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ELECTRICAL PROPERTIES OF CARBON NANOTUBE AND CARBON FIBER REINFORCED CEMENTITIOUS COMPOSITES

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Abstract- The addition of nano/micro scale carbon-based materials into cement-based composites is of significance for achieving reliable electrical properties in different civil engineering practices. The present study aims to disperse carbon-based materials homogenously for the improved electrical performance for non-structural functionalities. The investigation addresses the different mixing methods of carbon nanotubes (CNT) and carbon fibers (CF) on the electrical properties of cement mortars. To do this, two mixing methods for each carbon-based material were applied and the electrical properties of cement mortars were evaluated via alternating current (AC) measurements. Although both carbon-based materials were able to improve the electrical properties, CFs were more pronounced in terms of reducing the electrical resistivity values of specimens compared to CNT-based and reference specimens. It is worth noting that proposing different methods may also further enhance the electrical properties for the specific mixture design of cement-based composites.

Keywords- Carbon fibers, carbon nanotubes, cementitious mortars, electrical properties.

1 Introduction

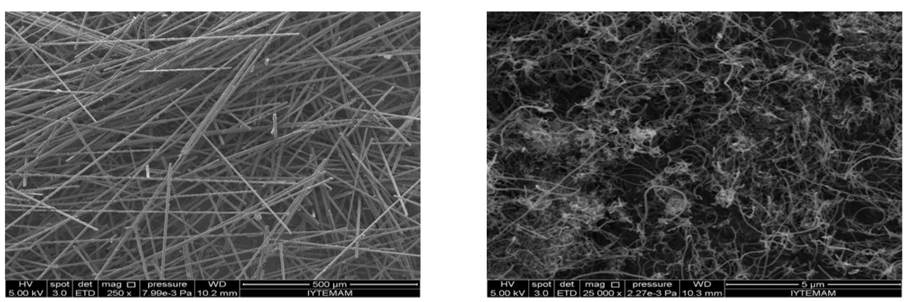
Despite the debate over the environmental effect of Portland cement [1], civil engineering industry is still in the necessity of huge amount of concrete production to sustain economic development. For different purposes, mechanical and durability performance of traditional concrete has been widely studied by researchers in terms of strength, ductility, toughness, impact resistance, environmental factors. Recently, additional efforts are given to design cement-based composites with different non-structural functionalities through maintaining or improving structural performance. For example, strain sensing, deicing, anti-static component, electromagnetic shielding applications can be integrated with the cement-based composites [2-5]. Achieving reliable non-structural functionalities is very interdependent with the best use of conductive materials. However, incorporation of the inert carbon-based materials is the initial challenge for the effective capturing of aforesaid non-structural properties. Carbon-based materials having nano/micro-scale physical properties are inert and they are in the need of homogeneous distribution within the cement matrix [6]. Unless uniform distribution is provided, pre-targeted non-structural functionalities may be improbable and weak zones may lead to inadequate mechanical performance. Several studies reported on the mechanical/electrical characterization of the cement-based composites [7-9] and the common conclusion is initially concentrated on the dispersion characteristics of the conductive fillers prior to tailoring electrical performance.

Dispersion of the nanoscale conductive fillers is interrelated with the van-der Waals forces acting upon the materials. Furthermore, synthesis of the nano conductive fillers results in entangled form and this is more prevalent for the carbon nanotubes (CNT) [10]. Besides synthesis methods, the high aspect ratio of CNTs possesses difficulties in multiphase composites such as cement-based matrices and disentanglement of CNTs becomes further challenge for efficient electrical performance. On the other hand, effective dispersion of the microscale carbon fibers (CF) is generally attributed to disentanglement instead of bundling in cement matrix. In the current study, effects of carbon fibers (CF) and carbon nanotubes (CNT) on the electrical properties of cementitious composites were investigated at curing age of 28 days. In experiments, different mixing methods were examined for each conductive filler aiming to obtain effective dispersion methods in comparison to reference mixtures. Investigations were performed basically on the electrical resistance of the specimens. Instead of laborious mixing, proposing a more practical and cost-effective mixing methods was aimed to achieve desirable electrical performance. The potential modification of the electrical performance may support the reliable use of cement-based composites having structural and non-structural abilities endowed through different carbon-based materials. For the multifunctional ability of cement-based materials, the current study deal with the novel dispersion methods for the carbon-based materials which is the initial step of the pre-targeted electrical performance. In comparison with the literature studies [8, 11-12], the current study presents new data with proposed methods comprising CNT and CF materials.

2 Experimental Procedures

2.1 Materials

Two conductive fillers used during the experimental study were carbon nanotubes (CNT) and carbon fibers (CF). CNTs had a diameter of ~10-20 nm, length of 10-30 µm and surface area of more than 200 m^2/g with the purity of %90. CFs had an aspect ratio of 800, tensile strength of 4200 MPa, elongation of 1.8% and density of around 1.76 g/cm^3. Scanning electron microscope (SEM) images of the carbon-based materials were given in Figure 1. On the other hand, traditional ingredients of the cement mortars were CEM I 42.R (PC) similar to ASTM type I, F-class fly ash (FA), silica sand having maximum aggregate 0.4 mm, and high range water reducing admixture (polycarboxyl ether-based). Nano-SiO_2 and calcium carbonate and methylcellulose-based dispersive agents were also used during the employed mixing methods. Chemical and physical properties of the PC, FA and silica sand were given in Table 1.



a) b)

Figure 1: Carbon-based materials, a. carbon fibers, and b. carbon nanotubes

Table 1. Chemical and physical properties of PC, FA and silica sand

Chemical composition	PC	FA	Silica sand
CaO (%)	61.43	1.64	34.48
SiO_2 (%)	20.77	56.22	38.40
Al_2O_3 (%)	5.55	25.34	10.96
Fe_2O_3 (%)	3.35	7.65	0.81
MgO (%)	2.49	1.80	7.14
SO_3 (%)	2.49	0.32	1.48
K_2O (%)	0.77	1.88	0.86
Na_2O (%)	0.19	1.13	0.18
Loss on ignition (%)	2.20	2.10	3.00
$SiO_2+Al_2O_3+Fe_2O_3$	29.37	89.21	50.17
Physical properties			

Specific gravity (g/cm^3)	3.10	2.31	2.60

2.2 Mixture proportions and sequence

In mixtures, water to total cementitious materials (PC+FA) ratio (W/C) and F-class fly ash to Portland cement (FA/PC) ratio were 0.26 and 1.2. In each mixture, HRWRA was used to provide adequate workable properties having 14-15 cm of mini-slump flow rate. Mixture proportions of the specimens were given in Table 2.

Table 2. Typical matrix mix design (ratios by weight)

Cement (PC)	Water	Silica Sand	F-Class Fly ash	HRWRA*	CNT	CF**
1.00	0.58	0.80	1.20	-	0.25	0.5

*: HRWRA was used based on the similar workability properties of each mixture.
**: by volume.

Two different mixing methods were performed for each carbon-based material type. In the preparation of CNT-based and CF-based cement mortars, 1st and 2nd mixing methods comprised the following sequence together with reference mixture:

- *CM/Ref:* Raw materials (PC, FA and silica sand) were mixed for 5 minutes in mortar mixer and then water and HRWRA were added gradually and 10 minutes of mixing was conducted additionally.
- *CM/CNT1:* Initially, dry mixing of raw materials (PC, FA and silica sand) was employed for 5 minutes. Then water and HRWRA were added and mixed for 10 minutes. In the separate homogenizer, 1st mixing method for the CNT-based cement mortars covered the mixing sequence of separate mixing of nano SiO_2 with CNT for 5 minutes. Then, separate mixing of CNTs was added to traditional mixing and 10 minutes of additional mixing was conducted.
- *CM/CNT2:* A separate mixing was prepared with CNT, water, HRWRA and calcium carbonate in nano/micro scale material homogenizer for 5 minutes. Then, the prepared suspension was added into ongoing dry mixing (PC, FA and silica sand) in mortar mixer and additional 10 minutes of mixing was performed in the 2nd of mixing method proposed for the CNT-based cement mortars.
- *CM/CF1:* Carbon fibers having 12 mm of length were mixed with dry raw materials (PC, FA and silica sand) for 10 minutes at 100 round per minute (rpm). Then water was added during 10 seconds into ongoing mixing and mixing speed was increased to 300 rpm after adding of HRWRA within 30 seconds. 10 minutes of mixing at 300 rpm was conducted additionally.
- *CM/CF2:* Carbon fibers having same properties in previous method were first mixed with the methylcellulose-based dispersive agent used by 0.2% of total binder. Mixing was made for 5 minutes at 100 rpm. The prepared mixing was added to ongoing raw material mixing (PC, FA and silica sand) and additional 10 minutes of mixing at 300 rpm was employed by gradual adding of HRWRA.

2.3 Testing

Produced fresh mortars reinforced with CNTs and CFs was poured into cylindrical mould having dimensions of 100^{mm} diameter and 200^{mm} length. After completion of casting, specimens were kept in molds at 50±5 relative humidity, 23±2 °C for 24 hours. After first day of curing, specimens were removed from the molds and kept in isolated bags until the curing ages of 7 and 28 days at 95±5 relative humidity, 23±2 °C. Cylindrical specimens having dimensions of 100^{mm} diameter and 200^{mm} length were cut into smaller cylindrical specimens having 100^{mm} diameter and 80^{mm} length for the electrical testing configuration. Electrical resistivity (ER) measurements were conducted using a concrete resistivity meter with uniaxial configuration similar to studies in the literature [13]. In this configuration, specimens were put into testing device and pre-saturated sponges were placed between the plates of the resistivity meter to sustain adequate electrical contact (Figure 2). The alternating current (AC) was employed with working frequency of 1 kHz to minimize the polarization effect [14]. Electrical measurements were made by calculating impedance and phase angle values and then resistivity values were made by using geometrical factors according to equation (1) given below;

$$\rho = Z * \cos(\theta) * \frac{A}{L} \qquad (1)$$

where, ρ, Z, θ, A and L stand for resistivity (Ω.m), electrical impedance (Ω), phase angle (°), cross-sectional area (m^2) and length (m) of the specimen, respectively.

Figure 2: Concrete resistivity meter (AC) and testing of the specimen

3 Results and Discussions

ER measurements of CNT and CB reinforced cement mortars are presented in Table 3. In addition to raw data given in Table 3, comparative results were also given for each carbon-based material modified cement mortars in Figure 3-4. As presented in Table 3 and Figure 3-4, ER values of the specimens showed a continuous increase from 7 days to 28 days without regard to mixing method and conductive filler type. The reason was related to the changes in the microstructure of the specimens resulting from porosity, tortuosity of pore network and pore solution [13]. The progress of hydration and pozzolanic reactions induced by fly ash may have led a substantial change in microscale level such as reducing pore solution and densification of matrix. Diminished conductive ions could be influential on the increase of the ER between 7 to 28 days of curing.

Table 3. Electrical resistivity measurements of cement mortars reinforced with CNT and CF

Mixture	7 days (Ω.m)	28 days (Ω.m)
CM/Ref	29.17	175.31
CM/CNT1	37.86	174.33
CM/CNT2	26.81	156.65
CM/CF1	13.60	41.50
CM/CF2	12.62	36.83

Figure 3 and Figure 4 indicate that incorporation of carbon-based materials was influential on the modifying of electrical properties of cement mortars. On the other hand, only CM/CNT1 mixture was not in this line at 7 days of curing compared to value of reference mixture. However, ER values of CM/CNT1 were able to present comparable results with the reference specimens at further curing (28 days). CM/CNT2 mixture had lower ER values compared to reference specimens both at 7 and 28 days. For the CF reinforced cement mortars (CM/CF1 and CM/CF2), a considerable reduction of ER values were obtained in comparison with the CNT reinforced cement mortars at 7 and 28 days. As seen from the results, CNT-bearing specimens had higher ER values and the reason can be attributed to hypothesis of nucleation occurred on the very fine surface of CNTs (around 200 m^2/g) that accelerate the formation of dense hydration products. It was likely that specimens reinforced with CNTs exhibiting higher ER values were due to lesser abundance of porosity, pore solution and tortuosity in the matrix system. On the other hand, another explanation can be given about the dispersion difference of the CNTs followed in the mixtures of CM/CNT1 and CM/CNT2. The clustering of CNTs during the mixing method of CM/CNT1 mixture may have been a disadvantage for the modifying electrical properties. For this reason, mixing method of the CM/CNT2 seemed to have more convenient dispersion for lowering the electrical resistivity of the reference specimens. (Figure 3). However, further microstructural analysis may be favorable for the precise interpretation of this finding and comparative analysis would then be possible especially between CM/CNT1 and reference mortars.

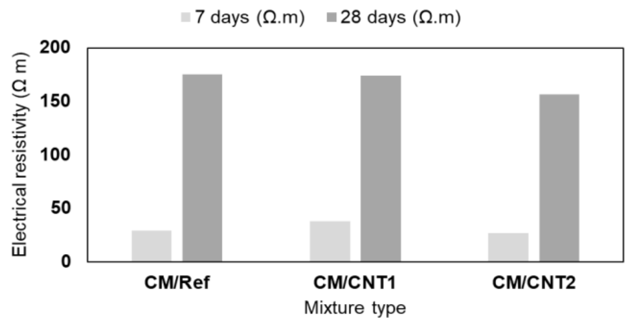


Figure 3: Electrical resistivity values of CNT reinforced cement mortars at 7 and 28 days

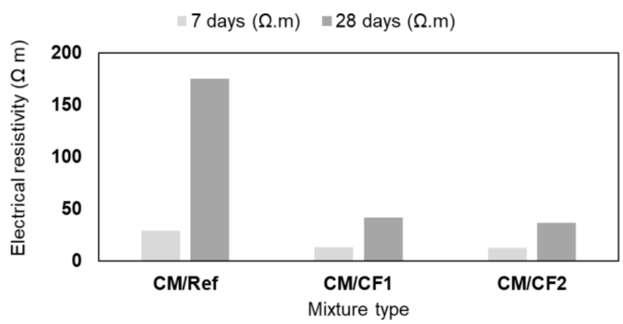


Figure 4: Electrical resistivity values of CF reinforced cement mortars at 7 and 28 days

For the CF-based cement mortars (Figure 4), it is clearly obtained that CFs were more promising in the modification of electrical performance. For example, an average of the both 7 day-old CF-based mixture (CM/CF1 and CM) was 13.11 Ω.m while it was 32.33 Ω.m and 29.17 Ω.m for the CNT-based and reference mixtures, respectively. The results imply that CF-modified specimens were able to present 55% and 59.4% lower electrical resistivity values compared to CNT reinforced and reference specimens. Similarly, average ER value of both CF-based mixtures was 76.30% and 77.66% lower than the CNT-based and reference specimens at 28 days, respectively. The advantage use of CFs can be related to longer CF fibers (aspect ratio of 1600 [12 mm]) may have provided a continuous conductive path by creating fiber-to-fiber contact [6]. Similar explanations are also available in the literature [15]. However, it is worth noting that similar testing should be addressed especially for the shorter CF fibers (3-6 mm) available in the market. The outcome of the study implies that electrical modification of the cement mortars is the first step of developing multifunctional cementitious composites which can be used in strain sensing, anti-static, thermal energy storage and deicing applications.

4 Conclusion

Following conclusions can be drawn from the conducted study:

- Two different mixing methods were applied for each mixture reinforced with CNT and CF. For the CNT-based specimens, CM/CNT2 mixing method was more promising compared to CM/CNT1 type both at 7 and 28 days. On the other hand, CNT/CM1 mixture had comparable ER values compared to reference specimens.

- Mixing methods proposed for the CFs were very promising without regard to both mixture types. A significant reduction of ER values was obtained for the CF reinforced cement mortars in contrast to CNT-based mixtures. The reduction is more pronounced particularly for CM/CF2 mixture type.

- Instead of elaborate mixing methods followed for the nanoscale carbon-based materials (herein CNT), employed mixing methods for the CFs provided practical and efficient benefits in the modification of electrical performance.

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