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Research Article

Use of silica particles to improve dispersion of -COOH CNTs / carbon fibers to produce HyFRCC

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Abstract

The development of hybrid fiber reinforced cement composite that has high strength, scope to be used as cement-based sensors has been investigated in this study by using a combination of carbon fibers and carbon nanotubes (CNT) at low volume fraction. The dispersion of CNTs was enhanced by using polycarboxylate based superplasticizer that resulted in a homogeneous aqueous stable solution, and profoundly improved dispersion when integrated with the cementitious matrix. Different siliceous additives were also incorporated into the mixes to improve the dispersion of CNTs in the matrix, where micro-silica outperformed as compared to nano-silica, confirmed morphologically. On the other hand, nano-silica enhanced dispersion of milled carbon fibers in the aqueous state. The sensing behavior was determined by the measurement of bulk resistance of mixes and the samples were subjected to compressive loading to study the strength improvement with the incorporation of fibers. The experimental results reveal that hybrid combination of chopped carbon fibers, micro silica, and low volume fraction of CNTs in a cementitious matrix results in a stronger and durable concrete that holds the potential for sensing applications. Thus, laying a strong foundation for the future of low cost smart cement based materials.

Keywords: Cement-based sensors; Carbon nanotubes; Carbon fibers; Silica particles; dispersion characteristics; mortar; compressive strength; smart materials; superplasticizer

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1. Introduction

Structural Health Monitoring (SHM) aims at the performance diagnosis of various constituent materials at different components of a structure to ensure that the structure stays in the state of serviceability as specified during design. All damage initiates at the material level and increments over time to a point where it is no longer safe to use the structure. This point is referred to as failure. SHM is an important tool that provides real time, reliable information about a structure as well as can assist in damage identification. Interestingly, it has been observed globally that some structures continue to be in service post their designed service life, generally owing to the economic issues. These structures thus, pose a risk as age related deterioration progresses. Hence, damage assessment of such structures is an important part of civil engineering.

Different techniques involved in SHM include use of optical sensors, electrical resistance strain gages and piezoelectric strain sensors. However, there are certain problems associated with these external sensors, which include low sensitivity and reliability along with the issue of long service life. Cement-based sensors manufactured by the integration of certain amount of nano-fillers not only help in the sensing of electro-mechanical properties but also help in strength improvement [1]. These intrinsic sensors unlike other methods of SHM do not use specialized electrical setups, and therefore have additional advantages of low maintenance cost (i.e. less wear and tear) and design flexibility (i.e. flexible proportions tailored for diverse application). These fillers which include steel fibers, carbon fibers, Carbon nanotubes amongst many others enhance the conductivity of the composite mixture, and hence help achieve the sensing objective.

Over the last two decades, extensive research has been carried out on carbon based nanofillers due to their multifunctional nature. Ever since their discovery in 1991 [2], Carbon nanotubes (CNTs) have become one of the most widely used carbon based nano fillers owing to the extended sp^2 carbon which impart extensive electrical and optical properties. In addition to these, CNTs are known to have excellent mechanical properties, their measured flexibility and rigidity being even higher than most reinforcing materials [3,4]. Further, due to their fiber like structure and high aspect ratio, they possess excellent load carrying capacities, Young's modulus up to 1 TPa and fracture strains in the order of 6% [4–7]. However, one of the significant challenges faced in the application of CNTs is obtaining uniform dispersion in the matrix. Because of their high aspect ratio and stronger van der Waals attraction forces, they tend to agglomerate when dispersed in a solvent. The practical properties of CNTs are dependent on the degree of graphitization, diameter and whether they are single or multi-walled. While, single walled carbon nanotubes (SWCNTs) are seamless cylinders made of a single graphene sheet, multi-walled carbon nanotubes (MWCNTs) consists of two or more seamless cylinders of graphene sheets that are arranged concentrically. MWCNTs are widely preferred both for academic and industrial purposes due to its lower specific surface area (SSA) of $200 \text{ m}^2/\text{g}$ [8] which further minimizes the carbon attractions and results in lower chances of agglomeration, better conductivity, ease of dispersion, greater availability and low cost, as compared to SWCNT.

Various researchers have suggested different ways to improve the dispersion of CNTs in solvents. One of the ways to achieve this is surface treatment which includes either of covalent or non-covalent modifications which increases the solvability of CNTs [8,10,11]. This is followed by mixing in magnetic stirrer or ultrasonication to obtain a more homogeneous dispersion in the solution [11,12]. Covalent methods involve surface functionalization of CNT walls that improve the solubility as well as bonding with the matrix. Non-covalent methods on the other hand involve non-covalent interactions such as physical adsorption of molecules on CNT surface. While the former modifies the π -electron conjugation, it is not disturbed in the latter case. Le *et al.* [13] investigated the effect of functionalization by different organic compounds on dispersion of CNTs and obtained a stable solution with COOH group and there was less entanglement of fibers. Similar results have been reported by various other researchers [12,13]. Other advantages of the carboxyl group are the ease with which it can be introduced in the CNT and its tendency to undergo a variety of reactions [16–18]. Fu *et al.* [19] suggest ozone treatment as another possible way to improve the dispersion. The report states that ozone treatment decreases the contact angle between fibers and water to almost zero, hence ensuring an increase in the bond strength between fibers and cement mix. It also significantly helped to reduce the drying shrinkage and increase the sensing capability of mix.

Furthermore, the dispersion of non-polar CNTs in high polar medium such as water is challenging as reported by Liebscher [20]. Hence, the use of a suitable surfactant in the solvent further helps in the dispersion of CNTs [21–24]. Study by Liu *et al.* [25] reported an increased dispersion with the use of anionic, cationic or non-ionic surfactant in comparison to an aqueous solution of CNTs. They further reported that dispersion of MWCNTs increased with the amount of COOH groups attached. Similarly, Randhawa *et al.* [26] investigated the effect of surfactant concentration on dispersion and functionalization using Triton X-100 and suggested better functionalization of CNTs with COOH after dispersion, the optimum surfactant being 1.3 wt%. Various researches have suggested that there should be an optimum surfactant to MWCNTs ratio for the most efficient dispersion [27–29]. Konsta-Gdoutas *et al.* [29] state that a weight ratio of surfactant to MWCNTs close to 4 is required for effective dispersion of nanotubes. They further suggested that improvement of fracture properties was observed by the proper dispersion of MWCNTs even at a very less concentration of 0.048% weight. Several researchers have proposed the use of polycarboxylate superplasticizer as a suitable surfactant for the effective dispersion of MWCNTs [20,23,30–32].

On the other hand, researchers have also explored the effectiveness of using silica-based particles to improve the dispersion and bonding of nanotubes in aqueous solutions. Kim *et al.* [23,33] studied the influence of siliceous materials and reported that micro-silica was also effective in dispersion of CNTs as compared to surfactants owing to the ball-bearing effect. Further, micro silica helped in reducing the resistivity of the samples when used at 10% weight of cement. On the contrary, an increase in resistance was observed on adding nano silica in higher concentration. However, nano silica when used at 1 wt% of cement had a stabilizing effect on the resistivity of

the samples [34]. Nano silica has recently gained popularity as a cement additive because of its high amorphous silica content, high surface area and lower dimension compared to micro silica. Further, it is well known from various research studies that the addition of silica particles (nano/micro sizes) in concrete leads to higher Pozzolan reactivity, forming a denser CSH gel which results in increased mechanical strength, and enhanced durability owing to their intrinsic properties [34–44].

The use of carbon fiber as a conductive material in cement based sensors have been adopted since a long time because of their superior mechanical properties as well as their lower cost as compared to carbon-based nano particles [45–48]. These fibers also hold the potential to enhance the durability of the cement mix upon addition against corrosion and abrasion resistance. The commercially available carbon fibers are either PAN-based or pitch-based. These two types vary on strength and texture aspects. The PAN-based fibers offer higher strength of the two and have a granular structure in contrary to the sheet like structure in pitch-based fibers. Sun *et al.* [49] proposed a model for conduction of current in carbon fiber-based composites. The model used Thermoelectric Force (TEF) method to predict the behavior and predicted that flow of electric current has four paths in composites, the primary path of them being dependent on the concentration of fiber used in the mix. The length of the fiber also plays a major role in determining the conductivity. However, studies pertaining to the use of this method for SHM is still sparse.

While a number of research studies have explored the feasibility to develop smart cement based sensors using carbon-based fibers, but little importance has been given to the cost perspective from application point of view [50–55]. Azhari and Banthia [56] suggested that hybrid mix of carbon fibers and CNTs can be used to address this problem. However, their studies reported that an improved dispersion mechanism for CNT particles in cementitious matrix would demonstrate superior sensing capabilities in smart concrete material. It has also been reported that adding CNTs to cementitious mixture not only improves mechanical performance but also enables the sensing capabilities [57–59] [Konsta-Gdoutos *et al.* 2017—Effect of CNT, Konsta-Gdoutos *et al.* 2017—Fresh and mechanical properties, Zhan *et al.* 2020], piezoelectric response [60] [Li *et al.* 2007], and potential to be used for crack repair in concrete [61,62] [Manzur *et al.* 2016, Souza *et al.* 2017]. Based on related recent studies, the authors identified a gap within the research scope of cement based sensors, i.e. how different fiber types would interact with f-CNTs, which consist of different aspect ratios and properties, at lower volume fraction, when used with suitable admixtures. Additionally, the authors have reported a novel processing methodology, i.e. using sonication along with magnetic stirring to obtain stable nano solution containing hybrid fillers along with cementitious admixtures in this paper.

Based on the literature review conducted by the authors, The authors observed limited and scattered findings in the literature on the effect of MWCNTs and carbon-based fibers in developing hybrid multi-faceted fiber reinforced cement mortars (FRCM) have been found. Therefore, this paper aims to experimentally evaluate the dispersion, mechanical and electrical behavior of cement mortars with different types of admixtures along with CNTs. Mortars were characterized in terms

of mechanical and bulk resistivity behavior. The dispersion efficiency and interfacial bonding of CNTs in the reinforcement of mortars were also analyzed by means of a scanning electron microscope (SEM). Hence, this research explores the first phase of development of economical cement-based composites for repair and sensing applications such as bridges, buildings, pavements, etc. ~~and all kinds of structures.~~ Further, it can be also used for electromagnetic interface shielding, lightning protection and electrical grounding ~~-applications.~~

2. Materials and Methods

2.1 Materials

In this study, smart nano cement based composites (with low resistivity or improved sensing capabilities) were fabricated. The matrix was reinforced by MWCNTs-COOH (COOH functionalized Multi-walled carbon nanotubes). Type 10 Ordinary Portland cement, conforming to the requirements of Type I as specified by ASTM C150 standards [63], was used for casting mortar specimens. The properties of the cement are listed in Table 1. The fine aggregates used for the experiments was obtained from the Sechelt pit in British Columbia (Canada), with a fineness modulus of 2.61 and a water absorption capacity of 0.79% by weight. Further, a polycarboxylate ether based superplasticizer (PC), SP (Master Glenium® 3030), containing 0.2 – 1.0 wt% sodium hydroxide and with a density of 1.05 g/cm³, was used in all mortar production. The SP was utilized to achieve good workability, and to act as a catalyst for the dispersion of carbon-based fillers in water.

Three different types of carbon-based fillers were used in the present investigation – functionalized MWCNTs, chopped carbon fibers and milled carbon fibers. The properties of long MWCNTs – COOH, procured from Cheap Tubes Inc., chopped carbon fibers and milled carbon fibers (PAN-based), provided by Zoltek Corp, U.S.A., are presented in Tables 2 (a, and b), respectively. Nano-silica (commercial product code: US 3438) and silica fume (commercial product code: K 811) used in the present study have different properties as mentioned in Table 3, which were supplied by US Research Nanomaterials Inc., and Kryton International, respectively.

Table 1: Properties of Portland Cement

Properties	Applicable	Type- I
Maximum air content of mortar, volume %	C185	12
Minimum fineness, specific surface, m ² /kg	C204	260
Maximum autoclave expansion, %	C151	0.80
3 days compressive strength, MPa	C109/C109M	12.0

7 days compressive strength, MPa	C109/C109M	19.0
Minimum setting time, min	C191	45
Maximum setting time, min	C191	375

1 Table 2 (a): Properties of MWCNT-COOH nanotubes

Properties	MWCNT-COOH values
Length	10-50 μ m
Outside diameter	8-15nm
Inside diameter	3-5nm
-COOH content	2.56 wt%
Purity	> 95%
SSA	> 233 m ² /g
Electrical conductivity	>100 S/cm
Bulk density	0.15 g/cm ³
Cost (\$) as of July 2019	\$18.9 per gram

2 Table 2 (b): Properties of milled & chopped carbon fiber (PAN-based)

Properties	Milled Carbon fiber values	Chopped carbon fiber values
Carbon content	95%	95%
Electrical resistivity	0.00155 ohm-cm	0.00155 ohm-cm
Linear resistivity	0.0761 Ω /cm	0.0761 Ω /cm
Density	1.81 g/cc	1.81 g/cc
Bulk density	490 g/L	350 g/L
Fiber diameter	7.2 μ m	7.2 μ m
Average fiber length	100 μ m (MF150) / 150 μ m	3, 6, & 13 nm
Filament shape	Round	Rectangular
Cost (\$)	\$0.0187 per gram	\$0.0212 per gram
Tensile Strength (MPa)	4, 137	
Tensile Modulus (GPa)	242	
Elongation (%)	1.5	

3 Table 3: Properties of Nano-silica & Silica-fumes

Properties	Nano-silica	Silica fumes
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SSA	180-600 m ² /g	15-21 m ² /g
Specific gravity	2.2	2.2
Bulk Density	<0.10 g/cm ³	600-650 kg/m ³
Average particle size (APS)	20-30 nm	~ 45 µm
Cost	\$250 for 500 grams = \$0.5 per gram	\$ 500 per ton = \$0.0005 per gram

2.2 Carbon nanotube dispersion

It is widely known that MWCNTs tend to agglomerate due to strong van der Waal forces, which results in making the dispersion difficult and laborious. Previous attempts by the authors to efficiently disperse MWCNTS-COOH in water (only) did not produce impressive results, mainly due to the lack of a chemical activator that resulted in sedimentation of CNTs. By referring to the findings reported by Shah *et al.* [30], the authors were able to overcome the major challenge and developed a methodology that resulted in effective dispersion of MWCNTs in water by adding dispersants / chemical admixtures and applying ultrasonic energy. According to Shah *et al.* [30], the optimum weight ratio of surfactant to CNTs (SP/CNT) closer to 4.0 was considered to obtain effective dispersion of nanotubes in water.

Typically, for CNT dispersion, MWCNT-COOH suspensions are prepared by adding the nano fillers to an aqueous polycarboxylate ether (PC) based solution [32]. In this study, the authors applied ultrasonic energy to the solution by a 500W cup-horn high intensity ultrasonic processor, with a ½ in. diameter titanium alloy probe. The sonicator was operated at an amplitude of 50% to deliver constant energy rate of 1900-2100 J/min at cycles of 20secs to prevent overheating of the suspension. The reasoning for the selected amplitude, time, and energy rate was based on information reported in recent publications [1,29,30].

The amount of dispersant / SP (0.35 wt% of total cementitious material) was mixed with water (25% of total cementitious material) and stirred magnetically for 5 min. Then the required CNT (0.06 wt%), corresponding to 0.173 g of absolute CNT mass, content was mixed with 25% aqueous solution (in a beaker) and sonicated for 20 min. The resulting superplasticizer to nanotubes, SP/CNT, ratio was calculated to be 5.83. Similarly, another CNT aqueous solution was prepared, but this time the SP/CNT ratio was kept at 4.0. The rationale behind a lower ratio are: (i) excess amount of superplasticizer would affect the workability as well as the strength of the CNT based mortar, (ii) lower manufacturing cost, and (iii) efficient dispersion of CNTs is obtained when its closer to 4.0 In the mixes containing nano-silica (NS) as an ingredient, NS (either at 0.5 wt% or 10.8 wt% of cement) was initially dispersed with PC solution using magnetic stirrer for 5 minutes, followed by mixing of CNTs using a sonicator probe for 2 hours. The beaker was partially submerged in ice-water bath during sonication to prevent the rise in temperature of the solution during the sonication process. The choice of dosages have been derived from studies by Hosseini et al. [34] who observed a stabilizing effect on resistivity at 1% NS incorporation. However, in mixes with both nano and micro silica, the weight incorporated is halved.

The dispersion and interaction of cementitious admixtures with CNTs were analyzed by means of SEM and EDX, using a liquid or powder (liquid dried) sample of about 2 ml, collected from the solution after the sonication process. SEM results have demonstrated that by using a surfactant and supplying appropriate ultrasonic energy, a stable and homogenous nano solution is obtained.

2.3 Mix compositions and sample preparations

Taking into consideration the gaps in literature, the authors decided to manufacture mortars with different admixtures (micro-silica (MS) or silica fume (SF), and/or nano-silica, NS) and weight fractions along with carbon-based fillers to cover a wide spectrum of engineered cementitious compositions, as mentioned in Table 4. The authors considered low dosage, 0.06 wt%, of long MWCNT-COOH to prepare mortar specimens, as it was recommended in previous findings [64]. An innovative approach was taken in the study to investigate if an equivalent weight fraction of carbon fibers (milled – CFM or chopped – CCF) could be substituted instead of CNTs (in the matrix) in-order to keep the manufacturing cost low, and obtain relative performance from the mortar sample. In parallel, control mortar (M1) without CNTs / CFs / NS & SF were also produced. The detailed mortar mixture proportion are given in Table 5.

Further, earlier studies had confirmed enhanced interfacial bonding and mechanical performance by introducing higher dosage of NS, but it also resulted in stabilization effect as the dosage of NS increased in the mortar mix. To address those limitations in this research, and propose a cost-effective mortar mix with admixtures the authors decided to choose three different weight proportions of NS, i.e. 0 wt%, 0.5 wt%, and 1.0 wt%. Additionally, authors after taking into consideration the intrinsic properties of NS and MS, effect on mixing with cement and CNTs, and cost decided to develop a mix with better properties while keeping the cost low. The resulting mortar mix, M4 (as listed in Table 5), integrated both nano and micro silica together; however, the relative dosages for both nano and micro silica were reduced by 50% as compared to when being used individually (i.e. refer to M2, M3, M5 mixes in Table 5).

Table 4: Various mix proportions studied

Mix ID	OPC	MS or SF	NS	CNT	CFM	CCF	Total % fillers
M1	✓	-	-	-	-	-	0
M2	✓	10%	-	0.06%	-	-	10.06
M3	✓	-	10.8%	0.06%	-	-	0.86 1.06
M4	✓	5%	0.5%	0.06%	-	-	5.56
M5	✓	-	10.8%	-	0.24%	-	1.04 1.24
M6	✓	10%	-	-	0.12%	0.12%	10.24
M7	✓	10%	-	0.03%	0.12%	-	10.15
M8	✓	10%	-	0.03%	-	0.12%	10.15
M9	✓	-	-	0.03%	0.12%	0.12%	0.27

Table 5: Mortar mixture proportion

	Cement	Sand	Water	Superplasticizer
Unit weight (kg/m ³)	752	1253	289	2.63

A traditional benchtop laboratory mortar mixer was utilized to produce mortar specimens. The mixing procedure to obtain nano-reinforced cementitious paste followed ASTM C305 [65] guidelines. The dispersed MWCNT aqueous solution was gradually added to the dry mix of OPC and sand, consisting of sand to cement ratio $s/c = 1.667$, and water was gradually added to the mix (quantity of water was calculated by taking water to cement ratio $w/c = 0.384$ (unless specifically mentioned)). On the other hand, mixes that contained micro silica, had silica particles (at either 10 or 5 wt % of cement) introduced in the dry mix of cement and sand and then subjected to rigorous mixing for 4 min prior to the addition of water and/or nano-aqueous solution. The mixing of the materials was performed for 3-4 min until all the MWCNT suspension was integrated with the cement mix. Following that, the remaining water was added gradually to the mix, while the mixer was running for 2-3 min, until the desired workability of the cement paste was attained, as per ASTM C143 [66]. For each composition, a minimum of three cube specimens of size 50 mm were fabricated. These molds were then kept on a vibration table for 5 min in order to ensure proper compaction and remove any voids that might be present in the cube samples, and then covered with a plastic sheet for 24h. After demolding, all the specimens, were water cured at ambient temperature (i.e. 22°C) for 28 days. At the end of 28 days of curing, the samples were removed from the water tank and air dried for 24 h before being subjected to compressive loads.

2.4 Testing procedures

For compressive tests, samples were tested after being water-cured for 28 days according to ASTM C109 [67]. The tests were conducted on a MTS ~~Criterion 64 (Model C64 206S)~~ universal testing machine at 0.01 mm/s. This approximately resulted in a loading range of 200 to 400 lbs/s [900 to 1800 N/s] as stated in the test standard. This loading rate is also in line with that suggested by B. Han et al. ~~The loading rate of sensing cementitious material has been obtained from the works of B. Han et al. [68].~~ For each mix, an average of 3 cubes were tested in Saturated Surface Dry (SSD) conditions. The maximum load (in ~~KN~~kN) was recorded for each sample, average was calculated for each mix composition, and used for comparative analysis.

Bulk resistivity test was performed using ~~‘RCON2’~~ non-destructive device ~~that was procured from Giatee Scientific Inc~~available commercially. The mortar samples with dimensions 50 x 50 x 50 mm were tested for bulk resistivity after various curing durations, i.e. 3, 5, 8, 10, 14, and 21 days for all mix proportions to study the connectivity effect of small numerous carbon particles in the mortar. The samples were removed from the curing tank, surface dried (maintaining SSD condition), and placed between the two metal plates, custom designed for either cylindrical or cubical specimens, (which act as electrodes) along with moist sponges for maintaining continuous flow of current. The bulk resistance values were recorded, which were later converted into resistivity values Azarsa and Gupta [69] describe the principle of this technique, and its application

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for concrete structures. The [Giatee-internal](#) software was able to impede AC current to the sample at a controlled frequency of 1 kHz and output the electrical resistivity of the sample. The mean resistivity of 3 samples for each mix proportion was calculated, based on the experimental test results, and used for comparative analysis.

3. Results and Discussions

3.1 Microstructure of CNT aqueous solution

The microstructure of carboxyl-functionalized nanotubes in water along with polycarboxylate ether based superplasticizer was investigated by SEM. Further the chemical interaction and effect of silica particles with CNTs and carbon fibers have also been discussed with regards to microstructure as observed under Transmission Electron Microscopy (TEM), and SEM analysis.

3.1.1 Influence of SP/CNT ratio on CNT dispersion

Polycarboxylate ether based superplasticizer (PC) plays an essential role in enhancing the dispersion of CNTs in water. Metaxa [70] illustrates that PC molecules have a comb like structure as illustrated in Figure 1, consisting of anionic backbone along with non-ionic side chains [71]. The latter, non-ionic side chains, primarily assist in the dispersion of nanotubes in water, as they form a layer on the outside surface that acts as a protection barrier and prevent carbon particles from being coagulated that ultimately leads to large agglomerates. On the other hand, the anchoring groups attached to the backbone consist of high polarity groups such as —COOH , —OH , etc., which upon interacting with cement particles develop a hydrogen bond, covalent bond and van der Waals forces [72]. Thus affecting the workability and strength of the cementitious material. The article also mentioned that longer PC chains have a more stabilizing effect on the dispersion of nanoparticles in aqueous solutions as well improved interfacial bonding between CNTs and the host matrix.

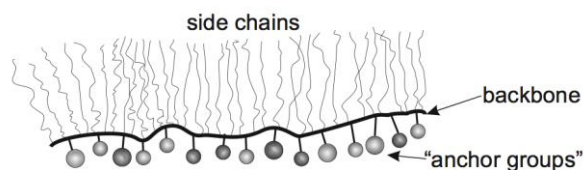


Figure 1: Schematic representation of the typical molecular structure of PC [Adopted from Open Access Article, Source:\[70\]](#)

Figure 2 presents a visual comparison between the dispersion stability of CNTs-COOH in water for two SP/CNT ratios. It can be seen that higher dosage of superplasticizer does not significantly affect the dispersion of nanotubes; however, it may affect the compressive strength of cement

mortars (discussed in Section 3.2). It's important to understand as to how the relative stability of CNT aqueous solutions with different SP/CNT ratios were determined.

Firstly, the suggested amount of SP, i.e. 0.35% of total cement (according to the supplier), was measured and mixed with one quarter amount of the total water required for casting cube samples. Accurately measured 0.06 wt% (about 0.173g—quantity required for making 3-cube samples) of COOH CNTs were added to the solution. The resulting superplasticizer to nanotubes, SP/CNT, ratio was calculated to be 5.83. The solution was then subjected to magnetic stirring for 5 minutes, followed by ultrasonication for 20 minutes to disperse CNTs homogenously within the solution. Similarly, another CNT aqueous solution was prepared, but this time the SP/CNT ratio was kept at 4.0. The rationale behind a lower ratio are: (i) excess amount of superplasticizer would affect the workability as well as the strength of the CNT-based mortar, (ii) lower manufacturing cost, and (iii) efficient dispersion of CNTs is obtained when its closer to 4.0 (refer to Section 2.2 for more details).

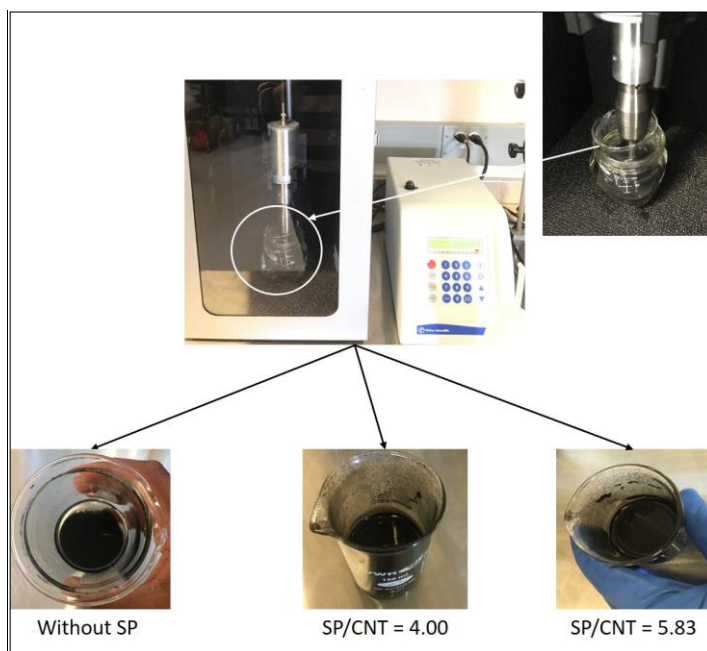


Figure 2: Suspension of nanotubes using superplasticizers - after sonication process

Further, the authors prepared the sample for SEM analysis (for preparation details, kindly refer to Section 2.4). Figure 3 depicts the morphological images (SEM) of the liquid sample (with SP/CNT = 4.0), and it can be observed that MWCNTs-COOH appear as coiled shape, but distributed evenly throughout the solution. The magnified image in Figure 3, reveals the length and diameter recorded

for various CNTs observed in the aqueous sample. Therefore, it can be stated that the length and diameter of the nanotubes seem to be not damaged by the sonication process. This became evident from the dimensions observed in the figure as those were within the limits as specified by the supplier. Hence, suggesting that the dispersion methodology, designed by the authors, is effective, safe and not detrimental to the physical characteristics of CNTs.

Lastly, from the cement reinforcement perspective, it is vital that an optimal SP/CNT ratio is chosen in-order to observe the improvement in mechanical and electrical properties of nano based concrete composite material. Hence, the integration of homogenously dispersed nanotubes in cementitious matrix would lead to improved mortar composition with enhanced properties.

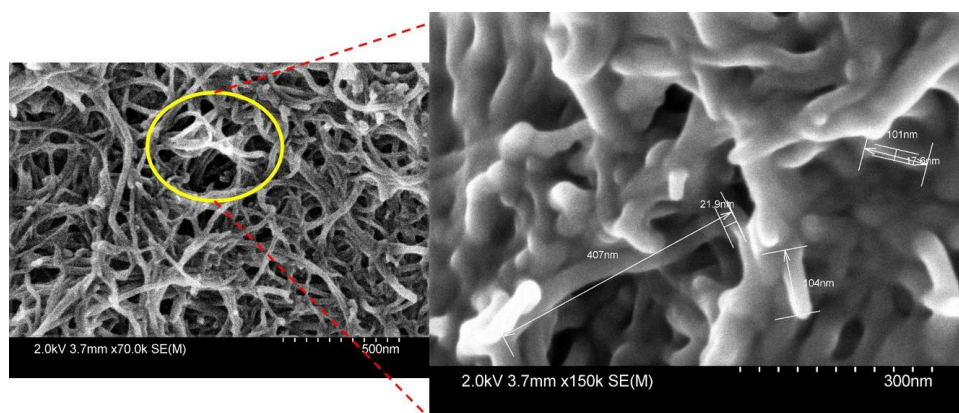


Figure 3: SEM images of CNTs dispersed in water by using PC superplasticizer

3.1.2 Effect of silica particles on CNT dispersion and microstructure

The utilization of silica particles such as micro silica (MS) in cementitious composites has shown promising results for more than two decades, with respect to durability and mechanical properties [74]. This profound effect has been reported due to the Pozzolanic reaction with cement and relatively smaller particle size vis-à-vis cement grain size. Therefore, silica particles have been incorporated by the authors in these experimental studies.

SEM images (refer to Figure 4) reveal the morphology of the dispersed MWCNT-COOH and micro silica (at 10 wt%). Spherical particles of MS were found to possess a variety of different diameters ranging from 90 nm to more than 250 nm. Further, the image on the left (in Figure 4) reveals the synergistic effect of silica fume particles in preventing re-agglomeration of dispersed nanotubes in the aqueous solution. In addition to that, it can be clearly seen that nanotubes are scattered throughout the matrix, and the very small spherical particles are spaced between neighboring CNTs which, while unwinding the CNTs also help to maintain a longer conductive network of fibers throughout the cement matrix even at a low concentration of conductive fillers.

1 The rationale behind this effect lies in the very small particle size of silica fume (i.e. 10 – 200 nm),
2 which tend to get intermixed with CNT bundles and thus help in breaking their agglomerates. As
3 a result, their presence helps to maximize benefit from limited volume fraction of fibers. This is in
4 contrast to Figure 3 (dispersion in the absence of silica particles) where the CNTs are much
5 conglomerated and exist in a coiled shape. Once again it can be seen in Figure 4, that individual
6 CNTs are randomly dispersed while maintaining their aspect ratio with the assistance of larger MS
7 spherical particles.

8 In addition to that, Figure 5 represents a higher magnified TEM image that illustrates the deposition
9 of silica oxide particles onto CNT wall surface, thus confirming the interaction between silica
10 particles and -COOH (found on the sidewalls of CNTs). Thus, authors believe that MS particles
11 mixed with CNTs in the solution, would tend to fill pores between cement particles, and thus
12 improve the interfacial bonding during cement hydration process. Similar behavior has also been
13 observed by other researcher [74].

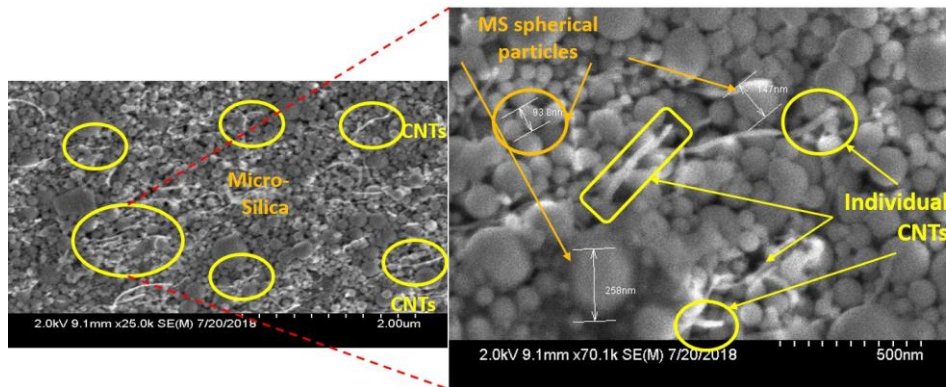


Figure 4: SEM images showing the synergistic effect of micro silica on dispersion of CNTs

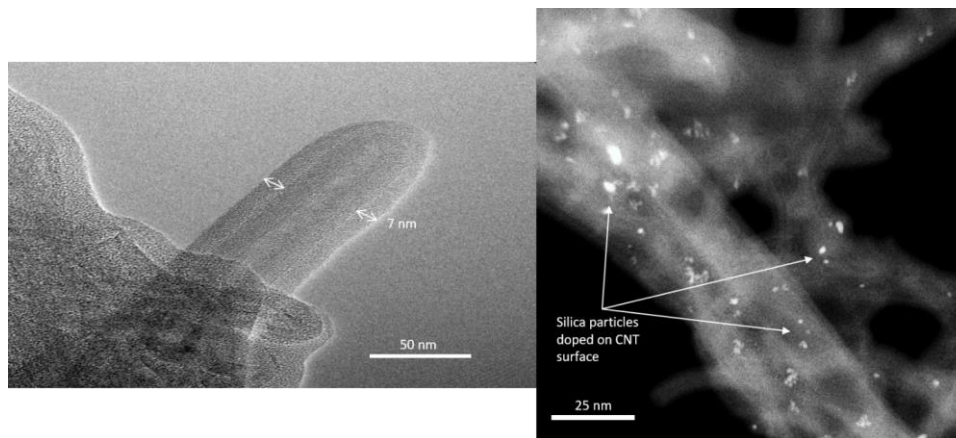


Figure 5: HRTEM image depicting Silicon dioxide (SiO_2) coating on f-CNTs walls

Kim [33] reported that the addition of nano-silica did not contribute to the dispersion of MWCNTs (pristine) in water. The rationale behind that lies in the irregular shape of nano-silica particles, and diameter of each particle, which were insufficient in increasing the distance between CNT particles inside the matrix. In order to investigate this further with functionalized CNTs (-COOH group), the authors produced a CNT-nano silica solution using the sonication process (described in Section 2.2). However, during the experiments, the authors observed initially that due to low bulk density as well as average particle size of the nano-silica particles, as compared to micro-silica particles, additional 25% water was required to mix 0.5 wt% of NS to prepare an efficient aqueous solution.

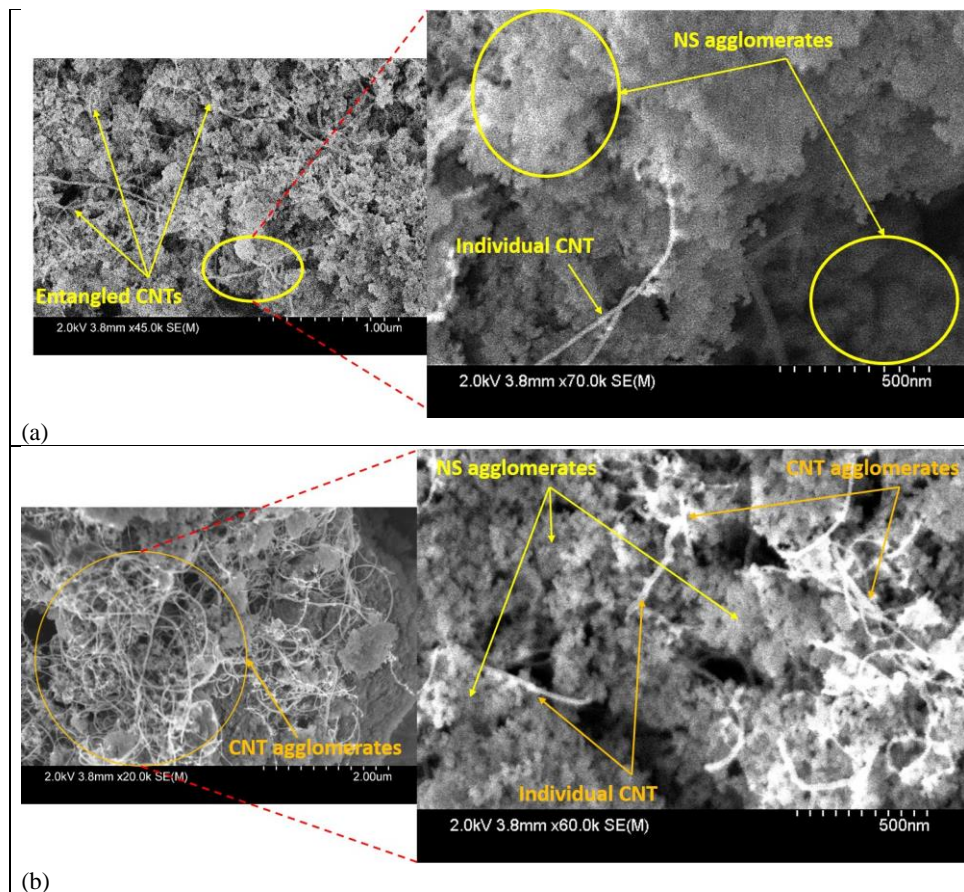
~~As a first step in the process to prepare the solution, weighed amount of NS was added to a CNT aqueous solution and stirred for 5 minutes. Following that, the CNT/NS aqueous solution was~~

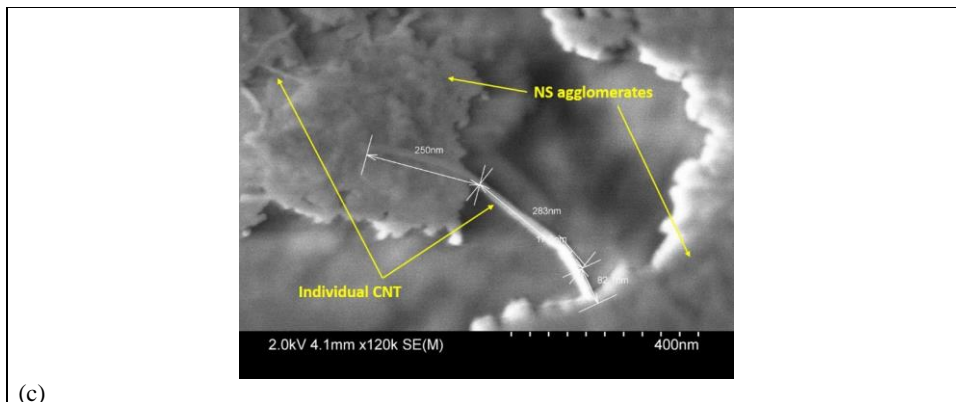
1 ~~stage 2: CNT/SP/NS solution~~ Key words: CNT/NS solution, low pressure, 2
 2 was: nano-silica appeared to form a dense mass inside the beaker (refer to Step 2 in Figure 6),
 3 some nano-silica particles dried out and were left on the surface of the beaker, as seen in Step 3 of
 4 Figure 6. Interestingly, the authors observed that a sample of the liquid solution left in a separate
 5 container (for SEM analysis) turned into a powder that depicted a separate layer of MWCNTs
 6 (blackish in color) and nano silica (appeared to be white in contrast).



8 *Figure 6: Suspension of nanotubes using nano-silica – after sonication process*

9 The nano-silica particles depicted a different effect when reacted with CNTs-COOH in-terms of
 10 dispersion stability, as well as morphologically in-comparison to the micro-silica particles. Figure
 11 7 presents the SEM images of the liquid (Figures 7 a & b) and powder sample (Figure 7c) of
 12 CNT/SP/NS aqueous solution. For the liquid sample under SEM, more number of entangled CNTs
 13 were observed surrounded by NS agglomerates. Only few spots in the sample illustrated long
 14 individual CNTs with NS agglomerated around it. Similar morphology of NS CNT embedded
 15 specimens has also been reported [33]. Whereas the liquid dried (powder) sample presented a long
 16 individual CNT strand as a bridge between two NS agglomerate particles under the microscope. It
 17 was interesting to observe that once again the length of the CNT (i.e. from 900 nm – 1 μ m) was
 18 not damaged during the sonication process, thus highlighting the repeatability and effectiveness of
 19 the dispersion methodology proposed in this study.





(c)
Figure 7: SEM images shows the effect of NS on dispersion of CNTs (a and b) liquid form; (c) powder form

3.1.3 Effect of silica particles on carbon fiber dispersion

Considering the two main objectives of this study, (i) identify an economical and practical hybrid mix (CNTs + CFs) for commercialization purposes; (ii) experimental observation - the behavior of silica particles with carboxylic functionalized carbon nanotubes, it became vital to understand if a similar interaction would also occur with carbon fibers.

Two different volume fractions (V_f) of nano-silica (0 wt% and 0.5 wt% of cement) were chosen to be mixed with milled type of carbon fibers (at 0.1 vol%) along with superplasticizer. The superplasticizer was initially mixed with 50% water quantity (of the total required for cement mortar) using a magnetic stirrer for 2 minutes. Following that, in Beaker 1, 0 wt% of NS was added along with milled carbon fibers (CFM); whereas in Beaker 2, 0.5 wt% of NS was mixed with CFM. The solution was then subjected to sonication process for 20 min.

At the completion of the sonication process, visually the solution in Beaker 1 appeared to be darkish in color, while a greyish solution could be observed in Beaker 2 (as shown in Figure 8 – a & b). The possible reason for change in color lies due to the addition and efficient mixing of nano-silica (whitish powder) in a black solution (CFM + water + SP). Interestingly, the final mixture maintained its dispersion stability and no drying of the solution was seen. Further, both the samples were analyzed using SEM-EDX to quantify their dispersion and chemical composition. The MCF/NS sample illustrated mostly the silica particles with traces of carbon, possibly due to efficient mixing of carbon particles with that of silica. The EDX during SEM analysis reported high carbon and silica content (each region shown in Figure 8c), thus validating the chemical interaction between the two.

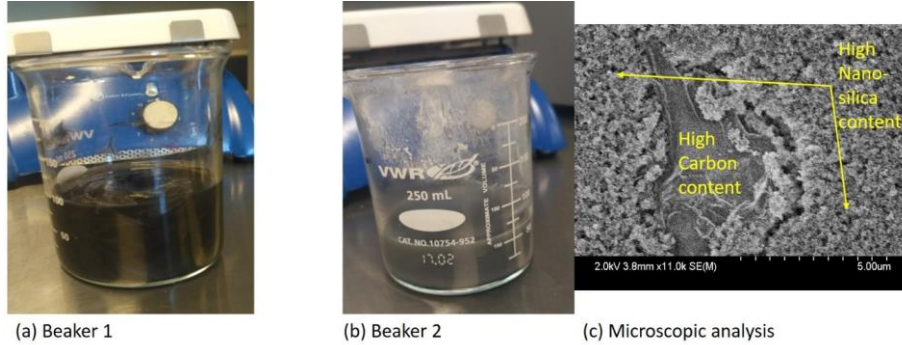


Figure 8: Dispersion of milled carbon fibers in an aqueous solution: (a) SP, (b) SP + NS, (c) SEM image

3.1.4 Summary of dispersion behavior of nanoparticles

Considering the dispersion behavior of silica particles with CNTs-COOH and carbon fibers it can be stated that micro-silica promotes enhanced dispersion of nanotubes, whereas nano-silica contributes towards stability of the solution with milled carbon fibers. Secondly, effective dispersion was achieved by applying ultrasonic energy with the use of a superplasticizer, PC. Lastly, the combination of visual and morphological analysis suggests that for stable and homogenous dispersion, a weight ratio of surfactant to MWCNT close to 4.0 is required.

3.2 Compressive Strength

3.2.1 Influence of CNTs-COOH

The ultimate compressive strength (UCS) results of the plain mortar and mortars reinforced with CNTs /MS/ NS after 28 d of hydration are depicted in Figure 9. Interestingly, the experimental results show that the addition of carboxyl functionalized nanotubes, irrespective of the additional admixtures such as MS and/or NS, improve the compressive strength of the mortar sample even at a low weight fraction (0.06 wt% of cement) vis-à-vis plain mortar specimen (M1 in Figure 9). This could be attributed to the development of strong bonding between CNT and matrix composites owing to the interfacial integration with cement hydration products such as C-S-H and surface functionalized CNTs. Thus, providing a very high strength mix for the industry. One possible reason for this enhancement is due to the strong interfacial interaction between cement and homogeneously dispersed nanotube particles. In-order to develop this covalent bonding, chemical reaction occurs between CNTs-COOH and cement hydration products either C-S-H or $\text{Ca}(\text{OH})_2$ as explained by Li [75], illustrated in Figure 10. The resulting long chains of carbon molecules allows efficient load-transfer capability from the cement matrix to the strong nanotubes. The other possible reason owes to reduced porosity of the cement paste. In general, there are several voids between the cement particles, which are filled by smaller particle sizes of nanotubes, micro-silica and nano-silica. As the pore sizes are reduced and compacted by the additional particles, it leads

1 to an increase in strength. Similar behavior has also been observed by other researchers globally
2 [40,41,75,76].

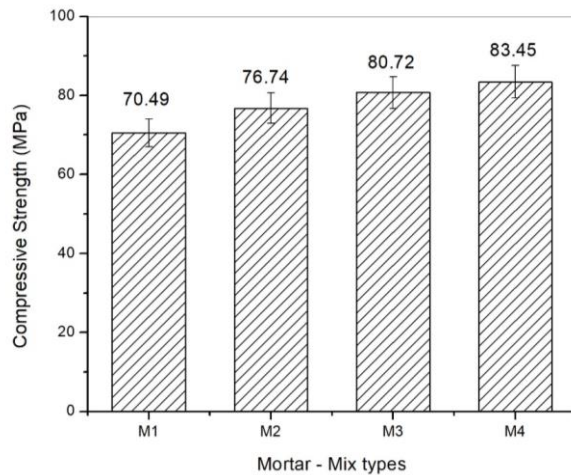


Figure 9: Compressive strength of plain mortar and mortars reinforced with CNTs and cement admixtures

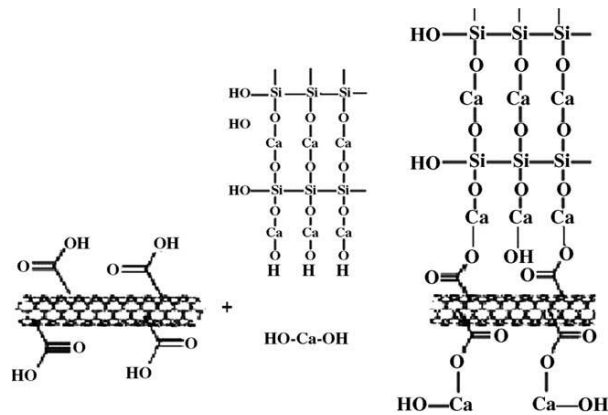


Figure 10: Reaction scheme between carboxylated nanotube and hydrated cement products
Source: [75]

3.2.2 Influence of silica particles along with CNTs

The modern developments in the construction industry created a need to develop high strength and durable concrete material. To address that issue, the micro behavior of the cementitious materials

² "Reprinted from ELSEVIER, Vol 53, Issue 6, Li G.Y., Wang P.M., Zhao X., Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes, 1239-1245, Copyright (2005), with permission from Elsevier."

needed modification, which was successful by reinforcing a portion of the cement with admixtures such as micro silica (or commonly referred to as silica fume) and nano-silica. The silica particles have high pozzolanic capability, which upon interacting with cement paste produces calcium silicate hydrate (C-S-H) gel during the pozzolanic reaction with the calcium hydroxide ($\text{Ca}(\text{OH})_2$) formed during cement hydration process [42]. As a result, concrete with high strength and low porosity is produced. Between MS and NS, the latter has superior properties owing to very high specific surface area, and smaller particle size when substituted in cementitious materials. Researchers have reported reduced hardening time, higher compressive strength and stable electrical resistivity by integrating nano-silica vs micro-silica in concrete [42,77,78].

With respect to results presented in Figure 9, the increase in compressive strength of the mortar specimens reinforced with functionalized CNTs along with micro-silica (MS) and nano-silica (NS), as compared to the control mortar, is 9% (M2 specimen) and 14.5% (M3 specimen), respectively. It can be seen that adding a limited amount of NS (0.8 wt%) had a greater influence on the compressive strength of mortar in-comparison to that with MS particles. The difference observed can be attributed to the pozzolanic reaction, where NS has higher pozzolanic effect vis-à-vis MS due to higher percentage of silica. The previous discussion in Section 3.1.2 about higher pozzolanic reaction between NS and CNTs has validated the positive effect on the mechanical performance of the material as well. Further, a combination of MS (at 5wt%) and NS (0.5%) with 0.06wt% of CNTs (M4 specimen in Figure 8), the compressive strength reaches a maximum value of 83.45 MPa, i.e. 18.4% increase as compared to the plain mortar specimen. The possible reason explaining this phenomenon can be attributed to the compactness and reduced porosity of the cement paste due to silica fume utilization. Additionally, when silica particles got intermixed with f-CNTs they got hydrated by Ca^{2+} ions from the cement paste. These products anchored onto CNTs, thus improving the interfacial bonding within the matrix. Further, during the experimental trials the authors observed that load-bearing capacity of the CNTs/NS sample was higher than the other specimens, while the failure strain enhanced for CNTs/MS specimen. The M4 sample illustrated a mid-range load bearing capacity along with higher strain rate, which makes it more suitable for real-life applications.

Based on the experimental results, the authors believe that an increase in the dosage of nanotubes (from 0.06 wt% to optimal 0.1 wt%), as well as nano-silica (from 0.8 wt% to optimal 2 wt%) would produce a very high strength material with enhanced durability and stable electrical resistivity. This has been considered as a future scope of this study. Lastly, the multi-faceted features of this new nano-concrete material would be beneficial and applicable for structural health monitoring of structures.

3.2.3 Influence of carbon fibers and hybrid mix with CNTs

The ultimate compressive strength (UCS) results of the plain mortar and mortars reinforced with carbon fibers (chopped – CCF, and milled – CMF), along with silica particles after 28 d of hydration are depicted in Figure 11. The volume fraction of the nanofillers was halved when used

1 in a combination. The objective of this methodology was to determine if the hybrid mix of carbon
2 fibers would have sufficient load bearing capacity, as found with nanotubes. Secondly, if found
3 feasible, the utilization of higher amount of carbon fibers over nanotubes would significantly drop
4 the manufacturing cost of the composite material.

5 In general, it was observed that in low volume fractions, the influence of carbon fibers on the
6 compressive strength was lesser in comparison with that of the nanotubes. The fibers inside the
7 cementitious matrix normally restrain and delay the crack propagation throughout the matrix.
8 During compressive loading, several micro-cracks are initiated throughout the mortar sample, the
9 carbon fibers deal with these cracks better because of their micro-scale, while the small diameter
10 of nanotube reduces porosity and promotes cement hydration products, which result in increasing
11 the compressive strength and strain failure. The authors observed a drop of 15.3% in strength for
12 M5 mortar mix in comparison to M1 (plain mortar) specimen. These results suggest the lack of
13 chemical interaction between carbon milled fibers (CMF) and NS particles during disperion
14 process, which probably resulted in creating more voids inside the cementitious matrix, thus
15 dropping the compressive strength. On the other hand, a hybrid combination of CCF and CMF
16 along with micro-silica particles (M6 in Figure 11) demonstrated slightly positive effect on the
17 strength of the material in comparison to M1.

18 Furthermore, the authors attempted to substitute carbon fiber with 0.03wt% of nanotubes, to
19 explore the effect on the compressive strength. As seen in Figures 11 and 12, between M7 and M8
20 mixture proportions, the latter demonstrated 13.2% improvement in compressive strength vis-à-
21 vis plain mortar. It must be noted that, dry mix of chopped carbon fibers (CCF) along with silica
22 fume particles have a more positive effect in-terms of reinforcement as compared to a CMF
23 aqueous solution. Additionally, the combination of carbon nanotubes and chopped carbon fibers
24 help to effectively reduce the voids and bridge the micro cracks being formed, respectively, thus
25 leading to a higher compressive strength and higher strain post peak load, as seen in Figure 12.

26 The load displacement graph was obtained from compressive loading on cube specimens of size
27 50mm. It can be seen that initially less displacement occurred compared to the load applied, during
28 which the clearances between the test fixture and the specimen eliminated. Following that applied
29 load increased linearly with the displacement till the peak load. Similar behavior has been observed
30 by other researchers as well [79,80]. It must be noted that the initial curvatures is due to the
31 displacement in machine before the actual loading begins on contact surface. On the other hand, a
32 small positive compressive strength improvement for M9 mix proportion suggests that the
33 presence of only carbon particles in the cementitious matrix is not sufficient to produce high-
34 strength concrete. The integration of silica particles (either at micro or nano-scale) is vital as they
35 reduce porosity, increase compactness, and promote the production of C-S-H gels, which results
36 in higher strength of the composite material.

37 On comparing M4 and M8 curves in Figure 12, it can be observed that substituting 0.03 wt% of
38 CNTs with 0.12% CCF, and 0.5 vol% of NS with 5 vol% of SF present a higher load-bearing
39 capacity, controlled micro-crack growth, and ductile fracture behavior.

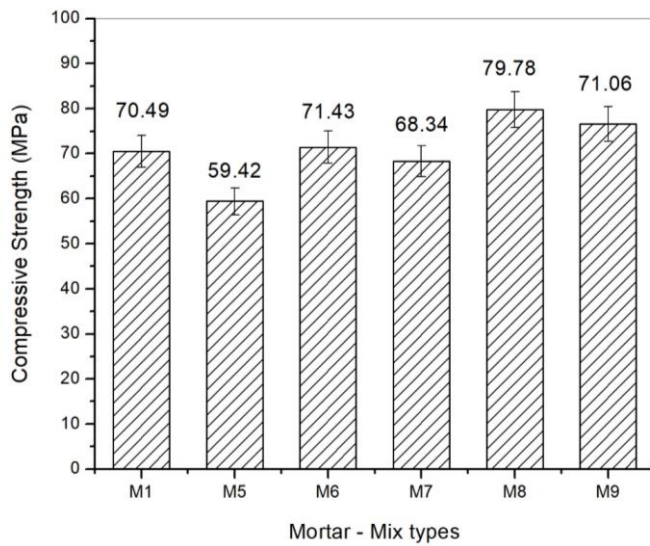


Figure 11: Compressive strength of plain mortar, mortars reinforced with carbon fibers, and hybrid mix (with CNTs)

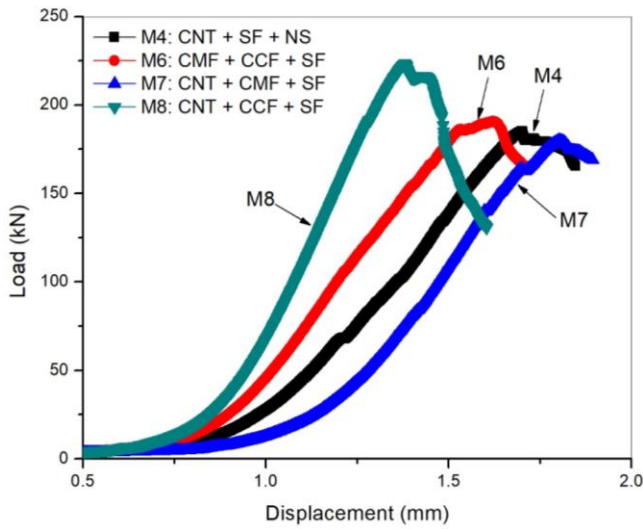


Figure 12: Load-displacement curve of Carbon fiber and CNT reinforced mortar specimens

3.2.4 Cost vs Strength

1 One of the objectives of this study was to explore an economical and high-strength / durable mix
2 proportion for concrete. For this, a cost analysis was carried out. The nominal cost associated with
3 producing plain mortar was considered the baseline, which includes the cost of cement, sand,
4 superplasticizer, and water. The normalized cost calculated represents the additional cost (per
5 cubic meters in Canada) required to manufacture 8 different mix proportions that utilize nanofillers
6 as well as silica particles. Since it is vital that the composite material be efficient for structural
7 applications it is important to plot the compressive strength and the manufacturing cost
8 simultaneously, which is represented in Figure 13.

9 It can be observed from sections A, B & C in Figure 13 that there is a significant cost difference
10 in the mixes. Firstly, the section A highlights that replacing micro-silica with higher Pozzolanic
11 ingredient, i.e., nano-silica, in a CNT reinforced mortar the strength increases as well as the cost
12 (referring to M3 mix proportion). It is interesting to note that, lowering the volume fraction of NS
13 and substituting it with MS (M4 mix) has a dual effect: it leads to an improved compressive
14 strength of 83.45 MPa; and also lowers the manufacturing cost by 15% (from \$12420 to \$10590).
15 This reduction in cost is significant when compared to a large scale production in construction
16 industry. Hence, it can be stated that higher cost in Section A mix proportions is due to two
17 constituents: functionalized nanotubes and 99.9% pure nano-silica. These both being at nano-scale
18 have distinct properties, thus have a great influence on the dispersion as well as mechanical
19 behavior of the concrete composite material.

20 On the other hand, the hybrid mixes significantly cut down the manufacturing costs as seen in
21 section B of Figure 13. For each of the four mixes (M5, M6, M7, and M8) containing carbon fibers,
22 the cost is reduced to less than half in-comparison to the ones containing only f-CNTs, as
23 mentioned in section A. The lowest cost is calculated for the mix that doesn't utilize any f-CNTs
24 (M6) \$76. The resulting cost is nearly only 1% of the total cost involved for a similar mix
25 containing f-CNTs, M2. Further, section B of Figure 13 illustrates that although the cost of
26 producing fiber reinforced mortar is low in comparison to section A, but at the same instance, the
27 strength is within $\pm 5\%$ as compared to the plain mortar. As discussed earlier in section 3.2.3,
28 carbon milled fibers (CMF) did not show promising results when reinforced with nano-silica as
29 well as MS/CNT mixture. Thus suggesting, other tests to be carried out before making a
30 recommendation for industrial application, such as for other mechanical and electrical properties
31 as it may show a different effect, which may then change the scope of these materials.

32 Considering once again the discussion of Figures 11 and 12, the combination of carbon chopped
33 fibers and f-CNTs along with micro-silica (M8 mix) in cementitious matrix produces a hybrid
34 mortar composite with strength that is similar to mix containing NS and f-CNTs only (referring to
35 M3). It is interesting to note that while the strength is similar, the manufacturing cost (as reported
36 in section C of Figure 13) is halved. Hence, M8 mix proportion seems to be outperforming in-
37 terms of mechanical behavior as well as from application perspective. However, the present set of
38 investigation only considers compressive loading. Hence, it is necessary to determine the behavior
39 of mixes under different forms of loading conditions. The authors are continuing to investigate

1 further combinations that could result in even higher compressive strength, about 100 MPa, and
 2 being more durable while keeping the cost low. The results of those experiments shall be reported
 3 in a future publication.

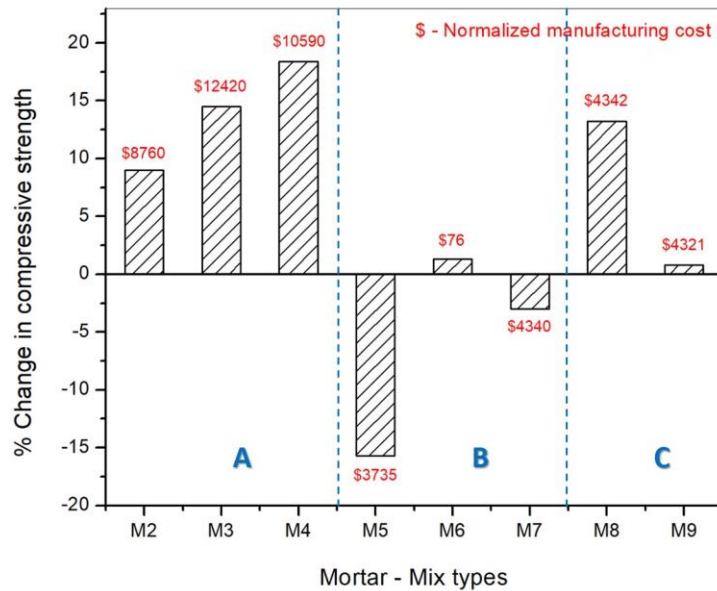


Figure 13: Normalized manufacturing cost vs % change in compressive strength for mortar mixes

3.2.5 Summary of compressive strength of nanoparticles

The experimental results reveal that the addition of carboxyl functionalized nanotubes enhance the compressive strength of the mortar sample even at a low weight fraction, owing to stronger covalent bonding with C-S-H gels and reduced porosity of the cementitious matrix. The addition of silica particles promote pozzolanic reactions with cement, producing more C-S-H gels, and improves the compactness of the matrix. Both micro and nano-silica improved the compressive strength when reinforced with CNT mortar mix, while the latter showed considerable effect. Furthermore, dispersed chopped carbon fibers (dry) in the cementitious matrix allowed the bridging of micro-cracks throughout the cement matrix, thus improving the compressive strength & strain failure, as compared to milled carbon fibers which increased the porosity and deteriorated the strength. Lastly, the cost vs strength comparative analysis provided a preliminary investigation, which confirms that with the possible hybrid application of fibers with f-CNTs, an economical method of cement-sensor based structural health monitoring technique can be developed.

3.3 Potential of CNT reinforced concrete as ‘cement-based’ sensors

The electrical resistivity is a property of the cementitious composite material which relates to the ability of the matrix to resist the flow of electrical current. The bulk resistivity of the material is dependent primarily on the specimen’s moisture content. In general, the normalized bulk resistivity of the cement material is considered a material property, however, the tests performed provide electrical resistance value. This value is then corrected by applying the geometry factor, as illustrated in Eq (1).

$$\rho = K \times R \quad (1)$$

In this study, R, which is the resistance was measured using a Giatec equipment (in Ω), and K is the shape factor (mm or cm). K can be calculated using the following formula, Eq (2):

$$K = \frac{A}{L} \quad (2)$$

Where, A is the cross-sectional area, and L is the length of the test specimen. In this study $A = 2500 \text{ mm}^2$, and $L = 50 \text{ mm}$. Thus, the equation to calculate the bulk resistivity ($\Omega\cdot\text{cm}$) of the cube shaped specimens (50x50x50mm) is given in Eq (3):

$$\rho = 5 \times R \quad (3)$$

Lastly, the conductivity (σ), in $(\Omega\cdot\text{cm})^{-1}$, of the nano reinforced mortars is given by Eq (4):

$$\sigma = \frac{1}{\rho} \quad (4)$$

The samples were tested after 3, 5, 8, 10, 14 and 21 days curing regime, and the average electrical conductivity for each mixture proportion is presented in Figure 14.

3.3.1 Bulk Resistivity of CNT based mortar

The bulk resistivity of fiber-reinforced mortar was significantly reduced by adding carbon fillers, especially 0.12 vol% of chopped carbon fibers (CCF) as presented in Figure 14 as compared to the reference specimen. For instance, after 3 days curing, the conductivity of the composites with 0.06 wt% CNTs (M2 in Figure 14) was found to be $2.15 \times 10^{-4} (\Omega\cdot\text{cm})^{-1}$, whereas the hybrid composite containing 0.03 wt% CNTs along with 0.12 vol% CCF (referring to M8 mix) recorded the maximum, i.e. $3.89 \times 10^{-4} (\Omega\cdot\text{cm})^{-1}$ at the identical age. This is probably due to the fact that more continuous pathways were formed due to the presence of chopped carbon (conducting) fibers. On comparing this hybrid mix to the reference mix (M1), 92% improvement in conductivity was recorded. It is also interesting to note that, CCF outperformed MCF in-terms of conductivity as well as strength. A possible reason is the higher bulk density of MCF vs CCF. On the contrary, the effect of CNTs alone (at 0.06 wt%) as a conductive filler in the mortar mix was insufficient to form enough continuous conductive pathways to allow electrical current to flow effectively (refer to M2, M3 & M4 in Figure 14), as it’s below the percolation threshold of 1 vol% and/or 1.15 vol%,

as suggested by other researchers [81,82]. Additionally, the presence of silica particles (either NS or MS) did not seem have to have a profound effect on conductivity of the material, while it did influence the strength (as discussed earlier).

Furthermore, the experimental results illustrate an increase in electrical resistance as curing time increases for most of the mix proportions. This effect is influenced by the water content inside the matrix, which initially increases the conductivity but with excess water absorption it decreases [83–88]. The highlight for this paper are hybrid combinations (containing CNTs) – SP, MS, NS, sonication and stirring, which have shown better performance in terms of SEM, compressive strength and resistivity properties. Thus, there is a potential for such mixes to be used as a sensing element in cement - based composites. However, further research would allow to develop strong intrinsic sensing capabilities in a hybrid fiber reinforced cementitious composite (HyFRCC) material, which shall be reported in a future publication.

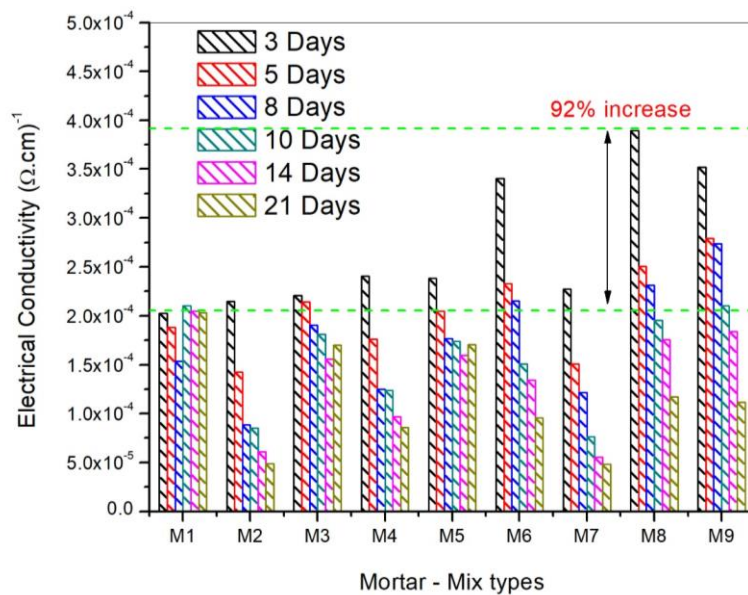


Figure 14: Electrical conductivity of cement composites reinforced with CNTs and carbon fibers

4. Conclusions

- The results presented in this paper indicate that efficient and homogenous dispersion of functionalized carbon nanotubes can be achieved with polycarboxylate-ether (PC) based superplasticizer-to-CNT ratio of 4.0 by applying optimal ultrasonic energy.

2. Small volume fraction of micro-silica particles in CNT aqueous solution builds synergistic effect that prevents re-agglomeration of dispersed nanotubes in the aqueous solution. Further, strong interfacial bonding is developed due to the Pozzolanic reactions between CNTs and silica particles.
3. Nano-silica also plays a significant role in improving the dispersion of CNTs in the aqueous solution, by acting as a cloud and thereby preventing any coagulations, but less in comparison to micro-silica. However, NS contributed significantly towards stability of the solution with milled carbon fibers.
4. Uni-axial compressive strength of mortar mix was improved by 9% (for MS and CNT mix), 14.5% (when NS and CNT were mixed), and 18.4% (for mix containing MS, NS, and CNTs) as compared to the control mix. The possible reason is the stronger covalent bonding with C-S-H gels and reduced porosity of the cementitious matrix. Also, the addition of silica particles promotes Pozzolanic reactions with cement, producing more C-S-H gels, and improves the compactness of the matrix.
5. Dispersed chopped carbon fibers (dry) in the cementitious matrix reported bridging effect between micro-cracks throughout the cement matrix that resulted in higher compressive strength & strain failure as well as better conductivity, as compared to milled carbon fibers which increased the porosity and deteriorated the strength.
6. Hybrid mortar mix containing SF, CNTs and chopped carbon fibers demonstrated 13.2% improvement in compressive strength, 92% enhanced conductivity for sensing capabilities, and optimal cost of production as compared to all other mixes.

Further, exploration of hybrid mixtures of fibers with f-CNTs would allow to develop a smart cement-based sensor that can be used as a structural health monitoring technique for the construction industry. The authors strongly believe that the issue of high cost of MWCNTs to be used as sensors in developing countries can be well addressed by using an optimal concentration of f-CNTs along with different type of fibers and siliceous admixtures.

Declaration of interest: none

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