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# Electrical resistivity reduction with pitch-based carbon fiber into multi-walled carbon nanotube (MWCNT)-embedded cement composites

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## HIGHLIGHTS

- Electrically conductive cement composites containing MWCNT and CF were prepared.
- Test specimens with various CF length, filler content, and w/c ratio were fabricated.
- The incorporation of CF into the MWCNT-embedded composite causes the bridge effect.
- The improved electrical and viscous properties of proposed composites was observed.

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## ABSTRACT

Recently, various functional construction materials based on carbon nanotubes (CNTs) are being researched; however, there are very few examples of practical use due to cost and workability obstacles. In order to overcome these limitations, we studied the electrical characteristics of multi-phase cement composites containing multi-walled carbon nanotubes (MWCNTs) and economical pitch-based carbon fiber (CF). Test specimens with various formulations of the CF length, content, and water/cement (w/c) ratio are manufactured and their properties are evaluated. The pitch-based CFs used in the experiments were analyzed by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The resistance of the conductive cement composites was measured by a two-probe method, and the viscosity was evaluated using a rheometer immediately after the mixing process. In addition, the internal structure of the specimens was analyzed using a scanning electron microscope (SEM) and by micro-computed tomography (Micro-CT) analyses. It was observed that the incorporation of CFs into the CNT-embedded cement composite causes the CFs to serve as a bridge between CNT particles, thus maintaining the homogeneity of the conductive network in the composites. In addition, although an increase of the w/c ratio improved the viscosity of the composites by 90%, the electrical resistivity was retained due to the bridging effect of the CF.



## 1. Introduction

Nanofiller- and cement-based multifunctional construction materials have attracted substantial interest as a basic element in future smart buildings [1–3]. Due to the nature of the construction field, which is most exposed to humans and the atmosphere [4], the development of nanofiller-embedded cement composites has the potential to have a considerable impact on our daily lives [5]. However, a significant challenge is the high viscosity and prices of final products, preventing additional technological developments. Despite various reports of the achievement of very high physical properties of the cement composites containing nanofillers, the scarcity of successful commercialization stems from the fact that these problems have not been solved.

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In the early days of applying nanofillers to a cement matrix, many studies paid attention to strength improvements. For instance, Li et al. [6] prepared surface-treated multi-walled carbon nanotubes (MWCNTs) which were mixed into cement materials. It was observed that the incorporated MWCNTs act as bridges across cracks and voids, ultimately improving the compressive strength, flexural strength, and failure strain of composites [6]. It was also reported that carbon nanotube (CNT)/cement composites with improved mechanical performance capabilities can be obtained by increasing the amount of high stiffness C–S–H and decreasing the porosity [7].

However, various inexpensive and convenient methods have been proposed to improve the mechanical characteristics of cement-based materials. The incorporation of steel or polymer fibers represents a typical means of achieving strength improvements without excessive cost and labor problems [8–12]. Hence, studies of the functional characteristics of cement composites containing nanofillers are actively underway in recent years, and one strand in this research seeks to improve the electrical conductivity [13–16]. The electrical conductivity of construction composites containing carbon fiber (CF) has been investigated with varying the CF volume, size, and relative humidity [10,13,17]. However, the improvement of the electrical conductivity caused by inserting CF into cement was not remarkable [13].

Kim et al. [14] proposed a means of improving the dispersibility of CNTs by the incorporation of silica fume. It was found that the addition of silica fume led to an enhancement of the CNT dispersion properties, and increased the mechanical and electrical characteristics of cement composites [14]. It was also confirmed that the electrical conductivity was enhanced by incorporating CNT and CF into the cement matrix [15]. Although the electrical properties were reduced in comparison to cases in which only CNT was added, the durability was measured and found to be superior. The cement composites with improved electrical conductivity could be applied to various fields, such as electromagnetic wave shielding [18], energy harvesting [19], sensing [20,21], heat generation [22], and in curing application based on the pyretic mechanism [23].

According to the studies carried out in the past, there are three limitations in the study of cement composites incorporating nanofillers: (1) decrease in workability due to high viscosity, (2) high price of the final product, and (3) low durability. In order to overcome the above problems, the present study is to develop cement composites with a low weight fraction of CNT and economical pitch-based CF. CNT is known to be a material that raises prices and lowers workability levels; thus, the weight fraction of CNT is fixed at the minimum level, near percolation thresholds with reference to the literature [14,15,18,22–24]. Pitch-based CF is a material produced from petroleum residue. The mechanical properties of pitch-based CF are lower than that of ordinary CFs; however, their electrical properties are known to be similar [25,26]. Above all, there is great potential to use CFs in the construction field given the advantage of a reasonable price. By adding CF, nanoscale and microscale changes occur simultaneously in the cement composite. From the viewpoint of durability, the addition of microscale CF filler is expected to induce the conductive path more rigid and minimize the deterioration of material properties.

In the present study, the electrical characteristics of multiphase cement composites containing MWCNT and pitch-based CF were investigated. Test specimens with various formulations of the CF length, content, and water/cement (w/c) ratio are manufactured and their properties are evaluated. The pitch-based CFs utilized in this study were analyzed by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). In addition, the electrical resistance levels of the cement composites were measured by a two-probe method, and the viscosity in each case was evaluated using a rheometer immediately after the mixing process. The internal structures of the specimens were analyzed by scanning electron microscopy (SEM) and by micro-computed tomography (Micro-CT) analyses.

## 2. Experimental program

### 2.1. Mix proportions and specimen preparation

It is important to note that the present study investigates the effects of MWCNT, CF, and the w/c ratio on the electrical characteristics of cement composite. Note that the w/c ratio was calculated on the basis of cement weight. The most essential factor during the production of cement composites is to ensure uniformity during the dispersibility of the fillers. In the literature [14,27] it is reported that the use of silica fume and a superplasticizer reduces the van der Waals force of CNT particles and effectively disperses the CNTs. Hence, silica fume (EMS-970 manufactured by Elkem Inc.) and a polycarboxylic-acid-based superplasticizer (GLENIUM 8008 by BASF Pozzolith Ltd.) were utilized in this study at 10 and 1.6 wt%, respectively. Herein, the weight percentage of silica fume and superplasticizer were based on the weight of cement. In addition, adding CNTs in an amount that exceeds the percolation threshold causes agglomeration in the cement matrix [15], which negatively affects the overall performance of the composites. The weight fraction of MWCNT (Jeno Tube 8© by Jeio Co. Ltd.) is thus fixed at 0.3 wt% in the present study. The length of MWCNT is 30–45 μm, and Supplementary Material regarding the SEM analysis of MWCNTs is available in the online version of the paper. The cement material used in the experiment was ordinary Portland cement (OPC). To investigate the effects of the pitch-based CF (GS Caltex Co.) length on the composites, samples with various lengths of CF (3, 5, and 10 mm) were also prepared. It should be noted that the length of CF was estimated based on reliable papers in the existing literatures [28–31]. In most studies, the length of the CF was considered to be 1–10 mm, and some studies reported that lengthy CFs can cause clumping and adversely affect the cement composites [28,29]. For these reasons, the length of the CF in the present study is estimated to be 3, 5, and 10 mm. The cement and silica fume were separately classified in the present study (Tables 1 and 2), and all weight fractions were based on cement.

Fig. 1(a) shows a schematic representation of the mixing procedure of the composites used in the experimental study here. The materials listed in Fig. 1(a) were incorporated into a mortar mixer (Heungjin, HJ-1150) and were mixed for 7–10 min [23]. Fig. 1(b) presents the notation method used for the specimens according to the combination of the material parameters, where L and F correspondingly denote the length and weight of the CF, W is the w/c ratio, and C means CNT. The mix proportions of the specimens in the study are listed in Tables 1 and 2. After mixing, the cement composites were fabricated by casting them into a mold 25 × 25 × 25 (unit: mm) in size, as shown in Fig. 1(c). The specimen size was determined in accordance with ASTM C 109 [32] and the relevant literature [23]. Copper electrodes with a height of 20 mm and a width of 10 mm were inserted into each specimen to measure the resistance. Each specimen was then sealed with wrapping material to prevent water evaporation after the manufacturing process.

### 2.2. Testing methods

The macro-morphology of the CF morphology was observed by field emission scanning electron microscopy (FE-SEM) (NOVA nanoSEM 450, FEI, USA) using Pt-coated samples. It is noted that the SEM images can be obtained by detecting the secondary electron signal on the surface of specimen, and a certain level of electrical conductivity is required for the specimen. However, the inherent conductivity of the cement is very low for SEM analysis, and thus the Pt coating was applied to the surface of the cement material to analyze the SEM image at the appropriate resolution. The Raman spectra were obtained using a Renishaw invia Raman microscope (514 laser lines). XPS (K-Alpha, source: Al Kα (1486.6 eV)) was adopted in order to measure the surface composition of the nanotubes.

The composite specimens were analyzed to assess their electrical and viscosity characteristics. The electrical resistances at different ages (3, 7, 14, and 28 days) were measured using a two-probe method (FLUKE, True-rms Multimeter), and the measured resistance was converted to the resistivity using the following equation

$$\rho = R \cdot \frac{A}{L} \tag{1}$$

where $\rho$ and $R$ denote the resistivity and the measured resistance, respectively, and $L$ and $A$ correspondingly represent the distance (cm) between the copper electrodes and the cross-sectional area (cm$^2$) of the electrode embedded in the cement composite. The electrical conductivity of cement composite was measured by referring to the ASTM standards [33,34] and previously published papers [15,23] related to conductivity measurement of materials. The viscosity of the specimens was measured using a Rheometer (TA instruments, Discovery Hybrid Rheometer-3). The uncured fresh specimen after mixing was placed on a static basal plate and measured at a temperature of 25 °C and a shear rate of 1–100/s.