinforced concrete exhibits promising potentials in these studies, its application to construction practice demands for a deeper understanding of the effects of graphene nano-particles on the durability-related properties of concrete. To meet this need, this study is focused on the strength, corrosion resistance and freeze-and-thaw performance of graphene-reinforced cementitious materials. In this investigation, the mortar specimens reinforced by different types of GNPs and GONPs are tested and then compared with the benchmark samples. To capture the reinforcement mechanisms of graphene, nano-scale characterization is carried out with a focus on the microstructure of the cement paste around the graphene nano-particles. The observed microstructure morphology and modulus profile show that GNPs and GONPs can significantly reshape the microstructure of cement paste. Based on the micro-characterization, atomistic models of the graphene-reinforced C-S-H gels are constructed and the freeze-and-thaw process is simulated. It is found that in addition to the reshaped microstructure, the effects of graphene and graphene oxides on water migration in the nano-pores of cement paste play an important role in the frost resistance of graphene-reinforced concrete.

1. Introduction

The rapid progress towards construction sustainability calls for high performance and smart cementitious materials to build safer, more durable and more economical infrastructure systems. Among many strategies and concepts improving the concrete performance and smartness, the idea using additives to reinforce cement paste as well as to tailor its physical, mechanical and transport properties has been widely explored and investigated [1–4]. The primary rationales underneath this reinforcement strategy are (1) to utilize the unique properties of the selected additives and (2) to minimize the deleterious influences of the pre-existing flaws and microcracks in concrete, which are an inherent byproduct of cement hydration and usually range from nano-scale to meso-scale in concrete.

During the initial exploration, fiber additives including steel fiber [5], carbon fiber [6] and polymer fiber [7–9] have been used to reinforce cement paste due to their positive effects on the tensile strength and fracture resistance of concrete. However, since the

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size of these conventional fibers is usually at or beyond millimeter scale, their effects on cement paste are inherently limited at macro- and meso-scales. Thus, little improvement can be achieved in the concrete microstructure, which is now deemed as the fundamental source of many mechanical and transport mechanisms critical for the performance of cementitious materials.

To overcome this obstacle, nano-sized additives have been attracting increasing attentions during the last decade [10–12]. Nanomaterials of high surface-volume ratios, e.g., carbon nanotube, titanium oxide, nanosilica and nanoalumina, are studied and used as additives to strengthen the microstructure of cementitious materials [10–13]. It is found that after proper treatment, these nanomaterials can significantly improve the microstructure strength of hydration gels. In addition, by enhancing the packing density of calcium-silica-hydrate (C-S-H), some nano-sized additives can effectively reduce the microstructure porosity, and thus greatly decelerate the transport rate of the deleterious agents in concrete. Therefore, despite certain challenges existing in dispersion, bonding and cost [1,14], incorporation of nano-sized additives in concrete is showing great potentials for producing stronger and more durable construction materials.

Recent advance in materials science and nano-technology provides another excellent nanomaterial, namely graphene, to be considered as a nano-sized additive for cementitious materials. Compared with other nanomaterials, graphene displays a unique atom-thick sp^2 bonded 2D structure [15,16]. Hinging on this atomistic structure, graphene exhibits many extraordinary properties highlighted by its super-high specific surface area, ultrahigh tensile strength and elastic modulus, and excellent thermal, electrical and optical conductivity [17–21]. Therefore, using it to produce smart and high performance materials garners increasing interests in a wide variety of engineering applications [22–26].

Graphene nanoplatelets (GNPs) and graphene oxide nanoplatelets (GONPs) are new types of nano-particles consisting of graphene stacks [14–27]. Different from pristine graphene, GONPs are oxides of GNPs, and thus contain the functional groups attained during oxidation and exfoliation process. Both GNPs and GONPs exhibit a 2D sheet-like structure with a thickness at nano-scale (less than 10 nm). GNPs and GONPs inherit many advantages of graphene and make themselves promising nano-sized additives and ideal reinforcement for high performance and smart structural materials. Furthermore, among the nanomaterials used as additives in many engineering applications, they are low-cost nanoparticles.

The study by Alkhateb et al. [28] showed that GONPs reshaped the morphology of C-S-H gels and altered the microstructure of cement paste. As a consequence, the C-S-H interfacial bond and concrete overall strength were both remarkably enhanced. Recently, Lv et al. [29] found that adding 0.03% GONPs (with respect to the weight of cement) strikingly increased the tensile, flexural and compressive strength of concrete by 78.6%, 60.7% and 38.9% respectively. Based on the XRD and SEM tests, they speculated that the intrinsic reinforcement mechanism was that the hydration gels reacted preferentially with the functional groups on the surfaces of GONPs. In addition, the unique 2D sheet-like structure of GONPs was found to form a barrier against crack propagation so as to provide a 2D isotropic reinforcement for cement paste [14]. This is an advantage over the nanofiber-like additives, which strengthen concrete microstructure only normal to their longitudinal direction, and thus cannot arrest the microcrack growth parallel to it.

In addition to strength improvement, GNPs and GONPs bring certain smartness to cementitious materials. Le et al. [23] used GNPs to quantify the damage extent in concrete by measuring the electric potential of specimens. They found that powered by the excellent electrical conductivity of GNPs, the graphene-reinforced concrete reacted to damage "smartly" by exhibiting the potential of self-sensing, and thus aided in crack detection and structural health evaluation. Furthermore, GNPs and GONPs display good dispersion ability in water, and thus avoid entanglement and agglomeration in large-scale structural application, which is a perplexing challenge to the nanofiber-like additives.

Although promising effects on strength and smartness are observed, the implementation of graphene-reinforced concrete in design and construction demands for a deeper understanding of graphene's influences on the durability-related properties of cementitious materials, which are expected to undergo complex mechanical and chemical processes during their lifespans. Information revealing the fundamental mechanisms of GNPs and GONPs to reshape the concrete microstructure and affect the transport characteristics not only provides physical insights in predicting the performance of graphene-reinforced concrete during service, but also sheds lights on optimizing the graphene-based additives by designing and tailoring their size, attached functional groups and other properties. Unfortunately, despite the research enthusiasm on the graphene-reinforced concrete, the study on its durability-related properties is limited and the fundamental mechanisms in microstructure are not fully understood.

To remedy this inadequacy, this study is focused on the durability-related performance of graphene-reinforced concrete, in particular, its strength, freeze-and-thaw behavior and corrosion resistance. In the present study, different types of GNPs and GONPs, characterized by their size and oxidation agent, are used to cast the mortar samples for experimental investigation. The macroscopic responses of samples to compression, chemical attack and freeze-and-thaw cycles are recorded and compared with the companion samples containing no graphene. To deepen the understanding of the experimental results, micro-characterization utilizing advanced nano-techniques, e.g., Atomic Force Microscopy (AFM), Scanning Electrical Microscopy (SEM) and Raman spectroscopy, is carried out to scan and quantify the microstructure characteristics of graphene-reinforced cement paste. It is found that the existence of GNPs and GONPs significantly alters the proportions of constituent phases in the microstructure of cement paste, which are directly correlated with the strength, porosity and corrosion resistance observed in the graphene-reinforced concrete. To capture the roles of GNPs and GONPs in frost resistance, atomistic models are constructed and a freeze-and-thaw cycle is simulated. Based on the water migration in the nano-pores, the freeze-and-thaw performance of the cement paste reinforced by different graphene nano-particles is discussed.

2. Experimental test

2.1. Materials preparation

In this investigation, Type I Portland cement and sieved sand are used for preparing the mortar specimens. Pristine graphene nanoplatelets (GNPs) procured from XG Sciences (MI, USA) are used as additives in the mix design. To identify the effect of nano-particle size, two types of GNPs, characterized by their in-plane diameters and thickness, are selected for the experimental investigation. Based on the physical properties listed in Table 1, the GNPs of grade M (xGnP-M-15, labeled as "GMs" hereafter) display greater average thickness and a larger mean in-plane diameter than the GNPs of grade C (xGnP-C-500, labeled as "GCs"

Table 1
The properties of GNPs used in the tests.

	Bulk density (g/cc)	In-plane diameter (μm)	Thickness (nm)	Surface areas (m^2/g)
xGnP-M-15 (GMs)	0.03–0.1	~15	6–8	150
xGnP-C-500 (GCs)	0.2–0.4	<2	~3	500