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Multifunctional properties of carbon nanotube/fly ash geopolymeric nanocomposites

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HIGHLIGHTS

- We examine the mechanical/electrical properties of geopolymers containing MWCNTs.
- Excellent mechanical and electrical properties at 0.1 and 0.5% MWCNTs.
- Good dispersion of MWCTs at 0.1 and 0.5% and agglomeration at 1% MWCNTs.
- Piezoresistive response with high sensitivity to crack propagation.

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ABSTRACT

Fly ash-based geopolymers are currently being considered as a viable replacement to ordinary Portland cement (OPC) due to multifold benefits such as cost efficiency, chemical stability, corrosion resistance, rapid strength gain rate, low shrinkage and freeze-thaw resistance. However, geopolymers tend to be more brittle than OPC and thus unsuitable for concrete structures due to safety concerns. Geopolymers with improved electrical properties can also be used as self-sensing materials capable of detect their own structural damage. Therefore, this paper is aimed at investigating the effect of multiwalled carbon nanotubes (MWCNTs) on the mechanical and electrical properties of fly ash (FA) geopolymeric composites. Geopolymeric matrices containing different MWCNTs concentrations (0.0%, 0.1%, 0.5% and 1.0% by weight) were synthesized and their mechanical properties (i.e., flexural strength, Young's modulus, flexural toughness and fracture energy), electrical conductivity and piezoresistive response were determined. A scanning electron microscope (SEM) was employed to evaluate the distribution quality of MWCNTs within the matrix and determine their crack-bridging mechanism. The experimental results showed that the MWCNTs were uniformly distributed within the matrix at 0.1 and 0.5-wt% and they were poorly distributed and severely agglomerated within the matrix at 1-wt%. The experimental results also showed that the addition of MWCNTs increased the flexural strength, Young's modulus and flexural toughness by as much as 160%, 109% and 275%, respectively. The MWCNTs also enhanced the fracture energy and increased the electrical conductivity by 194%. The geopolymeric nanocomposites exhibited a piezoresistive response with high sensitivity to micro-crack propagation.

1. Introduction

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 geopolymers is known as polymerization where the alumino-silicate oxides react with the alkali polysilicates to form a 3-dimensional polymeric Si–O–Al amorphous microstructure [1]. Geopolymers are currently being considered as a replacement to ordinary Portland cement (OPC) and has received considerable attention for their cost efficiency, chemical stability, corrosion resistance, rapid strength gain rate, low shrinkage and freeze-thaw resistance [2,3]. However, due to their cross-linked structure, geopolymers tend to be more brittle than OPC and therefore, they are unsuitable for structural applications when safety-based structural design is considered. Geopolymers were found to be more brittle than the OPC, and their fracture energy was about 40% of that of OPC [4]. Thus, improvement in fracture properties of geopolymers is deemed necessary.

Previous research investigated the mechanical properties of geopolymers reinforced with different macro-fibers such as steel, polypropylene (PP), polyvinyl chloride (PVC) and basalt fibers [5].

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The addition of these fibers increased the flexural strength, fracture energy and controlled the crack propagation [5]. Carbon nanotubes (CNTs) are being considered as a potential reinforcement in composites because they have mechanical, electrical, chemical and thermal properties superior to traditional fibers [6]. Nanoscale reinforcement of OPC with CNTs has been the focus of intense study recently. Chen et al. [7] provided a complete literature review of CNT-cement nanocomposites. Their review 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 [7–9]. The enhancement of mechanical and electrical properties depends on how well the CNTs are dispersed within the cement matrix. The literature review highlighted many inconsistent results on the effect of CNTs on the mechanical properties of OPC. However, it is well established that the current mechanical properties of CNT–OPC are not satisfactory for structural applications indicating further research is needed to find ways to uniformly disperse CNTs in cement [7]. In terms of durability, previous studies on the effect of CNTs on the pore structure of CNT–OPC composites suggested that CNTs can act as nucleating sites for the cement hydration and as a result, the overall porosity and pore continuity are reduced [7].

The addition of CNTs improves the multifunctional properties of OPC. Well dispersed CNTs increase the conductivity and piezoresistive sensitivity of CNT–OPC composites. This is attributed to the formation of conductive network in the cement matrix. In this case, the CNT–OPC exhibits an enhanced ability to sense its own damage based on the change in the electrical change upon loading [7].

A few studies have focused on the fabrication of CNT–OPC composites in relation to dispersion of CNTs and workability of mixtures. Collins et al. [10] 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 reduction was significant for mixtures with CNT contents of 1 and 2-wt%. This is consistent with the results from previous studies [11,12] where in order to achieve adequate dispersion of CNTs within the cement paste, a maximum content of 0.1 wt% was recommended [11].

The mechanical and electrical properties of FA-based geopolymers containing carbon nanotubes have not been reported apart from similar potassium-based aluminosilicate (clay) geopolymers reinforced with single walled carbon nanotubes (SWCNTs) [13]. Their investigation showed that the conductivity increased with increasing SWNCT content, whereas the tensile strength results were inconsistent. The tensile strength 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 geopolymers has the potential to enhance the interaction of MWCNTs with the geopolymeric matrix by two positive effects, leading to improved mechanical and electrical properties. The first one is the effect of sodium hydroxide (NaOH) on the dispersion of MWCNTs within the geopolymetric matrix. Previous studies have shown that NaOH 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 [14]. The other is the effect of NaOH on the electrical conductivity of the geopolymer. The 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 [15].

The present trend in research activities on CNTs has mostly been focused on their reinforcement effects in polymer and cement composites however; no work has been reported on FA-based geopolymeric composites containing CNTs. Therefore, the objective of this study is to examine the mechanical and electrical properties of MWCNTs reinforced geopolymeric nanocomposites as new multifunctional structural materials. The dispersion quality of MWCNT was evaluated and the improvement in mechanical properties, fracture energy and electrical conductivity of geopolymer nanocomposites was quantified. The piezoresistive response of the geopolymeric nanocomposites was also investigated.

2. Experimental program

2.1. Materials

Low-calcium FA was used to prepare the geopolymeric nanocomposites. The chemical composition of FA is given in Table 1 and the typical size of the FA particles is shown in Fig. 1. The alkaline solution consisted of a combination of sodium silicate (Na_2SiO_3 with 29.4% SiO_2, 14.7% Na_2O and 59.9% H_2O) and sodium hydroxide (NaOH). The CNT reinforcement phase used in this investigation consisted of MWCNTs synthesized with chemical vapor deposition (CVD). The outside estimated diameter and length of MWCNTs ranged from 30 to 50 nm and 10 to 20 μm, respectively. The density of MWCNTs was about 2.1 g/cm^3 and their electrical conductivity was more than 100 S/cm.

2.2. Dispersion of MWCNTs

Fig. 2 shows the dispersion steps employed in this study. The MWCNTs were first mixed with a surfactant. The surfactant consisted of 5% Glenium 51 polycarboxylate-based super plasticizer and 95% water. This polycarboxylate-based super plasticizer has been proven to be effective for CNTs dispersion [10]. The solution was sonicated using a Branson 450 Sonifier Analog Cell Distributor for 2 h. Solutions with concentration of 0.1, 0.5 and 1.0-wt% of the total weight of the matrix were used to identify the MWCNT concentrations for the mechanical and electrical percolation threshold. The sonication energy was 60 100 and 210 kJ/L for 0.1, 0.5 and 1-wt%, respectively. Fig. 3 shows a typical SEM image of the sonicated MWCNTs.

2.3. Fabrication of MWCNT/geopolymeric nanocomposites

Two geopolymer mixes M1 and M2 were produced. Both mixes (density of 2.3 g/cm^3) consisted of 50% of FA, 30% of fine sand and 18% of alkaline activator. The activator to FA ratio was 0.36. The alkaline activator was composed of 13% of Na_2SiO_3 and 5% NaOH with a concentration of 8 M (mole) for the mix M1 and 12 M for the mix M2. The NaOH solutions were prepared 24 h prior to casting and then mixed with Na_2SiO_3 1 h prior to casting. Each mix was reinforced with 4 MWCNT concentrations: 0.0 (control), 0.1, 0.5 and 1-wt%. During mixing, the sand and FA were first dry-mixed until thoroughly blended. The alkaline solution (Na_2SiO_3 + NaOH) was subsequently added and mixed for 3 min. The sonicated MWCNT solution was then added to the mix. Upon mixing, the molds were filled in two layers and vibrated on a vibrating plate for removing air voids. For electrical and piezoresistive characterization, copper electrodes were embedded into the finished specimens. Beams (100 mm × 100 mm × 500 mm) were produced in order to determine their mechanical and electrical properties, and their piezoresistive

Table 1
Main chemical composition of FA (wt%).

Element	Weight%
Silicon dioxide, SiO_2	53.50
Aluminum oxide, Al_2O_3	34.30
Iron oxide, Fe_2O_3	3.60
Calcium oxide, CaO	4.40
Loss of ignition	2.00