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Improved piezoresistive sensitivity and stability of CNT/cement mortar composites with low water–binder ratio

H.K. Kim [a], I.S. Park [b], H.K. Lee [b,*]

[a] School of Architecture, Chosun University, 309 Pilmun-daero, Dong-gu, Gwangju 501-759, South Korea
[b] Department of Civil and Environmental Engineering, Korea Advanced Institute of Science and Technology, Guseong-dong, Yuseong-gu, Daejeon 305-701, South Korea

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ABSTRACT

In previous studies by the authors, it was found that a lower water–binder ratio led to enhanced dispersion of carbon nanotube (CNT) in the cement matrix. The objective of this study was to investigate the piezoresistive sensitivity and stability of CNT/cement mortar composites with low water–binder ratio. The effect of absorbed water on the piezoresistivity of the composites was also investigated, since it strongly affects the electrical properties of the composites. The changes in the electrical resistance of composite specimens induced by external cyclic loading were measured to investigate their piezoresistive sensitivity and stability. The experimental results indicates that the stability of piezoresistivity under cyclic loading and their time-based sensitivity can be improved by decreasing the water–binder ratio of the cement composites. Moreover, the variation of piezoresistivity induced by the moisture content can be decreased by low water–binder ratio.

1. Introduction

Application of carbon nanotubes (CNTs) in cement-based composites for various purposes has been increasingly attracting attention [21,25–28]. One of the main purposes of incorporating CNTs is to provide electrical properties to cement composites. Conventionally, low-priced carbon materials (i.e. coke powder, graphite, and carbon black) and/or metallic inclusions (i.e. steel fibers and shavings) have been utilized in cement composites for this purpose [10–14,29]. Conductive cement composites incorporating these materials have been applied as anti-corrosion earth connectors for electrical-shock protection and electric-heating pavement materials for de-icing roads [11,12].

The conventional conductive materials, however, have some disadvantages. In the case of the metallic inclusions, such as steel fibers and shavings, corrosion of these materials leads to degrade the durability of cement composites. In the case of low-priced carbon materials, the required content is too high to provide sufficient electrical conductivity for cement composites. For example, the content of carbon black in a cement composite to obtain electrical resistivity lower than 100 Ω cm was more than 20% by weight of cement [13]. Similarly, the content of graphite powder in a cement composite to obtain electrical resistivity lower than 100 Ω cm was more than 40 vol.%, i.e. about 60–80% by weight of cement [15]. These high contents of the conventional carbon materials degrade the mechanical properties and durability of cement composites [13,23].

On the contrary, it was found that a small amount of CNTs (i.e. less than 1 wt.% by weight of cement) could provide cement composites with a similar level of electrical conductivity as obtained with high contents of carbon black or graphite [13,23]. Moreover, when small amounts of CNTs were incorporated, the mechanical properties of cement composites were not degraded or were even improved [23].

By the addition of CNTs, electrical conductivity was not only provided to cement composites, but piezoresistivity was also introduced at the same time [16,17]. Piezoresistivity is an effect of electrical resistance change induced by deformation of materials [6]. A number of studies on the piezoresistivity of cement composites containing conventional carbon materials have been reported ([9,13,6,8]; Wen and Chung, 2009). However, studies on the piezoresistivity of CNT/cement composites are on a preliminary level, and most have only dealt with the feasibility of the composites [7,4,7,1,3]. Few in-depth studies on the factors affecting the piezoresistivity of composites, such as the mix proportion of the cement matrix or the moisture content, have been reported to date.

In previous studies by the authors, the effects of mix proportion on mechanical and electrical properties of CNT/cement composites were investigated [21,22,2,23]. It was found that the dispersion of

* Corresponding author. Tel.: +82 42 350 3623; fax: +82 350 3610.
E-mail address: leeh@kaist.ac.kr (H.K. Lee).

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CNTs in the cement matrix was enhanced with lower water–binder ratio (W/B) and inclusion of some silica fume, without a sonication process [23]. This led to enhanced effects of CNTs on mechanical and electrical properties of cement composites [22,23]. In particular, for a cement paste composite containing 0.3% of CNTs, the electrical resistance was drastically decreased from 10^8 to $10^4\ \Omega$ (reaching a level of 1/10,000) when the W/B of the composites was decreased from 0.25 to 0.20 [23].

The objective of this study was to investigate the piezoresistive sensitivity and stability of CNT/cement mortar composites with low water–binder ratio. The effect of absorbed water on the piezoresistivity of the composites was also investigated, since it strongly affects the electrical properties of the composites [5]. Cement mortar composites with three different W/B values, 0.4, 0.5, and 0.6, were designed, and for each mixture, CNTs in amounts of 0.1%, 0.3%, and 0.5% by weight of cement were applied. Specimens with two different moisture contents, saturated-surface dry (S.S.D.) and oven dry (O.D.) conditions, were prepared for all experimental studies. The initial electrical resistance of the CNT/mortar composites was measured prior to loading. Also, the changes in the electrical resistance of the specimens induced by external cyclic loading were measured to investigate their piezoresistive sensitivity and stability.

2. Experimental program

2.1. Preparation of specimens

Type I Portland cement (C) and silica fume (SF), which is a proprietary product of Elkem Inc. (EMS-970 D), were used as binder materials. Crushed sand (A) having a specific gravity of 2.60 in the S.S.D. condition was used as a fine aggregate. A poly-carboxylic acid-based super-plasticizer (SP), a proprietary product of BASF Pozzolith Ltd. (GLENIUM 8008), was added to enhance the workability of the fresh mortar. Multi-walled carbon nanotubes, a proprietary product of Carbon Nano-material Technology Co. Ltd., were used as electrically conductive materials. The specifications of the CNTs are given in Table 1.

CNT/cement mortar composites with three different W/B values (i.e. 0.4, 0.5, and 0.6, and three different CNT contents; 0.1%, 0.3%, and 0.5% by weight of cement) were designed for this experiment. The mix proportions are shown in Table 2. It should be noted that since the piezoresistivity in the cement paste and mortar without CNT was negligible regardless of moisture contents in the specimens as shown in the previous studies by the authors ([24]; Jeon and Lee, 2012). The specimen without CNT was not prepared for the experiments in the present study.

The cement, silica fume, crushed sand, and CNTs were mixed by an electrical hand mixer for 6 min and the dry mixture was mixed again with water and a super-plasticizer by a standard Hobart mixer for another 3 min. $50 \times 50 \times 50\ mm^3$ cubic specimens were then cast for measuring compressive strength and electrical resistance. Two copper electrodes spaced 2 cm apart were embedded in the specimens for the measurement of their electrical resistance (Fig. 1). The copper electrodes were coated by silver paste before being embedded in the fresh mixture to prevent corrosion during the curing period. All specimens were demolded after a single day following fabrication, and then cured in a water bath with a temperature of 18 ± 5 °C for more than 28 days.

Table 1
Properties of carbon nanotube (CNT).

Diameter	Length	Purity	Bulk density	Electrical conductivity
5–15 nm	⩽10 μm	⩾95 wt%	0.02–0.04 g/cm^3	>10^2 s/cm

Table 2
Mix proportion of CNT/cement mortar composite and their mortar flow.

W/B	Weight composition[a]						Mortar flow (mm)
	W	C	SF	A	SP (×1000)	CNT (%)	
0.4	0.44	1	0.1	1.63	8.00	0.1	240
						0.3	165
						0.5	104
0.5	0.55					0.1	260
						0.3	206
						0.5	151
0.6	0.66					0.1	258
						0.3	250
						0.5	191

[a] Mass ratios of cement weight.

2.2. Experimental details

The flow characteristics of fresh mixtures were measured in accordance with ASTM C1437 [20,19]. The mortar flows of the mixtures are listed in Table 2. A field emission type SEM (Nova 230) manufactured by FEI Co. was used to observe the distribution of CNTs in the cement matrix. An SEM analysis was carried out using gold-coated samples under low vacuum mode with a low nitrogen pressure at 10–20 kV acceleration voltage. The detailed procedures for the SEM analysis can be found in Kim et al. [23]. The direct-current (DC) resistance of each CNT/cement mortar composite was measured according to a two-probe method that involves connecting two wires to the respective electrodes with a digital multimeter (Agilent Technologies 34410A). The details of the measuring process and the rationale for using the two-probe method are provided in Kim et al. [23]. It should be noted that, in the present study, the electrical resistance values of saturated specimens were measured for a period of time to prevent unwanted fluctuation of the electrical resistance induced by polarization [30]. It was found that the electrical resistance values for all specimens became stable nearly 1 h after the beginning of the measurement.

The compressive strengths of the hardened composites after 28-day curing were measured by a 300-ton capacity Universal Testing Machine (UTM) following the specifications of ASTM C109. The piezoresistivity of the specimens was measured as shown in Fig. 2. Compressive loading was applied by using a 10-ton capacity UTM. The loading was applied in the direction perpendicular to the electrodes embedded in the specimen, and the maximum stresses for the specimens were equivalent to 30% of the compressive strength. The compressive strengths of the specimens and the maximum stresses applied for measuring the piezoresistivity are presented in Table 2. The speed of loading and unloading was about 0.2 MPa/s for all specimens. When the specimens were under cyclic loading, the change in the electrical resistance of the specimens was synchronously measured by the digital multimeter and recorded in a computer (Fig. 2). The electrical resistance change induced by loading was calculated as follows (c.f. [7,17]) (Table 3)

$$\text{Electrical resistance change} = \Delta R/R_0 \times 100\ (\%), \quad (\Delta R = R - R_0) \tag{1}$$

where R is the electrical resistance of the specimens under loading and R_0 is the initial electrical resistance without loading [7,17].

Note that the electrical resistances of the specimens in the S.S.D. condition were measured directly after removing the specimens from the water bath. For the specimens in the O.D. condition, the electrical resistances were measured after drying in a laboratory oven with temperature of 105 °C for 2 days. Refer to ASTM C642 for details of the drying process of the hardened cement