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Enhancement of mechanical and electrical properties of graphene/cement composite due to improved dispersion of graphene by addition of silica fume

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HIGHLIGHTS

- Silica fume (SF) is helpful to improve the graphene (G) dispersion in cement paste.
- Appropriate addition of SF obviously enhances compressive strength of composite with low amount of G.
- Appropriate amount of SF significantly improves electrical properties of composite with high amount of G.

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ABSTRACT

Incorporation of graphene into cement-based materials has attracted extensive attention of many researchers. Achieving effective dispersion of graphene can contribute to improving the mechanical and other properties of the cement composite. In this study, the effects of silica fume content on compressive strength and electrical resistivity of the graphene/cement composite were investigated. The distribution of graphene and silica fume in cement matrix was observed by scanning electron microscopy (SEM) and the pore structure of the composite was analyzed by mercury intrusion porosimetry (MIP). Results revealed that silica fume was capable of facilitating the dispersion of graphene and increasing the interfacial strength between graphene and cement matrix. Moderate amount of silica fume can refine the pore structure of the cement paste. Incorporation of appropriate amount of silica fume can increase the compressive strength and reduce the electrical resistivity of the composite. However, the extra amount of silica fume had a negative effect on mechanical and electrical performances.

1. Introduction

Cement-based material is the most widely used construction material. However, it possesses some significant disadvantages such as low tensile strength, poor capacity to conduct electricity and so on, which limit application of this traditional material in certain conditions.

In recent years, many researches have concentrated on using additives to modify the performances of the cementitious materials. With the advancement of nanotechnology, some nanomaterials have raised interests of some concrete researchers owing to their superior mechanical, thermal and electrical properties, coupled with high specific surface area. Because of their tiny size, nanomaterials can fill the interconnected pores and densify the microstructure in cement paste, thereby resulting in enhancement in strength and barrier properties [1–8]. Furthermore, incorporation of them can improve the electrical conductivity of cement-based materials and create "self-sensing" capacity, which is the foundation of structural health evaluation [9–14].

Graphene (G) and graphene oxide (GO) are new members in nanomaterial family, which are in the form of two-dimensional (2D) sheets. Compared to graphene oxide, graphene is more useful in strongly modifying the electrical properties of cement composites [15]. Although recent studies have explored the enhanced effects of graphene on cement-based materials pertaining to mechanical and durability-related properties as well as sensing

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capacity based on excellent electrical properties, very few works has been reported on the dispersion of graphene in cement paste [16–22]. Achieving effective dispersion can contribute to improving properties of cement composite containing nanomaterials [23]. Because nanomaterials can migrate freely in the fresh cement paste and high van der Waals forces make them strongly attract each other, nanomaterials can form agglomeration easily, leading to defects and cracks within the cementitious matrix, and hence, performance degradation of cement composite. Now the most common method to prevent poor dispersion of graphene is using sufficient surfactants in combination with ultrasonication [24,25]. Although graphene layers are dispersed well in water using this method. But graphenes can easily aggregate again in the cement paste.

Silica fume (SF) is the by-product of manufacture of silica metal or ferrosilicon. Typically, the size of silica fume is in the range of 100–500 nm, around 100 times finer than that of cement grains. It also exhibits pozzolanic characteristics and consumes calcium hydroxide during the hydration process to produce C-S-H. The contribution of silica fume to the dispersion of nanomaterials in cement paste has been investigated by some researchers. Sanchez et al. [26] found that silica fume could serve as wedges to mechanically separate the carbon nanofibers (CNFs) so as to improve the dispersion of fibers. According to Yazdanbakhsh et al. [27], silica fume played a role in stabilizing the dispersion of CNFs in cement composite. The study by Kim et al. [28] showed that appropriate addition of carbon nanotubes (CNTs) could facilitate the dispersion of CNTs in cement-based materials, thereby yielding an obvious increase in compressive strength and electrical conductivity of this composite. Li et al. [29] reported that graphene oxide layers could be dispersed effectively when sufficient amount of silica fume was introduced into the cement paste, they also explained the reason that over-dosed silica fume can lead to a lower compressive strength. However, there is a lack of understanding about the influences of silica fume content on the dispersion of graphene and the related properties of the graphene/cement composite.

In this study, the effects of silica fume content on performances of cement paste containing graphene in terms of mechanical (compressive strength) and electrical properties were investigated. The scanning electron microscopy (SEM) was performed to observe the micro-morphology of fractured surfaces of the composite and the graphene dispersion. The pore structure of the cement paste was probed by mercury intrusion porosimetry (MIP). This paper can provide a guidance for design and application of graphene reinforced cement-based composite.

2. Experimental details

2.1. Materials

Graphene was manufactured by physical method and its purity exceeded 95%. The graphene consisted of 1–5 layers averaging 1.0–1.77 nm in thickness and 2–10 μm in diameter. Its specific surface ratio ranged from 360 to 450 m^2/g. Table 1 summarizes the properties of the graphene. Sodium dodecyl sulfate was chosen as the surfactant to uniformly disperse graphene in water. Cement used in this study was P.Ⅱ 42.5 Ordinary Portland Cement, which was in accordance with Chinese standard GB175-2007. The chemical composition of cement is presented in Table 2. The silica fume contained 85–96% SiO_2. The average particle size of the silica fume power was in the range of 0.1–0.3 μm, about 100 times smaller than that of cement grain. Its specific surface ratio was between 20 and 28 m^2/g. The chemical composition of silica fume is shown in Table 3. A large amount of water was adsorbed on large surface area of graphene and silica fume, so giving rise to degrading the workability of cement paste. The polycarboxylate superplasticizer was introduced as water-reducing agent to ensure the good workability of the cement paste.

2.2. Specimen preparation

In this investigation, graphene was added in concentrations of 0%, 0.1% and 2% by mass of total binder materials incorporating cement and silica fume. At each graphene concentration, Cement was partly substituted for equal weight of silica fume and amounts of silica fume were 0%, 5%, 10% and 15% of the total binder materials. The water to binder materials mass ratio (w/cm) of 0.48 was applied for specimens containing 0% and 0.1% of graphene. The specimens containing 2% of graphene were prepared with w/cm of 0.53. The amounts of water-reducing agent were adjusted according to amounts of silica fume so that the pastes can maintain similar workability. The mix proportions are presented in Table 4.

Graphene, the surfactant and the water-reducing agent were added into the water and sonicated for 40 min to produce graphene suspension. Two kinds of graphene water solutions, with and without surfactant were measured by ultraviolet visible spectroscopy (UV-Vis), the results are shown in Fig. 1. When the surfactant was used, there was an absorption peak at the wavelength of 260 nm, which was the specific absorption peak of graphene. The absorbency exceeded 0.5 g/L MC, which meant a good dispersion of graphene in the case of the graphene suspension containing surfactant. If silica fume needed to be used, the silica fume was mixed with graphene suspension and stirred for 10 min. Then, cement was added into the graphene-silica fume mixture and mixed for additional 4 min by using a mortar mixer equipped with a flat beater. The mixing method similar to this in GB/T1764-1999 was adopted. The fresh cement pastes were cast into moulds (60 mm × 20 mm × 20 mm) and vibrated on a vibration table for 2 min to ensure good compaction. Four stainless steel meshes (27 mm × 18 mm × 0.2 mm) were inserted into the specimen along the length direction with the same spacing, 18 mm. Specimens were demoulded after 24 h and cured in a moist-curing room (25 °C and 95% relative humidity) for 28 d until measurement.

2.3. Testing methods

To evaluate the influences of silica fume content on mechanical behavior of graphene/cement composite, the compressive strengths of specimens at 3 and 28 days of curing were measured by a testing machine. At least five specimens were repeated for each test.

Electrical resistivities of specimens at the ages of 3 and 28 days were measured by using the four-probe method (as shown in Fig. 2), which can eliminate the contact resistance between the specimens and the electrode [30]. This test was carried out by using a DC stabilized voltage source and two Fluke-15B multime-

Table 1
Properties of graphene.

Diameter (μm)	Thickness (nm)	Layers	Single rate	Purity (wt%)	Specific surface area (m^2/g)
2–10	1.0–1.77	1–5	>30%	>95%	360–450