Composites: Part A 101 (2017) 143–150

Contents lists available at ScienceDirect

Composites: Part A

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

Enhancing mechanisms of multi-layer graphenes to cementitious composites

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ARTICLE INFO

Article history:
Received 29 April 2017
Received in revised form 13 June 2017
Accepted 15 June 2017
Available online 16 June 2017

Keywords:
A. Graphene
B. Reinforced cement
B. Mechanical properties
C. Analysis

ABSTRACT

The mechanical property and underlying enhancing mechanisms of cementitious composites filled with multi-layer graphenes (MLGs) are investigated in this paper. Research results indicate that the addition of MLGs can achieve an enhancement of 54% in compressive strength and a reinforcement of 21% in flexural strength to cementitious composites, respectively. The strengthening effects can be attributed to extensive distribution network of MLGs inside matrix, decreasing ratio of water to cement and self-curing caused by water adsorption and release of MLGs, reducing primary cracks due to MLGs presence, strong bonding between MLGs and matrix, and lowering orientation index of calcium hydroxide crystal in hydration products of cementitious composites. It is therefore concluded that MLGs are effective nanoscale fillers for reinforcing cementitious composites.

1. Introduction

Nanotechnology was conceived with a vision to advance our understanding and control of matter at nanoscale. It enables changes at molecular level to optimize material behavior and performance of civil infrastructure systems such as buildings and highways at the macro-functional level. The resulting nano-modified high-performance construction materials and systems are characterized by higher strength, greater durability, increased speed of construction, and reduced environmental impact.

Both nano-materials and carbon materials are attracting more and more attention in the field of material science and technology. Carbon materials with nano-scale structures not only show better properties than those of conventional or micro-scale carbon materials, but also exhibit novel characteristics that conventional carbon materials do not have. For example, multi-walled carbon nanotubes are efficient in providing the material with strain-sensing capabilities, and graphene nanoplatelets (GNP) have an excellent effect on increasing thermal and electrical conductivities of the materials. They provide a new approach to developing composites with high-performance and multifunctional properties. Owing to the remarkable physical properties, significant nanosize effects, low density, and excellent chemical and thermal stability, nano carbon materials offer the possibility to develop a new generation of strong, durable and multifunctional/smart cementitious composites [1–4].

Multi-layer graphenes (MLGs), as 2D nano carbon materials, are stacking from monolayer carbon atom flat structure graphene. The extreme case of MLGs is single-layer graphene, of which the lattice is a hexagon formed by six carbon atoms. The carbon atoms are connected by σ-bonds and their combination modes are sp2 hybridization. These σ-bonds endow MLGs extremely excellent mechanical property and structural rigidity. It should be noted here that MLGs is different form GNP which also stacks from graphene. The differences lie in their layer number and properties. The layer number of GNP is larger than 10 with a thickness between 5 and 100 nm, so the properties fall in between those of MLGs and graphite. The layer number of MLGs is between 3 and 10 with a thickness less than 5 nm, and its properties are more like those of single-layer graphene. The stiffness of MLGs is 100 times higher than that of the best steels ever known, even higher than that of diamonds. The strength of MLGs is dozens of times stronger than that of steels. The coefficient of thermal conductivity of MLGs is as high as 5300 W/(m·K), which is higher than that of carbon nanotube and diamond [5–16]. Since MLGs possess such excellent properties, they may be useful for modifying the cementitious composites. Some researches have been done to ascertain the mechanical properties of the cementitious composites filled with MLGs. The mechanical properties of the cementitious composites

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http://dx.doi.org/10.1016/j.compositesa.2017.06.016
1359-835X/

filled with MLGs are closely related to not only the type, concentration, surface condition and dispersion quality of MLGs, but also the composition of cementitious materials. Therefore, different research results are obtained. For example, Hou et al. found that MLGs oxide can enhance the flexural strength of the material by 11.62% [17]. Huang et al. observed that the addition of MLGs increases the flexural strength of cement paste by 82% compared with the plain ones [18]. Duan et al. reported that MLGs oxide can improve the flexural strength of cement paste from between 41% to 59% and the compressive strength from between 15% to 33% [19]. Lv et al. found that MLGs oxide can remarkably increase the strength of the resulting cement mortar. The tensile, flexural and compressive strengths of cement mortar with MLGs oxide are increased by 78.6%, 60.7% and 38.9%, respectively [20]. In addition, researchers also tried to find the underlying strengthening mechanisms of MLGs to the mechanical properties of the cementitious composites, and they suggested such effects as template nucleating effect, pore size refinement effect, filling effect and crack arresting effect based on experimental phenomena [21–31]. However, the template nucleating phenomena does not occur in all previous research work. Furthermore, MLGs at low concentration is hard to have strong filling effect. Based on the above analysis, the reinforcing mechanisms of MLGs to cementitious composites are still not quite clear.

Therefore, this paper aims to further investigate the underlying mechanism of MLGs to cementitious composites through calculating MLGs distribution in matrix, measuring water adsorption characteristic of MLGs, testing hydration behaviors, nano hardness and thermal properties of the composites, and observing microstructure of the composites.

2. Materials and experimental method

Cementitious composites are fabricated with cement (type P.O. 42.5R) provided by Dalian Onoda Cement Company, MLGs (powder form, shown in Fig. 1, and their properties are presented in Table 1) provided by Shanghai Yuanrun new Energy Equipment & Technology Co., Ltd., polycarboxylate superplasticizer (Sika ViscoCrete 3301E, employed to disperse MLGs) provided by Sika (China) Ltd., Dalian, and water. Fine aggregate used is standard sand (Xiamen AI Ou standard sand Co., Ltd, China).

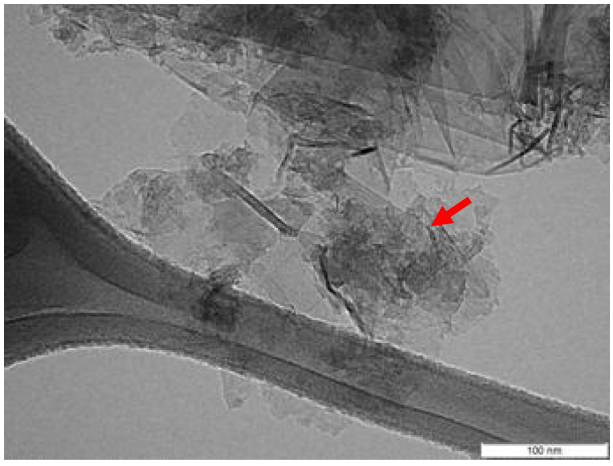

Fig. 1. Images of MLGs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The mix proportions of cementitious composites filled with MLGs are provided in Table 2 and Table 3. The detailed fabrication process of cementitious composites filled with MLGs is as follows: (1) Mix the polycarboxylate superplasticizer with water; (2) Add MLGs into the solution and then ultrasonicate the suspension for 1 h with a Branson 2510 E-DTH ultrasonicator (Bransonic Ultrasonics Corporation) to prepare uniform suspension; (3) Put the cement and sand in batches into the suspension slowly and stir them with a DW-2 DC Constant Speed Stirrer (Chinese Yu Hua Instrument Ltd.) at low speed firstly and then at high speed; (4) Pour the mixture into the moulds (20 mm × 20 mm × 40 mm for compressive test, 40 mm × 40 mm × 160 mm for flexural test, and 90 mm × 90 mm × 10 mm for thermal conductivity test); (5) Put the mould with the mixture on the electric vibrator and vibrate to eliminate bubbles; (6) Demold after 24 h; (7) Cure the specimens for 90 days in standard condition at a temperature of 20 °C and a relative humidity of 100%. Three specimens in each group were used to test. The standard deviation of compressive and flexural strength of three tested specimens is 3.2% and 4.5%, respectively. These indicate that the above fabrication progress is effective for uniformly dispersing MLGs in cementitious matrix.

The compressive and flexural loadings were exerted on the specimens by using a universal testing machine WDW-200E. Two strain gauges were fixed to the opposite sides of compressive specimens along the loading direction to test the compressive strain. Dynamic strain indicator (DC-204R by Tokyo Sokki Kenkyujo Co., Ltd.) was employed to measure the strain. The displacement control method was applied in this paper. The displacement speed for compression tests is 1.2 mm/min and 0.05 mm/min for flexural tests. RST-SST rheometer (American Brookfield Co. Ltd.) was employed to test the rheological property and the test procedures included preshearing and data acquisition processes: (1) Increase shear rate from 0 to 100 r/min in 30 s and then decrease shear rate from 100 r/min to 0 in 30 s. (2) Increase shear rate from 0 to 150 r/min in 75 s and then decrease shear rate from 150 r/min to 0 in 75 s. A Nano Indenter XP System (MTS Systems Co. Ltd.) was used to measure the nano hardness of cementitious composite. The samples were prepared by polished machine. The loading rate of nano intender XP system is 4 nm/s and the penetration depth is 2 μm. The area of nano-indentation test region is 160 μm × 160 μm. The hardness of nine test positions in the test region is measured. The separation between centers of adjacent test positions is 80 μm. The area of indentation is 98.24 μm^2. The quasi-steady-state method is applied to test thermal conductivity and special heat of specimens with a ZKY-BRDR Quasi Steady State Specific Heat/Thermal Conductivity Coefficient Tester (Cheng Du Century Science and Technology Co., Ltd., China). A Field Emission Scanning Electron Microscope (FESEM) (Nova NanoSEM 450, American FEI Ltd.) was used to observe the morphology of the MLGs and cementitious composites. Additionally, thermogravimetry (TG) analysis was performed using a Thermogravimetric Analysis (EXSTAR TG/DTA 6300, SII) to get the amount of calcium hydroxide (CH) and other hydration products. The condition of TG analysis was under nitrogen atmosphere at a heating rate of 10 °C/min up to 1000 °C. X-ray powder diffraction (XRD) (Bruker D8 Advance, Bruker German) was applied for studying the change

Table 1
Properties of MLGs.

Diameter	Thickness	Relative gravity	Thermal conductivity	Specific surface area	Oxygen content	Nitrogen content
<2 μm	1–5 nm	2–2.25 g/cm^3	>3000 W/(m·K)	500 m^2/g	6 wt.%	2 wt.%