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Influence of 2D rGO nanosheets on the properties of OPC paste

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ABSTRACT

In this experimental study, the effects of 2D reduced graphene oxide (rGO) sheets on the properties of Portland cement paste in comparison to popularly reviewed nanomaterials like aluminium oxide nanopowder (n-Al_2O_3) and colloidal silicon dioxide nanoparticles (n-SiO_2) were investigated. The addition of 0.02% rGO sheets by weight of cement increased the 7 and 28 days flexural strength up to 70% and 23% respectively when compared to control paste. Moreover, its incorporation substantially decreased the sizes of pores/voids in the paste, even compared to the other nanomaterials, as characterized by Mercury Intrusion Porosimetry (MIP) and 3D X-ray Computed Tomography (CT) aided with image analysis technique. The assessment of Portlandite content by Thermo-gravimetric Analysis did not indicate major differences between the pastes, with the exception of the paste incorporating nano-silica. Microstructural analysis by Fourier Transform Infrared Spectroscopy, X-ray diffraction and Scanning Electron Microscopy did not reveal any major differences between the control paste and the pastes incorporating nanomaterials. The overall results suggest that the performance of rGO was better in comparison to other two nanomaterials, despite the significantly lower amounts that were used in the paste.

1. Introduction

The diffusion of deleterious ions through the pore network of cementitious materials can be arrested by incorporating nano-sized materials, which have a high surface area to volume ratio. Minor additions of nanomaterials such as carbon nanotubes, nano silica, nano alumina and graphene nanosheets, which are effectively dispersed in the cement matrix, are beneficial in enriching the mechanical and durability properties [1]. The nanomaterials are suggested to be super-sorbents that physically adsorb the free water to a large extent. Due to such effects, the nanomaterials are perceived to act as nucleation sites for the growth of hydration crystals at early ages, which ultimately results in reducing the fraction of unhydrated cement [2,3]. Further, the issue of reduced workability that is caused because of the use of the high surface area nanomaterials can be overcome by the use of surfactants, which also help in reducing the agglomeration effect of nanomaterials due to van der Waals forces [4–7]. In addition to high surface area, the shape and structure of nanomaterials also play an important role in microstructural alterations of the cementitious compounds [8].

Graphene, a 2D planar sheet of single atom thickness having sp^2 bonded carbon atoms arranged in a honeycomb lattice pattern, gives excellent in-plane mechanical (modulus of elasticity 1100 GPa), thermal (conductivity 5300 W/mK), optical transparent, and electrical (conductivity 2000 S/cm) properties [9].

Lv et al. [10] have attributed the aforementioned behaviour of morphological changes to shape effects by the dispersion of graphene oxide (GO) into the cement mortar. It was reported that flower-like planar clusters at low GO dosage and polyhedral and lamellar form of hydration crystals were densely formed due to the effect of high GO dosage into OPC paste. The study claims that such flower clusters were easily produced in holes and cracks of the cementitious composites. By performing thermal analysis, Gong et al. [11] have reported that 0.03% GO by weight addition into cement paste increases the generation of Portlandite and non-evaporable water up to 6% and 9% respectively. Further, they also reported that the compressive, tensile and flexural strengths were increased up to 38%, 79% and 60% respectively compared to control

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specimens.

Bulk synthesis of graphene is difficult to achieve because of the significant van der Waals forces in these sheets of high surface area (2630 m^2/g) that cause irreversible agglomeration or even restacking to form graphite. Kuila et al. [12] have suggested that such an effect was overcome with the help of using Chemical Oxidation/Modified Hummers' method to synthesize graphene oxide. This method proves effective in synthesizing chemically converted graphene sheets which are able to form stable colloids through electrostatic stabilization. Without the use of surfactants, effective dispersion is achieved through hydrazine reduction of graphene oxide under controlled conditions [13]. The resultant material is termed as 'Reduced' Graphene Oxide (rGO).

In this study, the influence of reduced graphene oxide (rGO), dry aluminium oxide nanopowder (n-Al_2O_3) and colloidal silicon dioxide nanoparticles (n-SiO_2) on the properties of cement pastes such as workability, compressive and flexural strength, mass porosity and water sorptivity index were determined after curing for 7 and 28 days. Then the effect of nanomaterials on the pore refinement of OPC paste was investigated using Mercury Intrusion Porosimetry (MIP) and 3D X-ray Computed Tomography (CT) studies. Further, the alterations in microstructure of cement paste due to the addition of nanomaterials were characterized using Fourier Transform Infrared spectroscopy (FTIR), X-ray Diffraction technique (XRD), Thermo-gravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM) techniques.

The motivation behind choosing the popularly reviewed nanomaterials such as n-Al_2O_3 and n-SiO_2 for the comparative evaluation against the rGO cement composites was due to their effective dispersion into the cementitious matrix without the use of any surface modification agents [14,15].

2. Experimental

2.1. Materials

A top-down approach was followed to extract the rGO from natural graphite by redox reaction. Three steps such as pre-reduction, sulfonation and post-reduction were followed to synthesize rGO. Sodium borohydride was used for the pre-reduction of rGO at 80 °C for 1 h in order to remove the major amount of oxygen functionalities from graphene oxide. Then the water solubility (dispersion in water) was improved by adding sulfanilic acid in an ice bath for 2 h. In this stage, controllable structural defects were allowed to avoid alteration in the properties of graphene. In the post reduction process, hydrazine solution was mixed with as-synthesized graphene oxide and stirred at 100 °C for 24 h using rapid synthesizer. A majority of oxygenated groups are removed other than acid functionalities during such a reaction. Before its use, the synthesized graphene oxide of sheet sizes ranging from 5 nm to 1500 nm was kept under observation for 6 h to examine the stability of colloids [16,17]. The transformed colour of GO to rGO during its synthesis is shown in Fig. 1a. The TEM image of synthesized rGO as presented in Fig. 1b, indicating a wrinkled surface texture (image obtained from JEOL 3010 Transmission electron microscope). 53 grade ordinary Portland cement (OPC) conforming to IS 12269-1987 and polycarboxylic ether (PCE) based superplasticizer as dispersion agent were used in this study. Table 1 shows the chemical composition of the cement.

Dry aluminium oxide nanopowder (n-Al_2O_3) of mean size less than 50 nm and silicon dioxide nanoparticles of average size 12 nm dispersed in deionized water (n-SiO_2) having surface area of 40 m^2/g and 225 m^2/g respectively were obtained from Sigma-Aldrich. Energy dispersive X-ray analysis was performed on the nanomaterials, and the results are shown in Fig. 1c.

2.2. Sample preparation

Four different cement paste mixes with a water to cement (w/c) ratio of 0.32 and dispersion agent (PCE) of 0.05% by weight of cement were prepared. Table 2 specifies the type and amount of nanomaterials used in the different mixes.

For better dispersion, pre-mixing of the nanomaterials along with deionized water and PCE were carried out using a magnetic stirrer for 15 min, followed by ultrasonication in an ultrasonic bath for next 30 min Fig. 2 shows the well-dispersed rGO solution (black coloured liquid) used in this study.

For paste preparation, the ingredients were mixed in a high speed Hobart mixer for 12 min. After mixing, the mini slump test was conducted to determine the flowability; the remaining paste was used for casting specimens of size 25 × 25 × 25 mm and 20 × 20 × 160 mm for determining the compressive and flexural strength respectively. Consolidation was performed using a vibration table. The specimens were demolded after 24 h and then cured in saturated limewater solution at room temperature (25 ± 2 °C) for 7 and 28 days.

2.3. Testing methods

A mini slump cone as shown in Fig. 3a was used for conducting the mini slump test in order to determine the workability of cement paste. The procedure specified by Collins et al. [18] was followed in this study. To determine compressive and flexural strength, the specimens were tested at a loading rate of 143 N/sec and 50 N/sec respectively. Both tests were performed using Controls C9842 testing machine on different frames having the capacities of 250 kN and 15 kN respectively.

Water sorptivity test was performed on the specimens of size 25 × 25 × 12.5 mm (sliced from the 25 mm cubes) after 7 and 28 days. After curing, the specimens were stored in acetone for the next two days to arrest the hydration followed by air drying for two days. Further, the dried specimens were kept in a shallow tray of size not less than 150 × 75 mm with roller arrangement as shown in Fig. 3b. Then the tray was filled with limewater solution (5 g per 1 L of distilled water). The final water level was maintained slightly above the bottom edge of the specimen. The mass of the specimen was measured at specified intervals such as 0, 3, 5, 7, 9, 12, 16, 20 and 25 min. Before weighing, the adsorbed water at the specimen surface was removed with a moist cloth. Finally, the vacuum saturated mass of the specimens was measured.

The influence of rGO, n-Al_2O_3 and n-SiO_2 on the microstructure of cement paste cured for 28 days was characterized using XRD, FTIR, TGA and SEM. The paste samples were ground using mortar and pestle and sieved through 75 μm sieve for XRD, FTIR and TGA testing. Bruker XRD machine was used to determine the crystalline phases formed in the nanocomposites and the control paste. IR absorption spectra were collected using PerkinElmer FTIR instrument for all paste samples. Netzsch TGA testing machine was used for determining the amount of Portlandite in pastes cured for 28 days. For SEM investigation, the fractured surface of paste sample was tested using FEI Quanta 400 FEG-SEM device. To enhance its conductivity, a 3 nm thick Gold/Palladium layer was coated over the surface of the specimen.

The effect of nanomaterials on the pore structure of OPC paste was characterized using MIP and 3D X-ray CT. Firstly, the distribution of gel pores (<10 nm) and capillary pores (10 nm–10 μm) in a paste sample of size 7 × 7 × 7 mm was determined using Thermo Scientific Pascal 140/440 series MIP instrument. Secondly, the distribution of pores/voids (>100 μm) in a paste sample of size 10 × 10 × 10 mm was determined using tomographic images acquired through GE phoenix v|tome|x s 3D X-ray CT testing machine.