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Self sensing carbon nanotube (CNT) and nanofiber (CNF) cementitious composites for real time damage assessment in smart structures

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ABSTRACT

The self sensing properties of cementitious composites reinforced with well dispersed carbon nanotubes and carbon nanofibers were investigated. The electrical resistance of cementitious nanocomposites with $w/c = 0.3$ reinforced with well dispersed carbon nanotubes (CNTs) and nanofibers (CNFs) at an amount of 0.1 wt% and 0.3 wt% of cement was experimentally determined and compared with resistivity results of nanocomposites fabricated with "as received" nanoscale fibers at the same loading. Results indicate that conductivity measurements, besides being a valuable tool in evaluating the smart properties of the nanocomposites, may provide a good correlation between the resistivity values measured and the degree of dispersion of the material in the matrix. The addition of CNTs and CNFs at different loadings was proven to induce a decrease in electrical resistance, with the nanocomposites containing 0.1 wt% CNTs yielding better electrical properties. Furthermore, conductivity measurements under cyclic compressive loading provided an insight in the piezoresistive properties of selected nanocomposites. Results confirm that nanocomposites, reinforced with 0.1 wt% CNTs and CNFs, exhibited an increased change in resistivity, which is indicative of the amplified sensitivity of the material in strain sensing.

1. Introduction

Recent advances in the field of nanotechnology have led to the development of advantageous nanoscale fibers, making possible the development of new multifunctional, high performance, advanced sensing, cement based nanocomposites that could effectively act as sensors to monitor the health of the structures. Depending on their atomic structure, CNTs and CNFs may be metallic or semiconductors. When subject to stress/strain, their electrical properties change, expressing a linear and reversible piezoresistive response [1,2]. These electromechanical characteristics of CNTs and CNFs open new potential applications for cementitious nanocomposites with improved mechanical properties and added multifunctionality in stress monitoring of concrete structures, detecting damage, as well as traffic monitoring in highway structures.

Research efforts have been concentrated on developing cementitious composites with sensing capabilities using carbon microfibers [3–10]. Banthia et al. [3] conducted electrical resistivity measurements on cement pastes reinforced with carbon and steel microfibers as well as on several hybrid mixes containing both carbon and steel fibers. The addition of fibers significantly improved the conductivity of cement composites to a large extent. Fu and Chung [9] examined the strain sensitivity of carbon fiber/cement compared to that of normal cement since 1993, while cement composites containing carbon fibers have also been applied for monitoring traffic flow [10]. The results of their studies indicated that under loading, cement-based sensors with carbon fiber reinforcement develop a good correlation between resistivity changes and load changes, increasing in tension and decreasing in compression, sensing crack opening when the resistivity increases and crack closing when resistivity decreases.

A few studies have been carried out on the electrical properties, the piezoresistive behavior and sensing ability of cementitious nanocomposites embedded with carbon nanotubes (CNTs). Li et al. [11] conducted experiments using treated with acids (SPCNT) and untreated CNTs (PCNT) as reinforcement and concluded that both types reduce the electrical resistance and enhance the properties of the cementitious composites. In addition, they examined the variation of resistance by imposing cyclic compressive load. Yu and Kwon [12] investigated the electrical properties under compressive load of cement paste reinforced with multiwalled carbon nanotubes (MWCNTs). Results showed that the electrical resistance of the nanocomposite changed synchronously with the compressive stress levels. Recently, Han et al. [13] conducted experiments in the laboratory and in the field. They examined the electrical properties of nanocomposite samples under continuous and instant

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compressive load. Also they investigated the possibility of using the nanocomposite material for traffic control. Their results showed that under repeated compressive loading the electrical resistivity decreases upon loading and increases when unload, while the instant load also presented changes in the electrical resistance. In addition, road test results concluded that this nanocomposite can detect vehicular loads through remarkable changes in electrical resistance.

More recently, researchers investigated the effect of the MWNT content and water/cement ratio on the piezoresistive sensitivity of composites [14–16]. The piezoresistive properties are dependent on the conductive network in the composites, which in turn is influenced by the CNT or CNF concentration level and water/cement ratio. Han et al. [14] examined cement nanocomposites with amounts of multi-walled CNT (MWNT) of 0.05, 0.1 and 1 wt%. Experimental results indicated that the piezoresistive sensitivities of the composites first increased and then decreased with the increase of the CNT content concluding that the composite with 0.1 wt% of MWNT presents better sensing property. At the same time, they examined the effect of water/cement ratio on piezoresistivity by fabricating and testing samples with 0.45 and 0.6 water/cement ratios. The CNT/cement composite with $w/c = 0.6$ exhibited more sensitive response to compressive stress. Coppola et al. [15] observed that the sensitivity under compressive stress of cement pastes containing different percentages (0.1 and 1.0 wt%) of MWNTs is less evident in the composites with 1.0 wt% concentration of CNTs. Luo et al. [16] used cured multi-walled carbon nanotube (MWCNT) reinforced cement-based composites with 0.1 wt% and 0.5 wt% MWCNT and measured the electrical resistances under cyclic loading and unloading. Results revealed good piezoresistivity and strain sensitivity for both samples though the trendline of fractional change in resistivity ($\Delta\rho$) presented better stability for amounts of 0.5 wt%.

The considerable challenge in fully exploiting the properties of carbon nanotubes and carbon nanofibers as reinforcement in a composite is attributed to the lack of the fiber dispersion in the material matrix. The results of experimental studies on CNT/cement and CNF/cement specimens converge to the point that the addition of carbon nanotubes or nanofibers improves the mechanical [17] and electrical properties of the nanocomposite material by reducing resistivity and providing piezoresistive properties, under the condition that effective dispersion of nanofibers in the cement paste has been achieved [18–21]. Konsta-Gdoutos et al. [18] achieved effective dispersion of CNTs by applying ultrasonic energy along with the use of a surfactant (SFC) and observed that beyond the necessity for ultrasonication there is an optimum ratio of surfactant to CNTs for good dispersion. Considering this dispersion method Metaxa et al. [19] applied it on CNFs embedded in cement composites and investigated the appropriate amount of ultrasonic energy and the surfactant to CNF ratio (SFC/CNF) for effective dispersion. More recently, Han et al. [21] investigated the use of a polycarboxylate superplasticizer for effectively disperse CNTs and CNFs in a cement matrix given that the existing dispersants affect cement hydration and consequently its mechanical properties. Results concluded that proper dispersion is achieved with the use of a superplasticizer, due to its ability to disperse both cement particles and CNTs/CNFs. Through this procedure high performance cementitious nanocomposites with strong piezoresistive characteristics can be successfully fabricated.

Another issue that arises is that cementitious composites exhibit the effect of polarization which causes an increase in electrical resistance during measurement while even the current cannot accurately be measured [22]. Solution to this, beyond the use of dry specimens, can be the use of AC measurement method, as applied by Banthia et al. [23].

Finally, recent research focuses its interest in exploring the behavior of carbon nanotube cement based sensors under dynamically varying strain in concrete structures [24].

In this study the electrical resistivities and self sensing properties of cementitious composites reinforced with well dispersed carbon nanotubes and carbon nanbofibers were investigated. The electrical resistance of cementitious nanocomposites with $w/c = 0.3$, reinforced with well dispersed carbon nanotubes (CNTs) and nanofibers (CNFs) at an amount of 0.1 wt% and 0.3 wt% of cement, was experimentally determined using the 4-pole method, and compared with resistivity results of nanocomposites fabricated with “as received” nanoscale fibers at the same loading. The piezoresistive properties and the sensing ability of the cement-based nanocomposites were also investigated measuring the changes in resistivity under the application of compressive cycling loading. A set of preliminary resistivity experiments were also conducted on nanocomposites reinforced at an amount of 0.048 wt% of cement, for the purpose of determining the optimum applied voltage.

2. Experimental procedure

2.1. Materials

The cementitious material used in this study was Type I ordinary Portland cement (OPC). Experiments were conducted with MWCNTs of 20–40 nm diameter and length in the range of 10–100 μm. A type of highly graphitic, Pyrograf-III, carbon nanofibers was used. CNFs exhibit a tensile strength of 7 GPa, tensile modulus of 600 GPa and length range of 30–100 μm. Characteristic properties of MWCNTs and CNFs used can be seen in Table 1. For the preparation of CNT and CNF dispersions, a commercially available surfactant (SFC) Glenium 3030 is used. In a typical procedure of dispersion [18], suspensions are prepared by mixing the CNTs and CNFs in aqueous solution containing the surfactant and the resulting dispersions are sonicated at room temperature. Constant energy is applied to the samples by a 500 W cup-horn high intensity ultrasonic processor with a cylindrical tip and temperature controller. The sonicator is operated at an amplitude of 50% so as to deliver energy of 1900–2100 J/min, at cycles of 20 s in order to prevent overheating of the suspensions.

After sonication, cement was added into the CNT and CNF suspensions at a water to cement ratio $w/c = 0.3$ by weight. The materials were mixed according to ASTM 305 using a mixer capable of operating from 140 ± 5 revolutions/minute (r/min) to 285 ± 10 r/min. After mixing, the paste was cast in 20 × 20 × 80 mm oiled molds. For measuring the electrical resistivity of the samples, metallic grids with large opening (3 × 3 mm) were used as electrodes, which were incorporated into the specimens immediately after casting. Specimens were then covered with membrane until they were demolded after 24 h. Following demolding, the samples were cured in lime-saturated water for 28 days and then put in an oven to dry, first at 60 °C for three days, and then for another three days at 95 °C. The process of specimen drying aims at eliminating the effect of polarization. CNT/cement and CNF/cement nanocomposites were prepared at percentages of 0.1 and 0.3 wt% of cement. At least three specimens were prepared for each mixture (Table 2).

Table 1
Properties of multiwalled carbon nanotubes (MWCNTs) and carbon nanofibers (CNFs).

Type	Diameter (nm)	Length (μm)	Tensile strength (GPa)	Tensile modulus (GPa)	Aspect ratio
CNT	20–40	10–100	11–200	200–1000	1600
CNF	60–150	30–100	7	600	650