Construction and Building Materials 149 (2017) 378–385

Contents lists available at ScienceDirect

Construction and Building Materials

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

Enhanced properties of cement mortars with multilayer graphene nanoparticles

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HIGHLIGHTS

- Incorporating MLG into OPC mortars substantially increase their strength.
- Thermal stresses are reduced and hydration reactions increase within the composite matrix.
- Dispersing MLG with isopropanol prevents the flakes from agglomerating very efficiently.
- The addition of MLG has relatively low costs and may be extended to a large scale.

ARTICLE INFO

Article history:
Received 24 February 2017
Received in revised form 15 May 2017
Accepted 17 May 2017

Keywords:
Multilayer graphene
Cement mortars
Mechanical properties
Hydration heat

ABSTRACT

The present work aims to combine multilayer graphene (MLG) nanoparticles with Ordinary Portland Cement (OPC) mortar specimens, evaluating possible improvements on their mechanical properties and ultimately coming up with an ideal and effective concentration for future applications. Mortars with water/cement ratio of 0.4, MLG dosage varying from 0.015 to 0.033% by weight of cement and sand at a proportion of 3× the weight of cement were prepared. 50 × 100 mm cylindrical specimens were shaped and subjected to compressive and splitting tensile strength tests at the ages of 3, 7 and 28 days. In addition, SEM micrographs and metallographic images were collected and analyzed in order to better characterize the sample's morphology and also in attempt of explaining the MLG influence on cement paste. The optimal tensile strength was achieved with samples designed with MLG dosage of 0.033%, for which the corresponding increases were 100.0, 144.4 and 131.6%, after 3, 7 and 28 days, respectively, compared with samples without MLG. On the other hand, the optimal compressive strength increases were obtained with samples designed with MLG dosage of 0.021%, with improvements of 63.6, 94.1 and 95.7% after 3, 7 and 28 days, respectively, compared with samples without MLG. The addition of MLG is believed to accelerate cement hydration reactions, reduce the pore volume and harden cement properties. An improvement in thermal conductivity is also associated to MLG incorporation, and this favorable heat transfer in OPC-based mortars probably promoted the observed changes in the composite chemical structure and mechanical properties herein analyzed.

1. Introduction

Developments in nanotechnology over the last years have begun to demonstrate the potential applications of nanoscale fillers in composites material [1,2]. These developments have been driven by the prospects of using those nanoscale fillers for modifying the properties of well-known materials [1], for exploring their fundamental influence at microscopic and macroscopic levels [3,4], and for the development of new materials [5,6]. Indeed, nanoscale fillers are now being incorporated to different materials and composites to specific applications [7–9]. Additionally, those recent developments have also stimulated new ideas for processing techniques in order to improve the properties of many conventional materials significantly.

Over the last decades, many studies have been focusing on enhancing the properties of Ordinary Portland Cement (OPC), the

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http://dx.doi.org/10.1016/j.conbuildmat.2017.05.146
0950-0618/

main ingredient of concrete and mortar, by combining their ceramic matrix with different nanomaterials. In those nanocomposites, nano-sized particles and fibers, such as nanosilica [10], nanotitanium oxide [11], nanoalumina [12,13] and carbon nanotubes [14], could be used for engineering reinforcements and for enhancing a wide range of OPC-based materials properties [11–16]. Because of the unique mechanical, electrical, optical and catalytic properties of nanoparticles, the interaction between the nanoscale filler and the ceramic matrix material could offer the possibility of modifying cement chemical and physical properties, creating new mechanisms of interaction [17] that could be useful agents on self-cleaning processes [11] and procedures associated with abrasion resistance [15,16]. It has been anticipated that the application of nanocomposites within the civil construction industry could decrease the impacts of industrial activities over the environment, since structures with higher durability could be designed using less raw materials [18]. In addition, nanomaterials could be used to reduce and prevent the toxicity of nanoparticles in the environment more efficiently [19].

Carbon-based nanoparticles constitute elements of one important class of materials that is applied to cement and mortar based composites to enhance their tensile and flexural strength, or expand their thermal [20] and electrical [21] characteristics. In particular, reinforcing nanomaterials such as carbon nanofibers (CNF) and carbon nanotubes (CNT), have been shown to improve mechanical strength and stiffness of cementitious nanocomposites [22], although, some contradictory results have been reported [23,24]. One challenge of studying these nanocomposites is the difficulty in dispersing CNT's and CNF in the OPC matrix. CNT's and CNF tends to form agglomerates and adhere together, probably due to strong Van der Waals force, making difficult to archive a desired level of dispersion [25].

As CNTs and CNF, graphene-oxide (GO) sheets have been extensively used to improve the properties of mortar nanocomposites [24,26–28]. In this 2-dimensional material, the oxygen-containing functional groups attached to the GO sheets improves its dispersion in water [29–31], and in the cement matrix [24,26–28,32] affecting the mortar hydration and mechanical properties [33]. However, the process of oxidation and exfoliation might affect GO mechanical properties negatively, lowering the elastic modulus and tensile strength [34].

In addition to GO, a few studies have focused on graphene-based mortar composites [35–38]. Graphene exhibits many extraordinary properties including a high tensile strength and elastic modulus [39,40], high surface area, and also the fact that their edges can be functionalized to enhance its dispersion in composites [36,37]. Therefore, studies evaluating how multilayer graphene influences the parameters of cementitious composites are of great value and can certainly stimulate future research lines within civil construction technologies. Here, we report investigations on OPC-based mortar nanocomposites reinforced with multilayer graphene nanoparticles. We investigated the morphological properties of MLG and cement mortar specimens using SEM and metallographic microscopy. Their chemical structure were evaluated by using FTIR and Raman techniques, and their mechanical properties by undertaking compressive and splitting tensile strength tests.

2. Experimental

2.1. Materials and synthesis

Ordinary Portland Cement (OPC), type CP-II Z-32, which incorporates pozzolanic additions varying from 6 to 14% by weight of cement, and sieved sand with mass density of 3.57 g/cm^3 and fineness modulus equivalent to 2.4 were used to prepare the mortar specimens. Table 1 presents the characteristic properties of the OPC used in this work along with its chemical composition.

Fig. 1(a) shows a typical high oriented natural crystalline graphite flake used to synthetize multilayer graphene sheets (MLG) powder. Large natural graphite flakes, provided by Nacional de Grafite Ltda. (Brazil), were submitted to an acid bath: sulfuric and nitric acids, followed by rapid heat treatment at high temperature for some seconds, in order to obtain an expanded graphite structure (EGS) [41,42]. To exfoliate the graphite structure, analytical grade isopropanol alcohol was blended with the EGS in a 1-to-1 ratio (ml-to-mg) and the solution was further ultra-sonicated for 2 h. The combination of MLG and isopropanol yielded excellent dispersion conditions to prevent MLG from agglomerating and was directly poured into the dry sand. Fig. 1(b) displays a SEM image of a typical flake present in the MLG powder used to prepare the OPC nanocomposites reported in this work.

Scanning electron microscopy was conducted to characterize the morphology of the samples. In order to improve the imaging, the samples were covered by a thin gold film. All images were obtained in the secondary electron mode, using an electron beam of 5–10 kV and 0.4–2.1 nA. Metallographic characterizations were also made with the aid of a microscope from Inova Optical Systems. Atomic force microscope Shimadzu SPM9700 was used in dynamic mode to get the morphology of an isolated MLG flake representative of our samples.

To obtain the Raman spectra, we employed a Renishaw confocal microscope operating at room temperature. The spectrums were obtained in backscattering configuration using a 532 nm laser source operating at constant power of 5 mW. The Infrared spectra were obtained using an Agilent Care 640 FTIR Spectrometer, in the diffuse reflection mode. The spectral range measured was 4000–350 cm^{-1}. All samples were prepared with the same dimensions: 1 mm thick disk with 10 mm of diameter, cut directly from cement mortar specimens.

2.2. Sample preparation

Five different mortar recipes were prepared using a pan type mortar mixer. The water-to-cement ratio was kept at 0.4 and the quantity of sand at a proportion of 3× the weight of cement. The MLG powder content varied from 0% to 0.033% by weight of cement. In order to guarantee MLG dispersion through the composite we first poured the solution of MLG and isopropanol into the dry sand, and this resulting combination underwent mixing for approximately 10 min. The portion of sand was put to rest at room temperature, in a way that the isopropanol fully evaporated after 48 h. Only then cement and water were added to produce mortar.

It is important to notice that no additives, such as superplasticizer, water-reducing agents or surfactants, were employed for workability. Mix proportions of mortars with and without MLG are given in Table 2. All mixes were cast into cylindrical molds (50 mm diameter and 100 mm length), and maintained at 23 ± 2 °C and a relative humidity of 50 ± 15% for 24 h, then demolded and submerged into a tank of water for curing. 12 h before the intended mechanical investigations all samples were removed from the water tank and left to stand at room temperature. Compressive and splitting tensile strength were investigated at the ages of 3, 7 and 28 days. In order to verify the reproducibility of the results, we prepared at least two samples for each evaluation.

2.3. Mechanical property tests

Compressive and splitting tensile strength tests were performed using a HD200T Digital Servo-Hydraulic Press (2000 kN maximum load). The compressive strength tests were determined following the protocols described by the Brazilian Regulatory Agency in ABNT/NBR-7215:1996 "Portland Cement – Determination of compressive strength", using a loading rate of 0.25 ± 0.05 MPa/s; and the splitting tensile strength was measured following the procedures described by ABNT/NBR-7222:2011 "Concrete and mortar – Determination of the tensile strength by diametrical compression of cylindrical test specimens" with a loading rate of 0.05 ± 0.02 MPa/s.

3. Results and discussion

3.1. Morphology

3.1.1. MLG

AFM analyses (Fig. 2a-b) of the representative flake depicted in Fig. 1(b) shows an average thickness around 10 nm (Fig. 2b) and an average lateral size around 4 μm, in agreement with values observed in previous works [43,44] involving the exfoliation of natural crystalline graphite flakes to further obtain multilayer graphene flakes with thickness varying between 0.7 and 20 nm. It is important to observe that the MLG flakes display a low surface roughness and sharp corners. These characteristics suggest that the synthetized MLG flakes are composed of graphene layers with defects/irregularities at the borders. This was in fact observed through Raman analyses and is discussed in Section 3.2.