Construction and Building Materials 49 (2013) 121–127

Contents lists available at ScienceDirect

Construction and Building Materials

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

Effect of graphene oxide nanosheets of microstructure and mechanical properties of cement composites

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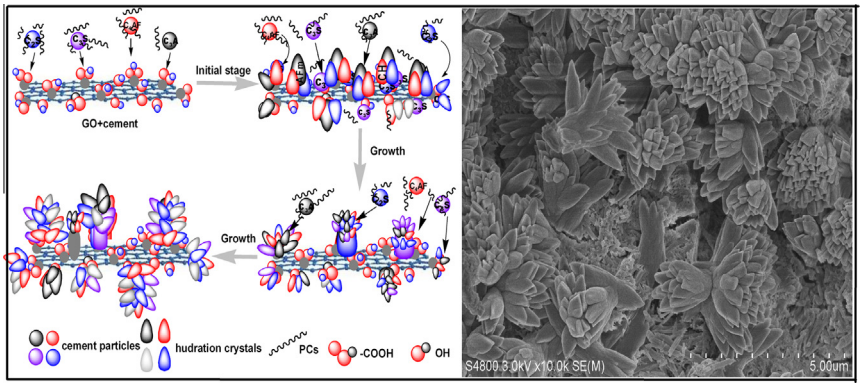
HIGHLIGHTS

- Graphene oxide (GO) nanosheets were prepared by oxidization and ultrasonic dispersion.
- GO nanosheets can regulate forming flower-like cement hydration crystals and sharply increase its toughness.
- The flower-like crystals were attributed to the template effect of GO naosheets.
- The research provides a pathway to significantly improving the toughness of cement composites.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 June 2013
Received in revised form 9 August 2013
Accepted 14 August 2013
Available online 4 September 2013

Keywords:
Graphene oxide
Cement
Hydration reaction
Microstructure

ABSTRACT

Graphene oxides (GOs) nanosheets were prepared by oxidization and ultrasonic dispersion. Effects of GO nanosheets on microstructure and mechanical properties of cement composites were investigated by observing shape changes of cement hydration crystals and testing mechanical strength. The results indicated that GO nanosheets can regulate formation of flower-like crystals and remarkably increase the tensile/flexural strength of the corresponding cement composites. A possible regulation mechanism was proposed and thought GO nanosheets exhibited the template effect and contributed to the formation of flower-like crystals. The research provide a new pathway to significantly improving the toughness of cement composites by a simple method.

1. Introduction

Cement composites are the most important and most abundant building material at present [1,2]. Though various high-performance cement composites have already been produced and applied worldwide, the inherent limitation of highly brittle and be likely to crack of cement composites are still here [3–5]. A noteworthy feature of the cement composites is their relatively high compressive strength and low tensile and flexural strength, indicating the fact that cement composites are brittle materials. In fact, how to significantly improve toughness has been the focus of attention since the appearance of cement composites. Now enhancing the strength of cement composites still mainly depends on reinforcing materials, such as steel bars [6], steel fibers [7], carbon fibers [8], polymer fibers [9–12] and mineral fibers [13,14]. These reinforcing materials can greatly improve the strength as whole, but high brittleness and associated cracking still occur. The main reason for this is because the high brittleness of cement composites originates from the hardened cement paste, which play adhesive role in cement composites and consists of complex cement hydration reaction products such as ettringite (AFt),

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http://dx.doi.org/10.1016/j.conbuildmat.2013.08.022

monosulfonate (AFm), calcium hydroxide (CH) and calcium silicate hydrate (C—S—H) gel. CH, AFt and AFm usually exhibit rodlike and needle-like crystals [1]. Previous toughening methods were over-dependent on reinforcing materials and neglected the regulation of the microstructure, such as the shape of hydration crystals, of cement paste. Therefore, seeking a method that can significantly improve the toughness of hardened cement paste through regulation of its microstructure is certainly worth considering. Graphene oxide (GO) has a high specific surface area, ultrahigh strength and flexibility [15–17]. It is reported that GO easily forms composites with polymer and ceramic materials, and can remarkably enhance toughness by control the microstructure of crystals [18,19]. Inspired by the structure and application properties of GO, meanwhile, considered the fact that effects of GO on structure and mechanical properties of cement composites has not been reported. Therefore, the effect of GO on the microstructure and strength, especially the tensile and flexural strength, of cement composites was investigated in this paper.

2. Experimental

2.1. Chemicals and materials

The chemicals used in this research were graphite (size <30 μm), concentrated sulfuric acid (H_2SO_4,98%), potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), hydrogen peroxide (H_2O_2,30%), which were all analytical grade. The polycarboxylate superplasticizer (PC, solid content 20%), standard sand and ordinary Portland cement type 42.5R were main materials used in this research. The chemical composition of the cement is shown in Table 1.

2.2. Preparation of GO

The following were sequentially added to a three-necked round-bottomed flask placed in an ice bath (<5 °C) under stirring: 5 g graphite, 30 g 98% H_2SO_4 and 2 g $NaNO_3$. With continuous stirring, 6 g $KMnO_4$ was slowly added to the flask. When the color of the solution had turned green, it was maintained at 5 °C for 1 h. Then it was heated to 35 °C and the temperature held for 12 h under stirring. Then 100 ml of deionized water was slowly added to the solution, the temperature raised to 90 °C and 300 ml deionized water and 30 g H_2O_2 (0.50 mol) slowly added to the solution in turn. The color of the solution changed from brown to bright yellow. Then the solution was purified by vacuum suction filtration and washed with deionized water repeatedly until the washing water contains no SO_4^{2-}. Then 300 ml of deionized water was added to the GO, stirred and dispersed by ultrasonication at 325 W for 1 h. A stable GO nanosheets dispersion aqueous solution was obtained. The GO concentration was controlled as 0.2%.

2.3. Preparation of cement composites

The cement composite was prepared by mixing 450 g cement, 1350 g standard sand, 165 g water, 0.9 g PC (solid dosage and by weight of cement) and a certain amount of GO. PCs is polycarboxylate superplasticizer, which is an indispensably admixture for cement composites, and its main function is to reduce the water consumption without losing fluidity of the cement pastes. The samples were molded into a rectangle with a size of 40 mm × 40 mm × 160 mm to test the flexural strength and compressive strength. The specimens for tensile strength testing were molded into a dumbbell shape length of 200 mm, which middle section is a rectangle with a size of 100 mm × 70 mm × 70 mm and the two ends of samples are rectangle with a size of 50 mm × 70 mm × 70 mm. Five samples were prepared at each measuring point for parallel determination and error reduction. Then the molds were removed after 24 h and the samples were continued to be cured in a standard curing box at 20 °C and 95% relative humidity until before testing.

2.4. Structural characterization of GO nanosheets

The sample was purified by precipitation and washing with deionized water, and then dried in a vacuum dry box at 50 °C for 10 h. Then the samples were used directly for detection of FTIR, XRD and EDS. The FTIR spectra were acquired using a Fourier transform infrared attenuated reflection spectrometer. The XRD patterns were acquired using an X-ray diffractometer. The GO samples were ground into fine powder, and then fixed in a metal plate. The EDS patterns were acquired using a field emission scanning electron microscope (FESEM) coupled with an energy-dispersive X-ray spectrometer (EDS). The samples for EDS were fixed on an aluminum stub and coated with gold by a sputter process.

The AFM images of GO nanosheets were acquired using an atomic force microscope (AFM). The GO sample was prepared by putting a drop of very dilute GO suspension solution (0.2% GO solution was diluted 200 times) on a piece of monocrystalline silicon (5 mm × 5 mm × 0.45 mm) and dried it in a vacuum oven at 50 °C for 2 h.

2.5. Microstructure and properties of cement composites

The SEM images of the fracture surfaces and EDS patterns of hydration crystals were obtained on a field emission scanning electron microscope. The XRD samples were ground into a fine powder and sieved to remove sand. Then XRD patterns were obtained on an X-ray diffractometer.

The flexural strength was determined by a three-point flexure testing machine according to GB/T 50080-2002 (National Standard of China) and the increasing ratio of pressure was 0.25 MPa/s. The compressive strength was acquired using a compression testing machine according to GB/T 50080-2002 and the increasing ratio of pressure was 0.8 MPa/s. Tensile strength measurements were obtained on a tensile strength tester. The tested results can be evaluated by the standard deviation. The standard deviation of tested data can be calculated by the following equation:

$$S = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N-1}} \quad (1)$$

where S is standard deviation (%), N is the total number of samples or all measurement times of each measurement point, x_i is a measurement of a sample, $\bar{x}$ is the average value of all measurement of a texting point.

Table 1
Chemical compositions of cement.

Component	SiO_2	Al_2O_3	MgO	CaO	Na_2O	K_2O	SO_3	Fe_2O_3	P_2O_5	TiO_2	MnO	Loss
Content (%)	21.25	4.21	2.90	65.16	0.50	0.97	0.72	3.35	0.10	0.21	0.07	0.56