The 2018 Structures Congress (Structures18)
Songdo Convensia, Incheon, Korea, August 27 - 31, 2018

Influences of CNT replacement on strengths and porosities of cement-silica fume mortars

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ABSTRACT

Carbon-Nanotube (CNT) is one of the novel construction materials to improve the mechanical properties and durability of concrete. The tensile strength of CNTs is 60 times higher than that of steel reinforcement, and the density is 6 times lower than the steel. Also, CNTs can be considered as great construction materials due to the high thermal and corrosion resistances. In this research, 0.5 wt% CNT solutions were implemented for the even dispersion in cement matrix. Cement and silica fume were used as binders. Composites with the CNTs/Binder ratio of 0.075 %, 0.125 % and 0.250 % were produced to conduct compressive and flexural strength test. Also, the pore characteristics of mixtures with CNTs replacement rates were investigated. The relationship between strengths and pore characteristics is discussed in this paper.

1. INTRODUCTION

Cement, which is the major component in concrete mixtures, contains Calcium silicates (C_3S, C_2S), Calcium aluminate (C_3A) and Calcium aluminoferrite (C_4AF). The compounds composed of cement react with water to form cement hydrates such as Calcium silicate hydrate, which is called C-S-H, and Calcium hydroxide ($Ca(OH)_2$), and the improvement of mechanical properties and denser microstructures can be obtained as time progressed. There have been various efforts to improve strength and durability of concrete such as the use of fly ash (FA) or ground granulated blast-furnace slag

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(GGBFS), which were by-products from the industry, and the using mineral admixtures such as silica fumes for last several decades.

Recently, the additions of CNTs or graphene into concrete appeared to improve durability of concrete as well as electrical and thermal conductivity of concrete. Li et al (2005) and Konsta-Gdoutos et al (2010) reported that the additions of CNTs improved the early age strength of concrete, and CNTs with large surface area caused the quick formation of cement hydrates and the increase in the ratio of C-S-H gel. 0.5 % of CNT additions developed 26 percent of compressive strength enhancement. The combination of cement and silica fume caused the strength improvement with 0.1 percent of CNT additions by Kang and Park (2014). Kim et al (2017) focused on the thermal conductivity of CNT-embedded cementitious composites. Choi et al(2015) presented an article that 1 percent of CNT addition enhanced the compressive strength more than 50 percent compared to OPC. In this study, the mechanical properties such as compressive strength and flexural strength and pore characteristics were investigated with various amounts of CNT additions.

2. Materials and experiments

2.1 Materials

Raw materials used in this study were research cement (RC), which does not contain $CaCO_3$. Also, 10 wt% of silica fume (SF) was substituted for RC to improve dispersion due to the addition of CNTs. The chemical compositions for RC and SF were presented in Table 1. Density and surface area for RC were 3.19 g/cm^3 and 3,680cm^2/g, respectively. Density and surface area for SF were 2.21 g/cm^3 and 15.4m^2/g. The surface area of silica fume was obtained by BET method, which was analyzed by ASAP 2020 from Micromeritics.

Table 1 Chemical compositions for RC and Silica fume

	CaO	SiO_2	Al_2O_3	MgO	SO_3	Fe_2O_3
RC	65.2	18.1	4.3	2.9	3.6	3.8
SF	0.2	91.8	0.4	1.2	0.4	0.9

CNTs used in this study were already resolved in the water solvent. The concentration of CNT solution was 0.5 wt%, and a small amount of chemical dispersant were added. Diameter and length of CNTs in the solution were 10 ㎚ and 1.5 ㎛, respectively. ISO standard sands, which were used to conduct strength tests, were used as the fine aggregate with a maximum grain size of 2 mm and a saturated surface dry density of 2.6 g/cm^3. The particle size distribution of the sand complied with the requirements of ISO 679 and the water absorption rate was less than 0.2%.

2.2 Experiments

The mix proportions were provided in Table 2. 90 percent of research cement and 10 percent of silica fume were used as binders in the study. Binder to water ratio in the

mix proportions were fixed as 0.5, and the water contents were calculated by taking out the amount of CNT solids.

Table 2 Mix proportions

Mix	RC	SF	CNT Solution*	ISO Standard Sand	Water
Plain	90	10	-	200	50
CN75	90	10	15	200	35
CN125	90	10	25	200	25
CN250	90	10	50	200	-

* CNT solution with 0.5 wt% of concentration

Paste specimens were produced to investigate pore characteristics and microstructures of mixtures with and without CNTs. Research cement and silica fume were pre-mixed in the mixer for 30 seconds. Then, CNT solution was put into the mixer, and then water was applied. The paste specimen was cast into 12 cubic molds with dimension of 10 mm × 10 mm × 10 mm. After 1 day of curing in a chamber at (20±3) °C and (90±5) % R.H., all specimens were demolded and placed in containers filled with water.

In order to evaluate mechanical properties such as compressive and flexural strengths of cementitious composites with CNTs, ISO sand was applied to the same paste mixtures as described above. Firstly, ISO sand was pre-coated with CNT solution for CNTs to disperse uniformly. Then, water and two binders, cement and silica fume, were applied. After mixing was completed, three prismatic specimens with dimensions of 40 mm × 40 mm × 160 mm were cast for compressive strength and flexural strength measurements. Demolding moment and curing conditions were identical with paste specimens.

The compressive and flexural strengths of the mortar specimens at 7 days and 28 days were tested according to ISO 679. Mercury Intrusion Porosimetry (MIP) analysis was performed at 7 days and 28 days using Autopore IV 9500 by Micromeritics to determine pore characteristics such as pore size distribution and total pore volumes of the samples. The surface tension and contact angle of the mercury were defined as 485 dynes/cm and 130°, respectively. The largest pressure applied to the paste specimens was 206 MPa, which could calculate pore diameter from 6 ㎚ to 120 ㎛.

SEM image of hardened paste specimen obtained in the research was carbon-coated and investigated under high vacuum conditions in a Tescan Mira LMH microscope.

3. Results and discussion

3.1 Strength

The compressive strength test results were provided in Fig. 1. At 7 days, Plain mixtures developed the highest compressive strength, 34.1 MPa, but the mixture with 0.25 percent of CNT added had 33.4 MPa, which was slightly lower than Plain. However, the highest compressive strength at 28 days was observed in CN250. 51.5 percent strength development was obtained. On the other hand, the compressive

strength at 28 days of Plain was 48.4 MPa, and just 40 percent strength development was observed. Other mixtures, CN75 and CN125, also developed 48 percent and 52 percent strength development from 7 days to 28 days, and this is because CNT played an important role in nucleation site to form hydration products and due to the filler effects at 28 days.

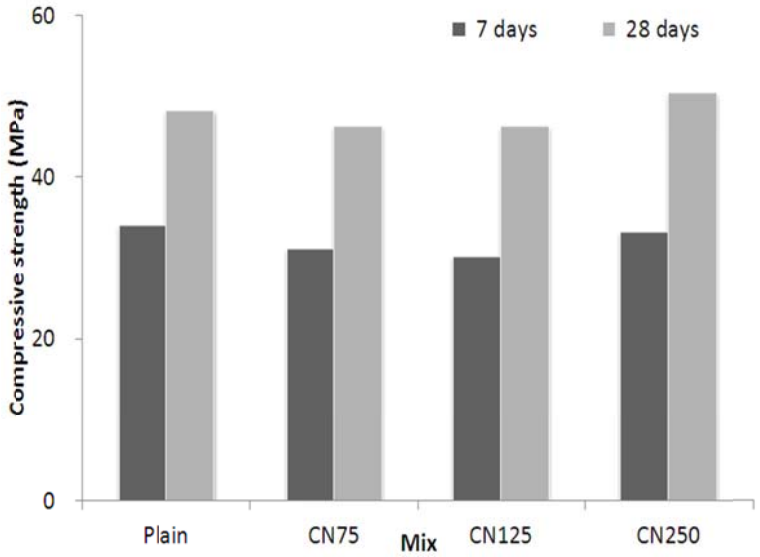

Fig. 1 The compressive strength test results

The flexural strength test results were provided in Fig. 2. At 7 days, most mixtures developed similar level of flexural strengths, which were between 6.3 MPa and 7.0 MPa. However, after 28 days of casting, the highest flexural strength development was observed in CN250, which was 10.1 MPa.

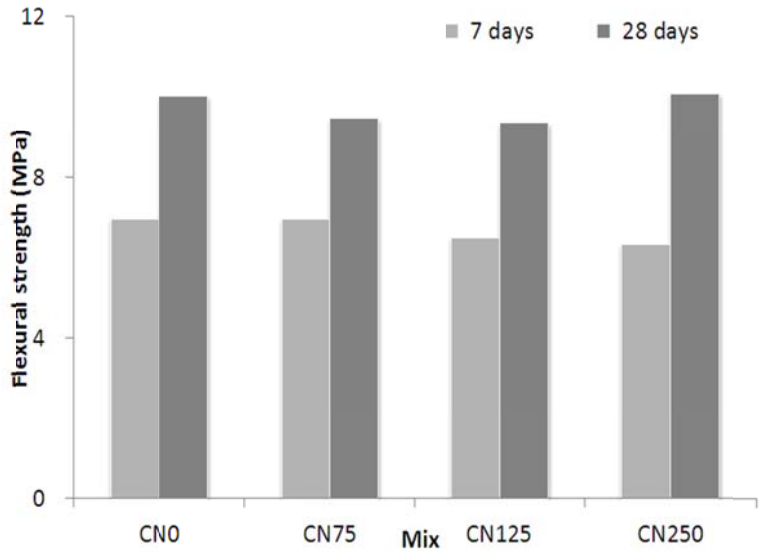

Fig. 2 The flexural strength test results

3.2 Pore characteristics

Table 3 shows the total porosities for all mixtures at 7 days and 28 days. The pore distribution for the mixtures at 7 days and 28 days were provided in Fig. 3 and Fig. 5, and pore distribution ranges were shown in Fig. 4 and Fig. 6. At 7 days and 28 days, the lowest porosity was observed in CN250 caused by CNT filler effects at the early age. The decrease rate in porosities was almost the same for all mixtures because of the same binders with water-to-binder ratio.

Table 3 Total porosities for mixtures at 7 days and 28 days

Mix	7 days (%)	28 days (%)
Plain	31.3	25.8
CN75	33.0	26.4
CN125	33.4	27.6
CN250	29.4	24.8

Most pore diameters were in the ranges between 50 ㎚ and 500 ㎚. As shown in Fig. 4, CN75 contains many pores with the diameter ranges between 50 ㎚ and 100 ㎚, and CN125 contains many pores with the diameter ranges between 100 ㎚ and 500 ㎚, compared to Plain and CN250 mixtures.

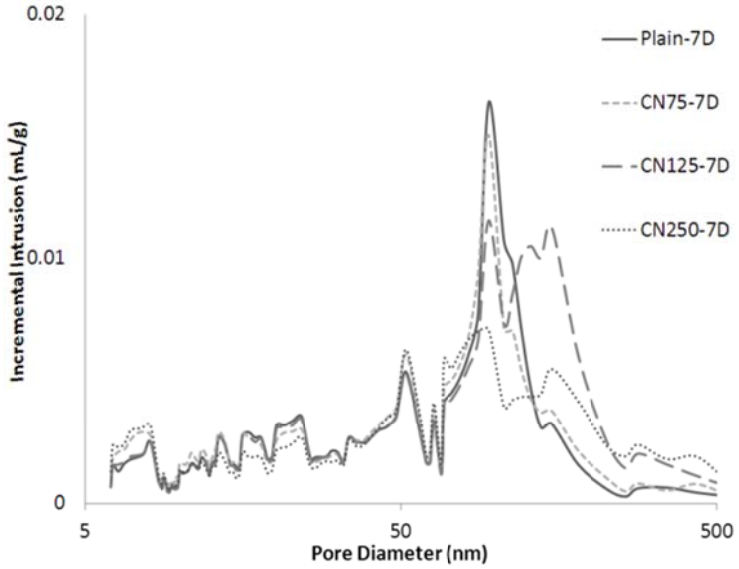

Fig. 3 The pore size distribution for mixtures at 7 days

Even large pores, which were from 500 ㎚ to 1,000 ㎚, were observed in Plain and CN250 in Fig. 4, the amounts of pores in that range were not influenced on the total porosity.

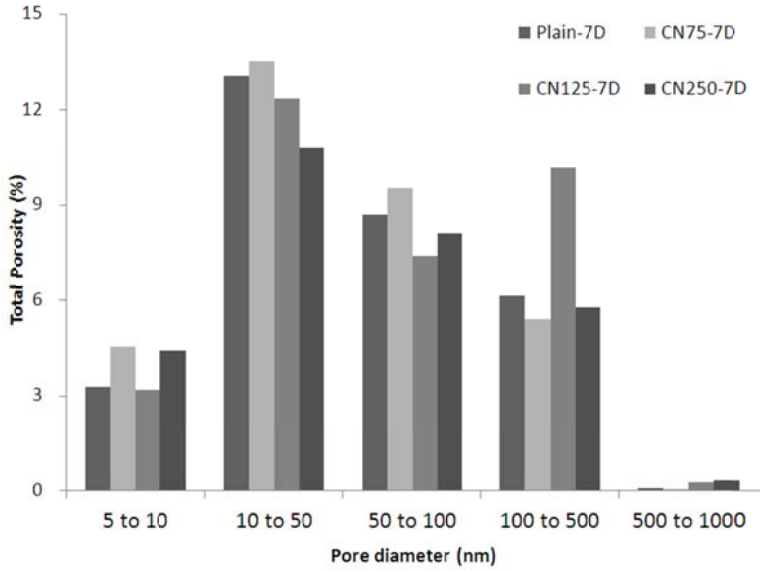

Fig. 4 The pore size distribution ranges at 7 days

As shown in Fig. 5, pore diameters between 100 ㎚ and 500 ㎚ were disappeared compared to results at 7 days. The pores in that range became smaller due to the further hydration during 28 days. Thus, the proportions of pore diameter, which ranges from 50 ㎚ to 100 ㎚. Also, the proportions of pore diameter ranges between 10 ㎚ and 50 ㎚ became smaller because of the filling hydration products in the meso-pores as shown in Fig. 6.

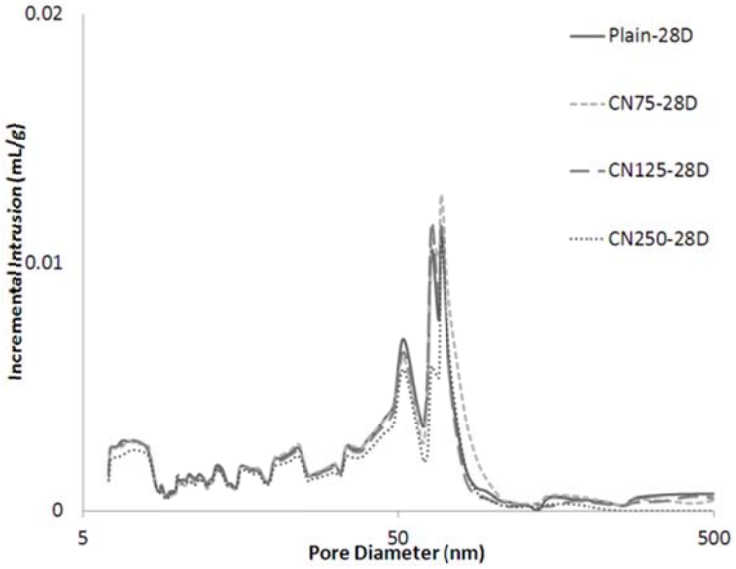

Fig. 5 The pore size distribution for mixtures at 28 days

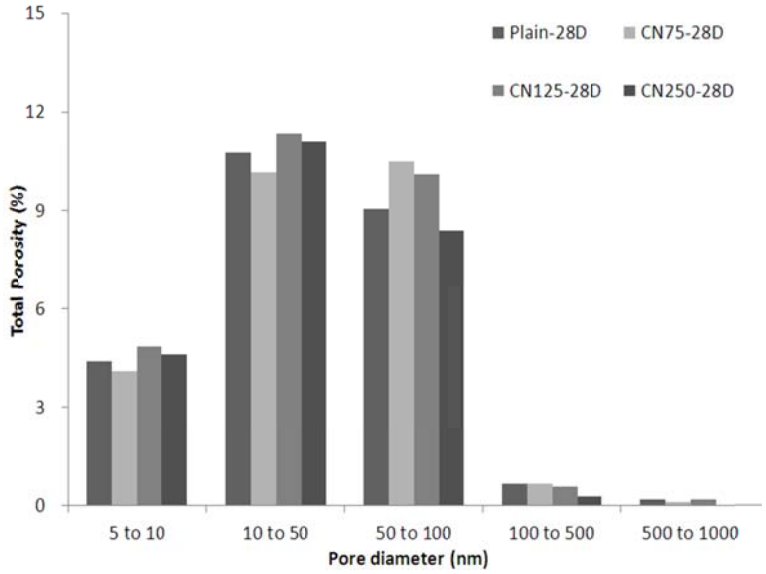

Fig. 6 The pore size distribution ranges at 28 days

From the most ranges, CN250 took the smallest proportions due to the filler effects and largest amount of nucleation sites presences by CNTs

3.3 SEM image

A slice paste specimens were obtained to investigate the CNT dispersion on the hydration products. Fig. 7 shows the silica fume on the plate shapes of hydration products, Calcium hydroxides. Most hydration products were C-S-H, discovered by SEM-EDS analysis.

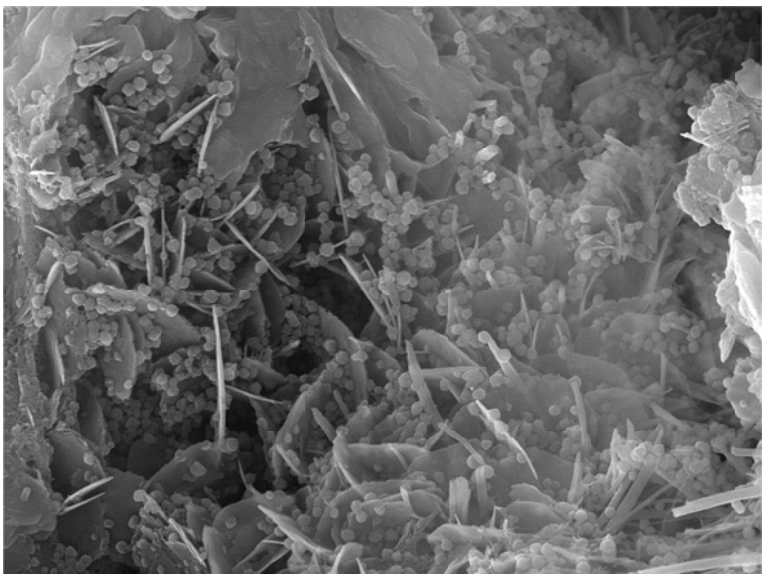

Fig. 7 SEM image for hydration products at 7 days with silica fume

Fig. 8 presented C-S-H and CNTs. CNTs were generally placed on the C-S-H or linked between hydration products. CNTs seem to be dispersed well in the image.

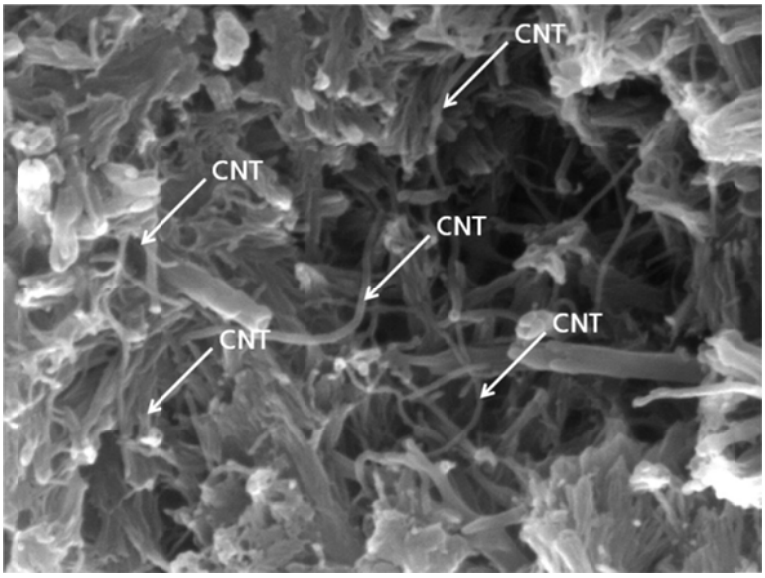

Fig. 8 SEM image for the mixture containing CNTs.

4. Conclusion

In order to investigate the mechanical properties, porosities and microstructures of cementitious composites with CNTs, the compressive/flexural strengths, mercury intrusion porosimetry and SEM-image analysis were conducted for the mixtures with 0 %, 0.075 %, 0.125 % and 0.250 % of CNT additions. There were not significant differences for all mixtures for the strength properties, but the mixture with 0.25 % of CNT additions developed the highest mechanical properties at 28 days. Also, the lowest porosities were observed in CN250, and this is directly related to the highest compressive strength. From the SEM image, CNTs were evenly dispersed to connect hydration products.

ACKNOWLEDGEMENT

This subject is supported by Korea Ministry of Environment (MOE) as “Public Technology Program based on Environmental Policy”.

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