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Synergistic effect of MWNT/fly ash incorporation on the EMI shielding/absorbing characteristics of cementitious materials

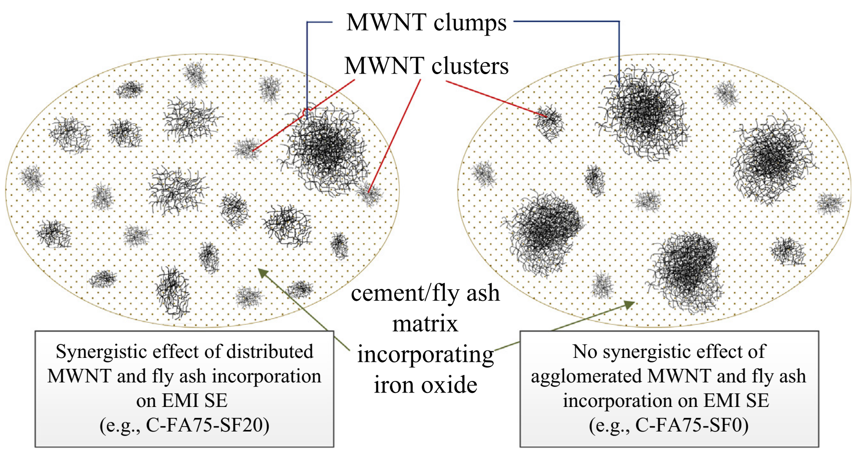
I.W. Nam, H.K. Lee *

Department of Civil and Environmental Engineering, Korea Advanced Institute of Science and Technology, 291 Daehak-ro, Yuseong-gu, Daejeon 34141, South Korea

HIGHLIGHTS

- A specimen consisting of CNT 0.6%, SF 20%, and FA 75%, exhibited the best EMI SE.
- Synergistic effect in EMI SE was attributed to CNT network and Fe_2O_3 in the matrix.
- The computational simulation work corresponded to the experimental EMI SE results.

GRAPHICAL ABSTRACT



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ABSTRACT

The present study aims to develop electromagnetic interference (EMI) shielding materials of which the EM wave shielding/absorbing capabilities were enhanced by a synergistic effect of multi-wall carbon nanotube (MWNT) and fly ash (FA) in terms of EM characteristics. The MWNT/FA-added cementitious materials were fabricated with various content ratios of FA and silica fume (SF). SF was incorporated as a dispersion agent of MWNT and EMI shielding effectiveness (SE) of the cementitious materials was assessed in an effort to determine optimum content ratios of FA and SF. The best EMI SE was achieved by the specimen comprised of MWNT 0.6%, SF 20%, and FA 75% (C-FA75-SF20) as exhibiting $-8.0 \sim -57.1$ dB at a frequency range from 1 to 18 GHz, indicating a synergistic effect of MWNT and FA. The superior EMI SE of the C-FA75-SF20 was assessed by three different tests, i.e., SEM observation, energy-dispersive X-ray spectroscopy analysis, and electrical & electromagnetic properties evaluation. Furthermore, a computational simulation work demonstrated that the experimental EMI SE results of the C-FA75-SF20 correspond to the simulation results.

1. Introduction

The role of electromagnetic interference (EMI) shielding is to shield and/or absorb electromagnetic waves emanating from electronic facilities, digital devices, etc. [1]. Such shielding is accomplished by using materials with high electrical conductivity or high permeability [2,3]. Electromagnetic waves radiating from electronic facilities and devices may interfere with adjacent electronics [2]. Similarly, the electromagnetic pulse (EMP) caused by a nuclear bomb can destroy any type of electronic device comprising electric circuits [2]. EMI shielding is also crucial to prevent

* Corresponding author.
E-mail address: leeh@kaist.ac.kr (H.K. Lee).

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military or corporate spy attacks aimed at gaining important information [2]. In this regard, EMI shielding is becoming a more important issue as electronics become more widely and repeatedly used not only in our living environments but also in industrial, military, and scientific fields [4].

Metallic EMI shielding materials such as steel, aluminum, copper, nickel, etc., are widely used to protect sensitive materials from electromagnetic waves, mainly on the basis of high reflectance attained by the impedance difference between air and the metal media [3]. However, high cost, heavy weight, and poor processability impede their application [4]. To overcome these disadvantages of metallic EMI shielding materials, carbon materials such as carbon fibers, cokes, graphite, carbon black, etc., have been utilized [5,6]. Among these carbon materials, carbon nanotubes (CNTs) have been suggested as an EMI shielding material since their high aspect ratio and electrical current density can endow CNT-added composite materials with high electrical conductivity [7]. For application of CNTs to EMI shielding materials, however, there are two primary obstacles: high cost and poor dispersion of CNTs in binding materials such as cement, one of the main construction materials throughout the world [8]. Recently, due to automated-mass production and competition among production companies, the cost of CNTs has been steadily decreasing, to cents per gram [9]. The dispersion of CNTs in binding materials has also been improved using various approaches such as polymerization, mixing with nano scale silica powder, etc. [8,10]. Accordingly, commercial production of CNT-added EMI shielding materials with low cost and good dispersion in binding materials is becoming feasible.

The EMI shielding by carbon material-added cementitious materials has been extensively researched; the following are some notable studies relevant to the present work. Fu and Chung (1996) attained EMI shielding effectiveness (SE) of 26.4 dB at 1.0 GHz with a cement matrix material incorporating carbon filament (0.1 mm in diameter) content of 0.54 vol.% [11]. Zornoza et al. (2010) reported EMI SE of 15 dB at 1.0 GHz with a carbon fiber-added cement matrix material incorporating carbon fiber (15 μm in diameter and 3 mm in length) content of 0.5 wt.% [12]. They also reported a synergistic effect on the EMI SE with the incorporation of carbon fiber in cement with fly ash (FA) [12]. The synergistic effect was enhanced as the aspect ratio of the carbon fiber added in the cement matrix materials increased [12]. On the other hand, a cementitious material with CNT was recently fabricated as an EMI shielding material and it can be found in the literature including previous works of the authors [10,13,14]. Nam et al. (2012) obtained a value of SE of 8 dB at 5.0 GHz using a cementitious material with CNT content of 0.6 wt.% and, as a dispersion agent, silica fume (SF) of 20 wt.% [10]. In addition, Micheli et al. (2014) reported EMI SE of 19 dB at 1 GHz using concrete composite incorporating CNT content of 2 wt.% [14].

The endeavors to enhance the EMI shielding capability of composite materials are a recent spotlighted subject and it can be accomplished by combined use of promising EMI shielding materials such as CNT and FA [15]. However, examination on EMI shielding characteristics of composite materials with CNT and FA, and verification on the combined use of them were scarcely reported.

The present work was carried out to determine the influence of FA incorporation in CNT-added cementitious materials on the EMI SE and to explain the variation of the EMI SE according to the ratios of SF and FA content [15]. FA was incorporated as a replacement for cement at 0%, 25%, 50%, and 75% of the sum of cement and FA weight [16]. SF was added as a CNT-dispersion agent in the cementitious materials at 0%, 10%, 20%, and 30% for each FA replacement ratio [16]. The fractured surfaces of the cementitious materials were observed via SEM in an effort to understand MWNT distribution, and the elemental compositions of the specimens were analyzed using EDS (Energy-Dispersive X-ray Spectroscopy) in an effort to figure out variations of chemical compositions of matrices in the specimens due to FA additions. The electromagnetic characteristics of the specimens were assessed in terms of scattering parameters (S parameters) by means of a network analyzer operated in conjunction with the coaxial transmission method [15]. AC conductivity of the specimens was extracted from S parameters and compared between specimen types in an effort to understand the CNT distribution. A comparison of the EMI SE calculated from S parameters was also made with regard to specimen types, and the maximum EMI SE was verified by means of a simulative work.

2. Materials and fabrication procedures

2.1. Materials and mix proportions

Multi-walled carbon nanotubes (MWNT), tap water, ordinary Portland cement, FA, SF, nylon fiber, and a super-plasticizer were used as constituent materials. The MWNTs processed by the chemical vapor deposition (CVD) method as used here were a proprietary product of Hyosung Inc. Their diameter and length were 16 ± 3.6 nm and 5 ∼ 20 μm, respectively. Type I Portland cement and F-Class FA were used. SF, a proprietary product of Elkem Inc. (EMS-970D) and 3 mm-long nylon fibers, a proprietary product of Nycon Fibers Inc. (NYMAX), were utilized. The super-plasticizer used here, a proprietary product of BASF Pozzolith Ltd. (Rheobuild SP8HU), was a polycarboxylic acid-based plasticizer [10]. In particular, on the basis of findings of the previous study, SF was used to enhance MWNT dispersion [10] and the chemical compositions of SF are listed in Table 1. A major chemical component of the SF was SiO_2 reaching content ratio of 90.7%; SF particles with diameters of less than 45 μm account for a minimum of 90% of the SF [16]. The specific gravity of SF, and its surface area, are 2.20 and 19,620 m^2/kg (BET), respectively. In addition, the chemical compositions of FA are also shown in the Table 1 and the specific gravity and surface area of FA are 2.38 and 290 m^2/kg (Blaine), respectively. The chemical composition of cement followed the typical composition of type I Portland cement, as can be found in the literature (e.g., Kim et al. (2012)) [17].

A total of twenty-four specimens were prepared with varying weight ratios of their constituent materials, as shown in Table 2 [15]. Eight specimens that have FA or SF and do not have MWNT in the mixtures, shown in the top four rows and bottom four rows of Table 2, were fabricated for comparison [15].

The specimens can be mainly classified into two groups according to the presence of MWNT. Specimens with MWNTs correspond to the experimental group and the remaining specimens comprise the control group. The mix variables in the experimental group were the content ratios of FA and SF.

The content ratio of MWNT was set at 0.6% of sum of cement and FA weight according to a previous work done by the authors [10,16]. It was possible to attain effective EMI SE with the addition of 0.6% MWNT and other materials [10]. To find the optimum content ratios of SF and FA, SF was added at three different weight

Table 1
Chemical compositions of SF and FA by weight (%).

Chemical component	Silica fume (SF)	Fly ash (FA)
CaO	1.30	2.60
Al_2O_3	4.00	33.00
SiO_2	90.70	46.00
Fe_2O_3	1.09	10.50
K_2O	2.00	–
SO_3	–	–
MgO	–	–
Cr_2O_3	1.30	