Construction and Building Materials 134 (2017) 336–345

Contents lists available at ScienceDirect

Construction and Building Materials

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

Enhanced mechanical properties of cement paste by hybrid graphene oxide/carbon nanotubes

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HIGHLIGHTS

- GO was used as a dispersant to disperse CNTs.
- The mechanical properties of cement paste were improved by the hybrid GO/CNTs.
- The hybrid GO/CNTs could refine the pores of the matrix.

ARTICLE INFO

Article history:
Received 16 August 2016
Received in revised form 25 October 2016
Accepted 24 December 2016
Available online 31 December 2016

Keywords:
Graphene oxide
Carbon nanotubes
Dispersion
Cement paste
Microstructure

ABSTRACT

The prominent mechanical properties of carbon nanotubes (CNTs) make them to be potential candidates for enhancing cementitious material. However, CNTs are hard to be dispersed uniformly due to the Van der Waals' force between them. Many methods have been attempted by researchers to improve the dispersion of CNTs. This research investigated the use of graphene oxide (GO) as a dispersant for CNTs to overcome the obstacles. UV–vis spectroscopy and scanning electron microscopy (SEM) results revealed that CNTs were highly dispersed by GO rather than by surfactants. More importantly, the excellent reinforcing capabilities of the hybrid GO/CNTs were demonstrated by the enhanced fracture resistance properties of the cementitious matrix. The hybrid GO/CNTs (0.02 wt% GO and 0.04 wt% CNTs by weight of cement) with poly-carboxylate superplasticizer had a great contribution to improving the compressive and flexural strength of cement paste by 23.9% and 16.7%, respectively, which was higher than cement paste reinforced by CNTs or GO. Scanning electron microscopy images showed that the hybrid GO/CNTs were well dispersed in the cement hydration products. Furthermore, mercury intrusion porosimetry (MIP) results indicated that the addition of the GO/CNTs promoted the refinement of pores in cement paste.

1. Introduction

Cementitious materials are extensively used worldwide for building and construction. However, cementitious materials are susceptible to cracking. The cracking process within cement begins with isolated nano-cracks, which then conjoin to form micro-cracks and in turn macro-cracks [1]. Traditional fibers (e.g. steel fiber or PVA fiber) show good crack resistance and restrain crack propagation in the macro scale, but were invalid for delaying micro-crack initiation. Recently, achievements in nanotechnology have produced nanofibers (e.g. carbon nanotubes and graphene oxide) that could be used as reinforcements to move the reinforcing behavior from the macroscopic to the nano-scopic level.

Compared to traditional fibers, carbon nanotubes (CNTs) regarded as a one-dimensional tube exhibit excellent mechanical properties and high aspect ratio ranging from 30 to more than many thousands [2,3]. The unique mechanical properties make them attractive for use as reinforcement to develop superior cementitious composites. However, the incorporation of high concentration CNTs in cement composites had proven to be re-agglomerate which will leads to weak bond in the microstructure [4]. CNTs tend to agglomerate, bundle together and entangle due to strong Van der Waal's attractive forces between particles. Therefore, dispersing CNTs uniformly in cementitious materials is probably the most critical issue for a successful production of CNTs/cement composite. Junqing Zuo et al. [5] used sodium dodecyl benzene sulfonate (NaDDBS) as surface-active agents to obtain uniform dispersed CNTs with the help of sonication, and found that the cement pastes with addition of 0.5 wt% MWCNTs could increase in the compressive strengths by 18.4%. But the treatment

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http://dx.doi.org/10.1016/j.conbuildmat.2016.12.147
0950-0618/

time or energy of the ultra-sonication process had strong influence on CNT dispersion. Shama Parveen et al. [6] reported that the flexural and compressive strengths of mortar increased by 7% and 19% through adding 0.1% single walled nanotube (SWCNT) with a novel dispersing agent, respectively. Some surfactants were successfully used to disperse carbon nanomaterials in other matrices have been reported [7]. Zoi S. Metaxathe et al. [8] also found that effective dispersion of different length MWCNTs in water was achieved by applying ultrasonic energy and in combination with the use of a surfactant. However, some surfactants of CNTs maybe entrap air in the cement paste. It was observed that the application of sodium dodecyl sulfate (SDS) as a surfactant of CNTs led to a severe drop in the strength of the hardened cement, which could be explained by the high porosity of the samples containing SDS caused by the formation of foam [9]. In addition, a lot of work had been done on the amination, fluoration, and long alkyl chain grafting of the carbon nanotubes through the chemical reactions [10,11]. The chemical functionalization of CNTs played an important role in improving the bonding of fibers and cementitious matrices. Acid treatment of carbon nanotube had also been found to benefit dispersion of the CNTs in aqueous media. Su-tae Kang et al. [12] reported that workability of the cement composites decreased with acid treatment of CNTs, compressive and tensile strength improved significantly. However, the functionalized CNTs due to the chemical modifications methods might cause a structure damage to CNTs, which resulted in a shorter length, a smaller diameter and a roughen surface in CNTs.

Similar to CNTs, graphene oxide (GO) with a unique atom-thick two-dimensional structure has excellent mechanical properties. The intrinsic strength and Young's modulus are estimated to 100 GPa and 1 TPa, respectively [13]. Moreover, GO is an excellent hydrophilic material with oxygen-containing functional groups such as hydroxyl, carbonyl and carboxyl, which could be dispersed well in water [14]. The unique structure and high surface area of GO could be beneficial for improving bonding between graphene sheets and cement products. Zhu et al. [15] demonstrated that the incorporation of 0.05 wt% GO in the cement paste increased the compressive and flexural strength by 33% and 41%, respectively. Shenghua Lv et al. [16] reported that the cement composites exhibited remarkable increase in tensile strength (78.6%), flexural strength (60.7%) and compressive strength (38.9%) comparing with those without GO, when the content of GO was 0.03%. This happened because the oxygen-containing function groups provided adsorption sites for water and cement, leading to the crystal nucleuses for cement hydrates [17]. Zeyu Lu et al. found that the addition of 0.05 wt% GO could improve the compressive and flexural strength of the magnesium potassium phosphate cement (MKPC) paste by 6.8% and 8.3%, respectively, compared with the fresh MKPC paste [18].

So far, there have been a lot of previous researches on CNTs or GO enhanced cementitious materials. But the study on co-effects of GO/CNTs on the mechanical behavior of cementitious materials is still few. In fact, the hybrid GO/CNTs has been extensively studied in the electrode and solar cells. Hejie Song et al. [19] prepared a "clean" three-dimensional architecture consisting of two-dimensional reduced graphene oxide (rGO) and one-dimensional CNTs supporting zero-dimensional Pd nanoparticles by using GO as a surfactant to disperse CNTs, which could be use as highly active and stable electro-catalysts. Leping Yu et al. [20] used GO sheets as the surfactant to disperse single-walled carbon nanotubes in water, and prepared GO/CNT electrodes that could be used in solar cells. Compared to CNTs or GO, the hybrid GO/CNTs may be better reinforcements in cement materials.

The aim of this paper is to investigate the dispersion of the hybrid GO/CNTs and the mechanical behavior of cement paste reinforced by GO/CNTs. The dispersion of CNTs used GO as a dispersant was characterized by Ultraviolet spectrophotometer (UV-s). And the properties of GO/CNTs/cement composites, involving Fourier transform infrared spectroscopy (FT-IR), Raman spectra, X-ray diffraction (XRD), scanning electron microscopy (SEM) and mercury intrusion porosimetry (MIP), were investigated.

2. Experimental

2.1. Materials

Ordinary Portland cement (OPC) type 42.5 was used in this paper. Multi-wall carbon nanotubes (MWCNT) with an outer diameter of 30–50 nm, was supplied by Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, China. The chemical compositions of cement and the physical properties of the CNTs were shown in Tables 1 and 2, respectively.

2.2. Preparation of GO

Graphene oxide was prepared from graphite flakes (325 mesh, Qing Dao) according to the improved Hummers' method [21]. First of all, graphite powder (3 g) and sodium nitrate (3 g) were added to 100 ml concentrated H_2SO_4 in an ice water-bath (below 5 °C). Successively, $KMnO_4$ (9 g) was gradually added under stirring for 30 min. Then the mixture was transferred to water-bath (35 °C) for 5 h. Deionized water (100 ml) was added into the mixture, followed by heating to 98 °C for 15 min. Finally, deionized water (230 ml) and 30% H_2O_2 solution (5 mL) was added to terminate the oxidation reaction. And the color of the solution turned from dark brown into yellow. After air cooling, the obtained sample was filtered and washed successively with 10% HCl aqueous solution to remove metal ions, and then centrifuged successively with warm deionized water completely until sulfate could not be detected with $BaCl_2$.

2.3. Preparation of GO/CNTs/cement composite

First, GO suspension (100 ml) was exfoliated by ultrasonic (420 W) for 30 min. The concentration of MWCNTs adding in cement paste was varied from 0 to 0.08 wt % by weight of cement. And the ratio of GO to CNTs was set as 0.5. Further, corresponding quality of CNTs was added into the GO suspension to disperse by ultrasonic (300 W) for another 30 min. And the ultrasonic was operated at a lower energy in order to prevent overheating of the hybrid suspensions, which might damage the structure of CNTs [22]. Based on the water to cement ratio (w/c) of 0.4, extra water and the GO/CNTs suspension were added to the cement powder for mixing. The mixing process and casting procedures of all the cement mixtures were similar. For compressive strength tests, the cement mixtures with or without poly-carboxylate superplasticizer (0.5 wt% of cement) were poured into the 20 mm × 20 mm × 20 mm steel molds. Specimens with a size of 25 mm × 25 mm × 140 mm were prepared for flexural strength tests. All the specimens were cured at a temperature of 20 °C and humidity of 98%. After demolding (24 h later), the specimens were stored in water at laboratory temperature for different curing ages.

2.4. Measurement

2.4.1. Tests of dispersion of hybrid GO/CNTs

UV–Vis absorption spectroscopy (Agilent Cary 60) was used to measure the stability of GO, CNTs and GO/CNTs in water at a scanning speed of 60 nm/min. The zeta (ζ) potentials of GO aqueous dispersions with CNTs or without were measured by the use of a zeta sizer nano-system (Malvern Instruments). XRD and Raman spectra was used to characterize the hybrid GO/CNTs. For the morphology observations of GO/CNTs, the dispersion of CNTs and GO/CNTs was measured by stereo microscopy and SEM (Carl Zeiss, Germany).

2.4.2. Mechanical property and micro-structure tests

The compressive and flexural strength tests of the specimens at different curing ages were carried out using a universal testing machine. Compressive and flexural strength of the specimens were performed at a constant strain rate of 2 mm/min and 0.1 mm/min, respectively. To measure the effects of GO/CNTs on the microstructure of cement paste, SEM and MIP were used.

3. Results and discussion

3.1. Characterization of graphene oxide (GO)

The XRD pattern (Fig. 1a) of GO and graphite gave reflection peak at $2\theta = 10.3°$ and $2\theta = 26.5°$, corresponding to interlayer spacing of 0.86 nm and 0.34 nm, respectively. The inter layer spacing