Visual Abstract

Graphene oxide on the microstructure and mechanical properties of cement based composite material

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ABSTRACT. To investigate the mixing amount of graphene oxide and water cement ratio on the microstructure and mechanical properties of graphene oxide reinforced cement based composite material, graphene oxide suspension was developed using improved Hummers method, and the structure, size and morphology of graphene oxide were represented using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and AFM. The results demonstrated that the bending and compressive strength of graphene oxide reinforced cement based composite material improved firstly and then declined with the increase of the mixing amount of graphene oxide, and moreover the improvement of the bending strength was obvious than that of the compressive strength. When the content of graphene oxide was 0.03%, the bending strength reached the maximum, 13.73 MPa. Under a high water cement ratio, the addition of graphene oxide was more effective in enhancing the strength of cement mortar. The representation of the microstructure of cement based composite material with scanning electron microscope (SEM) suggested that graphene oxide could optimize the microstructure of cement hydration products, improve the pore structure of set cement, reduce the volume of micropore in set cement, and increase the compactness of set cement, i.e. apparently strengthen the toughening effect of set cement. The research achievements are useful to improve the mechanical properties of cement based composite materials.

KEYWORDS. Graphene oxide; Cement based composite material; Mechanical properties.

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INTRODUCTION

Concrete is the most extensively applied cement based composite material [1, 2] which is composed of cement, dinas, rebars and reinforced fibers. Concrete has been extensively applied in the construction of buildings, roads, bridges and dams for its advantages of extensive source of raw materials, low cost, simple preparation techniques and high strength [3-6]. With the development of the construction field, concrete which was a traditional structural material with high bearing capacity has developed to be more functional and environmental-friendly. Currently, high performance concrete (HPC), an important development direction of concrete, is a cement based composite material with high strength, durability and workability [7, 8]. The cement composites have a noticeable feature of relatively high compressive strength and low tensile and flexural strength, which belong to brittle materials. New carbon materials such as carbon fibers and carbon nanotubes were used to enhance the strength of cement composites or provide the cement composites with improved thermal performance. Nevertheless, the reinforcing materials such as carbon fibers and carbon nanotubes only play a physical role in the cement composites and take no participation in the hydration and microstructural modification of the cement, especially the pore structure and crystalline structure of cement paste. The dispersion of carbon fibers and carbon nanotubes in the cement matrix is also challenging because of the hydrophobic surface of these reinforcing materials [9-11]. Therefore, it is urgent to find a new material which cannot only disperse uniformly in the aqueous system of hydrated cement, but also improve the toughness of hardened cement paste by microstructural modifications. Graphene oxide is an intermediate product in graphene preparation, which has many advantages as a reinforcing material such as excellent mechanical, electrical and thermal properties [12-14]. It is easy to disperse uniformly in cements, which is beneficial to the reinforcing effect. But the study on modifying traditional cement with graphene oxide is just getting started. Some scholars have investigated the modification of cement based composite material with graphene oxide. Cao et al. [9] added the modified graphene into cement and found that the addition of graphene could produce promotion and template effects on the formation of hydrate crystal product to improve the strength and tenacity of cement-based materials. Babak et al. [15] studied the mechanical properties of graphene oxide reinforced cement based composite material and found that the tensile strength had an improvement of 48% when the weight proportion of graphene oxide was 1.5%. In the study of Liang et al. [16], graphite oxide was dispersed to water via ultrasound and blended with polyvinyl alcohol solution. Then polyvinyl alcohol/graphene oxide composite was prepared by volatilizing solvent via solution casting. When 0.7wt% of graphene oxide was added, the tensile strength and Young's modulus of the composite was improved76% and 62% respectively compared to pure polyving alcohol, and moreover the thermal decomposition of the composite was also improved. In this study, graphene oxide was prepared using oxidation reduction to study the effects of different mixing amount of graphene oxide and water cement ratio on the mechanical properties (bending and compressive strength) and microstructure of cement based composite material and analyze the variation rules. This work aims to figure out the influencing mechanism of the mixing amount of graphene oxide and water cement ratio on graphene oxide reinforced cement based composite material to lay a basis for the application of graphene oxide in cement based material.

EXPERIMENTAL SCHEME

Experimental materials

Materials included graphite powder (granularity ≤ 30 μm, Sinopharm Chemical Reagent Co., Ltd., China), concentrated sulfuric acid (H_2SO_4, 98% mass fraction), potassium permanganate ($KMnO_4$, mass fraction ≥ 99.5%), concentrated phosphoric acid (HPO_3, mass fraction ≥ 85%), hydrogen peroxide (H_2O_2, 30% mass fraction), polycarboxylate superplasticizer, ordinary portland cement P.O.42.5 and ISO standard sand.

Preparation of graphene oxide

1 g of graphite powder and 46 mL of concentrated sulfuric acid were added into a conical flask. The temperature was kept below 3 °C. Then 6 g of $KMnO_4$ was slowly added during stirring for 2 h of reaction at 15 °C and 10 h (20 h/30 h/40 h) of reaction at 35 °C; the reactant turned to be green. Then 100 mL of deionized water was slowly added for 30 min of reaction at 80 °C. After the addition of 15 mL of 30% hydrogen peroxide, the reactant turned to be golden yellow; the reaction continued for 30 min. Next centrifugation and washing with deionized water were performed until there was no so_4^{2-} in the washing liquid. The value of pH was adjusted to 7.0. It was processed by ultrasonic wave under 500 W for 30 min to obtain graphene oxide dispersion liquid after the addition of polycarboxylate superplasticizer. Its mass fraction was controlled at 0.2%.

Representation of graphene oxide

The X-Ray Diffraction (XRD) of graphite and graphite oxide were detected using D/max 2200 PC X-ray diffractometer (Rigaku, Japn). Cu Kα was X-ray source. The test was performed under 40 kV and 40 mA, and the angle was between 2° and 70°.

IRPrestige-21 Fourier transform infrared spectrometer was used to represent the molecular structure and functional group of graphene oxide and identify the category of the functional group. Specimens used for Fourier Transform Infrared Spectroscopy (FTIR) was dried using a dryer and ground into powder. KBr pellet pressing method was used.

The size of graphene oxide nanosheets was detected using SPI3800N/SPA400 atomic force microscope (NSK, Japan). 0.5 % graphene oxide was diluted to 1500 times, and one drop was taken and dried on a monocrystalline silicon piece (10 mm × 10 mm) at 25 °C.

Preparation of graphene oxide reinforced cement based composite material

It has been found that the addition of a small amount of nanometer material can significantly improve various performances of composite materials [17, 18]. In this study, the mass fraction of graphene oxide was set as 0%, 0.01%, 0.03%, 0.05% and 0.07% to study the effects of the mixing amount of graphene oxide on the mechanical properties of test specimens. Water cement ratio is an important parameter determining the strength, working performance and durability of cement based composite material [19]. Water cement ratio was set as 0.35, 0.4, 0.45 and 0.5 to investigate the variation rules of the mechanical strength of specimens under the same mixing amount of graphene oxide and different water cement ratio. 0.2% polycarboxylate superplasticizer was added to all the specimens to solve the problem of reduced fluidity caused by the addition of graphene oxide [20].

According to the preparation techniques described in Method of testing cements - Determination of strength (GB17671-1999), cement mortar was put into a mould in a size of 40 mm ×40 mm × 160 mm for curing. Then the test specimens were developed as per the mix proportion shown in Tab. 1 for the compressive and bending strength tests. All the specimens were demoulded after 24 h of maintenance and then maintained in water under standard conditions, i.e. 20 °C and 90% relative humidity, before test.

No. of specimen	Cement/g	Water cement ratio	Standard sand/g	Graphene oxide/wt%	Polycarboxylate superplasticizer/wt %
1	450	0.35	1350	0	0.2
2		0.35		0.01	
3		0.35		0.03	
4		0.35		0.05	
5		0.4		0	
6		0.4		0.03	
7		0.45		0	
8		0.45		0.03	
9		0.5		0	
10		0.5		0.03	

Table 1: The mix proportion of cement mortar specimens.

Test on the mechanical properties of cement mortar

The test specimens were taken out from water and dried, and then the bending and compressive strength of the specimens were detected under 50 N/s and 2400 N/s following GB17671-1999. In each group, three test specimens were tested, and the average value was taken as the final result. Samples were collected from the crashed fracture surface of the test specimens and immersed in absolute ethyl alcohol to stop hydration, and finally preserved in a vacuum drier. Energy spectrum was analyzed using an American JSM-6360LV scanning electron microscope (SEM) and a spectrometer.

TEST RESULTS AND ANALYSIS

Analysis of Representation of Graphene Oxide

The XRD spectra of graphite powder and graphite oxide sample are shown in Fig. 1. The peak in the curve (a) of Fig. 1 was the characteristic peak of graphite, and the peak in the curve (b) was the characteristic peak of graphene oxide. The results demonstrated that the interlayer spacing of graphene oxide increased from 0.33855 nm to 0.83859 nm, which contributed to the introduction of oxygen-containing groups in graphite nanosheets under oxidation. Oxygen connected with graphene in the form of a covalent bond, leading to the changes of laminated structure and diffraction peak deviation of graphene oxide.

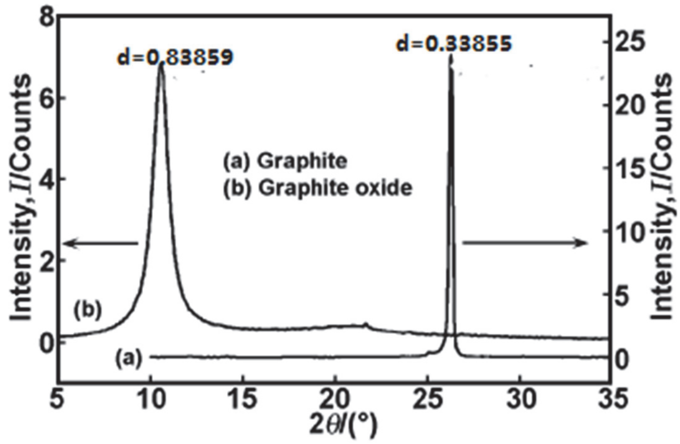


Figure 1: The XRD spectra of graphite and graphite oxide.

The FTIR spectrum of graphite oxide is shown in Fig. 2. As shown in Fig. 2, the stretching vibration and bending vibration peaks of -OH in water molecule were at 3394 cm^{-1} and 1622 cm^{-1} respectively, the the stretching vibration and bending vibration peaks of -OH in hydroxyl group were at 3141 cm^{-1} and 1401 cm^{-1} respectively, the stretching vibration peak of -C=O in carboxyl group and carbonyl group at the edge of graphite oxide nanosheets was at 1727cm^{-1} , and the stretching vibration peaks of C-O-C/-C-O were at 1116 cm^{-1} and 1075 cm^{-1}. The existence of those characteristic peaks suggested that oxygen-containing groups such as carboxyl group, epoxy group and carbanyl group were introduced in the preparation of graphite oxide, i.e. graphite has been successfully oxidized.

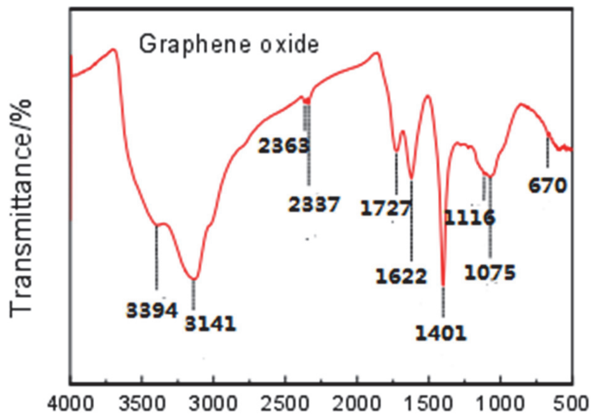


Figure 2: The FTIR spectrum of graphite oxide.

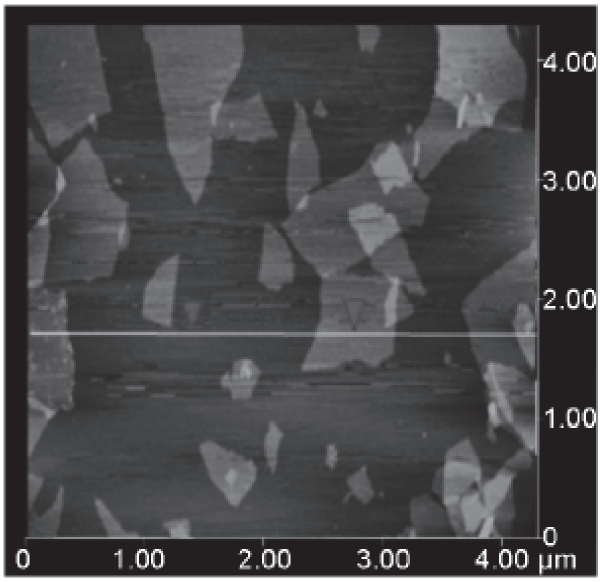


Figure 3. AFM image of graphene oxide nanosheets.

AFM image of graphite oxide is shown in Fig. 3. It can be seen from Fig. 3 that the size and thickness of graphite oxide sheet were 100-1000 and 0.7 nm, respectively, indicating that graphite oxide is one or two atom thick layers. It suggested that the prepared graphite oxide with oxygen-containing functional group on the surface had favorable dispersion and peeling.

Effects of the Mixing Amount of Graphene Oxide on the Mechanical Properties of the Test Specimens

The bending and compressive strength of the prepared graphene oxide reinforced cement based composite material were tested, as the results are shown in Tab. 2 and 3.

No. of test specimen	Water cement ratio	Mixing amount of graphene oxide/(%)	Bending strength/ MPa	Growth rate of bending strength/(%)	Compressive strength/MPa	Growth rate of compressive strength/(%)
1	0.35	0	11.07		65.66	
2	0.35	0.01	11.12	0.28	68.07	3.66
3	0.35	0.03	13.73	23.82	72.78	10.86
4	0.35	0.05	9.96	-10.21	55.42	-15.61

Table 2: The basic mechanical properties of cement mortar under different mixing amount of graphene oxide.

No. of test specimen	Water cement ratio	Mixing amount of graphene oxide/(%)	Bending strength/ MPa	Growth rate of bending strength/(%)	Compressive strength/MPa	Growth rate of compressive strength/(%)
1	0.35	0	11.07		65.66	
3	0.35	0.03	11.13	23.82	72.78	10.86
5	0.4	0	10.41		63.84	
6	0.4	0.03	11.85	10.49	67.95	6.42
7	0.45	0	9.32		60.44	
8	0.45	0.03	10.94	17.41	65.66	8.60
9	0.5	0	5.77		30.57	
10	0.5	0.03	9.98	73.10	52.66	72.36

Table 3: The basic mechanical properties of cement mortar under different water cement ratios.

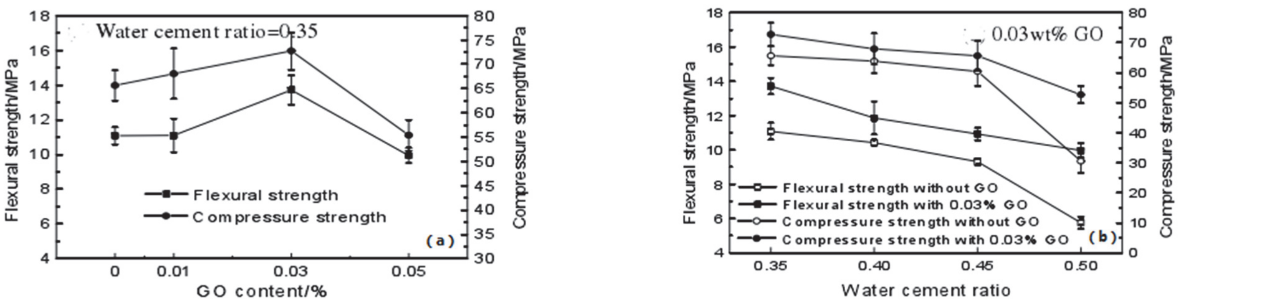


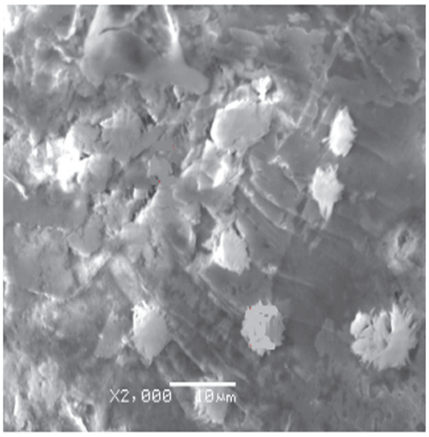
Figure 4: The variation of the bending and compressive strength of graphene oxide reinforced cement based composite material with the changes of the mixing amount and water-cement ratio of graphene oxide.

Fig. 4(a) described the variation rules of the mechanical properties of graphene oxide reinforced cement based composite material with the variation of the mixing amount of graphene oxide when the water-cement ratio was 0.35. As shown in the figure, the influence of the mixing amount of graphene oxide on the compressive and bending strength of the test specimens was consistent, i.e. increase firstly and then decrease; the compressive and bending strength was maximum when the mixing amount of graphene oxide was 0.03%, and there was a growth rate of 23.83% and 10.85%, indicating that the improvement of the bending strength was more obvious when the mixing amount of graphene oxide was within a certain range; when the mixing amount exceeded 0.03%, the bending and compressive strength had significant decline and even became lower than that of the blank samples. The first reason might be water demand significantly improved after the addition of cement-based materials because of the extremely large surface energy and specific surface area of graphene oxide. Zhu [21] found that the slump of cement paste which contained 0.05% graphene oxide reduced by 41.7%, which revealed that water demand sharply increased with the increase of the content of graphene oxide. The second reason might be graphene oxide was prone to gather because of van der Waals attraction when the content of graphene oxide was high. Moreover, many water molecules around were absorbed, leading to inconsistent water-cement ratio and uneven hydrate formation.

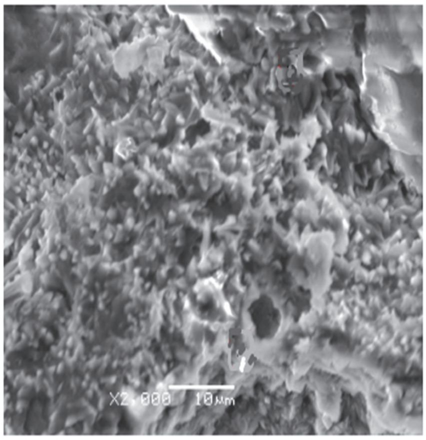
Fig. 4(b) shows the variation rules of the mechanical properties of compound cement mortar under different water cement ratio. The mechanical performance of the test specimens which were mixed with graphene oxide was superior to that of the specimens which were not mixed with graphene oxide, and the larger the water-cement ratio, the lower the strength of the test specimens. But when the water-cement ratio increased from 0.45 to 0.5, the strength of the test specimens which were not mixed with graphene oxide significantly declined, and the bending and compressive strength changed more gently. When the water-cement ratio was 0.5, the growth rates of the bending and compressive strength of the test specimens which were not mixed with graphene oxide were maximum, 73.09% and 72.35% respectively. On one hand, residual water evaporated during setting and hardening of cement paste, leading to the generation of large pores; on the other hand, graphene oxide was prone to fill in the micro-pores of the cement paste to improve the structure under a high water cement ratio. But graphene oxide as a nanometer material cannot fill in the large pores left after evaporation of water; therefore, the overall decrease tendency of the strength did not change with the variation of the water cement ratio.

Effects of graphene oxide on the microstructure of graphene oxide reinforced cement-based composite material

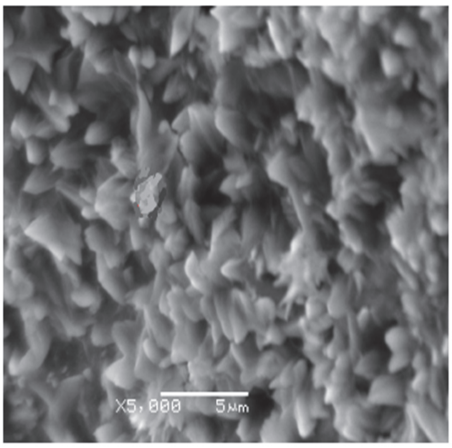
Fig. 5 exhibits the SEM images of the test specimens under different mixing amount of graphene oxide (0, 0.01%, 0.03% and 0.05%). The calcium silicate hydrate (CSH) gel and calcium hydroxide (CH) grew in the test specimens which were not mixed with graphene oxide. There were many pores in the hardened cement paste, and the insufficient ettringite inside the pores led to loose connection. But a large amount of ettringite scattering on the surface failed to play the roles of filling and connection, which was not beneficial to the structure of cement mortar. With the addition of graphene oxide, tiny CSH gels in a size of 1 μm distributed on the surface of cement particles like a roll leaf (Fig. 5(b)). When the content of graphene oxide was 0.03%, the structure of the hardened cement paste was significantly improved, no isolated hydration products were observed, and CSH structure in the shape of roll leaf which became more even and compact covered on the surface of other crystals and cement particles (Fig. 5(c)). When the content of graphene oxide was 0.05%, a compact and even structure which was composed of various hydrates was observed, but large pores and cracks appeared in the surrounding and flocculent CSH gel scattered on the surface (Fig. 5(d)).



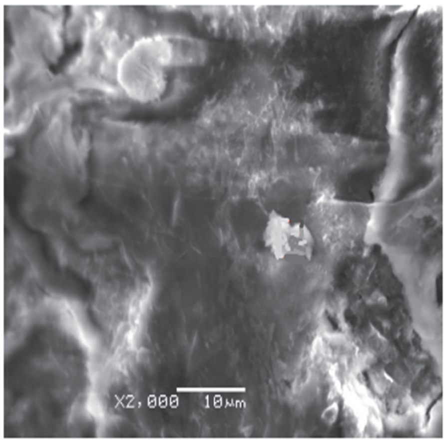
(a) The content of graphene oxide was 0.



(b) The content of graphene oxide was 0.01%.



(c) The content of graphene oxide was 0.03%.



(d) The content of graphene oxide was 0.05%.

Figure 5: The test specimens under different mixing amount of graphene oxide under scanning electron microscope.

Conclusions

Graphene oxide solution was prepared using the improved Hummers method and mixed with cement mortar to form cement-based composite material to investigate the effects of different mix proportion on the mechanical properties and microstructure of graphene oxide reinforced cement based composite material. The following conclusions were obtained.

(1) When the water cement ratio was fixed. The mechanical strength of cement mortar increased with the increase of the content of graphene oxide and reached the maximum when the content of graphene oxide was 0.03%; the increase of the bending strength (23.83%) was the most obvious. Those findings suggested the addition of graphene oxide could greatly improve the toughness of cement.

(2) When the content of graphene oxide was 0.03%, cement mortar was the same with the traditional cement; the larger the water cement ratio, the lower the strength. But the specimens which were added with graphene oxide effectively slowed the decline of the strength of the specimens with high water cement ratio (W/C=0.5). Compared to the blank specimens, the bending and compressive strength of the specimens which was mixed with graphene oxide had an improvement of 73.09% and 72.35%.

(3) The analysis of the microstructure suggested that the addition of graphene oxide could affect the growth form and number distribution of cement hydration products. The filling effect, hydration effect and nucleation effect of graphene oxide was notable when the content of graphene oxide was within a certain range. Graphene oxide became the zone for various hydration reactions because of its large specific surface area, which provided a better growth space for hydration products. It could reduce the porosity of the hardened cement paste and make the structure of cement mortar tighter; leading to the improved strength and ductibility.

The above research results which were similar to the research results of Xu et al. [22] were meaningful to improve the bending strength and crack resistance of cement-based materials and extend their service life, which can provide a reference for the future studies.

Acknowledgments

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