Contents lists available at ScienceDirect



Construction and Building Materials

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

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



IS

Hyeong Min Park^{a,1}, G.M. Kim^{b,1}, Sol Yi Lee^c, Haemin Jeon^d, Seong Yun Kim^e, Minkook Kim^a, Jae Woo Kim^{a,f,*}, Yong Chae Jung^{a,f,*}, B.J. Yang^{a,*}

^a Multifunctional Structural Composite Research Center, Institute of Advanced Composite Materials, Korea Institute of Science and Technology (KIST), 92 Chudong-ro, Bongdong-eup, Wanju-gun, Jeonbuk 55324, Republic of Korea

^b Korea Institute of Geoscience and Mineral Resources, 124 Gwahak-ro, Yuseong-gu, Daejeon 34132, Republic of Korea

^c Department of Polymer Nano Science and Technology, Chonbuk National University, 567 Baekje-daero, Deokjin-gu, Jeonbuk 54896, Republic of Korea

^d Department of Civil and Environmental Engineering, Hanbat National University, 125 Dongseo daero, Yuseong-gu, Daejeon 34158, Republic of Korea

e Department of Organic Materials and Fiber Engineering, Chonbuk National University, 567 Baekje-daero, Deokjin-gu, Jeonbuk 54896, Republic of Korea

^fDepartment of Nanomaterials and Nano Science, Korea University of Science and Technology (UST), 217 Gajeong-ro, Yuseong-gu, Daejeon 34113, Republic of Korea

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.

ARTICLE INFO

Article history: Received 28 August 2017 Received in revised form 8 December 2017 Accepted 27 December 2017

Keywords: Cement composites Pitch-based carbon fiber Electrical resistivity Viscosity Multi-walled carbon nanotube

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.

© 2017 Elsevier Ltd. All rights reserved.

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.

^{*} Corresponding authors at: Institute of Advanced Composite Materials, Korea Institute of Science and Technology (KIST), 92 Chudong-ro, Bongdong-eup, Wanjugun, Jeonbuk 55324, Republic of Korea (J.W. Kim, Y.C. Jung, and B.J. Yang).

E-mail addresses: jaewoo96@kist.re.kr (J.W. Kim), ycjung@kist.re.kr (Y.C. Jung), bj.yang@kist.re.kr (B.J. Yang).

¹ These authors contributed equally to this work.

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 Xray 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 senarately 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 \times 25 \times 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 specime 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 K α (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 ρ 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 (cm²) 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.

Table 1

Mix proportion of the specimen with variation lengths of CFs.

Specimen	CF Length	CF	CNT	Water	Cement	Silica fume	Superplasticizer
	(mm)	(g)	(g)	(g)	(g)	(g)	(g)
3L1F	3	1	3	220	1000	100	16
3L3F		3					
3L6F		6					
3L10F		10					
5L1F	5	1					
5L3F		3					
5L6F		6					
5L10F		10					
10L1F	10	1					
10L3F		3					
10L6F		6					
10L10F		10					
3L1F-C	3	1					
3L3F-C		3					
3L6F-C		6					
3L10F-C		10					
5L1F-C	5	1					
5L3F-C		3					
5L6F-C		6					
5L10F-C		10					
10L1F-C	10	1					
10L3F-C		3					
10L6F-C		6					
10L10F-C		10					

Table 2

Mix proportion of the specimen with variation of the w/c ratio.

Specimen	CF (g)	Water (g)	CNT (g)	Cement (g)	Silica fume (g)	Superplasticizer (g)
3L1F0.20W	1	200	3	1000	100	16
3L1F0.22W		220				
3L1F0.24W		240				
3L1F0.26W		260				
3L3F0.20W	3	200				
3L3F0.22W		220				
3L3F0.24W		240				
3L3F0.26W		260				
3L6F0.20W	6	200				
3L6F0.22W		220				
3L6F0.24W		240				
3L6F0.26W		260				
3L10F0.20W	10	200				
3L10F0.22W		220				
3L10F0.24W		240				
3L10F0.26W		260				
3L1F0.20W-C	1	200				
3L1F0.22W-C		220				
3L1F0.24W-C		240				
3L1F0.26W-C		260				
3L3F0.20W-C	3	200				
3L3F0.22W-C		220				
3L3F0.24W-C		240				
3L3F0.26W-C		260				
3L6F0.20W-C	6	200				
3L6F0.22W-C		220				
3L6F0.24W-C		240				
3L6F0.26W-C		260				
3L10F0.20W-C	10	200				
3L10F0.22W-C		220				
3L10F0.24W-C		240				
3L10F0.26W-C		260				

A SEM analysis (FEI, NOVA Nano SEM450) of the fracture surfaces in the cement composites was conducted for the specimens after curing them for 28 days. Through this analysis, we observed the distribution morphology and connectivity of each type of filler in the composites at a magnification level of 8–200 k (500 nm–10 μ m). A micro-CT (Bruker, SkyScan 1172) analysis was also carried out to

investigate the internal structure of the cement composites with different w/c ratios (0.20, 0.22, 0.24, and 0.26). A cylindrical specimen (ϕ 5 mm, length = 7 mm) was separately prepared for this analysis, and the measurement condition was as follows: an Al + Cu filter, voxel size of 4 K \times 2 K/3.3 μ m, 100 kVp X-rays, and object rotation angles of 360°.



Fig. 1. (a) A schematic of the mixing procedure of MWCNT/CF-embedded cement composites, (b) specimen notation method according to the combination of the material parameters, and (c) layout of the composite specimen with a copper electrode (unit: mm).

3. Results and discussion

3.1. CF characteristics

Fig. 2 presents the structure and spectroscopic characteristics of the pitch-based CF utilized in the present study. SEM images of the surface and cross-section of the CF are shown in Fig. 2(a). The figure shows a typical CF structure, in which the outer surface is smooth (or clean), with no pores observable on the fracture surfaces. The diameter distribution of the CF is approximately 10– 20 µm. A result of spectroscopic analysis performed using Raman spectra ($\lambda = 514$ nm) to confirm the structure and to search for the defectiveness in CF was shown in Fig. 2(b). The D-band (defect-induced mode) shown at the defect structure of CF was observed at 1300 cm⁻¹ and the G-band arising from the E_{2g} mode in graphite was confirmed at 1580 cm⁻¹ [35,36]. The G-band with a larger peak than the D-band indicates the typical CF structure found in general isotropic pitch-based CF [37,38].

An XPS analysis was also carried out to ascertain the presence of functional groups on the CF surface, and the results are shown in Fig. 2(c). The characteristic peak of C1s near 284.48 eV can be assigned to the sp^2 -bonded carbon atoms, while the broad peak at 286.2 eV originates from the sp^3 -bonded carbon atoms (i.e., dan-

gling bonds) [39,40]. In addition, the peak intensity of —COOH, and —C—O— at the binding energy of 288.5 and 286.2 eV indicate a substantial introduction of oxygen-containing functional groups on the outer surface of the CF. Also, Binding energy corresponding to O1s at 531.5 eV and 533 eV, which are ascribed C=O and C—OH on the outer surface of the CF. It was confirmed that the carbon content was 82.35% of the total; the oxygen content was 17.25% and a small amount of nitrogen was found at 0.4% on the surface of the CF. From these results, it can be concluded that the pitchbased CF used in this study is a pure CF material.

3.2. Electrical characteristics of composites

Figs. 3 and 4 present the electrical resistivity of the cement composites according to the length of the CF and the w/c ratio, respectively. For the specimen containing only CF, the resistivity exceeded $10^5 \Omega$ -cm regardless of the length of the CF (Fig. 3(a)). It was reported in previous studies that the electrical resistivity of cement composites with CFs was lower than 500 Ω -cm when the amount of the CF exceeded a percolation threshold (>1.5 wt %) [13]. The percolation threshold indicates that the electrically conductive fillers contained in a composite are continuously connected, leading to a significant reduction in the electrical resistivity



Fig. 2. Analysis results of the pitch-based CF used in the experiment: (a) SEM, (b), Raman spectroscopy, and (c) XPS analyses.



Fig. 3. Electrical resistivity outcomes of cement composites according to the variation length of the CF for specimens containing (a) CF and (b) MWCNT and CF.

of the composite [41,42]. Hence, an increase in the CF content did not clearly contribute to the reduction of the electrical resistivity of the composites in the present study because the CF contents added to the composites did not reach the percolation threshold value. In contrast, when MWCNTs were incorporated into the specimen together with CFs, it was confirmed from Fig. 3(b) that the resistivity was significantly reduced compared to that of the specimen using only CFs. Furthermore, the resistivity tends to decrease as the incorporated amount of CF increases. The effect of the CF length on the resistivity of the composites, however, did not show a clear trend, even for the specimens containing both MWCNT and CF (See, Fig. 3(a) and (b)).

Fig. 4 shows the electrical resistivity of the specimens with varying w/c ratios according to the curing age. It is well known that the electrical resistivity of cement composites containing conductive fillers is determined by the homogeneity of the filler network and the presence of an electrolytic pore solution [43]. According to the references [15,44], when the electrically conductive pathways in cement composites with electrically conductive fillers are not homogenous, the electrolytic pore solution. The pore solution in the 3L1F-C specimen possibly caused polarization and depolarization effects, thereby fluctuating the electrical resistivity.

For the specimens containing only CFs, it can be observed in Fig. 4(a) and (b) that the resistivity of the cement composites increased over time. This phenomenon likely stems from the effect of the electrolytic pore solution on the electrical resistivity of the composites, which increases when the electrically conductive



Fig. 4. Electrical resistivity outcomes of composites with w/c ratios of: (a) 0.20, (b) 0.22, (c) 0.24, and (d) 0.26.

pathways consisting of only CFs are not homogenous. The conductive network, consisting of CFs and the pore solutions, becomes more discontinuous as the electrolytic pore solution evaporates, leading to an increase in the electrical resistivity of the composites (Fig. 5(a)) [12]. Meanwhile, for the specimens with a w/c ratio of more than 0.24, the resistivity tends to increase sharply from 14 to 28 days. This occurs due to the presence of a sufficient amount of electrolytic pore solution in the composite to form a conductive network for up to 14 days. However, after 14 days, the electrolytic pore solution constituting the conductive network becomes mostly evaporated, causing damage to the conductive pathways in the composites. Consequently, a rapid increase in the electrical resistivity of the composites occurs.

For the composites containing both MWCNT and CF, an increase in the w/c ratio did not clearly affect the electrical resistivity, indicating that the electrical resistivity of the composites was less affected by the electrolytic pore solution because a homogeneous conductive network consisting of MWCNTs and CFs had already formed in the matrix. However, the influence of pore were also considered to be an important issue, and should be studied further in the future. It is also shown in Fig. 4(a–d) that the resistivity of the composites mixed with MWCNT and CF tended to decrease with the curing age. It was reported in previous studies that a growth of hydrates induced by hydration reaction may redistribute the fillers in the matrix of electrically conductive cement composites, which in turn reduces the electrical resistivity of the composites [45]. That is, this outcome is attributable to the formation of hydration products during the curing process, which lead to the redistribution of the conductive fillers (Fig. 5(b)) [45].

The synergistic effects of MWCNT and CF in the cement matrix can be explained by the experimental data illustrated in Fig. 4. The first synergistic effect was that the decrease in the resistivity of MWCNT-incorporated composites was more pronounced as the content of CF increased. Regardless of the w/c ratio, there was a more positive response when CF and MWCNT were used together than with MWCNT alone in all cases. Experimental evidences with

<u>Cement composites with CFs</u>





Fig. 5. Schematic descriptions of the variation of the electrical resistivity for cement composites (a) with CFs and (b) with MWCNT and CFs.

similar mechanisms have been published, and a more detailed description can be found in [22,23]. Herein, a direct comparison of the MWCNT/CF-incorporated composites with the composites containing only MWCNTs is not included since they are sufficiently comparable through the papers published previously [15,22,23,27,46]. With the same amount of MWCNT, it is obvious that the case where MWCNT and CF are mixed together into the composites is superior to the case where only MWCNT is used [22].

3.3. Synergetic effects between MWCNTs and CFs

Fig. 6 shows the viscosity results of the cement composites with MWCNTs and CFs. The test results show that the viscosity of the composites decreased with an increase the w/c ratio. Specifically, when the w/c ratio was 0.22, the viscosity is significantly reduced compared to that of the composite with a w/c ratio of 0.20. Nam

et al. [47] reported that as the w/c ratio increases, the connectivity of MWCNT in the matrix deteriorates significantly, which in turn simultaneously increases the flowability and the electrical resistivity of the composites. Based on the literature, it is presumable that an increase in the w/c ratio increased the distance among the MWCNTs, thereby leading to a decrease in the viscosity of the mixture [24]. In contrast, interlocking of the MWCNT particles in the composite occurred when the w/c ratio was lower than 0.22, leading to an increase in the viscosity. Meanwhile, it was reported that the rheological properties of cement materials with CFs were significantly affected when the content of CFs exceeded 1.0 wt% [48]. The content of CFs in this test was 0.1 wt%, indicating that the viscosity of the composites here is likely affected mainly by the MWCNT content. The second evidence of synergistic effect is that the resistivity of composites was maintained even with increasing w/c ratio. As the result, the change of resistivity was



Fig. 6. Viscosity results of the MWCNT and CF-embedded cement composites with 0.3 wt% of MWCNT and 0.1 wt% of CF.

minimized even though the viscosity decreased by 80.4% compared with the normal specimen as shown in Fig. 6.

Fig. 7 shows SEM images of the composite with MWCNT and CF. Fig. 7(a) illustrates that the conductive network was well constructed with MWCNT particles when the w/c ratio was 0.20; whereas the MWCNTs were more agglomerated when the w/c ratio used was 0.26 (Fig. 7(b)). In previous studies, it was observed that an increase in the w/c ratio increased the micro-sized pores that can act as a site in which the CNT agglomerates settle down [27]. Meanwhile, it can be observed in Fig. 7(b) that the CF connected the MWCNT agglomerates, consequently helping to maintain the homogeneity of the conductive network in the matrix. In summary, although the connectivity between the MWCNT particles was reduced by increasing the w/c ratio, the incorporation of CFs into the MWCNT-embedded cement composite caused a bridging effect between the MWCNTs and the CFs, thus improving the homogeneity of the conductive network in the composites. By considering the scale difference between MWCNT ($l_{MWCNT} = 30-45$ µm) and CF ($l_{CF} = 3-10$ mm), the agglomerated MWCNT particles in the cement can be bridged by CF penetration, and the related mechanisms were represented in Fig. 7.

Fig. 8 shows the results of micro-CT analyses of cement composites with various w/c ratios. Due to the limitations of the equipment available for use, we could observe the internal structures of the specimens only on the microscale. It is thus difficult to analyze the effect of CNT incorporation into the cement composites. However, the difference in the internal structure with respect to w/cratio, which was the object under analysis, could be observed, as shown in Fig. 8(a-d). It was found that black spots, considered to be voids, occur at a higher frequency in the composite as the w/c ratio increases. These pores increase as the w/c ratio increases due to the correlation between the moisture and the electrolytic pore solution, as shown in Fig. 5. Fig. 8(e) shows the volume fraction of void in the specimens with respect to w/c ratio measured by micro-CT. It is observed that the amount of void increases linearly as the w/c ratio increases. Internal voids are expected to have a negative effect on the electrical resistivity of these composites; however, the incorporation of CF serves to prevent this phenomenon. This is in accordance with the mechanism of the material described above.

Through previous studies [15,22,23,27,46], it have found that MWCNT-incorporated cement composites are very sensitive to



(b)

Fig. 7. SEM images of specimen: (a) conductivity network of the CNT/CF- embedded cement composite with a w/c ratio of 0.20 (3L1F0.20W-C) and (b) connections between CF and CNT particles within the specimen with a w/c ratio of 0.26 (3L1F0.26W-C).



Fig. 8. Micro-CT analysis results of the cement composites with different w/c ratios: (a) 0.20, (b) 0.22, (c) 0.24, (d) 0.26, and (e) measured porosity values.

w/c ratios, and increasing the w/c ratio deteriorate the resistivity of cement composites significantly. It should be noted that various cement composites incorporating CF and CNT were fabricated and evaluated in the present study, and meaningful values of electrical resistivity was confirmed at a relatively low viscosity.

4. Conclusions

This paper presents an experimental study of cement composites containing MWCNT and CF in an effort to resolve various obstacles of the conductive construction materials. With the addition of pitch-based CF, the utilization amount of MWCNT could be reduced, which promoted better viscosity and greater economic efficiency. In order to clarify the mechanism proposed in this study, SEM and micro-CT analyses of cement composites were carried out. It was observed that the incorporation of CFs into MWCNTembedded cement composites causes the CFs to bridge the CNT particles, thus maintaining the homogeneity of the conductive network in the composites.

There are various economical and functional fillers have recently been developed in the field of materials science, and the synergistic effects induced by the combinations of fillers should be studied. However, this is too broad to be covered in the present study and will present a new study for the future. In addition, the focus of this study is on the improvement of the electrical conductivity of cement paste level, and it is the previous stage of concrete which aggregate is mixed. The addition of coarse aggregates that is non-conductive materials can significantly deteriorate the connectivity between the electrically conductive fillers, thereby increasing the electrical resistivity of the cement composites. This is attributed that the aggregates can act as an insulation gap in the cementitious composites. Thus, it is beyond the scope of the present paper; however we plan to extend our work along this direction in the near future.

Acknowledgements

We thank Jungmin Lee at Jeonju University, Gookhwan Lee at Chonnam National University, and Jaehwan Lee at Chonbuk National University for assistance of the experiments.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.conbuildmat.2017. 12.205.

References

- L. Hollaway, The evolution of and the way forward for advanced polymer composites in the civil infrastructure, Constr. Build. Mater. 17 (6) (2003) 365– 378.
- [2] B. Yang, B. Kim, H. Lee, Micromechanics-based viscoelastic damage model for particle-reinforced polymeric composites, Acta Mech. 223 (6) (2012) 1307.
- [3] D. Snoeck, N. De Belie, From straw in bricks to modern use of microfibers in cementitious composites for improved autogenous healing–A review, Constr. Build. Mater. 95 (2015) 774–787.
- [4] P.M. Vitousek, H.A. Mooney, J. Lubchenco, J.M. Melillo, Human domination of Earth's ecosystems, Science 277 (5325) (1997) 494–499.
- [5] C.J. Kibert, Sustainable Construction: Green Building Design and Delivery, John Wiley & Sons, 2016.
- [6] G.Y. Li, P.M. Wang, X. Zhao, Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes, Carbon 43 (6) (2005) 1239–1245.
- [7] M.S. Konsta-Gdoutos, Z.S. Metaxa, S.P. Shah, Highly dispersed carbon nanotube reinforced cement based materials, Cem. Concr. Res. 40 (7) (2010) 1052–1059.
- [8] X. Fu, D. Chung, Effect of polymer admixtures to cement on the bond strength and electrical contact resistivity between steel fiber and cement, Cem. Concr. Res. 26 (2) (1996) 189–194.
- [9] B. Yang, Y. Hwang, H. Lee, Elastoplastic modeling of polymeric composites containing randomly located nanoparticles with an interface effect, Compos. Struct. 99 (2013) 123–130.
- [10] B. Yang, S. Ha, S. Pyo, H. Lee, Mechanical characteristics and strengthening effectiveness of random-chopped FRP composites containing air voids, Compos. B Eng. 62 (2014) 159–166.
- [11] S. Fallah, M. Nematzadeh, Mechanical properties and durability of highstrength concrete containing macro-polymeric and polypropylene fibers with nano-silica and silica fume, Constr. Build. Mater. 132 (2017) 170–187.
- [12] H. Lee, S. Song, Influence of fiber volume fraction and fiber type on mechanical properties of FRLACC, J. Reinf. Plast. Compos. 29 (7) (2010) 1089–1098.
- [13] B. Chen, K. Wu, W. Yao, Conductivity of carbon fiber reinforced cement-based composites, Cem. Concr. Compos. 26 (4) (2004) 291–297.
- [14] H. Kim, I. Nam, H. Lee, Enhanced effect of carbon nanotube on mechanical and electrical properties of cement composites by incorporation of silica fume, Compos. Struct. 107 (2014) 60–69.
- [15] G.M. Kim, S.M. Park, G.U. Ryu, H.K. Lee, Electrical characteristics of hierarchical conductive pathways in cementitious composites incorporating CNT and carbon fiber, Cem. Concr. Compos. 82 (2017) 165–175.
- [16] B. Yang, K. Cho, G. Kim, H. Lee, Effect of CNT agglomeration on the electrical conductivity and percolation threshold of nanocomposites: a micromechanicsbased approach, Comput. Model Eng. Sci. 103 (5) (2014) 343–365.
- [17] H. Jeon, J. Yu, H. Lee, G. Kim, J.W. Kim, Y.C. Jung, C.-M. Yang, B. Yang, A combined analytical formulation and genetic algorithm to analyze the nonlinear damage responses of continuous fiber toughened composites, Comput. Mech. (2017) 1–16.
- [18] I. Nam, H. Lee, Synergistic effect of MWNT/fly ash incorporation on the EMI shielding/absorbing characteristics of cementitious materials, Constr. Build. Mater. 115 (2016) 651–661.
- [19] T. Ji, X. Zhang, W. Li, Enhanced thermoelectric effect of cement composite by addition of metallic oxide nanopowders for energy harvesting in buildings, Constr. Build. Mater. 115 (2016) 576–581.

- [20] G.Y. Li, P.M. Wang, X. Zhao, Pressure-sensitive properties and microstructure of carbon nanotube reinforced cement composites, Cem. Concr. Compos. 29 (5) (2007) 377–382.
- [21] H. Souri, J. Yu, H. Jeon, J.W. Kim, C.-M. Yang, N.-H. You, B. Yang, A theoretical study on the piezoresistive response of carbon nanotubes embedded in polymer nanocomposites in an elastic region, Carbon 120 (2017) 427–437.
- [22] G. Kim, F. Naeem, H. Kim, H. Lee, Heating and heat-dependent mechanical characteristics of CNT-embedded cementitious composites, Compos. Struct. 136 (2016) 162–170.
- [23] G. Kim, B. Yang, G. Ryu, H. Lee, The electrically conductive carbon nanotube (CNT)/cement composites for accelerated curing and thermal cracking reduction, Compos. Struct. 158 (2016) 20–29.
- [24] H. Kim, I. Park, H. Lee, Improved piezoresistive sensitivity and stability of CNT/ cement mortar composites with low water-binder ratio, Compos. Struct. 116 (2014) 713–719.
- [25] A. Bright, L. Singer, The electronic and structural characteristics of carbon fibers from mesophase pitch, Carbon 17 (1) (1979) 59–69.
- [26] M. Endo, Structure of mesophase pitch-based carbon fibres, J. Mater. Sci. 23 (2) (1988) 598–605.
- [27] G. Kim, B. Yang, K. Cho, E. Kim, H. Lee, Influences of CNT dispersion and pore characteristics on the electrical performance of cementitious composites, Compos. Struct. 164 (2017) 32–42.
- [28] S. Wen, D. Chung, Carbon fiber-reinforced cement as a thermistor, Cem. Concr. Res. 29 (6) (1999) 961–965.
- [29] D. Chung, Cement reinforced with short carbon fibers: a multifunctional material, Compos. B Eng. 31 (6) (2000) 511–526.
- [30] M. Chiarello, R. Zinno, Electrical conductivity of self-monitoring CFRC, Cem. Concr. Compos. 27 (4) (2005) 463–469.
- [31] F. Azhari, N. Banthia, Cement-based sensors with carbon fibers and carbon nanotubes for piezoresistive sensing, Cem. Concr. Compos. 34 (7) (2012) 866– 873.
- [32] ASTM C 109, Standard Test Method for Compressive Strength of Hydraulic Cement Mortars, ASTM, West Conshohocken (PA), 2007.
- [33] ASTM D257-07, Standard Test Method for DC Resistance or Conductance of Insulating Materials, ASTM, West Conshohocken (PA), 2007.
- [34] ASTM B 193-02, Standard test Method for Resistivity of Electrical Conductor Materials, ASTM, West Conshohocken (PA), 2002.
- [35] M. Dresselhaus, P. Eklund, Phonons in carbon nanotubes, Adv. Phys. 49 (6) (2000) 705–814.
- [36] F. Tuinstra, J.L. Koenig, Raman spectrum of graphite, J. Chem. Phys. 53 (3) (1970) 1126–1130.
- [37] X. Jin, Q.Q. Ni, Y. Fu, L. Zhang, T. Natsuki, Electrospun nanocomposite polyacrylonitrile fibers containing carbon nanotubes and cobalt ferrite, Polym. Compos. 33 (3) (2012) 317–323.
- [38] T. McNally, P. Pötschke, P. Halley, M. Murphy, D. Martin, S.E. Bell, G.P. Brennan, D. Bein, P. Lemoine, J.P. Quinn, Polyethylene multiwalled carbon nanotube composites, Polymer 46 (19) (2005) 8222–8232.
- [39] H. Ago, T. Kugler, F. Cacialli, W.R. Salaneck, M.S. Shaffer, A.H. Windle, R.H. Friend, Work functions and surface functional groups of multiwall carbon nanotubes, J. Phys. Chem. B 103 (38) (1999) 8116–8121.
- [40] H. Murphy, P. Papakonstantinou, T.T. Okpalugo, Raman study of multiwalled carbon nanotubes functionalized with oxygen groups, J. Vac. Sci. Technol. B Microelectron. Nanometer Struct. Process. Meas. Phenom. 24 (2) (2006) 715– 720.
- [41] D. Chung, Self-heating structural materials, Smart Mater. Struct. 13 (3) (2004) 562.
- [42] J. Xu, W. Yao, R. Wang, Nonlinear conduction in carbon fiber reinforced cement mortar, Cem. Concr. Compos. 33 (3) (2011) 444–448.
- [43] T. Wu, R. Huang, M. Chi, T. Weng, A study on electrical and thermal properties of conductive concrete, Comput. Concr. 12 (3) (2013) 337–349.
- [44] J. Cao, D. Chung, Electric polarization and depolarization in cement-based materials, studied by apparent electrical resistance measurement, Cem. Concr. Res. 34 (3) (2004) 481–485.
- [45] Y. Song, Q. Zheng, Conduction stability of high-density polyethylene/carbon black composites due to electric field action, Eur. Polym. J. 41 (12) (2005) 2998–3003.
- [46] G. Kim, I. Nam, H. Yoon, H. Lee, Effect of superplasticizer type and siliceous materials on the dispersion of carbon nanotube in cementitious composites, Compos. Struct. (2017).
- [47] I. Nam, H. Souri, H. Lee, Percolation threshold and piezoresistive response of multi-wall carbon nanotube/cement composites, Smart Struct. Syst. 18 (2015) 217–231.
- [48] S. Park, B. Lee, Y. Lim, Experimental study on the engineering properties of carbon fiber reinforced cement composites, Cem. Concr. Res. 21 (4) (1991) 589–600.