Construction and Building Materials 177 (2018) 10–22

Contents lists available at ScienceDirect

Construction and Building Materials

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

Graphene oxide prepared from mechanically milled graphite: Effect on strength of novel fly-ash based cementitious matrix

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HIGHLIGHTS

- Effect of graphene oxide (GO) synthesized from milled graphite (MGP) on fly-ash based cement matrix was investigated.
- Mechanical strength and microstructure improved with addition of GO.
- Regulation of crystallization behavior of cement compounds with addition of GO.
- Pozzolanic activity of FA was hindered using high concentration of GO.

ARTICLE INFO

Article history:
Received 10 December 2017
Received in revised form 19 April 2018
Accepted 6 May 2018

Keywords:
Milled graphite
Graphene oxide
Fly ash based cementitious matrix
Microstructure
Crystalline phase composition

ABSTRACT

Graphene oxide (GO) has been synthesized from mechanically milled graphite (MGP) and characterized using SEM/EDS, TEM, XRD, Raman, FTIR, AFM and TGA/DTA/DTG techniques. Effects of GO on compressive and tensile strength, microstructure and crystalline phase composition of fly-ash based cementitious nanocomposites (FCNCs) have been addressed. Compressive and tensile strengths were improved by a maximum of 35% and 96% respectively for 0.125% GO incorporated. Addition of GO refined the microstructure of hardened nanocomposites by controlling the orientation of hydration crystals. Chemical composition of inorganic crystalline phases of hydration products was accelerated due to increased hydration on the active sites of GO.

1. Introduction

Cement is a widely used material for construction purposes at global level. It is a binder which glues the other ingredients in cement mortar and concrete and provides the integrity to the final structure. But the inherent quasi-brittle behavior of cement-based matrices leads to poor resistance to crack development [1]. This also creates a reduction in strength properties of these materials and ultimate failure to external loads. Additionally, the production of Ordinary Portland cement (OPC) releases huge amounts of greenhouse gases such as carbon dioxide into the environment. It has been estimated that nearly 5% of total global emissions result from cement production during the sintering process of clinkers at high temperatures [2,3]. Hence, the sustainable development of cement based materials with sufficient longevity requires the utilization of some alternate constituents.

Fly ash (FA) is an industrial waste material and has been extensively as replacement to cement in concrete structures [4–6]. It does not possess any binder properties of its own but contributes to the strength of concrete by taking part in chemical pozzolanic reaction in which FA particles react with calcium hydroxide (C-H) crystals produced during hydration of cement. The resulting product is calcium-silicate-hydrate (C-S-H) gel which imparts further strength to concrete [7]. Utilization of FA as replacement to cement provides other benefits such as improved workability, improved resistance to sulphate attack and abrasive environments [8–10]. But the major disadvantage of incorporation of FA is slow strength development at early ages due to which its use is avoided in practical cases where early age strength is desirable [11]. Previous researchers have tried to overcome this drawback by different approaches which mainly include chemical and mechanical treatments of FA particles [12–15], which makes the overall process costly.

The emergence of nanomaterials possessing different dimensionalities (0-D nanoparticles, 1-D nanotubes/nanofibers and 2-D nanosheets) and exceptional properties has created strong interest

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https://doi.org/10.1016/j.conbuildmat.2018.05.051
0950-0618/

among researchers to explore their effects on number of matrix materials including cement-based matrices. Use of nanoparticles such as nano-SiO_2, nano-TiO_2 and nano-ZnO has already been studied in past investigations and significant improvements in properties of both FA based cementitious matrices and OPC based matrices have been observed [16–18]. Effects of 1-D nanotubes have also been explored in detail [19–21], followed by recent studies on influence of normal graphene oxide (GO) on a range of properties of cementitious matrices [22–25].

Although many investigations have been conducted on the influence of GO on properties of cement-based materials, negligible studies have been performed to investigate the effect of GO on the strength behavior and microstructure of FA based cementitious matrix. Our previous studies have focused primarily on incorporation of either pristine GO (synthesized from commercial graphite) or ball-milled GO (derived by milling of pristine GO) in 100% OPC based matrix [26,27]. But none reports the results of GO synthesized from mechanically milled graphite in FA based cementitious matrix. Hence, in this paper, commercially available graphite powder (GP) has first been exfoliated and size-reduced using simple approach of mechanical milling to produce finer mechanically milled graphite (MGP). The graphite so produced has further been used as the precursor to synthesize nano-sized GO. As-produced GO has been investigated for its influence on mechanical, microstructural and crystallization behavior of FA based cementitious nanocomposites (FCNCs). This research is aimed to establish sustainable and economical cementitious matrices.

2. Experimental

2.1. Materials and Chemicals

Ordinary Portland cement (OPC) CEM I 42.5 complying IS 8112 (IS 8112, 1989) was procured from Ultratech Cement Company in Jalandhar district (Punjab). Class F Fly ash (FA) was used at a dosage of 30% as partial replacement to OPC in all the mixes. FA was procured from thermal power plant located at Ropar district (Punjab). Local sand available in market was used in all the mixes. A polycarboxylate ether based superplasticizer (Glenium 51) purchased from BASF India Ltd. was used in the mortar mixes containing GO as nanoadditive in order to improve the dispersion of the material within the matrix.

Commercially available Graphite powder (GP) was purchased from Loba Chemicals Pvt. Ltd. Other analytical reagents (AR) grades used were concentrated sulphuric acid (H_2SO_4, 98%), potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$) and hydrogen peroxide (H_2O_2, 30%) which were bought from Merck Specialty Pvt. Ltd., India.

2.2. Mechanical-Milling of graphite (GP)

High energy mechanical ball-milling of GP was carried out for continuous 3 days in Planetary Ball Mill. About 70 g of GP was put altogether into the planetary jar containing zirconium oxide balls (dimensions of 1.6 mm × 1.8 mm). An approximate ratio by weight of GP to Zirconium balls was 1:2.8. The mechanically milled product was collected and designated as milled graphite powder (MGP). The milling process was done to obtain exfoliated graphitic sheets with possible defects on the surfaces. This provides better chances of functionalization of graphite surface when treated using oxidizing agents [28].

2.3. Synthesis of graphene oxide (GO) from mechanically milled graphite (MGP)

The commonly used Hummer's method [29] was followed to obtain the surface functionalized graphene oxide (GO) from the milled graphite. The finally obtained suspension of graphene oxide prior to filtration was yellowish brown in appearance and has been shown as pictorial image in Fig. 1.

2.4. Structural characterization of GP, MGP and GO

The different materials namely GP, MGP and GO were structurally characterized using various analytical techniques such as field-emission scanning electron microscopy (FE-SEM), energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM), X-ray diffraction (XRD), raman spectroscopy, fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM) and thermogravimetric analysis (TGA).

2.5. Mix proportions

The composition of different mortar mixes prepared in the study has been shown in Table 1. In general, total six mixes were prepared and tested. All the mortar mixes were cast at binder (30% FA + 70% OPC) to sand ratio of 1:3 by mass. The details of sand used in the study have been given in Table 2. The grain distribution of the sand was the same as used by authors in their previous research [21]. A constant water-binder ratio (w/b) of 0.45 was used in each mix. The first mix was the basic mortar mix containing 100% OPC as binder. Second mix was the reference mix containing 30% FA as partial replacement to OPC, and GO was not added in it. The mix was designated as 0-FCNC (where FCNC denotes fly ash based cementitious nanocomposite). Remaining four mixes were all FA based mixes and were prepared by simply varying the concentration of GO in the range of 0.125% to 1.00% (by weight of binder i.e. FA + OPC). Before the addition of GO in the binder-sand mixture, aqueous dispersions of GO were prepared in the presence of distilled water and optimum dose of superplasticizer using ultrasonic shock waves. The time period of ultrasonication was

Fig. 1. Pictorial Image of Suspension of GO Synthesized.