



Autogenous shrinkage and electrical characteristics of cement pastes and mortars with carbon nanotube and carbon fiber

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HIGHLIGHTS

- Flow of cement pastes with CNT and CF was reduced as the CNT content increased.
- The addition of CNT to the cement pastes inhibited the hydration reaction.
- Compressive strength of pastes at 24 h was reduced as the CNT content increased.
- Incorporation of CNT and CF reduced the autogenous shrinkage of cement pastes.
- CF incorporation mitigated an adverse effect of aggregate on electrical resistivity.

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ABSTRACT

The autogenous shrinkage and electrical characteristics of cement pastes and mortars incorporating carbon nanotube (CNT) and carbon fiber (CF) were investigated in this study. The dispersion agents for the CNT and CF were polycarboxylate-type superplasticizer and silica fume, respectively. The electrical characteristics of the pastes and mortars were investigated by means of the two-probe method, while the autogenous shrinkage characteristics of the cement pastes and mortars were discussed in the light of the reaction characteristics of cement particles. The effects of the replacement ratio of the CF to CNT, the length of CF, and the fine aggregate content on the autogenous shrinkage and electrical characteristics of the cement pastes and mortars were examined. The test results showed that the CNT addition inhibited the hydration reaction at an early stage of curing, thereby reducing the autogenous shrinkage of the pastes and mortars. The addition of CF mitigated an adverse effect of the addition of fine aggregates on the electrical resistivity of the mortars.

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1. Introduction

Carbon nanotube (CNT) is a representative carbonaceous nanomaterial which has outstanding mechanical, electrical properties and high chemical stability [39,24,16]. The C atoms in CNT consist of C—C bonds with an angle of 120°, making its Young's modulus approximately 1.0–1.8 TPa [43]. The electrical conductivity of CNT is similar to those of metallic materials due to the presence of weak π bonds on the z plane [43]. The seamless structure of CNT contributes to its high chemical stability [40]. Studies on the application of CNT in cementitious composites were initiated in the early 2000s [11]. Many researchers initially focused on the applicability of CNT to improve the mechanical properties of

cementitious composites and the focus shifted to investigations of the electromagnetic interference shielding, heating and piezoresistive sensing properties of the composites, utilizing the semiconductor-like electrical conductivity of the composites [16,20,21,28,32,33].

Recently, few researchers have attempted to improve the electrical conductivity by adding carbon fiber (CF) to cementitious composites incorporating CNT [4,19,48,36]. Azhari and Banthia reported that the addition of CF and CNT at rates of 15.0% and 1.0%, respectively, to cementitious composites significantly increased the electrical conductivity and improved the piezoresistive properties [4]. Kim et al. investigated the influence of CF on the homogeneity of conductive pathways in cementitious composites incorporating CNT and reported that the addition of CF to the composites improved the electrical stability by forming hierarchical conductive networks [19]. However, the effects of different

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variables such as the replacement ratio of CF to CNT and length of CF are rarely investigated.

Meanwhile, the autogenous shrinkage of cementitious composites incorporating CNT and CF may be serious, since the composites generally do not include aggregates to ensure homogeneity of electrically conductive pathways [15,35]. The addition of fine aggregate can adversely affect the connectivity of electrically conductive fillers such as CNT and CF in cementitious composites, thereby increasing the electrical resistivity [17]. Minimization of w/c ratio is also desirable to form homogenous conductive pathways in cementitious composites [15,35]. However, hardened cement with w/c ratio often suffers from a serious autogenous shrinkage [42,45]. Furthermore, the addition of CNT, given that it is a nanomaterial, can affect the hydration reaction characteristics of cement particles, and the reinforcing effect of CNT and CF may affect the autogenous shrinkage characteristics [31,12]. Although the autogenous shrinkage characteristics of cementitious composites incorporating CNT, which can be used as functional materials as well as high-performance construction materials, is of important factors to apply these materials in practical sites, relevant studies conducted are few in number.

The electrical and autogenous shrinkage characteristics of cement pastes and mortars incorporating CNT and CF were investigated in the present study. The dispersion agents for the CNT and CF were polycarboxylate-type superplasticizer and silica fume. Specifically, the effects of the replacement ratio of the CF to CNT, the length of CF, and the fine aggregate content on the autogenous shrinkage and the electrical characteristics of the cement pastes and mortars were examined. The autogenous shrinkage characteristics of the cement pastes and mortars were discussed in the light of the reaction characteristics of cement particles. The electrical characteristics were investigated by means of the two-probe method.

2. Experimental program

2.1. Sample preparation

Ordinary Portland cement was used as a binder material. The dispersion agents used here were silica fume and a polycarboxylate-based superplasticizer. The specific gravity and

specific surface area of the silica fume (Elkem Inc. (EMS-970)) were 2.1 and 15.0 m²/g, respectively, while its diameter ranged from 100 to 200 nm. The fine aggregate used to fabricate the mortar specimens was standard sand as described in ASTM C778 [3]. Electrically conductive fillers were the multi-walled CNT (produced by Hyosung Inc. Korea) and PAN-based CF (produced by ACE &Tech, Ltd). The purity of the multi-walled CNT was approximately 95% and the specific gravity, length and diameter were 1.32, 10 μm and in the range of 12–40 nm, respectively. The specific gravity and diameter of the CF were 1.82 and 7.2 μm, respectively.

The mix proportion of the cement pastes and mortars incorporating CNT and CF is shown in Table 1. Independent variables were the replacement ratio of CF to CNT, the length of CF, and the fine aggregate content. The CNT was replaced with CF from 0% to 50% by weight of the CNT and the length of CF was varied from 3 mm to 12 mm. The fine aggregate content used to fabricate the mortar specimens was varied from 0% to 150% by weight of the cement. The amounts of silica fume and the superplasticizer added to all mixtures were fixed at 10.0% and 1.6% by the weight of cement, respectively. The paste and the mortar specimens used to measure the electrical resistivity were cast into cubic molds 50 mm × 50 mm × 50 mm in size, while the specimens used to measure the autogenous shrinkage were cast into the prism molds with dimensions of 25 mm × 25 mm × 285 mm in accordance with ASTM C490 [1]. The mixing sequence to produce the specimens was as follows: The dry materials (cement, silica fume, CNT, CF and fine aggregate) were mixed for 1 min, after which the water and superplasticizer were added for further mixing for 5 min. The fresh mixtures were then cast into the molds. To measure the electrical resistance of the composites, two copper electrodes covered with silver paste to reduce the contact resistance between the electrodes and the cementitious composites were inserted into the cubic specimens. The length and width of the electrodes were 70 mm and 30 mm, respectively, and the distance between them was 10 mm. The specimens utilized to perform the compressive strength test and to measure the electrical resistance were sealed and cured for the designated days at 25 °C.

Table 1
Mix proportion of the cement pastes and mortars incorporating CNT and CF (g).

Specimen	Cement	CNT	CF			Fine aggregate	SF	SP	Water/cement ratio
			3 mm	6 mm	12 mm				
N0	1000	–	–	–	–	–	100	16	0.24
N6	1000	6	–	–	–	–	100	16	0.24
N6-50	1000	6	–	–	–	500	100	16	0.25
N6-70	1000	6	–	–	–	700	100	16	0.26
N6-100	1000	6	–	–	–	1000	100	16	0.27
N6-150	1000	6	–	–	–	1500	100	16	0.30
N5F1(3)	1000	5	1	–	–	–	100	16	0.24
N5F1(6)	1000	5	–	1	–	–	100	16	0.24
N5F1(12)	1000	5	–	–	1	–	100	16	0.24
N5F1(3)-50	1000	5	1	–	–	500	100	16	0.25
N5F1(3)-70	1000	5	1	–	–	700	100	16	0.26
N5F1(3)-100	1000	5	1	–	–	1000	100	16	0.27
N5F1(3)-150	1000	5	1	–	–	1500	100	16	0.30
N4F2(3)	1000	4	2	–	–	–	100	16	0.24
N4F2(3)-50	1000	4	2	–	–	500	100	16	0.25
N4F2(3)-70	1000	4	2	–	–	700	100	16	0.26
N4F2(3)-100	1000	4	2	–	–	1000	100	16	0.27
N4F2(3)-150	1000	4	2	–	–	1500	100	16	0.30
N3F3(3)	1000	3	3	–	–	–	100	16	0.24
N3F3(3)-50	1000	3	3	–	–	500	100	16	0.25
N3F3(3)-70	1000	3	3	–	–	700	100	16	0.26
N3F3(3)-100	1000	3	3	–	–	1000	100	16	0.27
N3F3(3)-150	1000	3	3	–	–	1500	100	16	0.30

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