Research Progress of the Preparation and Properties
Graphene Cement Composite

Z L Huang, X T Qin*, Z X Mao, H Lan, W H Tong, S Y Zhu
School of Civil Engineering and Architecture, Wuhan Polytechnic University, Wuhan
430023, China

Corresponding author’s e-mail address: qinxiantao@whpu.edu.cn

Abstract: Graphene has extremely great mechanical, electrical and thermal properties that make them ideal reinforcing materials in cement by mixing them homogenously. In this paper, firstly, the dispersion methods of graphene, including physical stirring, surfactant treating and ultrasonication, are presented to obtain stable dispersed surfactant aqueous solution. Then, the mechanical properties of graphene cement composite are studied, such as Young’s modulus, shear modulus, compressive strength, flexural strength and toughness. Moreover, the piezoresistivity of graphene cement composite is researched in comparison with plain cement. At last, the durabilities, especially the resistance to chloride ion permeability, freezing-thawing and carbonization, are summarized and compared.

1. Introduction
Nowadays, cement concrete is the most widely used material in building construction, but the increasingly harsh use environment demands for higher requirements of cement concrete. Therefore, in recent years, the improvement of comprehensive properties of cement-based materials has been a research hotspot in the academic world. The development of interdisciplinary subjects such as material physics and chemistry has greatly promoted the research progress of intelligent cement-based composite materials. Specifically, advanced nanomaterials, such as carbon nanofibers, carbon nanotubes, carbon black graphene oxide and so on, have being used in the cement matrix to make the diagnosis, self-adjusting, self-healing smart cement-based composite materials. As one of the thinnest, strongest and most conductive and heat-conducting nanomaterial at present, graphene is known as the "king of new materials", has aroused a high tide of research and application in different matrix materials, specifically, a more smart and strong infrastructural material in cement concrete. Therefore, this review summarizes the researches on fabrication, mechanical and electrical properties as well as durability of graphene/cement composite material.

2. Dispersion of graphene in cement
Nanomaterials can migrate and aggregate easily in water and fresh cement slurry because of high van der Waals, π-π bond and capillary force, which make them attract each other strongly. Besides, the surface of graphene contains few oxygen-containing function groups with strong hydrophobicity and weak hydrophilicity, which make it difficult to disperse evenly and stably in water. Furthermore, there is a perception that the strengthening mechanism of graphene is filling effect and template effect-the addition of graphene makes the hydration products of cement develop towards orderly layered aggregate, and the formation of structured crystals makes the hardened cement become more compact.
Therefore, stable dispersion of graphene in aqueous suspension is the most important precondition of processing carbon-reinforced cement composites[1].

2.1. Physical method

In earlier research, the physical dispersion method of graphene, generally refers to ball-milling or mechanical stirring, was thought to be an effective way. In the former method, graphene are dispersed in cement by ball-milling treatment for hours in the ball mill before mixing with water. While in the later method, the dispersion of graphene in water is a short duration. The problem with this approach is that the graphene reaggregate again quickly when mixing the mixture of cement and graphene with water. Cui[2] tried to increase the mixing speed and time to improve the dispersion quality, but under the certain concentration and temperature, the dispersion caused by stirring and the agglomeration caused by its polarity will reach a balance. At that time, the agglomeration will not be reduced or even eliminated by only mixing. When the graphite content exceeds 15%, the graphite is difficult to disperse but tend to agglomerate in cement matrix.

2.2. Surfactants & ultrasonication

Then, the combination of surfactants and ultrasonication are used to disperse the graphene. Figure 1 shows the most common dispersion method of graphene nanosheets(GNS) in aqueous solution.

![Figure 1. Dispersion of GNS in aqueous solution][3]

Generally speaking, the common surfactants are classified into ionic surfactants and non-ionic surfactants. The surface of graphene is charged by ionic surfactants with the same charge, thereafter, graphene is dispersed by electrostatic repulsion[4]. Non-ionic surfactants contain hydrophilic groups and hydrophobic groups on their surfaces. Hydrophobic groups distribute on the surface of graphene, while hydrophilic groups interact with water. Because there has space steric resistance between groups, graphene can be dispersed[5]. In comparison, non-ionic surfactants are now more likely to be used to disperse graphene, because it can retain the excellent properties of graphene as much as possible and doesn’t destroy the conjugate structure of graphene. There has another explanation of the mechanisms of action of the surfactant, polyvinylpyrrolidone(PVP) was called as a “coating” polymer stabilizer to prevent graphene aggregation in aqueous dispersions[6].

Typically, cetyl trimethyl ammonium bromide(CTAB), polyvinylpyrrolidone(PVP), polyoxyethylene nonylphenyl ether(CO890), gum arabic(GA) are used as surfactants to dispersed graphene[7]. Table 1 shows the optimum concentration (OC) of surfactants.

| Types         | Non-ionic | Ionic | Complex         |
|---------------|-----------|-------|-----------------|
| OC (g/L)      | 0.4       | 0.5   | 0.7             |
|               | 0.7       | 0.3   | 0.3             |
|               | 0.3       | 0.6   | 0.7             |

3. Mechanical properties of graphene cement-based composites

3.1. Young's modulus and shear modulus

Graphene has good mechanical properties and its Young's modulus is 1.1TPa[8]. Therefore, graphene can improve Young's modulus and shear modulus of cement paste through Alkhateb’s research[9]. Resonant ultrasound spectroscopy (RUS) testing results show that in graphene-cement...
nanocomposites (GCNCs), shown in table 2, the addition of graphene is only 0.5wt%, but the Young's modulus and shear modulus increase obviously compared to plain Portland cement paste.

| Material                     | Young’s modulus (GPa) | Shear modulus (GPa) |
|------------------------------|-----------------------|---------------------|
| Portland cement              | 18.5                  | 6.7                 |
| Pristine graphene cement     | 19.7                  | 8.1                 |
| Functionalized graphene cement | 22.8                 | 9.2                 |

3.2. Compressive and flexural strength
Graphene is now the highest intensity material[10]. In order to investigate the effect of graphene on the compressive and flexural strength of cement-based materials, Wang[11] dispersed graphene nanosheets in cement matrix by ball grinding method, then obtained the compressive and flexural strength of cement-based composite materials after curing for 3d, 7d and 28d. The results showed that graphene could improve the flexural strength and compressive strength of cement matrix. Specifically, with the increase of dosage of graphene, flexural strength and compressive strength of cement-based composite materials first increases then decreases. When the content of graphene nanosheet is 0.04wt%, the flexural strength and compressive strength of cement-based composites reach the maximum value, shown in table 3. It is found that graphene is mixed with hydration silicate products generated from cement-based materials[9], which may be the reason for strengthening the mechanical properties of graphene cement-based composites.

According to Qin’s research, 0.05wt% addition of well-dispersed graphite nanoplatelets (GNP), treated with polyacrylate and sonication, maximizes the compressive strength of graphite nanoplatelets-reinforced cement (GNPRC) by 7.5% and 16.7% for 7d and 28d, respectively. While within the GNP dosage changes from 0 to 0.5wt%, the flexural strengths at 7 days and 28 days are continuously increasing, up to 55.6% and 53.3%, respectively[1].

3.3. Toughness
When the mass fraction of graphene does not exceed 0.02% in cement-based composites, the toughness of cement-based composites will be significantly enhanced[12]. The toughness enhancement of cement-based composites is due to the promotion effect and template effect of graphene on the formation of cement hydration products, which is leading to the formation of neat nanoscale microcrystals and the effect of toughness enhancement[13]. In addition, experiments show that well-dispersed graphene nanomaterials in cement matrix can prevent the destruction of cement matrix by external forces through bridging effect. When the graphene nanosheet is pulled out of the cement matrix under external load, it will dissipate some energy and share the stress from all directions, which is another mechanism for the toughness enhancement of graphene in cement composites[11].

4. Electrical properties of graphene cement-based materials
Sedaghat[14] found that adding graphene lamellae (GNP) to cement can significantly increase the conductivity and thermal diffusivity of cement. The results show that the conductivity of plain cement paste is about 10^{-8}S/m, and the conductivity of cement-based composites can be greatly improved by adding 1wt% graphene. The conductivity of cement-based composites can reach 10^{-2}S/m by adding 10% graphene, which shows that a small amount of graphene can significantly improve the conductivity of cement-based composites.

According to Zhu’s research[15], the addition of graphene sheets (GPs) leads to obvious decrease in volume resistivity and greater pressure-sensitivity compared to plain cement paste at each level of load. Especially, the GPs/ cement composite with 0.05 and 0.1% GPs have better piezoresistivities than that of composites paste incorporating 0.5% GPs. Typical pressure sensitive property is also
found in graphite nanoplatelets (GNP)-cement and reduced graphene oxide (RGO)-cement composite from Huang’s[16] and Ma’s test[17].

As a more comprehensive example, Pang[18] researched the piezoresistivities of cement composite with graphene nanoplatelet (GNP) under both cyclic and monotonically increasing compressive and tensile strain. The responses of specimens under tension and compression are different, which can be used to provide a quick and accurate assessment of the damage. According to the researches, the conductivity of the composite is improved significantly after adding graphene, which makes it possible to use the conductivity of the composite as an index to judge the damage degree.

5. Durability of graphene cement-based composites

In the study of graphene cement-based composite, the main concerns are its high mechanical properties and other improved properties. However, the durability of cement must be considered in order to meet the needs of engineering practice. The durability of graphene cement-based composites mainly includes permeability resistance, freeze-thaw resistance and carbonization resistance.

5.1. Resistance to chloride ion permeability

Graphene cement-based composites are porous matrix with different pore sizes (10 to 500 microns). When there is a pressure difference in the surrounding medium, the fluid mechanics of medium migration, namely permeability, is produced. The following part mainly introduces the chloride permeation resistance of graphene cement-based composites. In coastal and riverside areas and construction areas with high chloride ion concentration, the resistance of chloride ion erosion is the key of the service life for cement concrete. Therefore, it is of great significance to study the resistance to chloride ion permeability of graphene cement-based composites.

Du[19] concluded that graphene nanomaterials (GNP) can improve the barrier performance of cement mortar and the resistance of cement composites to chloride diffusion and chloride migration. Wang[20] and Muthusamy[21] observed that graphene nanoparticles can improve the pore structure of cement and reduce the chloride ion migration coefficient.

Mohammed[22] investigated the influence of graphene on the transport properties of cement-based composites and found that graphene cement-based composites can absorb chloride ions and increase the durability of cement-based materials.

5.2. Resistance to freezing-thawing

Gong[23] studied the influence of graphene oxide and carbon nanotubes on the frost resistance of cement matrix composites by comparing the mass loss and strength loss of specimens after 300 freeze-thaw cycles. The results indicate that incorporation of graphene oxide can indeed improve the frost resistance of cement.

Tong[24] analyzed the durability of cement-based composites with 0.1% graphene of different sizes. Through freeze-thaw experiments, it was found that the graphene with different sizes had different effects on the freeze-thaw resistance of cement-based materials.

Besides the resistance to chloride ion permeability and freezing-thawing, many studies have been made on other aspects of graphene-cement composite. Muthusamy[21] found that graphene can significantly improve the permeability resistance and carbonization resistance of cement by restricting the penetration depth of CO₂. Sedaghat[14] studied the thermal diffusion coefficient and cement density of graphene cement-based composites, as well as the mineral composition of cement. The results show that the addition of graphene can reduce the temperature crack of cement base and improve the durability. Zhou[25] investigated the frost resistance and corrosion resistance of graphene additive mortar induced by the addition of different grades of graphene particles and oxidative graphene particles. As the porosity of the cementitious material reduces rapidly after adding the oxidative graphene particles, the corrosion and frost resistance of cement are both slightly improved.

6. Conclusion
Due to its unusual mechanical, electrical, optical and other properties, graphene has huge potential in making a more smart and strong cement concrete.

First and foremost, dispersion is one of the most important preconditions of processing graphene-cement composites. Compared to physical method, graphene treated with surfactant and ultrasonication is more stable in aqueous solution as well as cement slurry. Therefore, different types of surfactants and different time of ultrasonication are often putting together into different approaches to obtain stable graphene-water system for processing cement composites.

Then, the mechanical properties of graphene-cement composites are studied based on well-dispersed graphene. In general, the mechanical properties, i.e. Young's modulus, shear modulus, compressive strength, flexural strength and toughness, are enhanced obviously by the help of graphene. The most possible mechanism for the strengthening effect is the fiber-like bridging effect in cement matrix.

Meanwhile, typical piezoresistivity is observed in graphene-cement composites under both compressive and tensile load, which can be used to develop self-sensing concrete. The durabilities of graphene cement-based composites, e.g., resistance to chloride ion permeability, freezing-thawing and carbonization, as well as the resistance to corrosion and frost, are all improved compared to plain cement. However, the mechanism needs to be studied further. Also, engineering application of graphene cement-based composite should be increased in future.

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