Heat conductivity properties of CNT-cement composites with various ranges of CNT dosages

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ABSTRACT

This study aimed to investigate the potential use of CNT (Carbon Nano-Tube), which are an innovative construction material preferred by many researchers. Long-term microstructure enhancement and onsite application are main reasons to conduct research on CNT-cement composites; thus, a study on mechanical properties as well as the heat conductivity of CNT-cement composites was carried out. As CNT contents increased, heat conductivity of cement composites was also enhanced. Strength development of CNT-cement composites at early ages was slow, although eventually CNTs containing water developed equivalent level of strengths at last as internal curing effects.

KEYWORDS: CNT-cement composites, Heat conductivity, Strengths, Internal curing

1. Introduction

In the last several decades, various methods to improve mechanical property of concrete have been examined by many researchers, such as the use of FA (fly ash) or GGBFS (ground granulated blast-furnace slag), and the use of mineral additives such as silica fumes [1, 2, 3].

Recently, the additions of CNTs or graphene to cement composites or concrete have been shown to improve the mechanical properties and durability of concrete as well as its electrical and heat conductivity. Li et al [4] and Konsta-Gdoutos et al [5] reported that the addition of CNTs improved the early age strength of concrete, and CNTs with a large surface area caused the quick formation of cement hydrates and an increase in the ratio of the C-S-H gel. A total of 0.5% of CNT addition enhanced the compressive strength of concrete by 26%. Kang et al [6] improved the strength by adding 0.1% CNTs to mixtures of cement and silica fume. Kim et al [7] focused on the heat conductivity of CNT-embedded cementitious composites. Choi et al [8] reported that 1% of CNT addition enhanced the compressive strength by more than 50% compared to OPC(ordinary Portland cement).

In order to develop surface treatment of CNTs for better dispersion [9, 10, 11], many researchers conducted researches on CNT surface treatment. Pavese et al [12] worked for the evaluation on wettablility before and after oxidation treatment in cement composites. Most research on CNT addition has been conducted to reveal the mechanical properties as well as the microstructures of CNT-cement composites [13, 14, 15, 16]. In addition, several studies have been conducted on the durability of CNT-cement mortars [17, 18].

In this study, the compressive strength was conducted with respect to the proportion of MWCNTs (Multi-Walled CNTs) in cement composites. Heat conductivity of CNT-cement composites was implemented for cement composites with high thermal capacity to be able to get rid of ice or snow on the roadways by applying electricity. For the large applications, this research was conducted in the lab scale. The amount of heat generated between two stainless steel meshes in the CNT-cement composites was measured to determine the optimal amount of CNT content in the composites. Flyash was added into the cement matrix for high flowability due to low workability of CNT-cement composite pastes.

2. Materials and Methods

2.1 Materials

A Blaine surface area of 358 m^2/kg and OPC density of 3.15 kg/m^3 were used in the experiment. A Bogue calculation of the OPC determined the composition to be 44.7% C_3S, 25.0% C_2S, 5.0% C_3A, and 11.9% of C_4AF by mass. The FA used was produced in South Korea, and its fineness and density were 410 m^2/kg and 2.29 kg/m^3, respectively. The chemical and physical properties of the binder materials are provided in Table 1 and Figure 2.

Table 1. Chemical and physical properties of raw materials

Material	Chemical Compositions (wt%)								Density (kg/m^3)	Blaine (m^2/kg)
	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	SO_3		
OPC	57.9	20.5	4.4	3.9	2.0	1.1	0.1	1.0	3.15	358
FA	1.7	64.3	20.6	7.5	0.9	1.1	0.3	0.1	2.29	410

In order to evaluate the effects of MWCNT additions on the chemical and mechanical properties of cement mortar, 2% concentrated MWCNT solution, which evenly disperses in solutions with high-range water reducer, was used. In the experiment, water was used as the main solvent of the MWCNT solution, with a dispersing agent for effective MWCNT dispersion. The viscosity of the MWCNT solution was 9.0 mPa·s, measured by Brookfield DV-II using an S-18 spindle at a speed of 100 RPM.

The MWCNT solution was placed in an oven at 105 °C to evaporate the water and obtain the image of MWCNT strands using SEM, as shown in Figure 1. Average diameter and length of the MWCNT strands were 20 nm and 1.5 μm with 1.3 g/cm^3 of density and 3.01 % of solid content from the FE-SEM analysis, respectively. Its electrical conductivity is 6,000 S/cm and thermal conductivity is 6,000 W/mK.

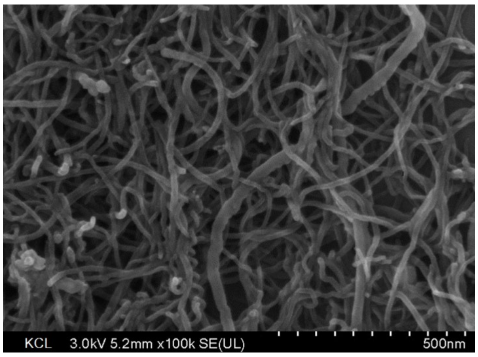

Figure 1. SEM image of the bulk dry MWCNTs

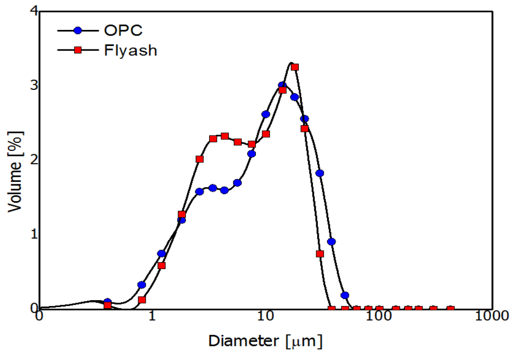

Figure 2. Particle size distributions of OPC and FA

2.2. Mix Proportions

Mix proportions are provided in Table 2. The binders used consisted of 80% OPC and 20% FA. Poly-carboxylate based superplasticizer, with a binder ratio of up to 0.4% by weight, was utilized to improve the workability of the cement mortar specimens due to the low water-to-binder ratio (0.28).

The proportion of binder to aggregate was 0.5 for the mortar mixtures. The aggregate used in this study, ISO standard sand, were natural and fine, and consisted of round particles with more than 98% silica contents. As shown in Table 2, the mortar mixtures were named as "MC-" with various amounts of MWCNT contents, ranging from 0 to 0.5% to binder mass. "MC00" is the mortar label of OPC and FA without MWCNT, and "MC05" indicates 0.5 mass% of MWCNT were added in binders to cast mortar specimens for the experiments. In order for water-to-binder ratio to be 0.28, extra water was added in the mixture. This is because MWCNT solution contained 2 wt% of solid contents.

The mixing procedures for the production of mortar specimens were similar to that specified by ISO 679. All binders were placed and pre-mixed in a 5-L bowl for 30 s with the automatic mortar mixer. Then, MWCNT solution and additional water were applied and mixed in the bowl for an additional 30 s at a low speed, 140 RPM for rotating and 65 RPM for revolving. Subsequently, 120 s of high-speed mixing, 285 RPM for rotating and 125 RPM for revolving, was performed to produce mortar specimens. In order to evaluate mechanical properties and heat conductivity of the mixtures, ISO sand was added to the fresh paste specimens by mixing at high speed for another 120 seconds.

Table 2. Mix proportions of mortar samples

Specimens	OPC (g)	FA (g)	Water (g)	MWCNT Solution (g)	ISO Standard Sand (g)
MC00	80	20	28.0	-	200
MC01			23.1	5	
MC02			18.2	10	
MC03			13.3	15	
MC04			8.4	20	
MC05			3.5	25	

2.3. Test Methods

Compressive strength test was conducted according to ISO 679 [19]. After 24 h of curing in a chamber at (21 ± 2) °C and (92 ± 5) % R.H., all specimens were demolded and placed in water containers at (21 ± 2) °C. The strength tests were performed at the ages of 3, 7, 28, 56, and 91 days to observe enhanced strength development.

Mortar specimens were cast in 50 mm-sized cubic molds, in which two sheets of stainless steel (SS) wire mesh, used as electrodes, were embedded. The SS wire meshes were 45 mm wide and 70 mm high, rectangular in shape, and designed for heat generation. The mortar cover for the SS wire meshes were secured with 10 mm distance, and thus, the distance between two electrode sheets was 30 mm.

One of the wire meshes was connected to the power supply as the positive electrode (cathode), and the other mesh was attached as the negative terminal (anode), as shown in Figure 3. CNT-cement composites are expected to be electrical materials because of the high conductivity of CNTs compared to that of ordinary cement composite. The initial voltage applied to the specimens for the heat generation experiment was 200 V. It took differing time periods to reach the highest temperature of each mortar specimen.

Furthermore, temperature data in the center of cube specimens were obtained by embedding thermocouples during the casting of fresh mortars. The thermocouples were directly connected to a data logger to measure the temperatures in real time (Figure 3). Elevated temperature data were utilized to calculate the heat conductivity of CNT-cement composites by observing the difference between ambient temperature inside the specimens and the peak temperature during the experiments, and the results are provided in Chapter 3.2.

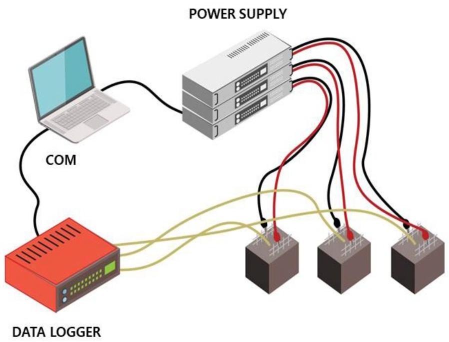

Figure 3. Experiment setup for heating carbon nanotube-cement (CNT-cement) composite blocks.

3. Results and discussion

3.1. Compressive Strengths

As shown in Figure 4, the compressive strength at three days for MC00 (40.0 MPa) was higher than that for mixtures from MC01 (37.7 MPa) to MC05 (33.4 MPa). As time progressed (up to 91 days) MC00 developed a higher compressive strength than the other mixtures. MC00 and MC01 developed almost identical compressive strengths for 91 days, except for the result at 28 days, which indicates that the addition of 0.1 wt% CNT to the total binder weight does not significantly influence the mortar strength.

The test results showed that an increase in the CNT dosages added to mixtures led to a decreasing compressive strength. At early ages (three and seven days), the compressive strengths ratio of MC03, MC04, and MC05 to MC00 were 80.4%, 90.9%, and 83.5% for three days and 81.2%, 86.8%, and 85.6% for seven days, respectively. However, compressive strengths for mixtures with 0.3 wt% of CNT solids developed as much as that of MC00 after 28 days.

Thus, it can be considered that CNT hindered the strength development due to the Van der Waals forces at early ages. Low water-to-binder ratio and large amount of CNT contents in the mixtures caused greater non evaporated water-to-binder ratio and chemical shrinkage, and it was influenced on the low hydration reaction at early age due to agglomerated CNT [20]. This caused the reduced compressive strengths at early age.

In addition, it can be considered that CNTs were not actively involved in cement hydration because they have the ability to absorb water. In theory, CNT was known for hydrophobic materials, but experimental results indicated that strength development for CNT mixtures was larger than reference mixtures. It is revealed that the entropy of water molecules increases in limited nano-spaces such as nano channels with hydrogen bonds [21].

Thus, strength development was relatively small in the mixtures with a large amount of CNTs owing to internal curing effects.

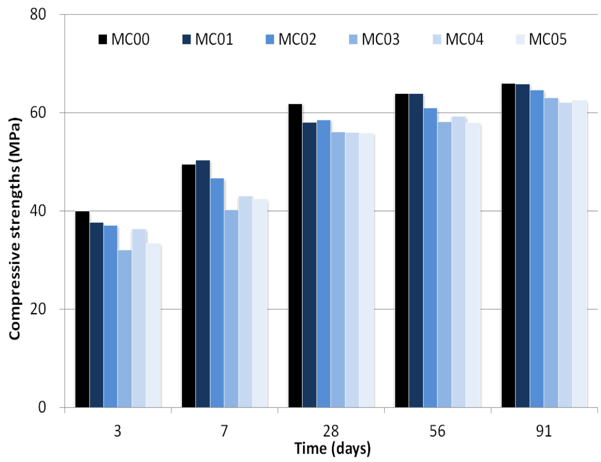

Figure 4. Compressive strengths of mortar mixtures.

3.2 Heat conductivity

As explained in Section 2.3, heat conductivity of CNT-cement composites was measured by applying a certain amount of electricity. Figure 5 shows the test results for heat conductivity for CNT-cement composites at the ages of 28 days. A constant 200 volts was applied, even as currents inside the samples differed. As higher temperature variation was detected, the higher current values were obtained, which showed linear relation.

The more CNT added in the mixtures, the higher the increase in temperature was observed. The ambient temperature started in the experiment was 20 degree Celsius, and the peak temperature for MC00 was just 38.8 °C. However, the highest temperature peaks MC01 and MC02 were 42.5 °C and 46.3 °C after 60 minutes elapsed, which was earlier than MC00.

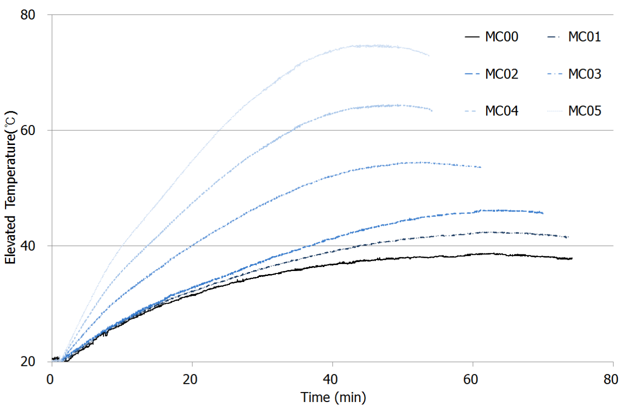

Figure 5. Heat conductivity plot for CNT-cement composites with peak temperatures with various CNT additions.

The slopes for the first 20 minutes for MC00, MC01, and MC02 were similar, but differences in peak temperature were relatively large. The highest temperature elevated during the experiment was observed on MC05, which contained largest amount of CNT added. MC04 and MC03 developed 64.5 °C and 54.6 °C at 47.2 and 51 minutes, respectively.

As shown in Table 3, as CNT additions increased in the mixtures, heat production inside the specimens increased, but the time to reach highest temperature for each specimen decreased. That is, CNT played an important role in enhancement of heat transfer capacity caused by electrical conductivity, low resistance, and high current migration [22].

Table 3. Experiment results for heat conductivity.

Specimen	Time to Reach the Peak Temperature (min)	Peak Temperature (°C)
MC00	63.0	38.8
MC01	61.0	42.5
MC02	63.7	46.3
MC03	51.0	54.6
MC04	47.2	64.5
MC05	44.9	74.9

4. Conclusions

CNT is a novel construction material because of its enhancement of the concrete property. Furthermore, electrical and heat conductivity were highly improved with the cement composites because CNTs have high conductivity. In this study, various experiments were conducted to investigate the mechanical properties and hydration reaction of CNT-cement composites with various CNT contents and low water-to-binder ratio (0.28).

Heat conductivity by CNT addition was simply estimated by designing a heat conductivity test with two stainless-steel electrodes to develop multi-functional cement composites in the near future. From the test results, heat conductivity capacity increased as CNT contents become higher in the mixtures. Figure 5 shows that peak temperature for MC00 and MC05 were 38.8 °C and 74.9 °C during the test, so large amount of CNT addition directly influences on the heat property on cement composites.

As the amount of CNT increased in the mixtures, the compressive strengths decreased initially owing to the water absorption of CNT. However, the strengths of specimens with large amount of CNTs rapidly increased as much as MC00 after 28 days. This was because of the internal curing effects of water contents in and around the CNT particles that released water. Thus, the compressive strength for MC04, which showed the lowest strength, was 94.0 percent of MC00.

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