Composites Part A 114 (2018) 188–195

Contents lists available at ScienceDirect

Composites Part A

journal homepage: www.elsevier.com/locate/compositesa

Microstructure and mechanical performance of graphene reinforced cementitious composites

Gen Li[a,b,1], J.B. Yuan[a,1], Y.H. Zhang[a,*], N. Zhang[a,*], K.M. Liew[b,*]

[a] Beijing Key Laboratory of Materials, Utilization of Nonmetallic Minerals and Solid Wastes, National Circular Economy, Engineering Laboratory, National Laboratory of Mineral Materials, School of, Materials Science and Technology, China University of Geosciences, Beijing 100083, China
[b] Department of Architecture and Civil Engineering, City University of Hong Kong, Kowloon, Hong Kong, China

ARTICLE INFO

Keywords:
Graphene-cement composites
Microstructure
Flexural strength
Ettringite
Mechanical properties

ABSTRACT

An experimental investigation of the microstructure and mechanical properties of graphene-reinforced cementitious composites is presented. The early-age microstructure of the grapheme/cement composites was examined by scanning electron microscopy (SEM). The SEM images revealed that ettringite, C-S-H gel and other hydration crystals were connected by graphene sheets, which formed a 3-D structure that could bridge the cracks and fill the pores in cement matrix. With the increase of hydration ages, the 3-D structure became more complicated and connection between the graphene and cement hydrates became stronger. The X-ray powder diffraction (XRD) analysis suggested that the amount of ettringite increased with the increase of graphene content, indicating that graphene sheets could promote the formation of ettringite. In addition, the mechanical strength of graphene/cement matrix was measured. The reinforcing effect of graphene is most obvious with the addition of 0.03 wt.% graphene, with which the flexural strength increased by 40%.

1. Introduction

Cement, as the most commonly used building materials in civil engineering, plays a crucial role in building construction. Because of its brittle characteristic and low strength against tension, it is difficult for them to meet many aspects of the engineering demands [1,2]. With the development of nanotechnology and nonamaterial, the concept of the introduction of nanomaterials into composites has attracted researcher's interests in order to enhance the performance of composites [3–5]. To date, various nanomaterials have been employed to reinforce cement paste, motor and concrete, for instance, graphene, carbon nanotube [6,7], nano-silica [8], nano-titanium oxide [9], fibers [10], and nano clay [11,12].

Since graphene was isolated and characterized in 2004 [13], it has been widely studied and employed in various fields. Due to its excellent properties such as large specific surface area, high Young's module [14] and promising electrical and thermal properties, graphene is one of the most ideal nanomaterials that can be used to enhance cementitious composites. This research topic has become popular and has attracted a lot of researcher's interests recently. The mechanical properties of graphene reinforced cement have been widely studied and it has been a common sense that graphene can greatly enhance the flexural strength of cement while the compressive strength can be barely affected [15–21]. Tong et. al [22] studied the function of graphene oxide (GO) in cement matrix. They found that the quantity of pores in cement decreased with the ratio of C-S-H gel increased significantly. Based on their experiments, it is proposed that GO can promote the hydration process and the formation of C-S-H gel, which results in the cement composites tougher, thus improves the properties of cement. Shang et al. [23] observed the microstructure of GO reinforced cement and discovered that GO can connect with cement matrix, offering a platform for C-S-H gel to grow. Bobak et al. [24] proposed the idea that GO can react with C-S-H gel and form chemical bonds, through which the hydration process was accelerated. Besides, the high surface energy and the presence of hydrophilic group on graphene structure can help the nucleation and growth of hydrated crystals. Wang et al. [25] studied the morphology of GO reinforced cement and built a 3-D model of GO. In the model, GO connected with each other through 3-D structure, offering a platform for hydration products to form and grow.

Graphene oxide has lots of advantages in modifying the performance of cementitious composites. Different from GO that requires a high cost and complicated process for oxidation, graphene also acquires lots of excellent properties. However, only few studies mentioned the working mechanism of graphene in modifying cementitious materials

* Corresponding authors.
E-mail addresses: zyh@cugb.edu.cn (Y.H. Zhang), nazhang@cugb.edu.cn (N. Zhang), kmliew@cityu.edu.hk (K.M. Liew).
[1] These authors contribute equally to this work.

https://doi.org/10.1016/j.compositesa.2018.08.026
Received 13 June 2018; Received in revised form 18 August 2018; Accepted 20 August 2018
Available online 22 August 2018
1359-835X/

Table 1
Physical properties of graphene.

Type	Density/g·cm^{-3}	Pack density/g·cm^{-3}	Particle size/μm	Chemical composition/wt.%	
Graphene	1.47	0.08–0.12	6–60	C 90%	O 10%

Table 2
Chemical composition of cement.

Element	SiO_2/%	CaO/%	MgO/%	Al_2O_3/%	SO_3/%	CO_2/%
Portland cement	27.67	39.63%	10.27	–	–	22.48
Belite cement	6.28	39.32	–	23.08	7.24	–

[26]. Besides, the connection and interface between graphene and cement matrix were barely studied. Thus, in this study, graphene sheets were employed to reinforce cement composites. Besides, the interaction between graphene sheets and hydration products was investigated in order to study the mechanism of the reinforcement.

2. Experimental studies

2.1. Materials

The materials used in the experiments are graphene (Nitrogen-doped graphene, Dayuan Materials., Co Ltd.), polycarboxylate superplasticizer (Qinfen Building Materials., Co, Ltd.), Portland cement (42.5 MPa/28 d Qinfen Building Materials., Co, Ltd.), Belite cement (42.5 MPa/28 d, Qinfen Building Materials., Co, Ltd) and sand (Xiamen ISO., Co, Ltd.). Table 1 gives the physical properties of graphene. The chemical compositions of Portland cement and Belite cement are presented in Table 2.

2.2. Preparation of specimens

The graphene reinforced cement paste was prepared by mixing cement, sand, graphene, polycarboxylate superplasticizer and water together. Polycarboxylate superplasticizer was used as solvent to dissolve graphene in the water. The weight ratios of water/cement and polycarboxylate superplasticizer/cement were kept at 0.27 and 0.1, respectively. In order to find the optimal weight ratio of graphene/cement, the dosage of graphene varies from 0.01 wt.% to 0.05 wt.% (as shown in Table 3) by the weight of cement. The mixture was stirred for 2 min at 300 rpm with a blender and poured into a 40 mm × 40 mm × 160 mm mold, then vibrated for 1 min in order to exhaust the entrapped air from the mixture. Finally, the fresh pastes were covered with fresh-keeping film to prevent the water evaporation. After samples were hardened, they were demolded and cured in moist at 20 ± 2 °C for 3 days and 7 days. For each batch, five replicates were made in order to get representative measurements for the mechanical strength [25].

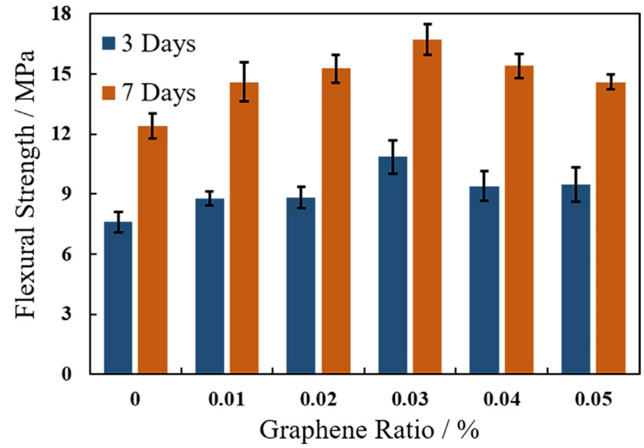

Fig. 1. The flexural strength of graphene-reinforced cementititous composites with the addition of 0.01–0.05 wt.% graphene.

2.3. Materials characterization

The flexural strength was tested according to GB/T 17671-1999 standard (the national standard of the People's Republic of China). A three-point bending testing machine was used to test samples at a loading rate of 50 N/s.

The scanning electron microscopic (SEM) – energy dispersive spectroscopic (EDS) analysis of graphene reinforced cement were obtained with a SU 8020 field emission scanning electron microscope coupled with a HORIBA EMAX ENERGY energy dispersive spectroscopy. In order to stop the hydration process, samples were immersed in ethanol for three days after 3-day and 7-day curing, and then dried under vacuum condition at 55 °C for 12 h. At last, specimens were treated with golden sputtering before taking SEM images. The atomic force microscope (AFM) of graphene was carried out using a FM-Nanoview 6800 (VEEVO, China).

The constituent analysis of all the specimens was carried out by X-Ray Powder Diffraction (XRD) (D8, ADVANCE) using Cu K α radiation (λ = 1.54056 Å) and operating at 40 kV and 40 mA with a step size of 0.026 degree. The qualitative analysis of cement hydrates was examined with a scanning rate of 6 degree/min in 2θ range of 5–70 degree and the quantitative analysis of ettringite was tested with a scanning rate of 2 degree/min in 2θ range of 5–25 degree. Powder samples of hardened graphene reinforced cement paste were produced by grinding. The refinement of XRD pattern was done with MAUD program.

3. Results and discussion

3.1. Flexural strength of graphene reinforced cement

The flexural strengths of graphene/cement composites after 3-day and 7-day curing are shown in Fig. 1. It is obvious that the strength of cement composites was enhanced greatly with the addition of graphene

Table 3
Ratio of materials.

Label	Standard sand/%	Portland cement/%	Belite cement/%	Polycarboxylate superplasticizer/%	Graphene/%	Water/ml
GB0	50	40	10	0.1	0	250
GB1	50	40	10	0.1	0.01	250
GB2	50	40	10	0.1	0.02	250
GB3	50	40	10	0.1	0.03	250
GB4	50	40	10	0.1	0.04	250
GB5	50	40	10	0.1	0.05	250

Note: the weight of each group was 1800 g. The ratio of polycarboxylate superplasticizer and graphene were the weight percentage of cement (Portland cement and Belite cement).