



Study on the three dimensional mechanism of graphene oxide nanosheets modified cement



Min Wang^a, Rumin Wang^{a,*}, Hao Yao^a, Shameel Farhan^a, Shuirong Zheng^{a,b}, Congcong Du^a

^aThe Key Laboratory of Space Applied Physics and Chemistry, Ministry of Education and Shaanxi Key Laboratory of Macromolecular Science and Technology, School of Science, Northwestern Polytechnical University, Xi'an 710072, PR China

^bNorthwestern Polytechnical University–East China University of Science and Technology Combined Research Institute of New High-speed Railway Materials, PR China

HIGHLIGHTS

- The first discovery of the 3D network structure of GO nanosheets in cement system.
- First demonstration of the chemical reactions between GO and hydration products.
- Provide a new direction of GO nanosheets were used for improving cement properties.

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ABSTRACT

This paper has established a 3D mechanism model of graphene oxide (GO) nanosheets modified cement. The GO nanosheets were compounded by the improved Hummers' method and characterized by Fourier transform infrared spectroscopy (FTIR), transmission electron microscope (TEM) and atomic force microscope (AFM). The mechanism of GO nanosheets modified cement was investigated by scanning electron microscope (SEM), differential scanning calorimeter (DSC), thermogravimetric analysis (TGA), FTIR and X-ray photoelectron spectroscopy (XPS). Based on these analyses, it was confirmed that the –COOH in the GO nanosheets reacted with the hydration product of cement ($\text{Ca}(\text{OH})_2$). The chemical reactions connected the GO nanosheets each other, producing a 3D network structure in the GO nanosheets modified cement. Moreover, the hydration products were also inserted into this 3D network structure. Therefore, the introduction of GO nanosheets improved the mechanical properties of cement composites.

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1. Introduction

At present, cement based composites are widely researched and playing an important role in building and construction fields. The global cement production has already exceeded 4.18 billion tones in 2014 [1]. Nevertheless, as we all know, cement is a brittle material due to its low flexural strength and poor strain capacity. Thus, the improvement of tensile properties has been one of the most important aspects in the field of cement modification [2–6]. Advancements in nanotechnology have provided exciting opportunities to tremendously raise the cement properties through the blending method. Various newly developed nanomaterials such as nano-silica, nanometer titania, carbon nano tube (CNTs), graphene and graphene oxide (GO) have been used in cement modification [7]. The nanomaterials used in modified cement system can be classified according to

their shapes in the space into zero-dimensional (0D) particles, one-dimensional (1D) fibers and two-dimensional (2D) sheets [8–16].

With the rapid development in GO research, GO nanosheets modified cement has provided a new method and direction towards the cement modification. According to the research by Pan et al. [17,18], introduction of 0.05 wt% GO in cement increased the compressive and flexural strengths by 15~33 and 42~59% respectively. Horszczaruk [19] reported an increase in Young's modulus by using 3 wt% GO in cement. Moreover, the microstructure changed but the kinetics of hydration process was not affected significantly with the addition of GO nanosheets. Lv et al. [20,21] observed that GO nanosheets could regulate formation of flower-like crystals and remarkably increase the tensile and flexural strengths of the corresponding cement composites. Despite these advances, the clear chemical mechanism of GO nanosheets modified cement is still unclear. The systematic mechanism research can provide not only the theoretical basis for further application of GO nanosheets in the modified cement field, but also bring

* Corresponding author.

E-mail address: wangmin19@mail.nwpu.edu.cn (R. Wang).

new train of thought for the development of new type of cements modified with nanomaterials.

It is well known that GO is a strong oxidation product of graphite and the intermediate product of graphene [22–26]. GO not only possesses the perfect mechanical properties, but also contains many active groups in the GO sheet, such as hydroxyl groups (–OH), epoxy group (–CH(O)CH–) and carboxyl group (–COOH) [27,28]. The oxygen functional groups, –OH and –CH(O)CH– attached on the basal planes, –COOH attached on the edges, significantly alter the van der Waals interactions between the GO sheets and therefore improve its dispersion and reactivity [29–31]. Furthermore, the violent hydrated reaction of cement can also produce some reactive compounds, such as $\text{Ca}(\text{OH})_2$ [32]. Therefore, it is necessary to study the probable reactions and structure in GO nanosheets modified cement.

Herein, we have used the modified Hummers' method to prepare the GO nanosheets and 0.05 wt% GO aqueous dispersion was incorporated into the cement [33–36]. The Fourier transform infrared spectroscopy (FTIR), transmission electron microscope (TEM) and atomic force microscope (AFM) were used to characterize the GO nanosheets. The effect of GO nanosheets on the flexural and compressive strengths of cement was investigated in this paper. In addition, we used scanning electron microscope (SEM) to reveal the morphology of GO nanosheets modified cement. The chemical reactions were studied by differential scanning calorimeter (DSC), thermogravimetric analysis (TGA), FTIR and X-ray photoelectron spectroscopy (XPS). Based on these analyses, the 3D mechanism and model of GO nanosheets modified cement has been proposed and discussed.

2. Experimental

2.1. Materials

The chemicals used in this research were graphite (Layer thickness <15 nm), potassium permanganate (KMnO_4), concentrated sulfuric acid (H_2SO_4 , 98%), sodium nitrate (NaNO_3) and hydrogen peroxide (H_2O_2 , 30%), which were all analytically pure. Ordinary Portland cement type 52.5R with chemical composition specified in Table 1, was used to make cement paste.

2.2. Preparation and characterization of GO nanosheets

2.2.1. Preparation of GO nanosheets

A three step process involving oxidation, filtration and exfoliation was used to prepare GO. The graphite powder (2 g) and NaNO_3 (2 g) were added to 96 mL concentrated H_2SO_4 (98%) using a three-necked round-bottomed flask placed in an ice bath (<5 °C) under stirring. Under continuous stirring, 4 g KMnO_4 was added slowly three times after 15 min each. The resulting mixture was reacted and cooled to room temperature over a period of 2 h. By this oxidation step, functional groups containing oxygen were inserted into graphite to make hydrophilic oxide. The color of the solution turned green. After oxidation, the remaining ions were removed by filtration using deionized water. The ice bath was removed, 80 mL deionized water was slowly added and the temperature was raised to 90 °C. At this point, 200 mL deionized water and 10 mL H_2O_2 were added to terminate the reaction and the color changed from brown to bright yellow. The solution was purified

by vacuum suction filtration and washed with deionized water repeatedly until the pH of the washing water was nearly 7. The resultant GO was subjected to ultrasonication at 325 W for 4 h, for exfoliation. At last, the GO was dried for 36 h in a freeze-dryer.

2.2.2. Characterization of GO nanosheets

The GO sheets were dispersed in the water by ultra-sonication. As noted in Fig. 1(a), TEM image depicts that the GO sheets appear typically wrinkled layer. From the XPS fitted result of C 1s in GO shown in Fig. 1(b), four strong peaks at 284.8, 286.7, 287.9 and 289.0 eV corresponding to C–C, C–O (hydroxyl and epoxide), C=O and O–C=O (carboxyl) groups of GO are noticed. The XPS analysis represents that there have many active groups in GO structure. From Table 2, it was noted that the C/O of the GO is 1.2. The AFM image of the GO sheets displayed in Fig. 1(c), the results represent that the single irregular lamellae of GO can be observed with a thickness about 0.79 nm (Fig. 1(d)). It means that the well dispersed GO nanosheets suspension was obtained.

2.3. Preparations of GO nanosheets modified cement paste

In this work GO oxide was used as water dispersion, which makes mixing cement paste very convenient. GO was incorporated in the cement mixture at five different percentages namely, 0.01 to 0.05% by weight of cement contents. The control mix (with no GO) was made following the mix proportions shown in Table 3. The water-to-cement ratio was kept constant at 0.33 for all mixes. In a typical experiment, distilled water was mixed with GO and ultrasonically dispersed for 1 h. Then, GO solution was added to dry contents and stirred for 3 min at 1500 rpm using a Hand-mixer (Sanyo, SHM500, China). The mixture was poured into 40 mm × 40 mm × 160 mm mold, vibrated and compacted for 25 s to remove the entrapped air. All specimens were immediately covered with a wet towel in order to prevent loss of water from the samples. Finally, the hardened cement specimens were demoulded and moist cured at 20 ± 2 °C for 6 d and then cured at 20 ± 2 °C / RH50 ± 5% for the next 21 d.

2.4. Materials characterization

The flexural and compressive strengths were tested according to GB/T 17,671–1999 of the national standard of the People's Republic of China. The flexural strength was determined using a DKZ-500 concrete three-point flexural strength tester at a load increasing rate of 0.05 KN/s. The compressive strength was tested on a JES-300 concrete compressive strength tester at a load increasing rate of 2.4 KN/s. To check for reproducibility of the results, three samples were tested each for compressive and flexural test, respectively and averaged the results.

SEM images of the fracture surfaces of GO nanosheets modified cement were obtained using a JSM-6700F scanning electron microscope. The samples were remnant pieces after mechanical testing, among which fresh surface were selected and cleaned with anhydrous ethanol. After drying at 40 °C for 24 h, the fractured surfaces were sputter-coated with a thin layer (1 nm) of gold for good conductivity prior to SEM imaging.

DSC of powder samples was performed with a DSC calorimeter (DSC1, METTLER TOLEDO, Switzerland). The specimens were prepared by grinding and filtering through a sieve (200 meshes). The

Table 1
Chemical composition of cement (%).

Composition	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	K ₂ O	Na ₂ O	LOI
Content	65.1	21.3	5.1	2.9	1.1	1.8	0.7	0.3	1.7

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