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Graphene oxide-deposited carbon fiber/cement composites for electromagnetic interference shielding application

Juan Chen, Dan Zhao, Heyi Ge *, Jian Wang

Shandong Provincial Key Laboratory of Preparation and Measurement of Building Materials, University of Jinan, Jinan 250022, PR China
School of Material Science and Engineering, University of Jinan, Jinan 250022, PR China

HIGHLIGHTS

- Graphene oxide-deposited carbon fiber (GO-CF) was obtained.
- The GO-CF showed good dispersion in water and cement matrix.
- GO-CF was found to be more effective than CF in providing EMI shielding of cement.
- SE of GO-CF/cement had a 31% increase than that of CF/cement in the mass of 0.4 wt.%.

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ABSTRACT

Graphene oxide-deposited carbon fiber (GO-CF) was obtained by introducing GO onto CF surface through electrophoretic deposition method. GO-CF was found to be more effective than CF in providing electromagnetic interference shielding of cement-based composites. With 0.4 wt.% GO-CF and a shield thickness of 5 mm, a shielding effectiveness of 34 dB was attained at X-band region (8.2–12.4 GHz), which had a 31% increase than that of CF/cement (26 dB) in the same mass fraction. The GO-CF is believed a promising filler of cement-based composites for high electromagnetic interference shielding.

1. Introduction

With the rapid development of the electronics industry, the dominant frequency range of communication devices has shifted toward a higher range in order to enhance the data transfer rates [1]. As a result, the demand for the microwave absorbers and electromagnetic shields in this frequency range is greatly increasing, to solve the electromagnetic interference (EMI) problems, especially in the X band (8.2–12.4 GHz).

Cement material which has rich resource and good environmental adaptability is attractive for the development of composites for EMI shielding [2–4]. However, cement is slightly conducting, so the use of a cement matrix needs to fill conductive fillers, such as carbon fiber (CF), carbon nanotube, carbon black, in composites to be electrically connected [5,6]. CF has aroused tremendous attention due to its excellent properties, such as high conductivity, large aspect ratio and high thermal stability [7–10]. Ji Sun Im a used electrospinning and heat treatment methods to prepared CF and added additives (Fe_2O_3/$BaTiO_3$/multi-walled carbon nanotubes) to increase the electromagnetic shielding effectiveness (SE), which observed an average of 37 dB over a frequency range of 800 MHz–4 GHz [7]. Chung attained a SE of 40 dB at 1 GHz in a cement-based composite containing 1.5 vol.% discontinuous 0.1 mm diameter CF [8]. Zhen-jun Wang investigated the electromagnetic SE of CF cement-based composites after freezing–thawing cycles [9]. Although CF has received much attention as it imparts cements with high electrical and EMI shielding properties, its further application is hampered due to the poor interfacial properties between CF and matrix as well as the poor dispersion in matrix. Normally CF volume fraction is typically less than 1% in a cement-based composite because of its poor dispersion. The cement paste with CF at 0.54 vol.% gave an effectiveness of 26 dB at 1.5 GHz [8], whereas the mortar with CF (isotropic pitch based, 3 mm long) at 0.84 vol.% gave an effectiveness of 15 dB at 1.5 GHz [10].

* Corresponding author at: Shandong Provincial Key Laboratory of Preparation and Measurement of Building Materials, University of Jinan, Jinan 250022, PR China. Tel.: +86 53182767151.
E-mail address: geheyi@sina.com (H. Ge).

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Graphene oxide (GO) sheets have attracted enormous attention in recent years due to their remarkable properties and large specific surface area [11–14]. GO sheets bear various oxygen-containing groups, mainly epoxides and hydroxyls on their basal planes and carboxyls on the edges, which can facilitate the dispersion of GO in water [15,16]. Therefore GO has been accepted as a well agent to improve the interfacial properties between fiber and matrix [17]. Furthermore, the defects and groups in GO will arise relaxation processes [1,18–20], which is favorable in enhancing microwave absorbing ability.

In this work, GO was introduced onto CF surface through the electrophoretic deposition method to improve CF hydrophilicity, thus to achieve the purpose of good CF dispersibility in cement matrix, excellent interfacial properties between CF and cement as well as higher EMI SE. The EMI SE of GO-CF/cement composite in the X-band frequency region (8.2–12.4 GHz) has been investigated for the first time.

2. Experimental

2.1. Materials

Portland cement 42.5 was used. The sand met ISO standard. T700SC CF (12 K, 0.8 g/m), with an average diameter of 7–8 μm, was supplied by Toray Company, Japan. Graphite powder (8000 meshes, 99.95%) and methyl cellulose were purchased from Aladdin Industrial Corporation. Concentrated sulfuric acid (H_2SO_4), sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), and ammonium hydrogen carbonate (NH_4HCO_3) were of analytical grade and purchased from Sinopharm Chemical Reagent (Shanghai, China).

2.2. Preparation of GO

The GO was synthesized by chemical exfoliation of flake graphite through a modified Hummers' method [21,22]. Briefly, 3 g graphite powder, 1.5 g $NaNO_3$ and 75 mL H_2SO_4 were sequentially added to a three-necked round-bottomed flask placed in an ice bath under stirring. 9 g $KMnO_4$ was slowly added to the flask. Once it was thoroughly mixed, the ice bath was removed and the solution was stirred at 35 °C for 2 h. Then 150 mL of deionized water was slowly added to the solution, the temperature raised to 98 °C and 500 ml deionized water and 15 mL H_2O_2 slowly were added to the solution in turn. The mixture was filtered and washed with 10 wt.% HCl aqueous solution. Finally, it was purified by dialysis for one week to remove the remaining metal species and acid. Exfoliation of GO was realized in an aqueous solvent by sonication for 1 h, and the non-exfoliated GO was removed by centrifuge (4000 rpm, 10 min), which were the optimized conditions for this experiment. A well dispersed GO colloid solution was obtained and used to immobilize onto CF surface in the subsequent process.

2.3. Introduction of GO on CF

The electrophoretic deposition method was used to introduce GO sheets on CF surface [23]. To exclude the possible effects of commercial sizing and to enhance the interfacial adhesion of GO/CF, the electrochemical corrosion method was firstly used to remove the commercial sizing before the introduction of GO on CF [24].

The electrolytic treatment system of a potentiostat/galvanostat analyzer was established with CF used as the working electrode (positive), and a graphite cathode served as the counter electrode. During electrochemical corrosion, NH_4HCO_3 was used as the electrolyte solution. The direct voltage was 3 V. CF was treated for 5 min. Then CF was washed by distilled water twice and then used 1.5 mg/ml GO instead of NH_4HCO_3 as the electrolyte solution (as shown in Fig. 1). The direct voltage changed to 15 V. CF was treated for 40 min. After electrophoretic deposition, the GO-deposited CF (GO-CF) was washed with distilled water and then immersed in distilled water for 30 min to remove the residual GO absorbed on the GO-CF.

2.4. Mixing procedure and sample preparation

The mortar mixtures were prepared in a mortar mixer. The CF and the GO-CF were cut to 3–5 mm before added to the mortar. They were used in the amount of 0.1%, 0.2%, 0.3%, 0.4% by mass of cement, respectively. Methyl cellulose was used as primary dispersant in the amount of 1% by weight of water. Water/cement (w/c) mass ratio was 0.48. Sand/cement (s/c) mass ratio was 1.0. Firstly the methyl cellulose was added in water and stirred. Then the CF or the GO-CF was added to form a uniform mixture. Finally the cement was mixed with this mixture (as shown in Fig. 2) and then cast in silicone molds. After 24 h, the specimens were removed from the molds and transferred to a moist-curing room for 7 days before EMI SE testing. The specimen size for EMI SE measurement was 22.6 mm × 10 mm × 5 mm and for the flexural strength/the compressive strength tests was 40 mm × 40 mm× 160 mm.

2.5. Characterization of specimens

The morphology of GO was performed on an atomic force microscope (AFM) system (Veeco NsIV, USA). The GO sheets were dispersed in water and dip-coated onto freshly cleaved mica surface before testing. Scanning electron microscopy (FEI QUANTA FEG 250 fieldemission SEM system) was used to investigate the surface morphology of GO-CF. Fourier transform infrared (FTIR) measurement was performed on a Nicolet 380 infrared spectrometer (Thermo electron corporation, United States). The specimens were prepared by potassium bromide pellet technique.

EMI SE was obtained according to the waveguide method using a network analyzer (Agilent, N5234A) equipped with an amplifier and a scattering parameter (S-parameter) test set over a frequency range of 8.2 GHz–12.4 GHz.

3. Results and discussion

3.1. The morphology and structure of GO sheets

The GO sheets were dispersed in water for ultra-sonication and centrifuged to obtain a stable suspension (as shown in the photo of colloid suspension of GO (1 mg mL^{-1}), Fig. 3(a)). GO sheets in water hydrolyze to form negatively-charged thin platelets that consist of single to multi-layer carbon [25]. The AFM image of the lamellae of GO is displayed in Fig. 3(b). The results indicate that single irregular layer of GO can be observed with a thickness about 1 nm. It suggests that the GO nanosheets suspension solution was obtained. As shown in Fig. 3(c), SEM image shows that the GO sheets appear typically flat yet wrinkled.

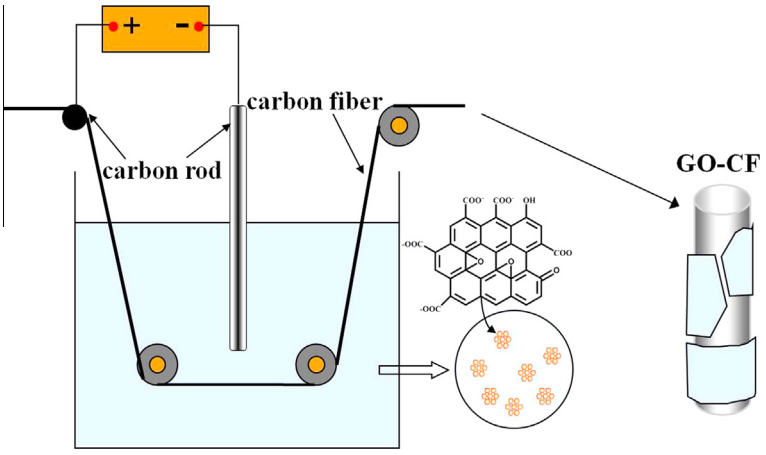

Fig. 1. Schematic of electrophoretic deposition.