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Characterization of alkali activated geopolymer mortar doped with MWCNT

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HIGHLIGHTS

- Geopolymeric matrices containing different MWCNTs concentrations (0.0:0.4 by binder weight).
- Marked decrease in the drying shrinkage as well as water absorption especially at 0.1%.
- An increase in the compressive strength specially when using 0.1% MWCNT.
- Further increase in MWCNTs results in agglomeration in MWCNT.
- XRD and SEM of mortar nanocomposites confirmed an increase in amorphous geopolymer up to 0.1%.

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ABSTRACT

This paper aimed to investigate the effect of MWCNTs on properties of slag geopolymeric mortar. Geopolymeric matrices containing different MWCNTs additions (0.0, 0.1, 0.2, 0.3 and 0.4% by weight of the used binder) were synthesized. The materials were prepared at water/binder ratios in the range of 0.34–0.39% depending on the amount of MWCNT; using of 6% NaOH as alkaline activation, whereas the Gelenium Ace-30 superplasticizer was used in the ratio of 1.4–2.2% from the total dry weight. Curing was performed under temperature of 40 °C and 100% R.H. Results showed that the addition of MWCNTs enhanced the resulting amorphous geopolymer structure with a marked decrease in the drying shrinkage as well as water absorption specially by using 0.1% MWCNT; further increase in WCNTs addition resulted in the agglomeration of MWCNT within the matrix and, therefore, hinder the propagation of geopolymerization reaction and negatively affect the formed geopolymer structure. XRD, FTIR, and SEM of mortar nanocomposites with MWCNT concentrations of 0.1 and 0.4-wt.% confirmed an increase in amorphous geopolymer as well as CSH up to 0.1% where the individual MWCNTs spread throughout the geopolymer matrix with uniform density.

1. Introduction

Nano-particles have proven to be an effective reinforcement in a variety of cement composites [1–3]. When fine aggregate particles are dispersed in the cement paste, they generate large number of nucleation sites causing the paste more homogeneous and dense as for the distribution of the fine pores. In addition, the physical effect of the fine grains allows denser packing within the cement and reduces the wall effect in the transition zone between the paste and aggregate. This weaker zone is strengthened due to the higher bond developed between these two phases, thus improving the microstructure and mechanical strength properties and durability when compared to the blank paste.

Recently, CNT has shown a high potential to improve the properties of materials. Since discovery of CNT by Iijima in 1991 [4], it has been widely used for a variety of applications due to their excellent physical properties: high strength and Young's modulus of individual CNT is about 1.8 TPa [5]. CNT was exhibited great mechanical properties along with extremely high aspect ratios (length-to-diameter ratio) ranging from 30 to more than many thousands. They are expected to produce significantly stronger and tougher cement composites than traditional reinforcing materials (e.g. glass fibers or carbon fibers). However, the properties and dimensions of CNT strongly depend on the deposition parameters and the nature of the synthesis method, i.e., arc-discharge [6], laser ablation [7] or chemical vapor deposition (CVD) [8]. In view of a commercial application, the arc-discharge technique is the only one that can offer a path towards low-cost and large scale production [9,10]. In fact, CNT obtained with a complete graphitization

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process achieved by heat-treatment at high temperature [11], either in vacuum or inert environment, show outstanding mechanical properties [12].

Geopolymer-based composites are a novel class of low-embodied carbon binders formed by a combination of low-calcium fly ash (FA) and alkaline solution. The curing process of geopolymer known as polymerization where the alumino-silicate oxides react with the alkali polysilicates to form a 3-dimensional polymeric Si–O–Al amorphous microstructure [13,14]. Geopolymers are currently being considered as a replacement to ordinary Portland cement(OPC) and have received considerable attention for their cost efficiency, chemical stability, corrosion resistance, rapid strength gain rate, low shrinkage and freeze–thaw resistance [15,16]. Geopolymers the fracture energy of geopolymerization was about 40% of that of OPC [17]. A previous research investigated the mechanical properties of geopolymer reinforced with different macro-fibers such as steel, polypropylene (PP), polyvinyl chloride (PVC) and basalt fibers [18,19].

Chen et al. [20] provided a complete literature review of CNT-cement nanocomposites and focused on the effect of CNTs on the properties of OPC including fabrication, hydration, mechanical properties, porosity and transport, conductivity and piezoresistivity. It was found that the dispersion of CNTs in cement remains one of the main challenges in improving the fabrication of CNT–OPC mixtures. Adequate dispersion of CNTs in cement is challenging as van der Waals forces are responsible for their bundling and agglomeration even at very low concentrations, thereby limiting their potential benefits [20–22]. The enhancement of mechanical and electrical charge properties depends on how well the CNTs are dispersed within the cement matrix.

In terms of durability, previous studies on the effect of CNTs on the pore structure of CNT–OPC composites suggested that overall porosity and pore continuity are reduced [20]. Well dispersed CNTs increase the conductivity and piezoresistivity sensitivity of CNT–OPC composites exhibiting an enhanced ability to sense its own damage based on the change in the electrical change upon loading [20]. Collins et al. [23] conducted a comprehensive study aimed at investigating the effect of different types of dispersion agents on the dispersion of CNTs and workability of CNT–OPC composites. Polycarboxylate-based superplasticizer and lignosulfonate dispersant agents provided adequate dispersion of CNTs (up to 0.5-wt.% CNTs) whereas styrene butadiene rubber and calcium naphthalene sulfonate dispersant agents promoted the agglomeration of CNTs. The addition of CNTs reduced the consistency and strength of CNT–OPC mixtures; this is consistent with the results obtained from previous studies [24,25], where in order to achieve adequate dispersion of CNTs within the cement paste, a maximum content of 0.1 wt.% was recommended [24].

The mechanical and electrical properties of FA-based geopolymers containing carbon nanotubes [26] have shown that the conductivity increased with SWNCT content, whereas the tensile strength results were inconsistent and slightly decreased at 0.2 wt.% SWCNTs and increased at 0.25-wt.% SWCNTs, and then sharply decreased at 0.35 wt.% SWCNTs. Although it has not previously been investigated, the alkaline solution used to process geopolymer has the potential to enhance the interaction of MWCNTs with the geopolymeric matrix by two positive effects; first one is the effect of sodium hydroxide (NaOH) on the dispersion of MWCNTs within the geopolymeric matrix. Where it acts as a surfactant and removes the oxidation debris from the surface of CNTs and consequently allowing them to de-bundle and form well-dispersed nanotubes within the matrix [27]. The other is the effect of NaOH on the electrical conductivity of the geopolymer, where pores solution of NaOH in the form of electrolytes allow the electrons to easily move within the matrix, resulting in an improved conductivity which could be enhanced further by integrating CNTs into the matrix to develop self-sensing structural materials. With an electrical conductivity between 0.05 and 0.1 S/m, fly ash-based geopolymers are considered as semiconductor materials [28].

The object of this study is to examine the mechanical, mineralogical and geopolymer functionality characteristic using Fourier transmitted infra-red (FTIR), X-ray diffraction XRD, water absorption and drying shrinkage of the resulted geopolymeric nanocomposites mortars reinforced with various ratios of MWCNTs from 0 up to 0.4 wt.%, as new multifunctional structural materials; the dispersion quality of MWCNT was evaluated and the improvement in mechanical properties of geopolymer nano-composites was also quantified.

2. Experimental

2.1. Materials

The materials, which used in this investigation, are ground granulated water cooled blast furnace slag (GGBFS), air cooled slag (ACS) as obtained before from Iron and Steel Factory-Helwan, Egypt. The used sand dunes for mortar preparation are sourced from fine sand (<1 mm) from Oases (Wahat)-Road, Egypt. The chemical compositions of the starting raw materials are given in Table 1. Sodium hydroxide (NaOH) produced by Fisher scientific company with 99% purity as used as alkaline activator. The mineralogical compositions of GGBFS and ACS are represented in Fig. 1; where ground granulated blast furnace slag material is composed of amorphous materials and air cooled slag is composed of crystalline minerals of quartz and gehlenite.

Carbon nano-tubes which used for enhancing of geopolymeric mortar properties are of multiwall type consisting of many nested cylinders whose successive radii differ by roughly the interlayer spacing of graphite. The morphologies and microstructures of the as-synthesized carbon nanomaterials were characterized by transmission electron microscope (TEM), as shown in Fig. 2, which depicts the representative TEM images of as-synthesized carbon nanotubes deposited on 50% Co/MgO by Acetylene gas decomposition at 700 °C reaction temperature and ~4 h time-on-stream. These images show that the morphologies have tubular structures, i.e., they are multi-walled carbon nanotubes (MWCNTs) and the boundaries between MWCNT tubes are clear. The diameters of the MWCNTs are mostly in the range of 14–24 nm. It is obvious in Fig. 2A and B the dark object in the pictures is related to the Co-metal particles of the catalyst.

Raman spectroscopy was employed to analyze the degree of graphitization of the produced CNTs as represented in Fig. 2C; where the two major bands were observed, representing D- and G-bands. The D-band, observed at 1250–1350 cm^{-1}, is known as either the disorder induced due to the wall disorder or the presence of amorphous carbon deposited on the outer surface of nanotubes. The G-band (observed at 1550–1600 cm^{-1}) can be attributed to the degree of graphitization of CNTs. The ratio of ID/IG of the D and G-band can be regarded as an index for the crystalline order of CNTs; the high ID/IG value (>1) indicates that there is high structural disorder in the carbon nanotubes obtained on the catalysts. However the lower ID/IG value (<1) suggests the enhancement in graphitization of deposited carbon. The high intensity of the G-band (417 cm^{-1}) relative to D-band (270.7 cm^{-1}) (ID/IG ratio ≈0.65) suggests that the CNTs synthesized under the optimum conditions were highly graphitized [29].

Thermo-gravimetric analysis (TGA) is very important tool for clarifying the yield, stability and quality of the as-grown MWCNTs, as indicated in Fig. 2D, where the catalyst presented a single oxidation inflection, which indicates that the amorphous carbon is extremely low and high purity MWCNTs are produced. Also, TGA data determine the onset, and offset (end) temperatures represent the temperature at the initial weight loss, (496 °C) and the final weight loss, (692 °C) respectively. The large difference between the onset and offset temperatures (192°) is attained on the catalyst. This can be attributed to the formation of large diameters of CNTs, which are proved by TEM photos (Fig. 2A and B). Based on these results, the formation of ideal graphitized carbon nano-materials and the highest carbon yield are gained on it. The properties of the produced MWCNT are summarized in Table 2.

2.2. Dispersion of MWCNTs

The research at the National Research Council of Canada has shown that a small amount of CNTs can be dispersed by ultrasonication in the water containing 5% superplasticizer [30]. Shah et al. also achieved an effective dispersion of MWCNTs with different lengths and concentrations in cementitious materials by applying polycarboxylate-based superplasticizer [31].

In the current work, MWCNTs were first mixed with Gelenium Ace 30-polycarboxylate-based superplasticizer and 50% of the added water. This Polycarboxylate-based superplasticizer has been proven to be effective for CNTs dispersion [23]. The solution was sonicated using a Fritish 450 Sonifier Analog Cell