Journal of Physics and Chemistry of Solids 85 (2015) 39–43

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

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

Co-effects of graphene oxide sheets and single wall carbon nanotubes on mechanical properties of cement

Xueguang Li [a,b], Wei Wei [b], Hao Qin [b], Yun Hang Hu [b,*]

[a] College of Mechanical and Electrical Engineering, Changchun University of Science and Technology, 7089 Weixing Road, Changchun 130012, China
[b] Department of Materials Science and Engineering, Michigan Technological University, 1400 Townsend Drive, Houghton, MI 49931-1295, USA

ARTICLE INFO

Article history:
Received 28 January 2015
Received in revised form
9 April 2015
Accepted 24 April 2015
Available online 25 April 2015

Keywords:
Nanostructures
X-ray diffraction
Mechanical properties

ABSTRACT

The enhancement of mechanical properties of cement composites by a carbon nanomaterial is an important topic. However, the co-effect of two (or more) carbon nanomaterials on the mechanical properties of cement has not been explored. In this paper, it was found that the mixture of graphene oxide (GO) sheets and single-walled carbon nanotubes (SWCNTs) exhibited an excellent co-effect, leading to 72.7% increase in bending strength of cement, which is much larger than the strength enhancements of 51.2% by GO and 26.3% by SWCNTs. Furthermore, it was demonstrated that the bending strength of cement composite materials with GO and SWCNTs is proportional to the sizes of crystal SiO_2 particles.

1. Introduction

As the most common construction material, cement composites have widely been used. However, their inherent cracks due to lesser tensile strength and strain capacity constitute a main drawback [1–3]. To solve the issue, the effect of filler particles and fibers on the growth of cracks in cementitious materials has been evaluated [4–12]. It was found that titania particles accelerated the hydration rate more than limestone particles [6]. The flexural and compressive strengths of the cement mortars can be increased by incorporating nano-Fe_2O_3 and nano-SiO_2 particles into cement mortars [13]. Furthermore, the content effect of colloidal silica on the mechanical performance and microstructure of cement composites was examined, showing that the average values of the rupture modulus of the cement decreased with increasing colloidal silica content [14]. On the other hand, the mechanical properties of cement could also be reinforced by carbon fibers and natural fibers [4,10,11]. For example, the mechanical properties of concrete could be reinforced by coconut fiber [9]. The effect was dependent on the length and content of coconut fibers, namely, the largest reinforcement was observed with a fiber length of 5 cm and a fiber-content of 5%.

In the past 30 years, carbon nanomaterials have attracted the most attention in science and engineering. Carbon nanotubes (CNTs), which are one-dimensional carbon nanomaterial with hollow tubular structure, are formed either by single wall (SWCNTs) or multi walls (MWCNTs) of rolled carbon sheets [15]. The effect of carbon nanotubes (CNTs) on the compressive strength of hydrated cement paste has been investigated with two techniques: the mixture of CNTs with cement in powder form and the mixture of CNTs with cement in hydrated form [16]. The two mixing techniques led to 8.5 and 22% increase in the strength, respectively [16]. The improvement in the hydration process of cement by SWCNTs or MWCNTs was also observed [17]. Furthermore, the bending strength, compression strength, porosity and density of mortars were correlated with CNT dosages [18,19].

Graphene is a star of carbon nanomaterials due to its unique properties [20], such as a large specific surface area (2630 m^2g^{-1}), high intrinsic mobility (200,000 $cm^2\,v^{-1}\,s^{-1}$) [21,22], and high Young's modulus (~1.0 TPa) [23]. As an atomic sheet, graphene is the strongest (over 100 times stronger than the strongest steel) and the stiffest material (stiffer than diamond) as well as the most stretchable crystal (up to 20% elastically) [20]. Its second- and third-order elastic stiffnesses, which were measured by nanoindentation in an atomic force microscope, are 340 Nm^{-1} and 690 Nm^{-1} respectively, and its breaking strength is 42 Nm^{-1} [23]. Those impressive mechanical natures stimulated interesting research in applying graphene as a superlative filler in reinforced composites [24,25]. Graphene oxide (GO), which possesses a high specific surface area and ultrahigh strength [26], can easily form composites with polymer and ceramic materials with chemical bonds, affecting cement hydration crystal shape and increasing its flexural and compressive strength [27–31].

So far, although the effects of various additives to cement on its

* Corresponding author.
E-mail address: yunhangh@mtu.edu (Y. Hang Hu).

http://dx.doi.org/10.1016/j.jpcs.2015.04.018
0022-3697/

mechanical properties were intensively investigated, the co-effects of multiple additives have not been explored. In this work, we combined graphene oxides (GO) and single walled carbon nanotubes (SWCNTs) as multiple-additives for cement, leading to a remarkable enhancement in its mechanical properties, which is larger than that by a single additive.

2. Experimental

2.1. Materials

Portland cement type II (No. 1124), which was used in this work, consists typically of 51% tricalcium silicate (C_3S), 24% dicalcium silicate (C_2S), 6% dicalcium aluminate (C_3A), 11% tetracalcium aluminoferrite (C_4AF), 2.9% MgO, 2.5% SO_3, 0.8% Ignition loss, and 1.0% CaO. Single-walled carbon nanotube (SWCNT) sample was purchased from Carbolex. Graphene oxide (GO) was synthesized from graphite powders (Sigma-Aldrich) via the modified Hummers method described as follows [32,33]: potassium permanganate (3 g) was added into the mixture of graphite (0.5 g), sodium nitrate (0.5 g), and sulfuric acid (25 mL) at room temperature, followed by heating to 35 °c with a water-bath and then stirring at 35 °C for a selected oxidation time (5 h) to form a thick paste. Deionized water (40 mL) was added into the thick paste with stirring, followed by heating to 90 °C over 30 min, then adding more deionized water (100 mL), and finally gradually adding 10 mL of H_2O_2 (30%). The obtained sample was filtered and washed with 100 mL of deionized water. The filter sediment was dispersed in deionized water again, followed by ultrasonic treatment for 24 h and then centrifugal treatment to separate the solid from the water. The obtained solid sample of graphite oxide was dried in a vacuum furnace at 50 °C. The as-prepared graphite oxide was re-dissolved in deionized water, followed by ultrasonic treatment (for 48 h) to achieve full exfoliation from graphite oxide to graphene oxide (GO).

2.2. Cement sample preparation and bending strength measurement

To make cement samples with and without GO (and/or SWCNTs), the cement composite was prepared by mixing 40 g cement, 120 g stand sand, 12 g water, and 4 g polycarboxylate superplasticizer (PC) solution that contains a certain amount of GO and/or SWCNTs. Polycarboxylate superplasticizer is an indispensably admixture for cement composites to reduce the water consumption without losing fluidity of the cement pastes. The specimens for bending strength testing were placed into a mold at the relative humidity of 50% for 24 h and then removed from the mold and continued to be cured in water at $23 \pm 2°$ for 7 days before bending test. The fracture strengths of the cement composites were measured using MTS ReNew upgrades 4206 at room temperature. The relative standard error of fracture strength measurements, which were obtained with 42 samples of GO/cement composites, is 5.78%.

2.3. Material characterization

Microstructures of GO sheets and single walled carbon nanotubes (SWCNTs) were further evaluated by JEOL JEM2010F transmission electron microscopy (TEM). The compositions of GO and SWCNTs were measured with Elemental Analysis method using the Control equipment corporation Model 240XA instrument. Fourier transform infrared (FTIR) spectra were obtained using FT/IR-4200 spectrometer. Crystal structures of cement composites were determined by using Scintag XDS 2000 powder diffractometer with Cu Kα ($\lambda = 1.5406$ Å) radiation at a scan speed of 1 °/min and a step size of 0.03°.

3. Results and discussion

The structures of graphene oxide (GO) sheets and single walled carbon nanotubes (SWCNTs) were evaluated by transmission electron microscopy (TEM). As shown in Fig. 1, one can see curved GO sheets and bundled SWCNTs with a diameter of about 1 nm. Elemental analysis revealed that the GO sheets contain 32.5% oxygen. Furthermore, the FTIR spectra of GO were employed to evaluate oxygen functional groups and various absorption bands were observed (Fig. 2): A broad and intense band at 3000–3700 cm^{-1} associated with O–H stretching vibrations, a band at 1714 cm^{-1} due to C=O stretching vibration, a band at 1410 cm^{-1} corresponding to stretching vibrations of C–O bond, and a band at 1146 cm^{-1} caused by epoxy C–O–C bond [34–38]. Furthermore, one can see an additional band located at 1590 cm^{-1}, which can be assigned to the unoxidized graphitic domain [39]. Those indicate that the functional groups of graphene oxides are carboxyl, epoxy, and hydroxyl groups [37–41].

The bending tests were carried out to examine the fracture strength of the cement composites. Fig. 3 shows that the fracture strength increased with increasing GO content and then decreased. The optimum GO content is 1.5 wt% at which the fracture strength reaches the maximum value (13 MPa). This is 51.2% larger than that (8.5 MPa) of the cement without GO additive, indicating that GO sheets can remarkably enhance the mechanical property of cement. The SWCNTs exhibited a similar effect on fracture strength of the cement composites as GO, namely, the fracture

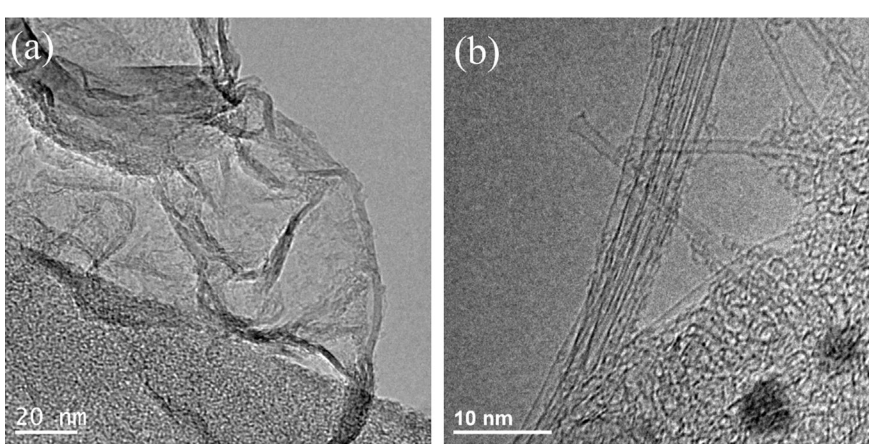

Fig. 1. TEM images of (a) GO and (b) SWCNTs.