Materials Today Communications 8 (2016) 196–204

Contents lists available at ScienceDirect

Materials Today Communications

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

Carbon nanotubes and nanofibers as strain and damage sensors for smart cement

Panagiota T. Dalla, Konstantinos G. Dassios*, Ilias K. Tragazikis, Dimitrios A. Exarchos, Theodore E. Matikas

Department of Materials Science and Engineering, University of Ioannina, Dourouti University Campus, Ioannina GR-45110, Greece

ARTICLE INFO

Article history:
Received 3 June 2016
Received in revised form 22 June 2016
Accepted 27 July 2016
Available online 28 July 2016

Keywords:
Carbon nanotubes
Carbon nanofibers
Smart cement
Electrical properites
Percolation theory
Damage sensing
Strain sensing

ABSTRACT

The present paper reports on the strain and damage sensing potential of carbon nanotubes and carbon nanofibers embedded in cement mortars. Prismatic and three-point bending specimens were prepared at various nano-inclusion concentrations for measurement of the material's surface electrical resistivity, establishment of its electrical percolation threshold, assessment of its piezoresistive response under cyclic compressive loading and for damage detection under pure bending of the mortars. Percolation theory conditions were met at a tube concentration of ca. 0.6% by weight of cement while both nanotubes and nanofibers endowed smartness to the mortars which exhibited remarkable electrical sensitivity to applied load, with fully-recoverable electrical resistances varying in an inverse relation with compressive stress. The potential of nanotubes and nanofibers as damage sensors in percolated mortars was manifestedby dramatic increases of in situ electrical resistivity under three-point bending testing, at loading instances as early as the maximum load, hence providing timely failure warnings. Differences in the strain and damage sensing potentials of the two types of nano-inclusions is presented and discussed in the text.

1. Introduction

Electrical conductivity, the property which quantifies how strongly the material assists electric current transport, is currently the most desirable characteristic of next-generation smart cement-based materials. The property is often expressed by means of its inverse, electrical resistivity, which can attain values ranging from 10^{-6} Ohm cm for highly conductive metals, to 10^{19} Ohm cm for highly insulating rubber and certain polymers. As a porous material, concrete exhibits a wide range of resistivities depending mainly on moisture content [1], temperature [2], cement type, water-to-cement ratio and amount and type of aggregates, admixtures and supplementaries in the raw materials [3].

Electrical resistivity is extremely significant for a variety of cement-based applications such as concrete railway ties on long-line railroads, transit lines, hospital operating room floors and cathodic protection systems [4]. Moreover, electrical resistivity measurements as non-invasive methodologies, have been suggested for assessment of the effect of re-alkalisation of carbonated concrete [5], monitoring the health of carbon fiber-reinforced concrete [6,7], and monitoring water, ionic penetration and moisture displacement within the materials [8–15]. Electrical resistivity measurements have also been suggested for assessing microstructural alterations in hydrating cement-based materials [16]. Elastic waves and electrical resistivity measurements were used by Kang et al. for studying the effect of the freezing-thawing process on sand-silt mixtures [17].

Carbon nanotubes (CNT), the one-dimensional allotropes of carbon considered as one of the most remarkable materials of the 21st century, are particularly efficient in endowing electrical transport potential to low-conductivity matter such as cement [18,19]. With average diameters as low as 1.2 nm the tubes can be conducting or semiconducting by adjustment of the imposed electrical field [19]. CNTs have attracted extensive scientific attention due to their remarkable physical, mechanical and electrical properties. Not long after the announcement of some unique CNT applications such as electrically conducting polymer composites, field emission electron sources for flat panel displays, hydrogen storage media in electric vehicles or laptop computers and microwave generators [20–24], the tubes demonstrated potential also in cement-based materials to which they can endow multi-functional characteristics such as enhanced electrical and thermal transport properties while simultaneously acting as nano-reinforcement to the mechanical behavior [19]. In smart cements, the tubes can act as internal self-

* Corresponding author.
E-mail address: kdassios@cc.uoi.gr (K.G. Dassios).

http://dx.doi.org/10.1016/j.mtcomm.2016.07.004

monitoring sensors for inner defects hence eliminating the need for embedded, attached or remote sensing systems [25]. The sensing ability of cement-based composites was firstly documented by Han et al. [26] and is associated with their piezoresistive effect, i.e. the change in their electrical resistance under external mechanical stimulus. The piezoresistive behavior of nano-modified cement stems from the variation, due to external loading -usually of compressive nature- in the contact resistance between the electrically conducting nano-inclusions and the bulk cement-based material [27].

Efficient improvement of the electrical transport properties of cement by embedded carbon nanotubes requires that percolation theory conditions are satisfied. Therein, establishment of a critical nanotube concentration is required for adjacent nano-inclusions to critically contact one another so that a continuous, electrically conductive path is formed throughout the material which leads to a sudden dramatic decrease in resistivity. The tube concentration where such conditions are met is known as the electrical percolation threshold of the given material system [27]. At the threshold, the curve of resistivity versus inclusion concentration renders S-shaped [27]. The percolation effect has been studied in great extent for CNT-loaded polymers however extremely limited information is available for cement-based materials [27–29]. Ambrosetti et al. [30] studied theoretically and numerically the percolation of electrical properties of carbon nanotube composites.

Measurement of the in-plane electrical resistance of cement-based materials in situ during testing can reveal the damage state of the materials due to either damage infliction (and corresponding subsequent opening of microcracks) or healing by microcrack closing [31]. For example, Bontea et al. monitored damage in short carbon fiber-reinforced concrete by measurement of DC electrical resistance and found that resistance decreased during compression and increased upon damage development [32]. In this manner the strain/stress state during dynamic loading could be related to the origin of the damage.

Electrical resistivity measurements in cement-based materials are typically conducted by one-, two- or four-probe methods. The latter, also called Wenner method [33], is considered as the most accurate; it uses four electrodes fixed onto the concrete surface and the current is applied to the two outer electrodes while the two inner ones measure the difference in potential. In the case of homogeneous materials like concrete, an additional factor, K, accounting for probe spacing, specimen dimensions and temperature must also be taken into consideration in calculation of the resistivity as suggested by Morris et al. [34]. Resistivity data from cylindrical and prismatic specimens also require correction as suggested in [35]. Coppola et al. [36] and Cao et al. [37] recently demonstrated the effectiveness of the four-point method in monitoring stress in CNT-loaded cement and in assessing the steel fiber dispersion in cement mortars, respectively.

The main objective of the present paper is to investigate the strain and damage sensing capabilities of two types of carbon nano-inclusions, namely carbon nanotubes and carbon nanofibers, in imparting smartness to cement. For this task, a series of nano-modified cement mortars were prepared at varying nanotube and nanofiber loadings and their electrical transport performance was examined in terms of surface electrical resistivity measurements for establishment of the percolation threshold, piezoresistivity measurements under cyclic loading for assessing the strain sensing capacity of the nano-inclusions and bending tests for establishment of their potential as instant damage sensors and early warning indicators.

Table 1
Properties of multi-wall carbon nanotubes.

Parameter	Value
Length range	5–15 μm
Diameter range	20–40 nm
Synthesis method	catalytic CVD
Purity	≥95%
Ash	≤0.2 wt.%
Specific surface area	40–300 m^3/g
Amorphous carbon content	≤3%

Table 2
Properties of carbon nanofibers.

Parameter	Value
Length	20–200 μm
Average diameter	100 nm
Average pore volume	0.12 cm^3/g
Purity	≥98%
Molecular Weight	12 g/mol
Iron content	<14,000 ppm

2. Experimental procedure

2.1. Materials

Five cement mixtures, each with different CNT loading, were prepared according to standard protocol "BS EN 196-1" intended for measurement of surface electrical resistivity. Sets of six prismatic specimens, dimensions of 40 × 40 × 160 mm^3 were fabricated for each mixture/loading value. Mixtures contained ordinary Portland cement type "I 42.5t", regular tap water, natural sand, long multi-wall carbon nanotubes commercially available by Shenzhen Nanotech Port Co. Ltd. (Shenzhen, China) and Viscocrete Ultra 600 superplastisizer (Sika AG, Baar, Switzerland) as CNT dispersant agent, in a 1:1 weight ratio to CNT. The specific superplastisizer is a native concrete additive which proved highly effective for CNT dispersion and rendered employment of conventional dispersion methods, such as surfactant use and chemical tube functionalization, unnecessary [38]. The main properties of the nanotubes used in this study are given in Table 1. Water to cement ratio was maintained at 0.5 while the tubes were added at varying concentrations of 0.2, 0.4, 0.6 and 0.8%, by weight of cement and a reference mixture without nano-inclusions was prepared.

For piezoresistivity measurements under three-point bending tests and for monitoring damage, six additional prismatic specimens, same dimensions as before, were fabricated at a tube loading of 0.6 wt.% of cement. The particular loading value was selected following the surface electrical resistivity measurements according to the rationale presented in Section 3.3. The initial notch of the bending specimens was 20 mm and crack opening displacement was measured using an external clip-on digital extensometer. External electrical contacts were prepared by direct embedment in the fresh mortars of four stainless steel grids, dimensions of 50 × 20 × 1 mm^3, immediately after the mortars were poured in the molds. The grids were embedded 30 mm deep into the samples to ensure good contact of the electrodes to the sensed material over a large, statistically representative material volume. The two inner probes (used for voltage measurement) were positioned symmetrically at a distance of 40 mm while the outer (used for passing current) at a 60 mm distance (Fig. 1). Two additional mixtures were prepared with carbon nanofibers as nano-inclusions at loadings of 0.2 and 0.6% by weight of cement. The particular mixtures were produced following the same protocol with CNT-based mixtures while the properties of the nanofibers used are shown in Table 2.