Construction and Building Materials 138 (2017) 333–339

Contents lists available at ScienceDirect

Construction and Building Materials

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

Mechanical performance, pore structure and micro-structural characteristics of graphene oxide nano platelets reinforced cement

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HIGHLIGHTS

- GONPs significantly enhanced the mechanical strength of OPC pastes.
- An enhancement in tensile strength by 41% was achieved at 0.03 wt% GONPs.
- GONPs considerably modified the pore structure of the cement pastes.

ARTICLE INFO

Article history:
Received 2 November 2016
Received in revised form 5 January 2017
Accepted 7 February 2017

Keywords:
Graphene oxidenanoplatelets
Cement paste
Mechanical strength
Pore structure
Thermal analysis
Microstructure

ABSTRACT

Graphene oxide nanoplatelets (GONPs) have unique physical properties that make them effective reinforcing materials. The attractive properties of graphene oxide have led to enhance the graphene-polymer nanocomposites. However, limited studies have been performed on using graphene oxide in cementitious nano composites. This article investigates the effect of GONPs reinforcement on mechanical properties, pore size distribution and the micro-structural characteristics of the hardened cement composites. GONPs were added at different percentages of 0, 0.01, 0.02, 0.03, 0.04 and 0.05 wt% of cement. Compressive and indirect tensile strengths were determined at 28 days of hydration. Thermogravimetric analysis (TGA) and X-ray diffraction (XRD) were used for studying the phase composition, the pore size distribution was studied using nitrogen adsorption at 77.35K technique and the microstructure was examined using scanning electron microscopy (SEM). Results revealed that, considerable enhancements in both compressive and indirect tensile strengths by about 13 and 41% have been achieved by incorporating GONPs into cement matrix by about 0.02 and 0.03%, respectively. The integration of GONPs into cement has significantly reduced the pore size of the GONPs-modified cement pastes and led to a considerable improvement in the microstructure, with a consequent improvement in the mechanical properties of these composites.

1. Introduction

Cementitious materials are the most widely utilized for many decades for different sorts of structures [1]. Although; cement based materials are used over a wide range of a structural applications, they are brittle and possess poor tensile strength. The brittleness of cement structures comes from the inferior characteristics of the cement pastes in the hardened state [2]. Enhancing the strength of cement materials generally can be achieved by using reinforcing microfibers, such as steel fibers [3], carbon fibers [4] polymeric fibers [5,6] and natural fibers [7]. These reinforcing materials can greatly improve the strength characteristics as a whole and increase the stress at which cement starts to crack, i.e. they delay the crack growth in the cementitious matrix however do not inhibit the crack formation [8].

Nowadays, nanotechnology (NT) has provided nano-scale particles/fibers; including, nano silica (NS), carbon nano tubes (CNTs) and nano graphene oxide (NGO); these might be utilized as reinforcements to inhibit the formation and delay the propagation of micro cracks. The use of nano fibers for improving the mechanical performance of cementitious materials are found to be more efficient than ordinary steel fibers (at millimeter scale) as they help in restricting cracks before they develop into micro cracks. NS [9–14] and nano metakaoline were found to enhance the mechanical performance of cement-based materials [15–20].

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http://dx.doi.org/10.1016/j.conbuildmat.2017.02.021
0950-0618/

Nowadays, great attention was paid to the graphene oxide nanoplatelets (GONPs) being the most beneficial nano reinforcing materials. It is an oxide-functionalized graphene and belongs to the hydrophilic materials, evidently, GO was utilized as a surfactant for many organic ingredients in water [21]. GO is characterized by high degree of dispersion in water and various solvents, due to the presence of oxygenated function groups. This favors its use as a nano reinforcement in different matrices like polymer, ceramic or cement for improving their mechanical performance [22].

The characteristics of GO composites were studied by some researchers; the introduction of GONPs by 0.05 wt% of cement has increased the compressive strength considerably by 15–33%; in addition, an enhancement of about 41–59% has been achieved in the flexural strength [2], the incorporation of GONPs by 0.03 wt% of cement can enhance the compressive strength of GO-cement composite and tensile strength by more than 40%; also the total porosity (TP) of cement paste decreased [23]. When GO was added to plain cement and cement mortar at different percentages 0.01, 0.02, 0.03, 0.04 and 0.05 wt% of cement, significant improvements in the flexural and compressive strengths of the hardened cement pastes by about 90.5 and 40.4% have been attained at 28 days of hydration, respectively. The flexural and compressive strengths of cement mortar modified with GO at ratios of 0.01, 0.03 and 0.06% increased by 70.5 and 24.4 wt% after 28 days of hydration, respectively [24]. Incorporating the reduced graphene oxide (RGO) into geopolymers at concentrations of 0.00, 0.10, 0.35 and 0.50% by weight has improved the microstructure and resulted in pore free condensed composites with enhanced mechanical performance, previous work reported an enhancement in flexural strength and Young's modulus by 134 and 376%, respectively [25].

It was found from the literature survey that, there are many conflicts regarding the development of GONPs reinforced cement especially in the GO incorporation ratios and the percentages of enhancements achieved. The main issue to be addressed in this work is to add an extended study to investigate the role of GO in enhancing the properties of hydrated cement by using different analytical techniques.

2. Experimental program

2.1. Preparation and characterization of GONPS

GONPs were synthesized according to the modified Hummer's technique [26]. Typically, add 1 g of graphite + 0.5 g of $NaNO_3$ in a flask, then add 50 ml of H_2SO_4 (98%) under constant stirring at 5 °C for 1 h, after that, add gradually 3 g of $KMnO_4$ (1 g every 15 min.) taking into consideration that, the temperature of the solution have to be less 20 °C to avoid overheating and explosion. Dilute the solution by slowly adding100 ml warm distilled water, and then treat the solution with 3 ml of 30% H_2O_2 solution and 100 ml of distilled water to be sure that, $KMnO_4$ is completely reacted. After that, wash the mixture with HCl and water, respectively, finally filtrate and dry to get the final product (GO).

The obtained material was examined by HRTEM to confirm the formation of GONPs and to investigate their morphology. The HRTEM images presented in Fig. 1(A, B) displayed the formation of transparent particles consisting of ultrathin layers with thickness less than 100 nm. The prepared GONPs surface appears as a wrinkled paper that may be due to the strong acid treatment and the high aspect ratio. Yang et al. (2011) explained the wrinkle appearance of GO sheets; that was caused by high aspect ratio (i.e) the GO sheet has several hundred nanometers of length compared to just several nanometers of thickness [27]. As seen also, GONPs appeared in the form of stacked / non-exfoliated thin sheets [28].

Fig. 2 shows the Raman shifts for graphite and GO. There are two main Raman shifts characterizing carbon nano materials ranged from 1200 to 1700 cm^{-1}. In this context, the first band at 1604 cm^{-1} can be attributed to the graphite mode (G band). While, the second band at 1363 cm^{-1} attributed to diamondoid mode (D band) [29]. An increase in the intensity of D band in GONPs spectrum over than that of a graphite which is observed at 1350 cm^{-1} may be due to the amorphization of graphite lattice that is arising from the transformation of some in-plane

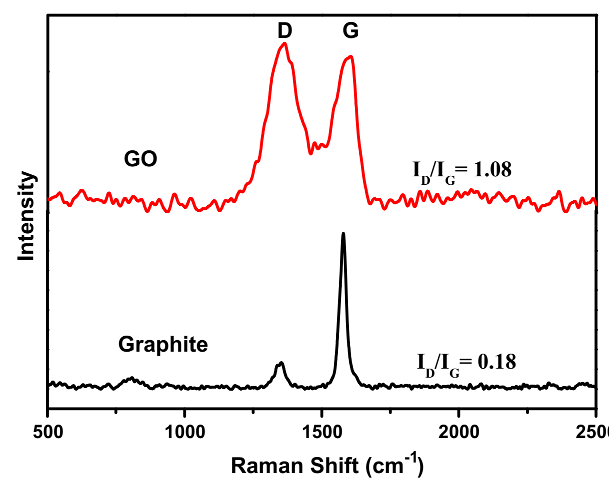

Fig. 2. Raman spectroscopy of graphite and GO.

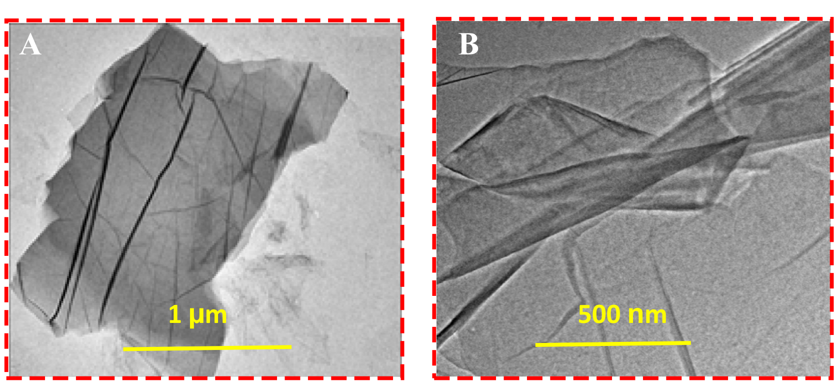

Fig. 1. TEM of GO.