COMPARATIVE APPLICATION OF TWO NANOPARTICLES IN CEMENT MORTAR

by

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ABSTRACT

COMPARATIVE APPLICATION OF TWO NANOPARTICLES IN CEMENT MORTAR

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Carbon Nanotubes (CNTs) and Carbon Nanofibers (CNFs) are two of the most promising advanced materials in the construction industry due to their excellent material properties. In this study, their application in cement mortar is studied comparatively as possible choice for concrete repair. CNT and CNF have very high aspect ratio due to which the Van der Wal forces between the CNT and CNF tend to agglomerate; thus forming bundles. In order to achieve proper dispersion, ultrasonic energy was used to disperse the CNT and CNF in the aqueous solution. The mechanical properties such as compressive strength and flexural strength of CNT and CNF cement composites were studied and compared with cement mortar. Flow test was conducted to investigate the workability of the cement composites.

In this study, 0.1% and 0.2% of both CNT and CNF by weight of cement and ratio of 0.008 (super plasticizer to cement) was used. Water cement ratio of 0.35, 0.40, 0.45 and 0.50 were used along with a super plasticizer. Samples with water cement ratio of 0.45 and 0.1% performed better compared to all other composites. There is a significant increase in compressive strength for both CNT and CNF samples by 54.5% and 67.5%, and a significant increase in flexural strength by 14.06% and 8.84% at 28 days, respectively. SEM (Scanning Electron Microscope) images were taken to verify the rate of dispersion in CNT and CNF composites. Bleeding, setting time and slant shear test results of the CNF and CNT composites were examined to assess the quality of cement composites as a repair material. Similar to ordinary cement paste, no bleeding was found for both the CNT and CNF cement composites. The CNF and CNT composites exhibited faster setting time compared to the ordinary cement paste containing super plasticizer. Slant shear test results indicated that the bond strength of epoxy resin was relatively close to the CNT composites at 28 days considering the effect of thermal aging for epoxy. Bond strength of CNF samples was low compared to both CNT composites as well as epoxy resin. Thus, the excellent compressive strength and flexural strength makes the CNT and CNF material to as a strong candidate for the repair of cracks and spalling of concrete.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Carbon Nanoparticles are one of the most promising advanced materials in the construction industry. Carbon Nano particles, especially Carbon Nanotubes (CNTs) and Carbon Nanofibers (CNFs), have promising material properties like tensile strength, elastic modulus, hardness and electrical properties. Carbon Nanoparticles have been used primarily in the industrial sectors like electronics, automotive, aeronautics, sports, marine, etc. [1] Introduction of nanoparticles in the cement based materials have gained popularity in recent years due to their mechanical properties and application. In construction industry, concrete is a premier material which is composed of cement, fine aggregates, coarse aggregate and water. Concrete is very good in compression but is weak in tension. To strengthen, the concrete has to be reinforced with bars, rods, fibers, pre- or post-tension. The strength of concrete is based on certain factors such as water-cement ratio, size of pores in the cement, binding between the aggregate and the cement and micro cracking in the cement, among others. Introduction of carbon nanoparticles in the cementitious materials provides extraordinary strength increase as well as controlling cracks, forming bridge mechanism within the cement matrix at the nanoscale level. Carbon Nanofibers have an average diameter of 70 ~ 200 nanometers (nm) and an average length of 50 ~ 200 microns [2] whereas Carbon Nanotubes have an average diameter ranging from <1 nm up to 50 nm and an average length ranging from 1 micron to 1 cm [3].

Attempts have been made previously to include carbon nanomaterial to the cementitious materials to improve the mechanical properties. Carbon nanoparticle enhanced cement mortar is a promising material for repair of concrete for bridge decks, pavements and crack repair of structural elements.

1.2 Research Significance

The term “Nanocomposites” refers to a material in solid state in which one of the phases has one, two or three dimensions of less than 100 nm, or structures having nano-scale repeat distances between the different phases [4]. Nanocomposites are different from other composite materials because of their exceptionally high surface to volume ratio of the reinforcing phase or exceptionally high aspect ratio [4]. CNTs have very high aspect ratio of 1:1,000,000, whereas CNFs have an aspect ratio of 250-2000.

CNFs have higher electrical conductivity, thermal conductivity and mechanical properties such as compressive strength and tensile strength. They are now cheaper and easily available as compared to the early 2000s. Short fibers were used earlier as an admixture for reducing drying shrinkage, to increase flexural toughness and also to increase the flexural strength [5]. Introduction of CNFs in cement based materials was not initially successful because of the high aspect ratio. If the aspect ratio is high, the dispersion of CNF is difficult. (Van der Waal’s interaction tends to agglomerate them in bundles).

CNTs have high electrical conductivity and tensile strength. They are highly flexible, elastic, have high thermal conductivity, low thermal expansion coefficient and high aspect ratio (length = ~1000 x diameter) [6]. Like CNFs, CNTs also have a very high aspect ratio, due to which van der Waal’s forces may cause them to form ropes or bundles when mixed with the cement paste [6]. Better dispersion could be achieved by ultrasonic agitation, and chemical treatment for sorting the fiber and treating with chemical solvents, thus making carbon nanocomposites a promising material for improving the mechanical properties of the material [7].

Repair and rehabilitation of concrete structure is a challenging area in the field of structural engineering. The three basic indications of distress in concrete structures are cracking, spalling and disintegration. The technique available for the repair of concrete structures is patch repair, spraying concrete, micro-concrete, non-shrinkage grout and sealing. Patch repair test mainly consist of two types; one is by using cementitious mortars and other is by using resin-based mortars. To repair the cracks on the pavements and bridges, an easy solution is to apply epoxy coating on the crack surfaces and for spalling of concrete, the solution is the overlay of cementitious grouts. But Epoxy coating does have some problem related to durability and performance as there is difference in stiffness and modulus of elasticity and also difference in the bond strength between the concrete substrate and the epoxy material. Temperature and humidity plays a vital role as thermal aging accelerates when epoxy is exposed to extreme conditions. Hence CNT and CNF reinforced mortar may be a potential candidate for overcoming the above mentioned problems.

1.3 Objective of the Study

Past studies on mortar nanocomposite mainly focused on dosage rate, percentage of CNTs and CNFs in the cement mortar and the mechanical properties of the cementitious composites. One of the problems with the nano composites is that, due to high aspect ratio it attracts each other to form bundles when mixed with water. To overcome, proper dispersion techniques have to be developed. Effect of CNT concentration and the aspect ratio has been studied [8]. Also, the effect of ultrasonic energy and surfactant concentration were investigated [9]. The effect of treated and untreated CNT and the optimum ratio of surfactant to cement have also been studied [11]. The objective of this study is to compare the performance of nanofibers and nanotubes in enhancing mechanical properties of cement mortar. To achieve this objective, the study is divided into three phases.

First Phase:

The objectives for the first phase are as follows:-

- To compare the compressive strength of the control sample (plain cement mortar) with the nanocomposite mortar with CNTs and CNFs.
- To compare the flexural strength of the control sample with the nanocomposite mortar with CNTs and CNFs.
- To determine effective w/c ratio for the nanocomposites.
- To inspect the workability (flow value) of the nanocomposites mortar through the addition of super plasticizer.

Second Phase:

The objective for the second phase was as follows:-

- To verify the proper dispersion of the particles within the cement matrix through SEM images of the failed specimens.

Third Phase:

Based on the first phase results, an effective ratio for the CNTs and CNFs were selected for the third phase. The objectives of this study were as follows:-

- To determine the setting time of cementitious mortar with addition of CNT and CNF.
- To inspect the bleeding of cementitious mortar having CNTs and CNFs.
- To investigate the bond strength between the old concrete substrate and nano composites through slant shear test and to compare with epoxy resin.

1.4 Research Plan

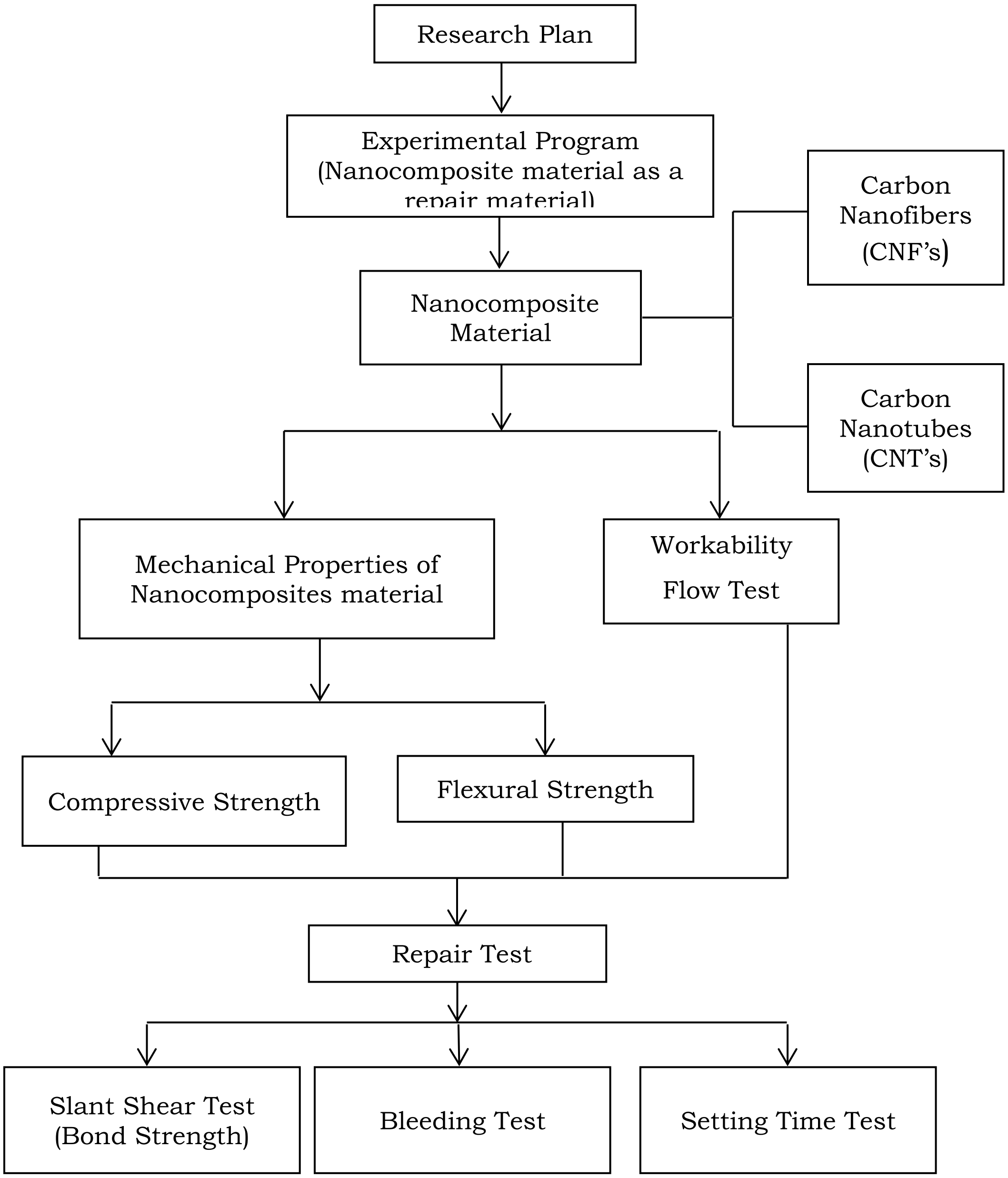


Figure 1.1: Research Plan

Note:

1. 0.1 % and 0.2% of weight of cement of CNTs and CNFs were used.
2. Water-cement ratio of 0.35, 0.40, 0.45 and 0.50 were used.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

A detailed literature review was carried out on nanocomposites (CNT and CNF reinforced cement mortar). The physical and mechanical properties of CNT and CNF were discussed in this chapter. Also, the effects of addition of CNT and CNF on the cementitious material were reviewed along with its mechanical properties (compressive strength and flexural strength).

Concrete is the most prominent construction material which covers half of the infrastructure projects in the world. However, concrete or other cementitious materials are known for their lower tensile strengths. Typically in order to increase the tensile strength, reinforcing bars are introduced. The tensile strength may be enhanced by introducing steel fibers while achieving significant improvements in the mechanical properties. The next step in improving the mechanical properties of the cementitious material would be nanotechnology.

Lately nanotechnology a new phenomenon, where nanoscience and nano-engineering being the two main prospects of application is introduced in concrete research [12]. Nanoscience is a science that deals with the measurement and characterization of nano/micro scale structure of cementitious materials. Nano-engineering enables the structure at a nanometer scale to form a new engineering, multifunctional materials with superior properties, performance and durability. These concepts help us understand the macro scale properties and performance of structural materials.

Concrete can be modified by using nanosized building materials to improve material properties and to control cracking within the cement matrix. Mechanical properties of the cementitious material depend on structural elements and phenomenon that occur at the micro and nanoscale [12]. Since nanocomposites have excellent mechanical properties, they have the potential to function as a high performance cementitious material and also as a promising repair material.

2.2 Carbon Nanofibers

2.2.1 History

CNFs were first patented by Hughes and Chambers in 1889 on the synthesis of filamentous carbon. The research on the CNF came into the limelight in 1950 when the electron microscope was popular in analyzing the specimens at nanoscale [13]. In the year 1970, Japanese researchers Koyama and Endo manufactured vapor grown carbon fiber (VGCF) with a diameter of 1 μm and a length greater than 1 mm [14]. VGCF and VGCNF (Vapor Grown Carbon Nanofiber) are the shortest carbon fibers and draw attention for their excellent thermal, electrical, chemical and mechanical properties.

2.2.2 Configuration of CNF

CNFs are cylindrical structures with graphite layers and are available in shapes of stakes, cones or cups. They are generally obtained in a very fine powder form. CNFs are available in diameters varying from 70 to 200 nm and in lengths varying from 50 to 100 μm.

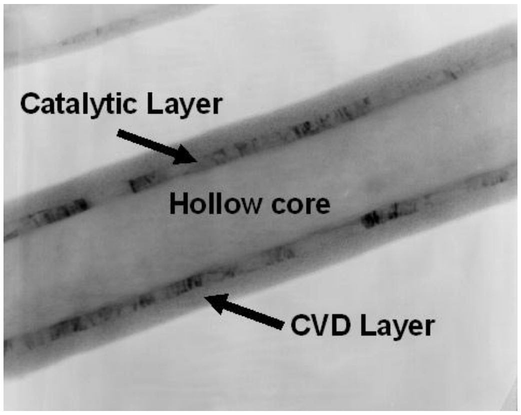


Figure 2.1: Vapor grown CNF (Source: Pyrograf III)

2.2.3 Properties of CNF

CNFs have high electrical conductivity, high thermal conductivity and excellent chemical properties. CNFs possess exceptional mechanical properties like elastic modulus as high as 600 Gpa and tensile strength as high as 8.7 Gpa. CNFs are highly adsorptive for organic materials [15]. CNFs can withstand heat up to 3000 ° C due to which it has superior electrical properties.

2.3 Previous research on CNF as a cementitious material

The utilization of carbon fibers in the cement matrix started in the early 1990s, when Pu-Woei Chen and DDL Chung introduced short carbon fibers in the cement mortar. The amount of carbon fiber used for the study was 0.2% by weight of cement. This research produced an increase of 85% in flexural strength, 205% in flexural toughness and 22% in compressive strength [16].

In 2000, Chung presented a review paper on cement-matrix structural composites for smart structures. In this paper, smart functions were addressed such as strain sensing; damage sensing, temperature sensing, vibration reduction and electromagnetic radiation reflection. The study revealed an increased flexural strength & flexural toughness, improved impact resistance, reduced drying shrinkage and enhanced freeze-thaw durability [17]. Li et al. (2004) displayed the microstructure of the cement mortar with nanoparticles. The compressive strength and flexural strength of the cement mortar with nanoparticles were higher than the plain cement paste [18].

In 2005, DDL Chung investigated the dispersion of fibers in the cement which led to a major breakthrough in the usage of micro carbon fibers in the cement paste. The dispersion of fibers was determined by measuring the electrical resistivity. The electrical resistivity is inversely proportional to dispersion of fibers. This research concluded that the usage of silica fume (15% by weight of cement) and methyl cellulose (4% by weight of cement) had a lesser electrical resistivity and a higher tensile strength [19].

In 2006, Li et al. studied the abrasive resistance of concrete containing nanoparticles. The abrasive resistance of concrete was improved significantly by the addition of nanoparticles and PP fibers. The compressive strength and flexural strength were also improved when the nanoparticles and PP fibers content was 1% by the weight of the cement [20].

In 2007, Li et al. conducted the flexural fatigue performance of concrete having nano particles. The test indicated that the concrete containing 1% of nanoTio2 by the mass of cement had the best flexural fatigue strength [21]. In 2009, Gao et al. performed a test on mechanical and electrical properties of self-consolidating concrete with CNF [22]. The concrete containing 1.0% of CNF produced the best performance in terms of compressive strength as well as electrical resistivity [22].

2.4 Carbon Nanotubes

2.4.1 History

In 1952, V. Radushkevich and V. M. Lukyanovich published images of carbon tubes in 50 nm diameter in the journal of physical chemistry in the Soviet Union [23].

It was unidentified since it was published in Russian language. Oberlin, Endo and Koyama (1976); presented the hollow-shaped CNTs [24]. In 1981, several Soviet scientists published papers on CNT and suggested that CNTs were either circular or spiral in shape. In 1991, Iijima discovered multi walled CNT and because of this discovery CNT became a popular material [25].

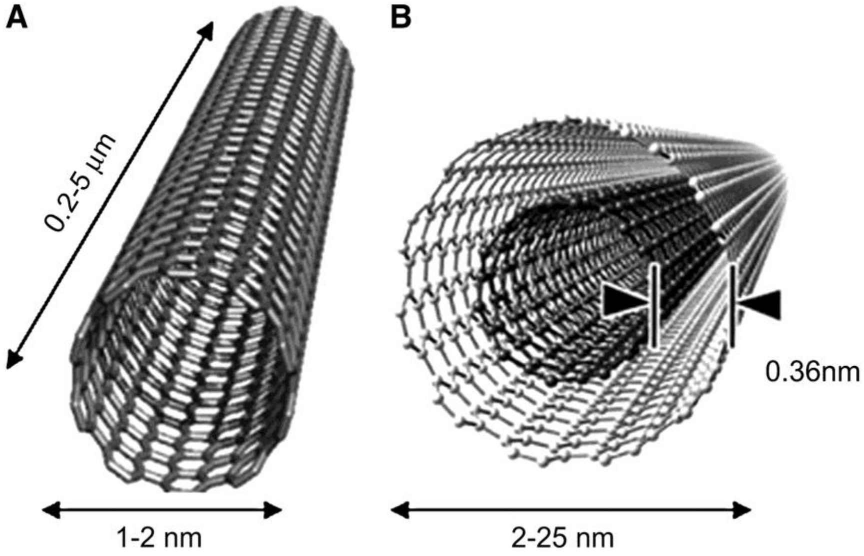


Figure 2.2: Molecular structure of SWCNT and MWCNT [26]

2.4.2 Configuration of CNT

CNTs are tube shaped material made up of carbon with diameter measuring less than a nm scaling up to 50 nm. CNTs are arranged either in spiral or circular shape. The length varies from few microns to even a centimeter. CNT has a high aspect ratio ranging from 1000:1 to 2,500,000:1. CNTs are categorized in to two main sub divisions namely single walled CNT (SWCNT) and multi walled CNT (MWCNT). SWCNT are the tubes of single graphite layer which are capped at the ends. They are available in diameter close to 1 nm. MWCNT consists of multi rolled layers of graphene tubes, which are arranged in concentric cylinders. They are available in diameter from 5 to 50 nm.

2.4.3 Properties and application of CNT

CNTs are the strongest material in terms of tensile strength and elastic modulus [27]. It has a specific density of 1.3 to 2, Young's modulus of 1 Tpa and tensile strength of 60 Gpa [27]. They have excellent thermal conductivity & electrical conductivity. CNTs are used in electrical circuits, electric cables and wires, paper batteries, ultra capacitors. They have wide spread applications ranging medical industry for cancer therapy, textile industry for improving the mechanical properties of the spinning fiber and aerospace industry for high strength and flexibility in highly stressed components. CNTs application in the construction industry has gained popularity, yet there is research progressing in different areas mainly as a filler material and as a repair material for pavements and bridges.

2.5 Previous Research on CNT as a Cementitious Material

The idea of introducing CNTs in the cement composites started when Makar et al. (2005) presented a paper about the developments in the production of CNT cement composite. He suggested that the addition of SWCNT in the cement composites accelerates the hydration process. Vickers's hardness test was done as it directly relates the elastic modulus and compressive strength. CNT composites showed a classical reinforcing behavior of crack bridging and fiber pull out mechanism, which was identified by SEM images [28].

Cwirzen et al. (2007) conducted a research on the wettability of MWCNT and the mechanical properties of the cement paste. He recommended that the most efficient method of dispersion was the tip sonication whereas the bath sonication destroys the tube length. Since the length of CNT was more significant in yielding the compressive strength and flexural strength. The research attained a 50% increase in the compressive strength of the sample containing 0.045% of the polyacrylic acid polymer-treated MWCNTs compared to the control samples [29].

Li et al. (2007) presented a paper on pressure-sensitive properties and the mechanical properties of the CNT reinforced cement composites. The properties of both treated CNT (with sulphuric acid and nitric acid) and the untreated CNT were studied. SEM images of both the cases revealed that the dispersion was uniform and bridging effect was observed. The treated CNT had more effect in pressure sensitive properties whereas the untreated CNT had more effect on reducing the electrical resistivity [30].

Shah et al. (2009) investigated the fracture characteristics and early strain capacity of CNT cement composites. The results proposed that the CNT of long length having smaller quantities (0.025 – 0.048%) and short length having higher quantities (0.08%) could achieve a good dispersion. The Nano indentation results indicate the CNT composite has a higher amount of stiffness and also less porous. This reduction of pores leads to significant effect on the early strain capacity of composites [8]. Shah et al. (2010) examined the highly dispersed CNT reinforced cement materials. The effect of ultrasonic energy, surfactant concentration and reinforcing effects of CNT were discussed. The test concluded that the optimum ratio of surfactant to CNT was 4.0 as it controls the mechanical properties significantly [31].

Yazdanbakhsh et al. (2011) inspected CNT for the enhancement of the mechanical properties of cementitious materials. The test includes MWCNT of 0.1% and 0.2% by weight of cement, w/c ratio of 0.40 and ratio of 0.005 (surfactant to cement) were used. Sonication time used for CNT was 30 minutes and 15 minutes for

CNF. The result yielded an increment of 150% in the peak displacement compared to ordinary cement paste [32].

2.6 Discussion

The physical and mechanical properties of both CNT and CNF make them a strong candidate for improving the strength properties when mixed with cementitious material and also as a repair material. The mechanical properties of nanocomposites, dosage rate of CNT and CNF, effect of admixtures and dispersion of nanocomposites were studied by researchers in the past. In order to perform nanocomposites as an alternative material for crack repair and overlay of grouts, an optimal combination of nanocomposites is utmost vital because this optimal combination should yield significant strength increase, good workability, accelerated setting time, negligible bleeding effect and superior bond strength.

CHAPTER 3

PHASE I

CNT AND CNF IN CEMENTITIOUS COMPOSITES

3.1 Introduction

In this chapter, the materials and their properties used for the experiments are discussed. The mixing technique, experimental setup and testing procedure are also discussed in detail. The mixing technique of nano composites involves ultra sonication, which was used to disperse the CNT and CNF in an aqueous solution. The testing procedures were carried out according to ASTM (American Standards and Testing Materials) standards. Compressive strength and flexural strength of the CNT cement composites and CNF cement composites were examined. The flow value of the nanocomposites, which is so critical for the workability of the cementitious materials, was analyzed. Detailed comparisons of compressive and flexural strength, and flow values of the nanocomposites with the control samples were reviewed.

3.2 Materials and Mixing Technique

3.2.1 Materials

Table 3.1: Composition of ordinary Portland cement (Source: TXI)

Composition	Percentage, %
Cement	90 - 96
Gypsum	2 - 5
Calcium Carbonate	0 - 5
Blast Furnace Slag	0 - 5

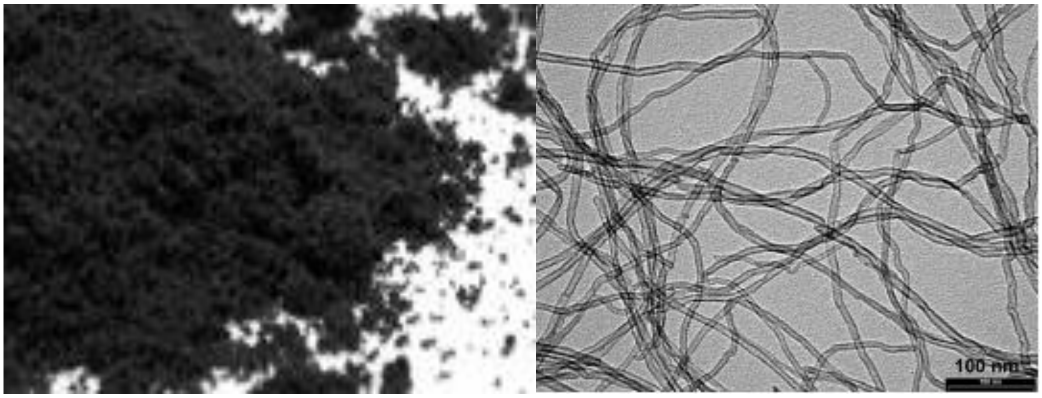
Ordinary Portland cement Type I/II low of alkali with a compressive strength 3500 psi (24 Mpa), in accordance with ASTM standard C150 was used for the experiment. The composition of ordinary Portland cement is listed in Table 3.1.Graded sand having bulk density of 1497 kg/m^3 and specific gravity of 2.65 was used in accordance to ASTM standard C778. The sieve analysis showed #16 sieve retained 0%; #30 sieve retained 2%; #40 sieve retained 30%; #50 sieve retained 75% and #100 sieve retained 98% of the quantity. Glenium 7700 from BASF (Baden Aniline and Soda Factory) was used as a surfactant and also as a dispersing agent. NC7000, CNT from Nanocyl and PR-24-XT-LHT, CNF from Pyrograf was used for the experiment. The properties of CNTs and CNFs are shown in Table 3.2 and Table 3.3. The scanning electron microscope (SEM) image of the CNT and CNF are shown in Figures 3.2 b and 3.3 b.

Table 3.2: Properties of CNT – NC7000 (Source: Nanocyl)

Property	Unit	Value	Method of Measurement
Average Diameter	Nanometers	9.5	TEM
Average Length	Microns	1.5	TEM
Carbon Purity	%	90	TGA
Metal Oxide	%	10	TGA
Amorphous Carbon	-		HRTEM
Surface Area	m2/g	250-300	BET

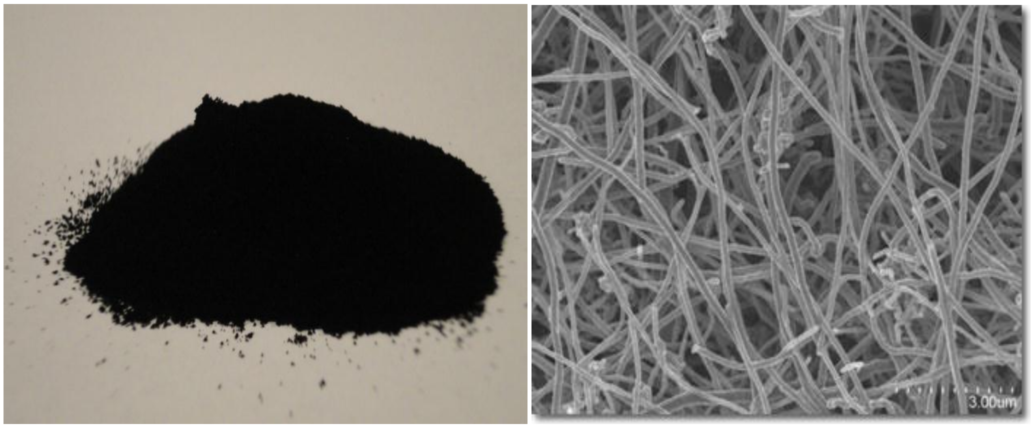
Table 3.3: Properties of CNF – PR-24-XT-LHT (Source: Pyrograf)

Fiber diameter, nm (average):	100
CVD carbon overcoat present on fiber:	No
Surface area, m2/g:	43
Dispersive surface energy, mJ/m2:	155
Moisture, wt%:	<5
Iron, ppm:	<14,000
Poly aromatic hydrocarbons, mg PAH/gm fiber:	<1



(a) (b)

Figure 3.1: (a) CNT (NC7000) in powder form (b) SEM image of CNT (NC7000) at 100 nm (Source: Nanocyl)



(a) (b)

Figure 3.2: (a) CNF in powder form (b) SEM image of CNF at 3µm (Source: Pyrograf)

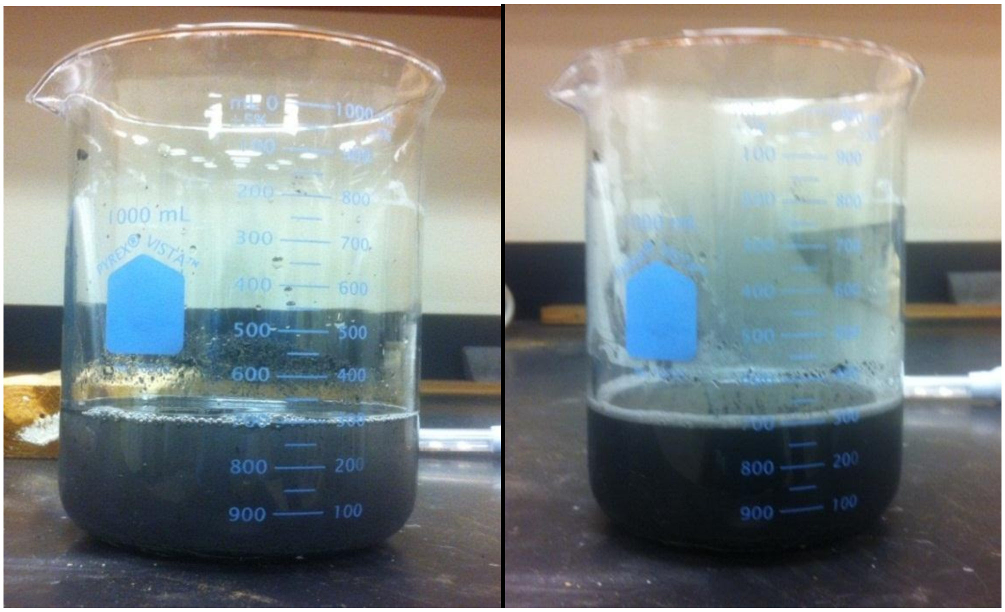
3.2.2 Mixing Technique

The mixing technique of producing highly dispersed nonmaterial in a cement mortar is highly crucial as it directly affects the mechanical properties of the cementitious composites. The dispersion of nonmaterial in the aqueous solution is most important before adding it to the cement mortar. Van der Waals forces attract the nonmaterial to form bundles since their aspect ratio is too high. A surfactant (plasticizer) was used in order to get a homogenous dispersion of CNT and CNF in water.

Optimum dosage rates for CNTs and CNFs were 0.1% and 0.2% by weight of the cement [9, 10], and ratio of 0.008 (super plasticizer to cement) was selected [11]. Water cement (w/c) ratio of 0.35, 0.40, 0.45 and 0.50 were selected since there is no clear evidence from the previous research to select a specific w/c ratio. CNT was sonicated for 30 minutes while the CNF was sonicated for 15 minutes [10].

In this research CNTs and CNFs was dispersed in water with surfactant using a sonicator. Sonication is a procedure where ultrasonic energy is passed from the probe tip to the water, forming a cavity with high intensity and thereby facilitating the dispersion. Tip horn sonicator (Misonix 4000) from Misonix was used for sonication. It had a titanium tip, which was effective in dispersing the carbon nonmaterial in water compared to the bath or cup horn sonicator types. The tip diameter determines the quantity of the sample to be sonicated. The tip used for the sonication was 0.5 inch (12 mm) and had a high intensity with amplitude of 120μm. The CNTs and CNFs were sonicated with amplitude of 50% in cycles of 30 seconds interval in order to prevent overheating of the suspensions. Overheating destroys the length of CNTs and CNFs as the length plays a vital role in yielding the mechanical properties.

Figure 3.3 and 3.4 display the effect of sonication for CNF and CNT. Figure 3.3a shows a pale color which shows that CNF did not disperse uniformly when stirred with hand, whereas 3.3b shows a uniform dispersion of CNF in water after 15 min of sonication. Similar effect of dispersion was obtained for CNT and shown in Figure 3.4. The setup of sonicator is shown in Figure 3.5.



(a) (b)

Figure 3.3: a and b CNF mixture before and after sonication

(a) (b)

Figure 3.4: a and b CNT mixture before and after sonication

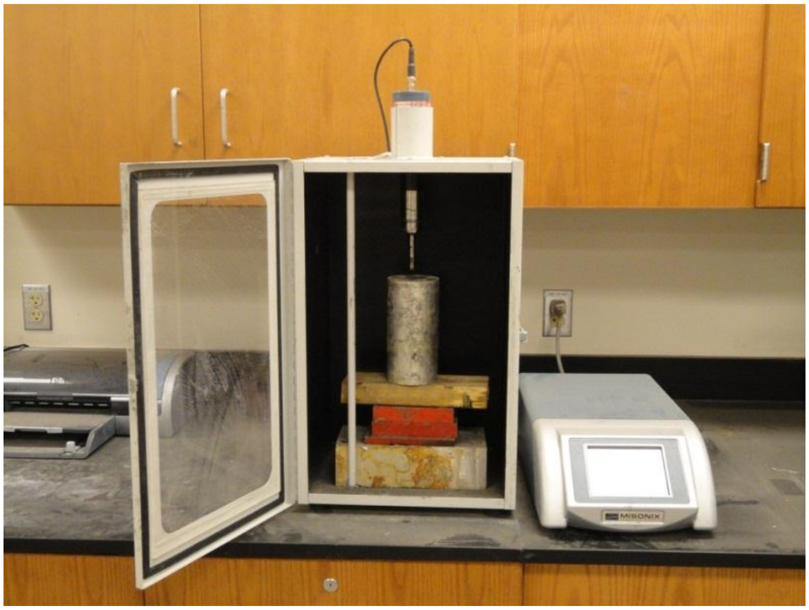


Figure 3.5: Setup of sonicator - Misonix 4000

3.3 Experimental Setup and Test Procedure

In this section, the experimental setup and test procedure for the compressive strength, flexural strength and flow tests are explained in detail.

3.3.1 Compressive Strength Test

The ASTM standard C109 test procedure was used to determine the compressive strength of a hydraulic cement mortar using 2 inch (50mm) cube [33]. All the testing materials were kept at ambient temperature i.e., 73° ± 5.5 ° F. The mortar consisted of 1 parts of cement and 2.75 parts of graded sand. Water cement ratio of 0.35 to 0.50 with increment of 0.05 was used for this research. A Hobart mixer with flat beater was used for the mixing of the mortar.

After sonication, both CNTs and CNFs were mixed with cement and sand for 4 min. After mixing the mortar, they were placed in the mold in two layers and tampered 32 times in 4 rounds. All the molds were demolded after 24 hrs and stored in a lime saturated water tank. Before testing of each sample at 7, 14 and 28 days, the surface was dried. The loading rate of 200 to 400 lbs/s was applied until the specimen failed. The maximum load of the each sample was recorded, and the compressive strength was calculated as follows:-

$$fm = P/A \qquad \text{[Eq. 3.1]}$$

Where, fm – compressive strength,

P - Total maximum load in lbf or N

A - Area of the loaded surface in^2 or mm^2.

The loading setups for the compressive strength is shown in Figures 3.6 and 3.7

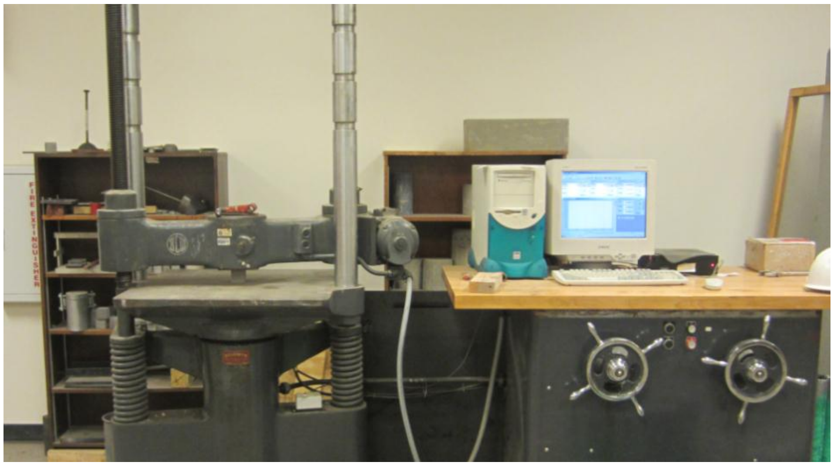


Figure 3.6: Compressive strength - Loading system connected with the data acquisition system

Figure 3.7: Compressive strength - 2 inch (50mm) cube under the loading plane

3.3.2 Flexural Strength Test

The ASTM C348 test procedure was used to evaluate the flexural strength of the hydraulic cement mortar using a sample size of 40mm by 40mm by 160mm [34]. The mixture proportion and the mixing procedure are same as mentioned in compressive strength test. After the completion of mixing, the mortar was placed in a layer of 20mm in thickness. Then the mortar was compacted in 2 layers by 12 strokes in 4 rounds. After 24 hrs the molds were demolded and stored in a lime saturated water tank. The flexural strength of the sample was determined by using a center point loading test. The loading rate of 2640 ± 110 N was applied on the sample, and the maximum load to break the sample was recorded.

The loading frame and center point loading setup for flexural strength test are shown in Figure 3.8.

Figure 3.8: Flexural strength - (a) Loading frame for flexural strength test, (b) Center point loading setup for flexural strength test

The flexural strength of the specimen is calculated by

$$S_f = 0.0028\ P \qquad \text{[Eq. 3.2]}$$

Where sf – flexural strength, Mpa

P –total maximum load.

3.3.3 Flow test

The ASTM C1437 test procedure was used to calculate the flow of a hydraulic cement mortar [35]. The mixture proportion and the mixing procedure were similar to the compressive strength test. The flow table was wiped clean and dry and the flow mold was placed at the center of the flow table. Then the mortar was placed 1 inch from bottom of the mold and compacted 20 times in 2 layers. The compacted mortar was flushed with the surface of the mold. The flow mold was removed and the flow table was dropped 25 times in 15 seconds. The diameter of the mortar along the four lines marked on the flow table was recorded. The flow value is the increase in the average base diameter of the mortar mass which is expressed as the percentage of the original diameter. Flow table and flow of the nanocomposites cement mortar are shown in Figure 3.9.


(a) (b)

Figure 3.9: (a) Flow table and (b) Flow of nanocomposite after the drop

3.4 Compressive Strength of Composites

CNT percentages of 0.1 % and 0.2%by the weight of the cement were used in the cement composites to determine the compressive strength. Four different w/c ratios were used as mentioned in section 3.2.2. Compressive strength of the CNT and CNF cement composites was calculated at 7, 14 and 28 days. For control samples, w/c ratio of 0.40 yielded the maximum strength at 7, 14 and 28 days. The average compressive strength of the control samples is shown in Table 3.4.

Table 3.4: Compressive strength of control samples

Mix Proportions	No of Samples	Days		
		7 MPa (ksi)	14 MPa (ksi)	28 MPa (ksi)
0.35 w/c	6	8.55 (1.24)	19.87 (2.88)	17.13 (2.48)
0.40 w/c	6	24.80 (3.60)	32.72 (4.74)	35.63 (5.17)
0.45 w/c	6	24.00 (3.48)	26.90 (3.90)	29.27 (4.24)
0.50 w/c	6	23.50 (3.41)	31.30 (4.54)	34.83 (5.05)

3.4.1 Compressive Strength of CNT cement composites

Table 3.5: Compressive strength of 0.1% CNT composites

Mix Proportions	No of Samples	Days		
		7 MPa (ksi)	14 MPa (ksi)	28 MPa (ksi)
0.1% CNT + 0.35 w/c + 0.008 SP	6	39.88 (5.78)	40.09 (5.81)	43.44 (6.30)
0.1% CNT + 0.40 w/c + 0.008 SP	6	34.81 (5.05)	36.81 (5.34)	37.30 (5.52)
0.1% CNT + 0.45 w/c + 0.008 SP	6	24.47 (3.55)	42.07 (6.10)	45.22 (6.56)
0.1% CNT + 0.50 w/c + 0.008 SP	6	26.70 (3.87)	30.95 (4.49)	33.73 (4.89)

Note: - SP denotes Super Plasticizer

The compressive strength of CNT composites possessed high strength at 7 days due to early hydration process. Average compressive strength of the CNT cement composites is tabulated in Table 3.5 and Table 3.6. Maximum strength of 39.88 MPa was obtained for 0.1% CNT cement composites having w/c ratio of 0.35 at 7days while w/c ratio of 0.45 displayed a lower strength at 7 days. However at 28 days 0.1% CNT cement composites with w/c ratio of 0.45 revealed a higher strength of 45.22 MPa than the other CNT cement composites. From the test results, w/c ratio of 0.45 effectively improves the compressive strength for 0.1% CNT cement composites.

Table 3.6: Compressive strength of 0.2% CNT cement composites

Mix proportions	No of samples	Days		
		7 MPa (ksi)	14 MPa (ksi)	28 MPa (ksi)
0.2% CNT + 0.35 w/c + 0.008 SP	6	24.45 (3.55)	23.54 (3.41)	23.46 (3.40)
0.2% CNT + 0.40 w/c + 0.008 SP	6	38.51 (5.58)	35.46 (5.14)	30.96 (4.49)
0.2% CNT + 0.45 w/c + 0.008 SP	6	34.86 (5.05)	35.31 (5.12)	37.13 (5.38)
0.2% CNT + 0.50 w/c + 0.008 SP	6	24.59 (3.57)	28.88 (4.19)	38.76 (5.62)

Similar trend of high strength at 7 days was obtained for 0.2% CNT composites. CNT percentage of 0.2 composites also displayed higher strength than the control specimens at all tested ages. Water cement ratio of 0.40 achieved a maximum compressive strength of 38.51 Mpa while 0.35w/c showed a lower compressive strength at 7days. Water cement ratio of 0.50 achieved highest strength of 38.76 Mpa at 28 days compared to other w/c ratios. Dosage rate of 0.2% CNT cement composites performed better when the w/c ratio was high. The reason is that the CNTs have a large surface area of 250 – 300 m^2/g which requires higher water content to disperse.

From Table 3.5 and 3.6 w/c ratio of 0.45 exhibited significant strength increase for both dosage rates of CNT.

3.4.2 Compressive Strength of CNT cement composites vs. Control samples

Detailed comparisons were made to find the percentage increase of 0.1% and 0.2% CNT composites over the control samples at 7, 14 and 28 days. Table 3.7 reveals that 0.1% CNT cement composites had a higher strength in all mix proportions as compared to the control samples except for w/c ratio of 0.50 which is similar to the control samples. It is also clearly evident that w/c ratio of 0.45 was the effective combination for 0.1% CNT composites to achieve significant strength gain. Even though w/c ratio of 0.35 had increased compressive strength, the workability decreased substantially.

Table 3.7: Compressive strength - Percentage increase of 0.1% CNT cement composites vs. Control samples

Mix Proportions	Days		
	7	14	28
	% Increase	% Increase	% Increase
0.1% CNT + 0.35 w/c + 0.008 SP	366	102	154
0.1% CNT + 0.40 w/c + 0.008 SP	40	12	-1
0.1% CNT + 0.45 w/c + 0.008 SP	2	56	54
0.1% CNT + 0.50 w/c + 0.008 SP	14	-1	-3

Table 3.8: Compressive strength - Percentage increase of 0.2% CNT cement composites vs. Control samples

Mix Proportions	Days		
	7	14	28
	% Increase	% Increase	% Increase
0.2% CNT + 0.35 w/c + 0.008 SP	186	18	37
0.2% CNT + 0.40 w/c + 0.008 SP	55	8	-13
0.2% CNT + 0.45 w/c + 0.008 SP	45	31	27
0.2% CNT + 0.50 w/c + 0.008 SP	5	-8	11

Table 3.8 reveals that 0.2% CNT composites produced considerable strength gain at all mix proportions except for CNT composites with w/c ratio of 0.40. Maximum % increase was obtained for w/c ratio of 0.35 followed by w/c ratio of 0.45. Considering the workability of the cement composites, w/c ratio of 0.45 exhibited good results. Therefore from the test results, w/c ratio of 0.45 performed well for both the dosage rates of CNT composites. Compressive strength of the CNT composites vs. control samples at 7, 14 and 28 days are shown in Figure 3.10 and Figure 3.11. Each bar represents the average of 6 samples and the error bars are ± 1 standard deviation (SD).

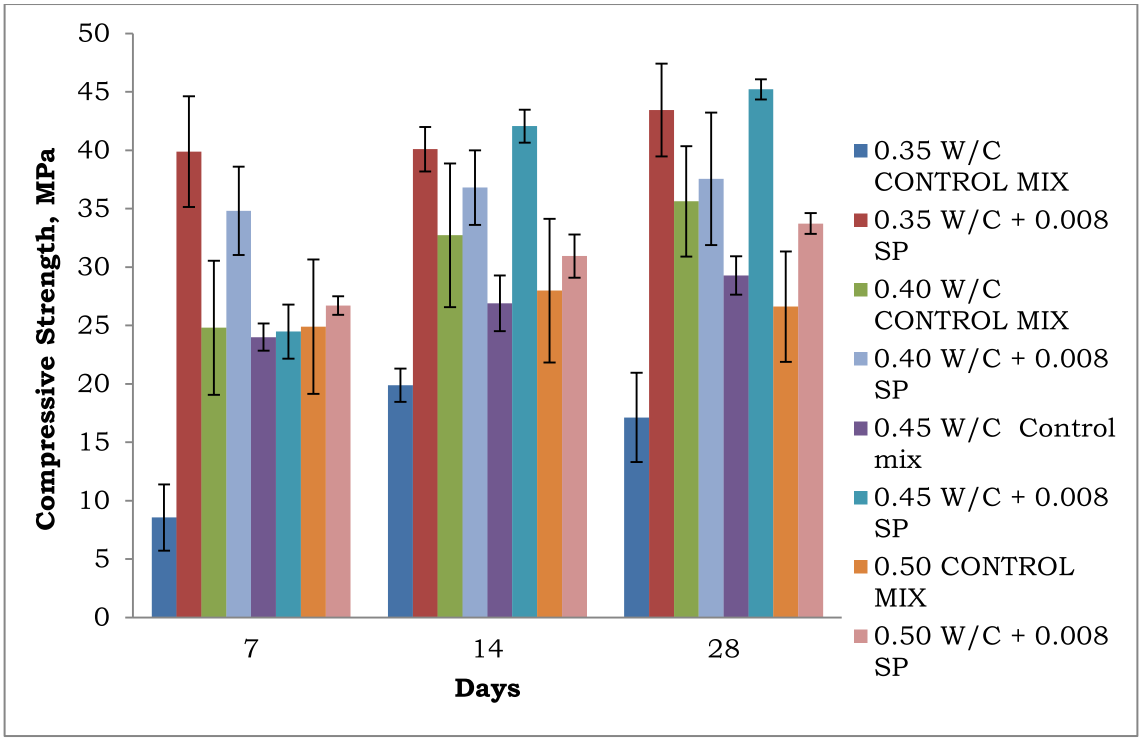


Figure 3.10: Compressive strength of 0.1% CNT composites vs. Control samples

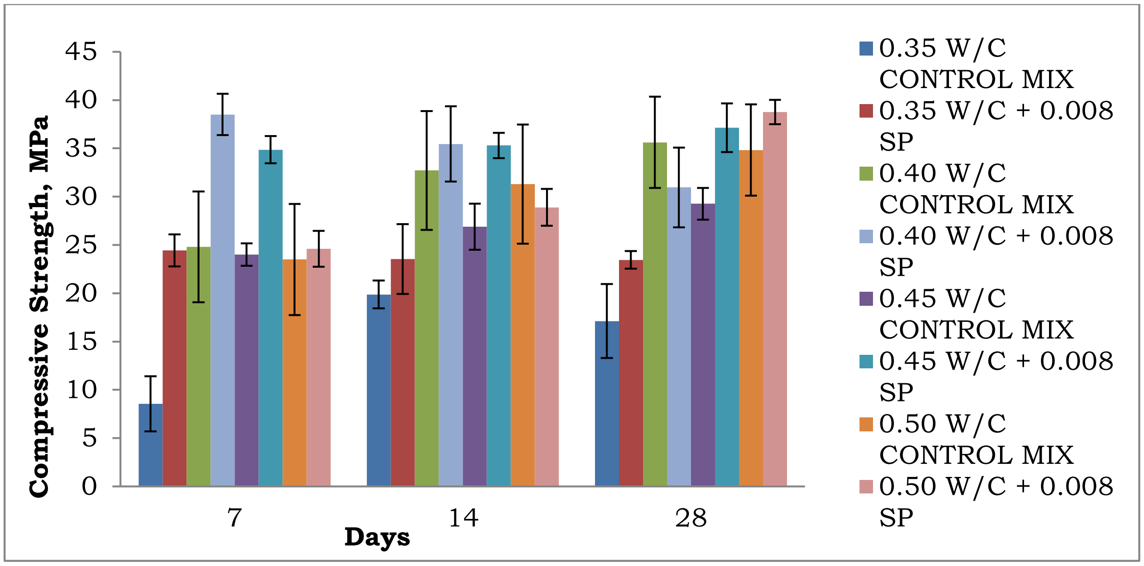


Figure 3.11: Compressive strength of 0.2% CNT composites vs. Control samples

3.4.3 Compressive Strength of CNF cement composites

Table 3.9: Compressive strength of 0.1% CNF cement composites

Mix Proportions	No of Samples	Days		
		7 MPa (ksi)	14 MPa (ksi)	28 MPa (ksi)
0.1% CNF + 0.35 w/c + 0.008 SP	6	37.84 (5.49)	46.70 (6.77)	51.30 (7.44)
0.1% CNF + 0.40 w/c + 0.008 SP	6	40.23 (5.83)	44.55 (6.46)	51.92 (7.53)
0.1% CNF + 0.45 w/c + 0.008 SP	6	31.79 (4.61)	42.25 (6.13)	49.13 (7.12)
0.1% CNF + 0.50 w/c + 0.008 SP	6	24.90 (3.61)	27.99 (4.06)	26.61 (3.86)

Dosage rate of 0.1% CNF composites showed very high strength at 7 days similar to CNT composites as both nanoparticles (CNTs and CNFs) accelerates the hydration process. From Table 3.9, it is evident that w/c ratio of 0.40 displayed maximum strength of 40.23 Mpa and w/c ratio of 0.50 yielded minimum strength of 24.90 Mpa at 7 days. Even at 28 days w/c ratio of 0.40 produced superior strength of 51.92 Mpa. As a result, w/c ratio of 0.40 achieved significant strength gain at all tested ages compared to the other CNF composites. This mix proportion is the optimal combination for 0.1% CNF composites. Since CNFs have less surface area than CNT it requires much less water content.

Table 3.10: Compressive strength of 0.2% CNF cement composites

Mix Proportions	No of Samples	Days		
		7 MPa (ksi)	14 MPa (ksi)	28 MPa (ksi)
0.2% CNF + 0.35 w/c + 0.008 SP	6	42.17 (6.11)	53.03 (7.69)	54.32 (7.88)
0.2% CNF + 0.40 w/c + 0.008 SP	6	43.56 (6.32)	45.94 (6.66)	45.36 (6.58)
0.2% CNF + 0.45 w/c + 0.008 SP	6	38.64 (5.60)	35.69 (5.17)	39.69 (5.76)
0.2% CNF + 0.50 w/c + 0.008 SP	6	23.14 (3.36)	28.64 (4.15)	27.11 (3.93)

CNF cement composites of 0.2% gave high early strength at 7 days compared to 0.1% CNF cement composites. Table 3.10 shows that the w/c ratio of 0.35 produced superior strength at 7, 14 and 28 days. Maximum compressive strength of 54.32 Mpa was observed for 0.2% CNF composites with w/c ratio of 0.35 at 28 days, which was the maximum of all the CNF and CNT composites. When the dosage rate is high, CNF composites performs better with lower w/c. But the difficulty in having lower w/c ratio is the workability issue. Therefore, an optimum w/c ratio which gives maximum strength yet achieving good workability is the key for CNF composites.

3.4.4 Compressive Strength of CNF cement composites vs. Control samples

Analogous to CNT cement composites, detailed comparisons were made to find the percentage increase of 0.1% and 0.2% CNF cement composites over the control samples at 7, 14 and 28 days. Compressive strength of 0.1% CNF composites achieved better results than the control samples except w/c ratio of 0.50. Water cement ratio of 0.35 displayed extraordinary percentage increase for 0.1% CNF. Water cement ratios of 0.40 and 0.45 also produced higher strength compared to control samples. As a result an effective w/c ratio exist which gives better compressive and flexural strength and also good workability. From Table 3.11 and Figure 3.12, it is clear that 0.1% CNF cement composites performed better when the w/c is less. Similar to CNT cement composites, CNF composites with w/c ratio of 0.45 also achieved highest strength gain as well as superior workability.

Table 3.11: Compressive strength - Percentage increase of 0.1% CNF cement composites vs. Control samples

Mix Proportions	Days		
	7	14	28
	% Increase	% Increase	% Increase
0.1% CNF + 0.35 w/c + 0.008 SP	342	135	200
0.1% CNF + 0.40 w/c + 0.008 SP	62	36	46
0.1% CNF + 0.45 w/c + 0.008 SP	32	57	68
0.1% CNF + 0.45 w/c + 0.008 SP	6	-11	-24

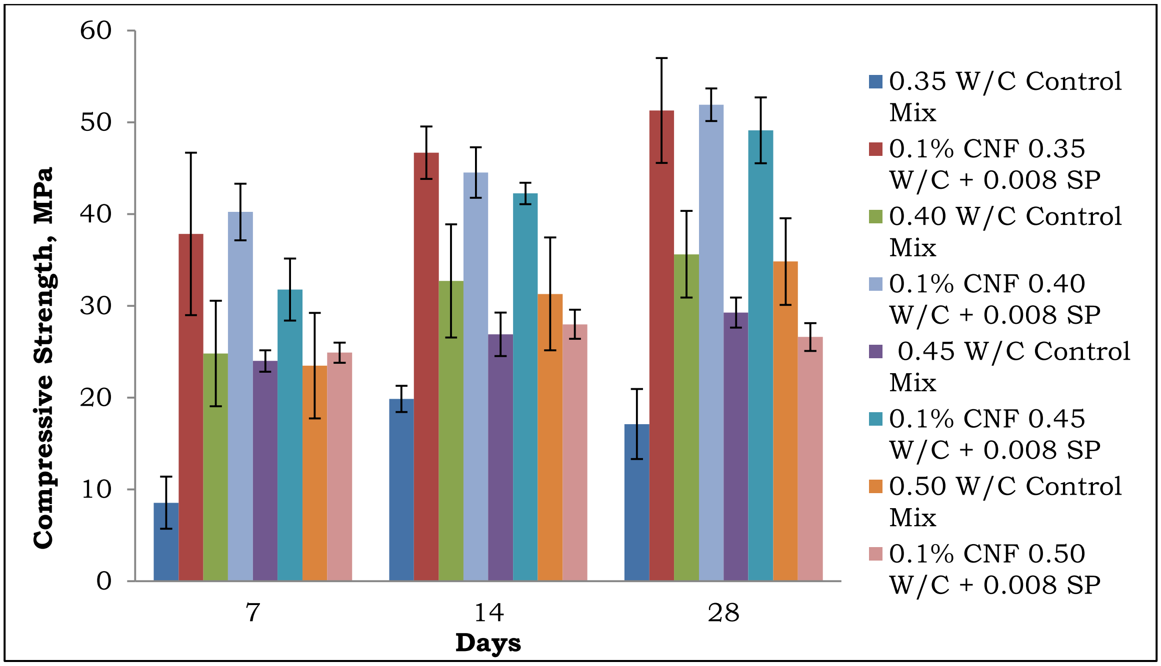


Figure 3.12: Compressive strength of 0.1% CNF composites vs. control samples

Table 3.12: Compressive strength – Percentage increase of 0.2% CNF cement composites vs. control samples

Mix Proportions	Days		
	7	14	28
	% Increase	% Increase	% Increase
0.2% CNF + 0.35 w/c + 0.008 SP	393	167	217
0.2% CNF + 0.40 w/c + 0.008 SP	76	40	27
0.2% CNF + 0.45 w/c + 0.008 SP	61	33	36
0.2% CNF + 0.45 w/c + 0.008 SP	-2	-9	-22

Table 3.12 reveals that 0.2% CNF cement composites displayed higher strength at 7, 14 and 28 days over the control samples except w/c of 0.50. Similar pattern was seen even for 0.1% CNF cement composites. CNF cement composites showed lower strength compared to control sample when the w/c ratio exceeded 0.45. The surface area of CNFs is less compared to CNTs. As a result CNF requires less quantity of water for sonication and vice versa. From the overall results, w/c ratio of 0.40 to 0.45 generated remarkable results for CNF whereas w/c ratio of 0.45 to 0.50 produced significant results for CNT.

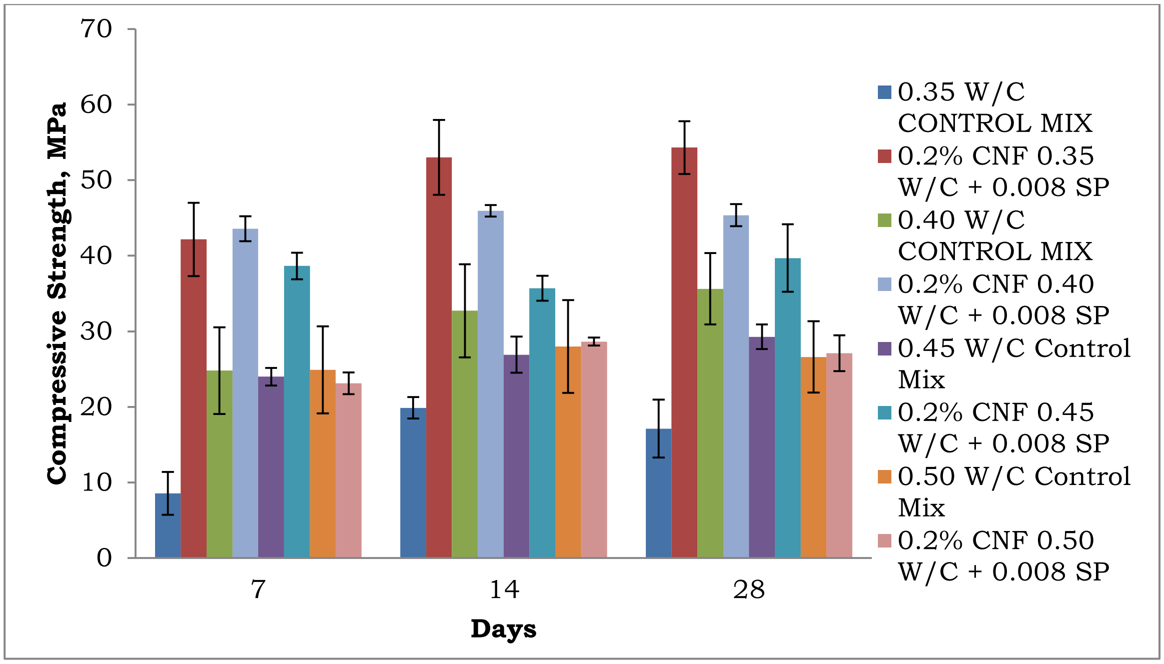


Figure 3.13: Compressive strength of 0.2% CNF composites vs. control samples

3.5 Flexural Strength of Composites

Water cement ratio of 0.35, 0.40, 0.45 and 0.50 was used for the flexural strength test. Ratio of 0.008 (Super plasticizer to the cement) was used for the CNT and CNF cement composites in order to achieve uniform dispersion. Samples were tested using a central point loading setup. Dosage rate of 0.1 % and 0.2% of CNT and CNF by weight of cement was used in this research. The mix proportions and the mixing procedure were followed as mentioned in 3.2.2. Table 3.13 reveals that w/c ratio of 0.50 yielded higher strength at 7 and 28 days for control samples.

Table 3.13: Flexural strength of control samples

Mix Proportions	7 Days, MPa (ksi)	28 Days, MPa (ksi)
0.35 w/c	4.36 (0.63)	5.51 (0.80)
0.40 w/c	6.58 (0.95)	7.17 (1.04)
0.45 w/c	6.34 (0.92)	8.18 (1.19)
0.50 w/c	7.37 (1.07)	8.88 (1.29)

3.5.1 Flexural Strength of CNT cement composites

Table 3.14: Flexural strength of 0.1% CNT cement composites

Mix Proportions	7 Days, Mpa (ksi)	28 Days, Mpa (ksi)
0.1 % CNT + 0.35 w/c + 0.008 SP	6.30 (0.91)	8.46 (1.23)
0.1 % CNT + 0.40 w/c + 0.008 SP	7.83 (1.14)	8.08 (1.17)
0.1 % CNT + 0.45 w/c + 0.008 SP	6.29 (0.91)	9.33 (1.35)
0.1 % CNT + 0.50 w/c + 0.008 SP	8.77 (1.27)	10.08 (1.46)

Table 3.15: Flexural strength of 0.2% CNT cement composites

Mix Proportions	7 Days, Mpa (ksi)	28 Days, Mpa (ksi)
0.2 % CNT + 0.35 w/c + 0.008 SP	5.23 (0.76)	7.02 (1.02)
0.2 % CNT + 0.40 w/c + 0.008 SP	7.60 (1.10)	8.16 (1.18)
0.2 % CNT + 0.45 w/c + 0.008 SP	7.00 (1.02)	9.97 (1.45)
0.2 % CNT + 0.50 w/c + 0.008 SP	8.16 (1.18)	9.83 (1.43)

CNT composites by dosage rate of 0.1%displayed high strength at 7 days due to early hydration process similar to compressive strength. From Table 3.14, it is evident that 0.1% CNT cement composites with w/c ratio of 0.50 performed better at both 7 and 28 days. Maximum strengths of 8.77 Mpa and 10.08 Mpa were observed at 7 and 28 days. The maximum flexural strength of 9.97 Mpa was obtained for w/c ratio of 0.45. Water cement ratio of 0.50 also achieved higher strength closer to the maximum.

Like 0.1% CNT composites, 0.2% composites also produced high early strength at 7 days. The flexural strength of 0.2% composites at 7 and 28 days was tabulated in Table 3.15. The flexural strength of 0.2% CNT composites increases when the w/c ratio increases and similar effect was found for 0.1% CNT composites.

3.5.2 Flexural strength of CNT cement composites Vs. Control Samples

Table 3.16 shows that 0.1% CNT composites displayed higher strength compared to control samples at 28 days. Water cement ratio of 0.35 shows highest percentage increase in flexural strength both at 7 and 28 days, followed by w/c ratio of 0.45. Water cement ratio of 0.45 actually performs well if the workability is taken in to account. This pattern was observed even for the compressive strength of 0.1% CNT composites.

Table 3.16: Flexural strength – Percentage increase of 0.1% CNT cement composites vs. Control samples

Mix Proportions	Days	
	7	28
	% Increase	% Increase
0.1 % CNT + 0.35 w/c + 0.008 SP	44	53
0.1 % CNT + 0.40 w/c + 0.008 SP	19	13
0.1 % CNT + 0.45 w/c + 0.008 SP	-1	14
0.1 % CNT + 0.50 w/c + 0.008 SP	19	14

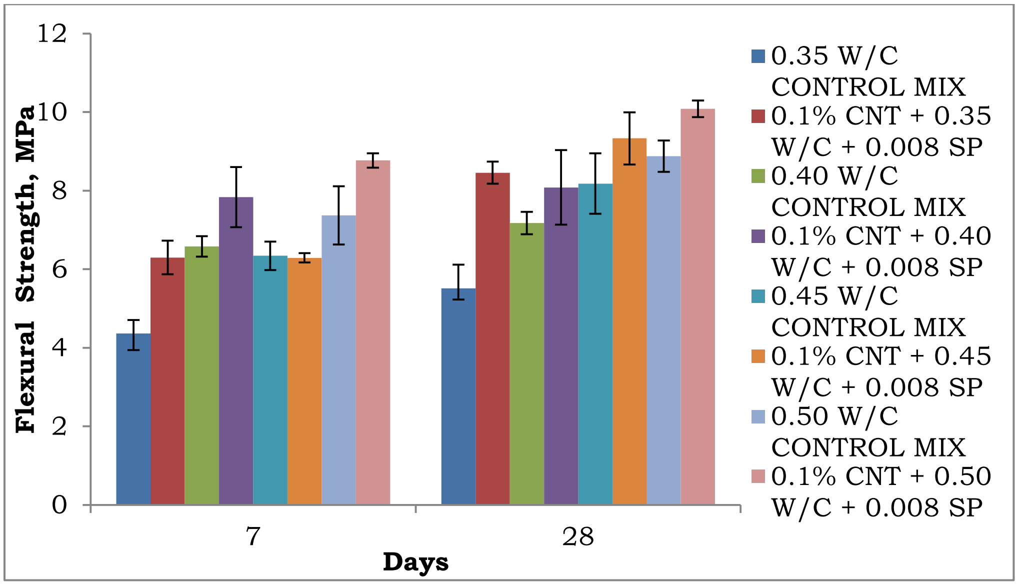


Figure 3.14: Flexural strength of 0.1% CNT cement composites vs. Control samples

Figure 3.14 illustrates the strength increase of 0.1% CNT composites over the control samples at 7 and 28 days. The percentage increase of 0.2% CNT composites versus the control samples at 7 and 28 days are tabulated in Table 3.17. CNT composites by dosage rate of 0.2% produced better flexural strength over the control samples at 7 and 28 days. Water cement ratio of 0.45 produced the maximum percentage increase of flexural strength considering the flow values of the mortar. From both the test results it is obvious that irrespective of dosage rates of the CNT composites, w/c ratio of 0.45 enhanced the flexural strength of the CNT composites satisfying both strength and workability parameters.

Table 3.17: Flexural strength – Percentage increase of 0.2% CNT cement composites vs. Control samples

Mix Proportions	Days	
	7	28
	% Increase	% Increase
0.2 % CNT + 0.35 w/c + 0.008 SP	20	27
0.2 % CNT + 0.40 w/c + 0.008 SP	15	14
0.2 % CNT + 0.45 w/c + 0.008 SP	10	22
0.2 % CNT + 0.50 w/c + 0.008 SP	11	11

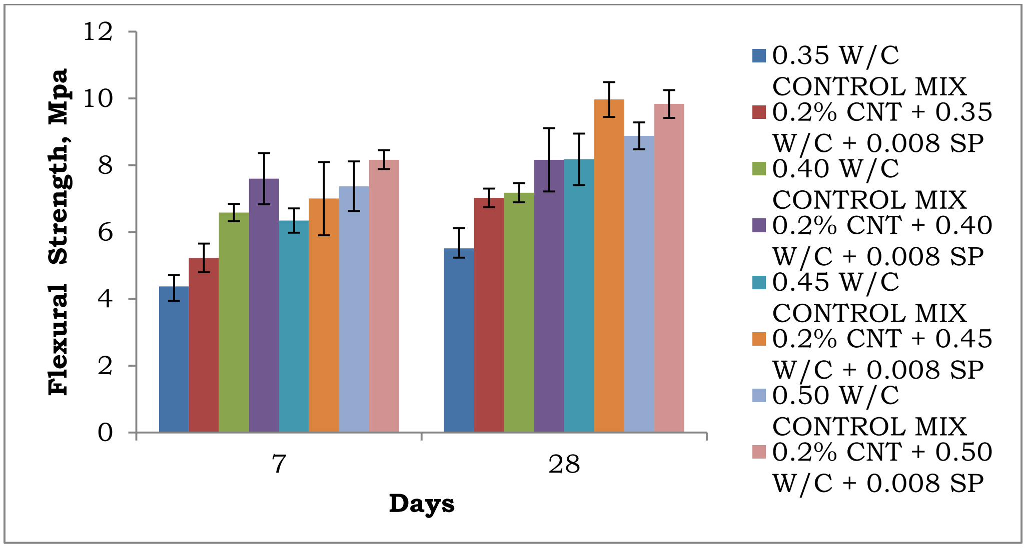


Figure 3.15: Flexural strength of 0.2% CNT cement composites vs. Control samples

3.5.3 Flexural Strength of CNF cement composites

Water cement ratio, ratio of super plasticizer to cement and dosage rate of CNF cement composites were maintained as same as that of CNT cement composites. Water cement ratio of 0.45 yielded the maximum flexural strength for 0.1% CNF composites at both 7 and 28 days. Table 3.18 shows that the flexural strength of 0.1% CNF composites at 7 and 28 days are very similar. This shows that the CNF composite exhibits very high strength due to early hydration process.

Table 3.18: Flexural strength of 0.1% CNF cement composites

Mix Proportions	7 Days, MPa (ksi)	28 Days, MPa (ksi)
0.1 % CNF + 0.35 w/c + 0.008 SP	7.77 (1.13)	7.82 (1.13)
0.1 % CNF + 0.40 w/c + 0.008 SP	6.94 (1.00)	7.63 (1.11)
0.1 % CNF + 0.45 w/c + 0.008 SP	6.95 (1.01)	8.84 (1.28)
0.1 % CNF + 0.50 w/c + 0.008 SP	5.69 (0.83)	6.54 (0.95)

Table 3.19 Flexural strength of 0.2% CNF cement composites

Mix Proportions	7 Days, Mpa (ksi)	28 Days, Mpa (ksi)
0.2 % CNF + 0.35 w/c + 0.008 SP	8.22 (1.19)	8.27 (1.20)
0.2 % CNF + 0.40 w/c + 0.008 SP	8.12 (1.18)	8.87 (1.29)
0.2 % CNF + 0.45 w/c + 0.008 SP	6.53 (0.95)	9.72 (1.41)
0.2 % CNF + 0.50 w/c + 0.008 SP	6.35 (0.92)	7.30 (1.06)

The flexural strength of 0.2% CNF composites at 7 and 28 days are presented in Table 3.19. Water cement ratio of 0.35 produced maximum strength at 7 days whereas w/c ratio of 0.45 gave highest strength at 28 days. Maximum flexural strength of 9.72 Mpa was obtained for 0.2% CNF composites, the highest of both dosage rates of CNF composites. Irrespective of dosage rate w/c ratio of 0.45 achieved the maximum flexural strength. Therefore, an effective w/c ratio exists for CNF composites to perform better than the control samples. The comparative results of flexural strength of 0.2% CNF composites were graphically shown in Figure 3.26.

3.5.4 Flexural strength of CNF cement composites Vs. Control Samples

Table 3.20 reveals that 0.1% CNF composites achieved superior results except the w/c ratio of 0.50. CNF composites in proportion of 0.1% by weight of cement did not perform well in both compressive and flexural strength once the w/c ratio reaches above 0.45. From the results w/c ratio of 0.45 produced appreciable results compared to other mix proportion. The graph representing the flexural strength of control sample versus CNF composites are shown in Figure 3.16 and Figure 3.17. Dosage rate of 0.2% CNF composites also behaved the same way as that of 0.1% CNF composites. Therefore from the test results, dosage rate of 0.1% with w/c ratio of 0.45 exhibits superior flexural strength.

Table 3.20: Flexural strength – Percentage increase of 0.1% CNF cement composites vs. Control samples

Mix Proportions	Days	
	7	28
	% Increase	% Increase
0.1 % CNF + 0.35 w/c + 0.008 SP	78	42
0.1 % CNF + 0.40 w/c + 0.008 SP	6	6
0.1 % CNF + 0.45 w/c + 0.008 SP	10	8
0.1 % CNF + 0.50 w/c + 0.008 SP	-23	-26

Table 3.21: Flexural strength – Percentage increase of 0.2% CNF cement composites vs. Control samples

Mix Proportions	Days	
	7	28
	% Increase	% Increase
0.2 % CNF + 0.35 w/c + 0.008 SP	88	50
0.2 % CNF + 0.40 w/c + 0.008 SP	23	24
0.2 % CNF + 0.45 w/c + 0.008 SP	3	19
0.2 % CNF + 0.50 w/c + 0.008 SP	-14	-18

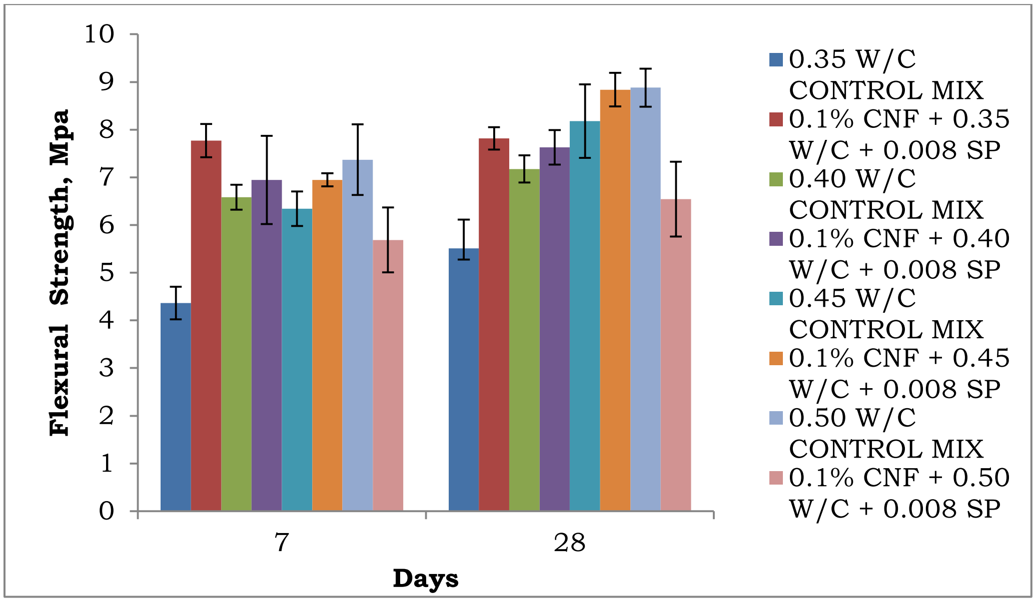


Figure 3.16: Flexural strength of 0.1% CNF cement composites vs. Control samples

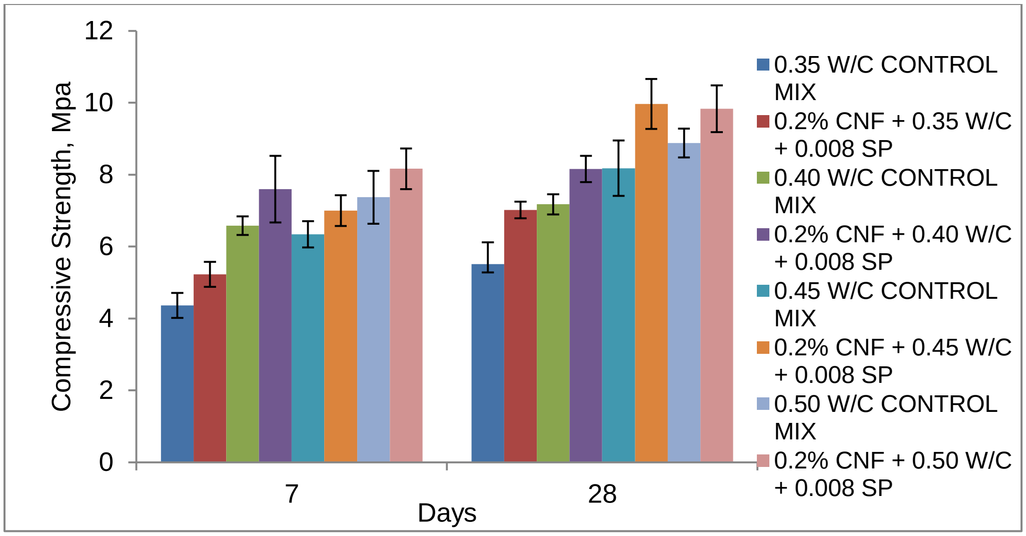


Figure 3.17: Flexural strength of 0.2% CNF cement composites vs. Control samples

3.6 Statistical Analysis

Statistical analysis was performed to compare the compressive and flexural strength of CNT and CNF reinforced cement composites over the control samples. The t-test was adopted for statistical analysis. A t-test is the statistical hypothesis test in which the test follows student t distribution if the null hypothesis is supported. T distribution test is one of the powerful tools in manipulating the mean of a normally distributed population where the sample size is very small and the standard deviation is unknown. Two sample t-test was performed to see if the differences in the mean of each sample were statistically different. P-value method was used for determining the hypothesis testing. Null hypothesis can be rejected if the P-value is less than the significance level α (0.05).

P value <0.05 indicates that the difference between the group means are statistically significant. Statistical analysis on compressive strength of CNT and CNF reinforced cement mortar at 28 days are tabulated in Table 3.22.

Table 3.22: T-test analysis on compressive strength of nanocomposite cement mortar

Mix Proportion	Control samples, Mean Mpa(ksi)	Composites, Mean Mpa(ksi)	P Value
0.1% CNF + 0.35 W/C + 0.008 SP	17.13	51.30	**P < 0.05**
0.1% CNF + 0.40 W/C + 0.008 SP	35.63	51.92	**P < 0.05**
0.1% CNF + 0.45 W/C + 0.008 SP	29.27	49.13	**P < 0.05**
0.1% CNF + 0.50 W/C + 0.008 SP	35.06	26.61	**P < 0.05**
0.2% CNF + 0.35 W/C + 0.008 SP	17.13	54.32	**P < 0.05**
0.2% CNF + 0.40 W/C + 0.008 SP	35.63	45.36	**P < 0.05**
0.2% CNF + 0.45 W/C + 0.008 SP	29.27	39.69	**P < 0.05**
0.2% CNF + 0.50 W/C + 0.008 SP	35.06	27.11	**P < 0.05**
0.1% CNT + 0.35 W/C + 0.008 SP	17.13	43.44	**P < 0.05**
0.1% CNT + 0.40 W/C + 0.008 SP	35.63	35.30	P > 0.05
0.1% CNT + 0.45 W/C + 0.008 SP	29.27	45.22	**P < 0.05**
0.1% CNT + 0.50 W/C + 0.008 SP	35.06	33.73	P > 0.05
0.2% CNT + 0.35 W/C + 0.008 SP	17.13	23.46	**P < 0.05**
0.2% CNT + 0.40 W/C + 0.008 SP	35.63	30.96	P > 0.05
0.2% CNT + 0.45 W/C + 0.008 SP	29.27	37.13	**P < 0.05**
0.2% CNT + 0.50 W/C + 0.008 SP	35.06	38.76	P > 0.05

From Table 3.22, it is clearly evident that the P-values for the CNF cement composites were less than 0.05 indicating that increase in the compressive strength of the CNF cement composites are statistically significant than the control samples at 28 days. For 0.1% CNT composites w/c ratio of 0.40 and 0.50 revealed the P- value greater than 0.05. Similar effect of significant strength difference was observed from the average compressive strength of composites. The statistical analysis reveals that w/c ratio of 0.45 for both dosage rate of CNT and CNF cement composites displayed statistically significant difference than the control samples.

Table 3.23: T-test analysis on flexural strength of nanocomposite cement mortar

MIX PROPORTION	Control samples, Mean Mpa(ksi)	Composites, Mean Mpa(ksi)	P Value
0.1% CNF + 0.35 W/C + 0.008 SP	5.51	7.82	**$P < 0.05$**
0.1% CNF + 0.40 W/C + 0.008 SP	7.17	7.63	$P > 0.05$
0.1% CNF + 0.45 W/C + 0.008 SP	8.18	8.84	$P > 0.05$
0.1% CNF + 0.50 W/C + 0.008 SP	8.88	6.54	$P > 0.05$
0.2% CNF + 0.35 W/C + 0.008 SP	5.51	8.27	**$P < 0.05$**
0.2% CNF + 0.40 W/C + 0.008 SP	7.17	8.87	**$P < 0.05$**
0.2% CNF + 0.45 W/C + 0.008 SP	8.18	9.72	$P > 0.05$
0.2% CNF + 0.50 W/C + 0.008 SP	8.88	7.30	$P > 0.05$
0.1% CNT + 0.35 W/C + 0.008 SP	5.51	8.46	**$P < 0.05$**
0.1% CNT + 0.40 W/C + 0.008 SP	7.17	8.08	$P > 0.05$
0.1% CNT + 0.45 W/C + 0.008 SP	8.18	9.33	$P > 0.05$
0.1% CNT + 0.50 W/C + 0.008 SP	8.88	10.08	**$P < 0.05$**
0.2% CNT + 0.35 W/C + 0.008 SP	5.51	7.02	$P > 0.05$
0.2% CNT + 0.40 W/C + 0.008 SP	7.17	8.16	$P > 0.05$
0.2% CNT + 0.45 W/C + 0.008 SP	8.18	9.97	$P > 0.05$
0.2% CNT + 0.50 W/C + 0.008 SP	8.88	9.83	$P > 0.05$

From Table 3.23 it is seen that the flexural strength of CNT and CNF reinforced cement composites produced mixed results. Although there is a clear increase in the flexural strength at 7 and 28 days, P-values of some of the CNT and CNF cement composites were less than 0.05 and vice versa indicating some CNT and CNF composites show a statistically significant difference and some did not. Flexural strength does not show a clear trend as seen in compressive strength. On the whole the results were promising even though some of the CNT and CNF cement composites did not reveal statistically significant differences. One possible reason could be the small sample size.

3.7 Significance of Flow Value

In this section, flow values of control samples, CNT and CNF composites are presented. Flow value was recorded for every sample set tested for compressive strength. Flow test values were calculated as per ASTM standard C1437. As per ASTM, the flow value has to be 110 ± 5 in 25 drops of the flow table. Flow value of the control samples, CNF and CNT cement composites are tabulated in Table 3.24. Relationship between the flow value and compressive strength of CNT and CNF composites was reviewed.

Table 3.24 illustrates that the flow value had greatly influenced the compressive strength of the nanocomposites. Increase in flow value contributes to the increase of compressive strength of the nanocomposites at 28 days. The maximum strength obtained for the 0.1% CNT was 45.22 Mpa which had the highest flow value of all the 0.1% CNT composites. A similar effect was found for the 0.2% CNT composites at 28 days which had a compressive strength of 38.76 Mpa. In case of CNF, the increase in flow value resulted in decreased compressive strength. The maximum strength obtained for 0.1% CNF was 51.92 Mpa and 54.32 Mpa where the flow values were extremely low.

Relationship between the flow values and the compressive strength of CNF & CNT composites were shown from Figures 3.18 to 3.22. The compressive strength of CNT cement composites increases when the flow value was higher. This phenomenon indicates that the dispersion of CNT was more uniform in the cement matrix.

Table 3.24: Flow value and compressive strength of control samples, CNT and CNF composites at 28 days

Mix Proportions	Flow Value, %	28days Compressive Strength, Mpa
0.35 w/c CONTROL MIX	66.67	17.13
0.40 w/c CONTROL MIX	70.00	35.63
0.45 w/c CONTROL MIX	75.00	29.27
0.50 w/c CONTROL MIX	76.67	26.61
0.1% CNF - 0.35 w/c + 0.008 SP	57.50	51.30
0.1% CNF -0.40 w/c + 0.008 SP	83.33	51.92
0.1% CNF -0.45 w/c + 0.008 SP	120.83	49.13
0.1% CNF -0.50 w/c + 0.008 SP	141.67	26.61
0.2% CNF - 0.35 w/c + 0.008 SP	45.00	54.32
0.2% CNF - 0.40 w/c + 0.008 SP	83.33	45.36
0.2% CNF - 0.45 w/c + 0.008 SP	132.50	39.69
0.2% CNF - 0.50 w/c + 0.008 SP	161.67	27.11
0.1% CNT - 0.35 w/c + 0.008 SP	36.67	43.44
0.1% CNT -0.40 w/c + 0.008 SP	73.33	37.30
0.1% CNT -0.45 w/c + 0.008 SP	113.33	45.22
0.1% CNT -0.50 w/c + 0.008 SP	111.67	33.73
0.2% CNT - 0.35 w/c + 0.008 SP	37.50	23.46
0.2% CNT - 0.40 w/c + 0.008 SP	79.17	30.96
0.2% CNT - 0.45 w/c + 0.008 SP	74.17	37.13
0.2% CNT - 0.50 w/c + 0.008 SP	101.67	38.76

On the other hand, the compressive strength of CNF cement composites decreased when the flow value was higher. Thus this pattern indicates that the CNF composites resulted in strength reduction after reaching an optimum flow value, thereby indicating the effective w/c cement ratio for the CNF cement composites. Therefore, flow value is an important tool to assess the proper reinforcing effect of the CNT and CNF composites.

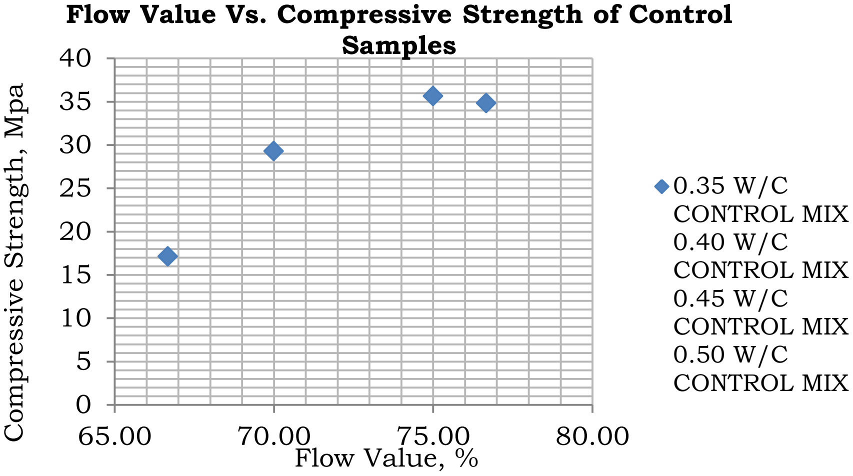


Figure 3.18: Flow value vs. Compressive strength of control samples at 28 day

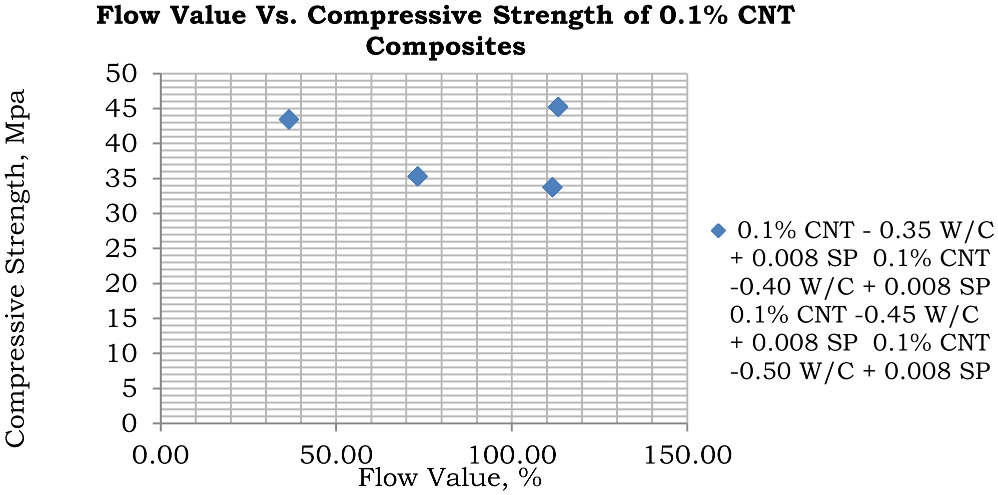


Figure 3.19: Flow value vs. compressive strength of 0.1% CNT composites at 28 day

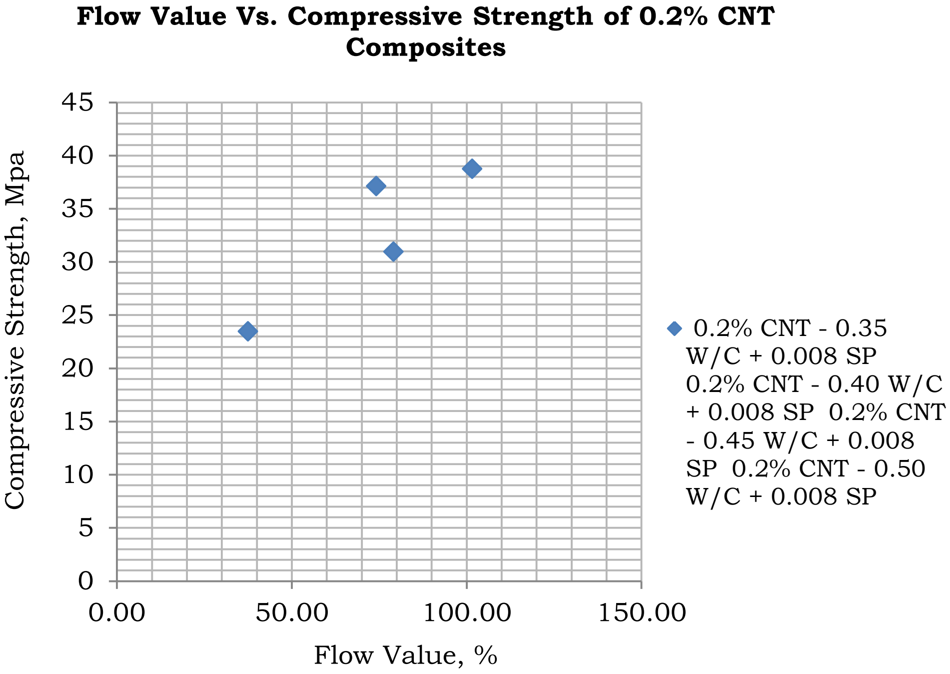


Figure 3.20: Flow value vs. compressive strength of 0.2% CNT composites at 28 day

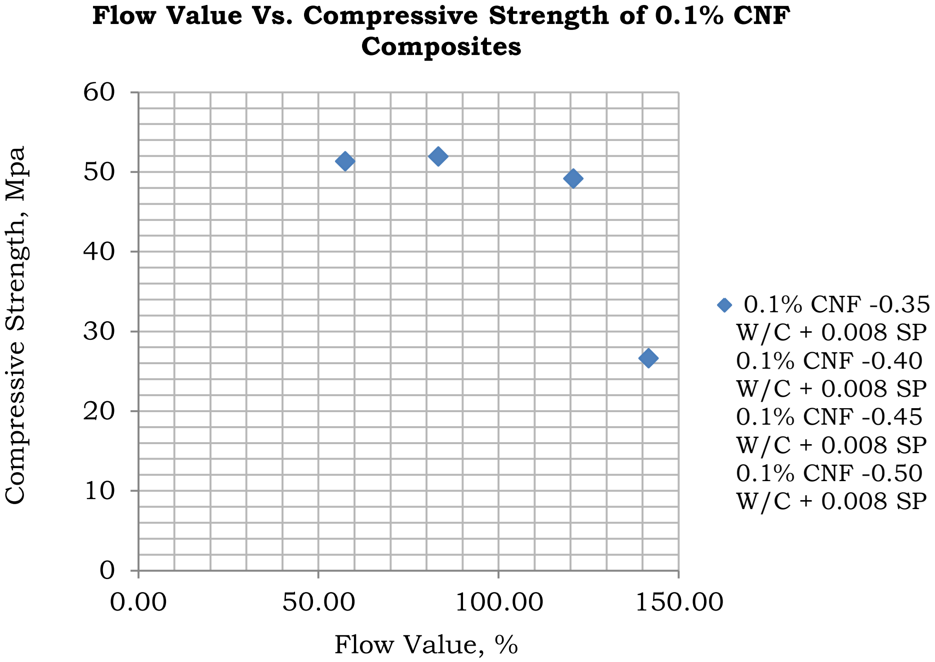


Figure 3.21: Flow value vs. compressive strength of 0.1% CNF composites at 28 day

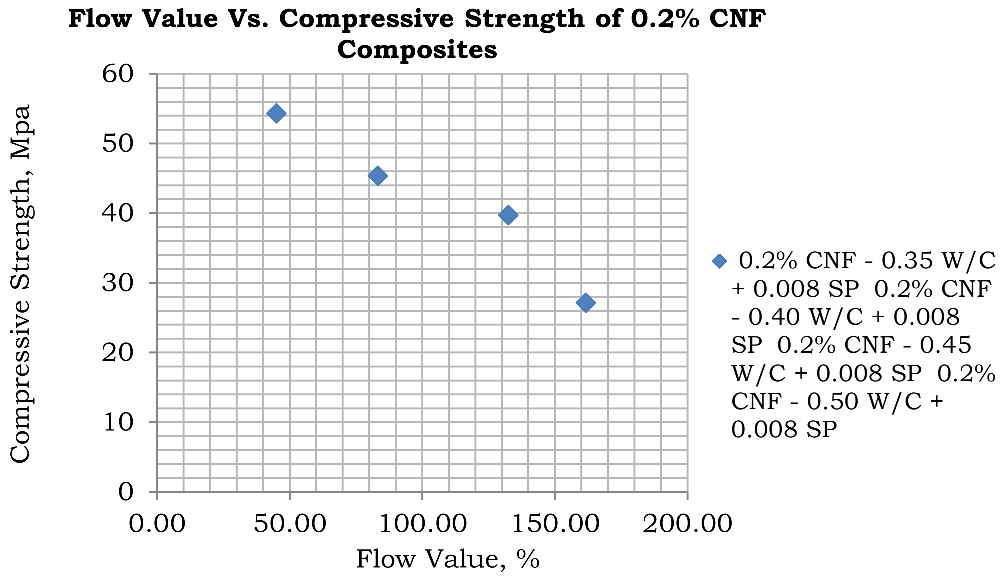


Figure 3.22: Flow value vs. compressive strength of 0.2% CNF composites at 28 day

3.8 Discussion

It is apparent that there is an optimum w/c ratio for CNT and CNF composites to achieve better strength properties. Water cement ratio of 0.45 produced highest compressive and flexural strength in all combinations. The dosage rate of 0.1% of CNT and CNF cement composites exhibited highest strength than the 0.2% composites. The optimum test results for the compressive and flexural strength and the flow value are tabulated in Table 3.25.

Table 3.25: Optimum results from compressive & flexural strength and flow value

Mix Proportions	Compressive strength, Mpa	Flexural Strength, Mpa	Flow Value, %
0.1% CNT +0.45 w/c + 0.008 SP	45.22	9.33	113.33
0.1% CNF+0.45 w/c + 0.008 SP	49.13	8.84	120.83

CHAPTER 4

PHASE II & III

SEM OBSERVATION and APPLICATION OF NANO COMPOSITES AS A REPAIR MATERIAL

4.1 Introduction

The degree of dispersion for CNFs and CNTs in the cement matrix was verified using SEM images and dispersion of CNTs and CNFs in the cementitious composites was analyzed. In this chapter, the application of nanocomposites as a repair material for pavements and bridges were discussed. From Phase I test results, an effective combination of nanocomposites producing substantial strength (compressive and flexural) and good workability was selected for further repair test. Setting time, bleeding effect and bond strength are one of the factors which evaluate the life and quality of the nanocomposites as a repair material. Dosage rate of 0.1% CNTs and CNFs cement composites with w/c ratio of 0.45 were selected to assess the above mentioned factors. Results and discussion of these three tests are presented.

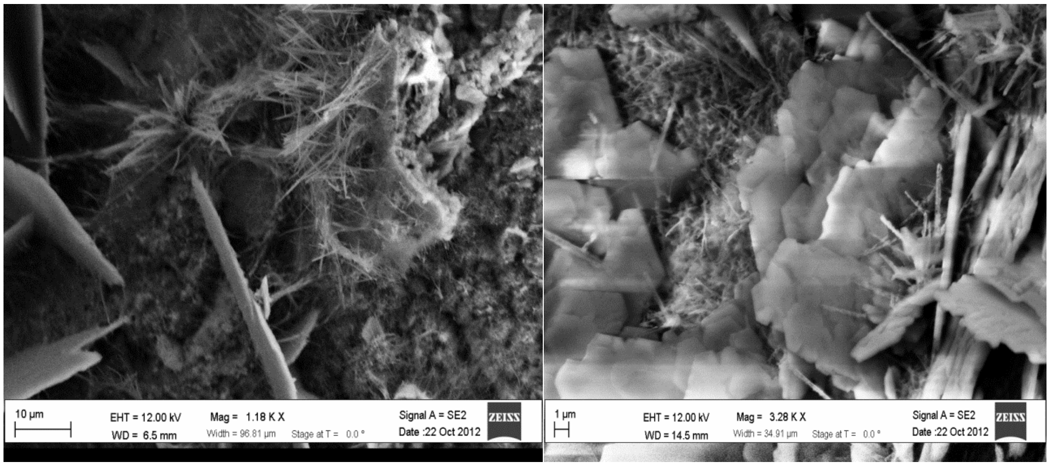
4.2 SEM Observation

SEM images of CNF and CNT cement composites were taken to verify the rate of dispersion and the bonding properties in the cement matrix. The ZEISS Supra 55 VP, (High performance variable pressure FE-SEM with patented GEMINI column technology) scanning electron microscope, was used to study the dispersion of CNT and CNF in the cement matrix. A broken sample from 28 days compressive strength test of CNF and CNT cement composites was used for obtaining the SEM images. Four combinations from CNF and CNT cement composites each, which yielded the maximum strength from compressive strength test and flexural strength test, were chosen for SEM imaging and the results were tabulated in Table 4.1.

Table 4.1: Best results from compressive strength and flexural strength tests

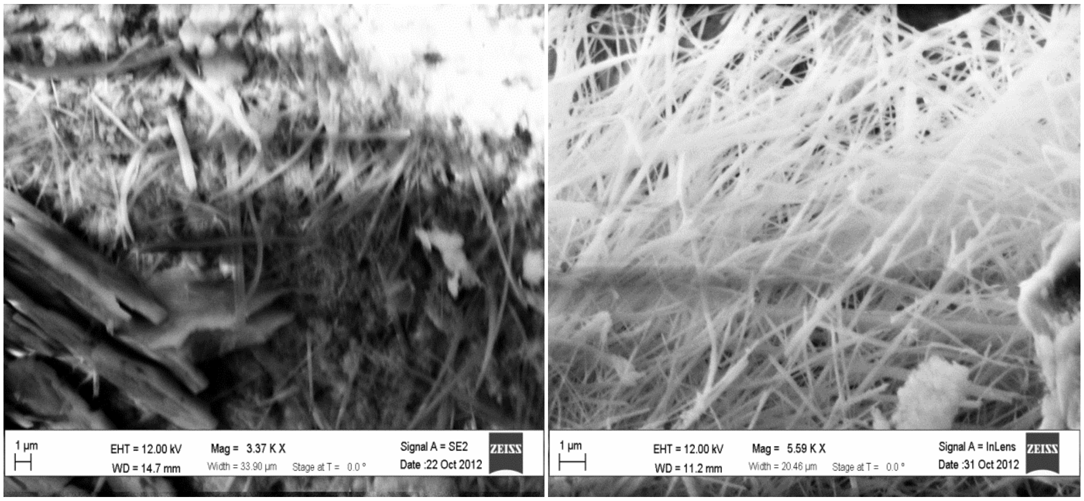
Mix Proportion	Compressive Strength, MPa	Flexural Strength, MPa
0.1 % CNF - 0.40 W/C + 0.008 SP	51.92	7.63
0.1 % CNF - 0.45 W/C + 0.008 SP	49.13	8.84
0.2 % CNF - 0.40 W/C + 0.008 SP	45.36	8.87
0.2 % CNF - 0.45 W/C + 0.008 SP	39.69	9.72
0.1% CNT - 0.45 W/C + 0.008 SP	45.22	9.33
0.1% CNT - 0.50 W/C + 0.008 SP	33.73	10.11
0.2% CNT - 0.45 W/C + 0.008 SP	37.13	9.97
0.2% CNT - 0.50 W/C + 0.008 SP	38.76	9.83

From the SEM images of CNF and CNT cement composites (from Figure 4.1 to 4.4), it was clearly observed that the CNF and CNT composites were in bundles (agglomeration due to Van der Waal’s force). The compressive strength and flexural strength of these combinations performed better than the control samples in spite of bundling effect. Although CNF and CNT exhibit darker dispersion in aqueous medium after sonication, the dispersion was not fully achieved when mixed with the cement. Re-agglomeration of CNF and CNT in the cement matrices takes place due to absorption of water from the cement. Dispersion of CNT and CNF in the cement matrix may possibly depend on the size and cluster of cement grains.



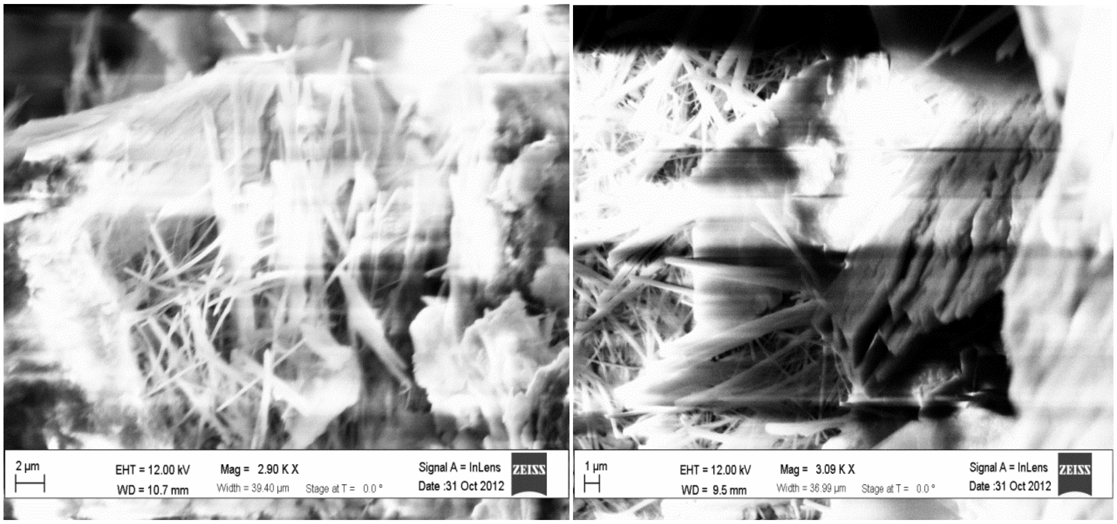
(a) (b)

Figure 4.1: SEM image of (a) 0.1% CNF cement composite with 0.40w/c and (b) (b) 0.2% CNF cement composite with 0.40w/c



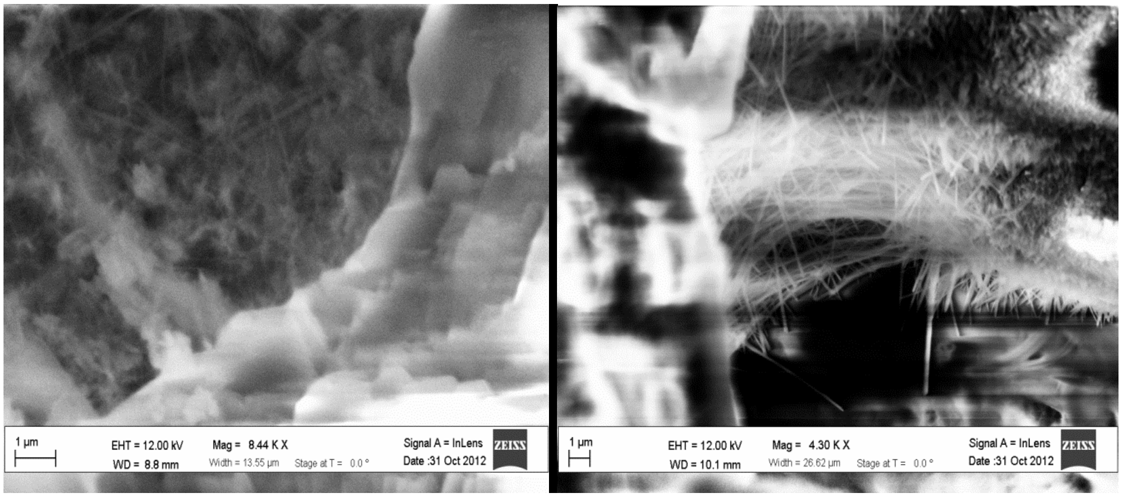
(a) (b)

Figure 4.2: SEM images of (a) 0.1% CNF cement composite with 0.45w/c and (b) 0.2% CNF cement composite with 0.45w/c



(a) (b)

Figure 4.3: SEM images of (a) 0.1% CNT cement composite with 0.45w/c and (b) 0.2% CNT cement composite with 0.45w/c



(a) (b)

Figure 4.4: SEM images of (a) 0.1% CNT cement composite with 0.50w/c and (b) 0.2% CNT composites with 0.50w/c

4.3 Bleeding Test

Bleeding of cement mortar is the existence of excess water on the surface of the freshly set mortar. Bleeding normally occurs when the mix is highly wet, improper mix proportion and insufficient mixing. Severe bleeding of the cement mortar leads to the mortar mass more porous and weak. Bleeding normally occurs by uniform discharge over the surface and also in channel form. When the water flows through these channels it washes away cement and sand forming pores or cavity. These channels are the sources for the durability issues such as freezing and thawing damage and corrosion of rebar. Nanocomposites which will be used as a repair material should possess bleeding within permissible limit or free from bleeding.

ASTM C940 – 10a test procedure was used to determine the expansion and bleeding of freshly mixed grouts [36]. The test procedure involves the materials to be maintained at an ambient temperature of 73 ± 3 °F. The mortar was placed in a glass graduated up to 800 ± 10ml on a vibration free surface. The glass graduated was covered in order to prevent evaporation of bleed water. The time and volume were recorded every 15 minutes for the first hour and thereafter hourly intervals until two readings were the same. Then the excess water on the mortar surface was decanted in to a 25 ml graduate and calculated to the nearest 0.5 ml. Dosage rate of 0.1% of CNT and CNF cement composites with w/c ratio of 0.45 was tested for bleeding effect and comparisons were made with the control samples. The test results of bleeding of 0.1% CNF and CNT composites and control samples were tabulated in Table 4.2.

Table 4.2: Bleeding test results of control samples, CNF and CNT cement composites

Mix Proportion	No of Samples	Amount of Plasticizer	Bleeding %	Temp °F
0.45 W/C Control Mix	3	NA	None	74
0.1% CNT -0.45 W/C + 0.008 SP	3	0.008	None	82
0.1% CNF -0.45 W/C + 0.008 SP	3	0.008	None	79

From the test results it was observed that none of the samples exhibited bleeding. The bleeding of control samples, CNF and CNT composites are shown in Figures 4.5 and Figure 4.6.

Figure 4.5: Bleeding test on control sample.

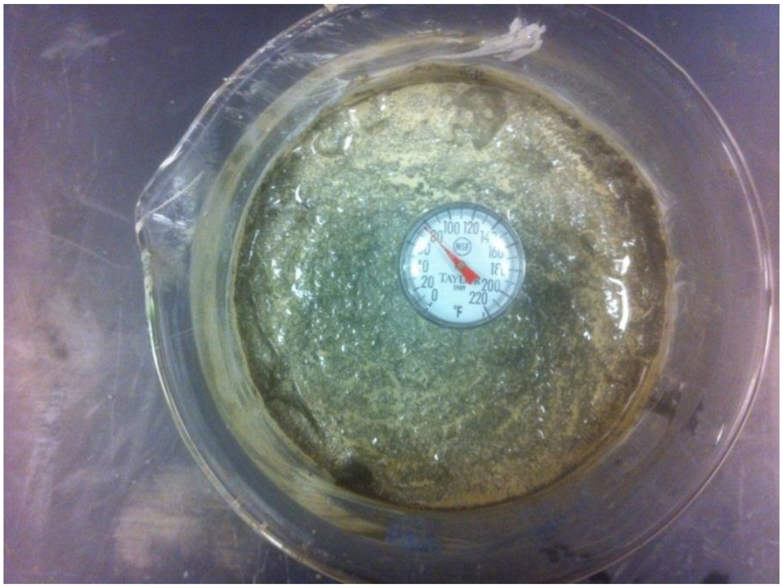


Figure 4.6: Bleeding test on 0.1% CNF composites

Figure 4.7: Bleeding test on 0.1% CNT composites

4.4 Setting Time Test

The terminology “Setting” is used to denote the stiffening of the cement mortar. It is the change of fluid state to a solid state which is caused by the hydration of C_3A and C_3S. Setting time is very vital for repair material for the application of crack repair and disintegration of concrete. ASTM C807-08 test procedure was used to determine the setting time of cement mortar using vicat apparatus [37]. The materials and mixing procedure were same as mentioned for the compressive strength and flexural strength test. The mortar was placed in the mold of about 20mm from the bottom and compacted. The remaining mortar was placed and compacted inside the mold till it gets flushed with the top of the mold. Then the sample was kept idle for 30 minutes in a moist closet room. After 30 minutes, the vicat needle was placed on contact with the surface of the mortar. The vicat needle of 1 mm was used for setting time test. The reading was set to 0 mm and the needle was dropped. The corresponding the reading was recorded. The procedure was repeated at every 30 minutes until the needle failed to touch the bottom of the mortar. Thereafter the readings was recorded for every 10 minutes till it reached less than 10mm. Setting time testing images for control samples, CNF and CNT composites are shown in Figures 4.8 to Figure 4.11.

Figure 4.8: Setting time test - Vicat's needle touching the surface of mortar

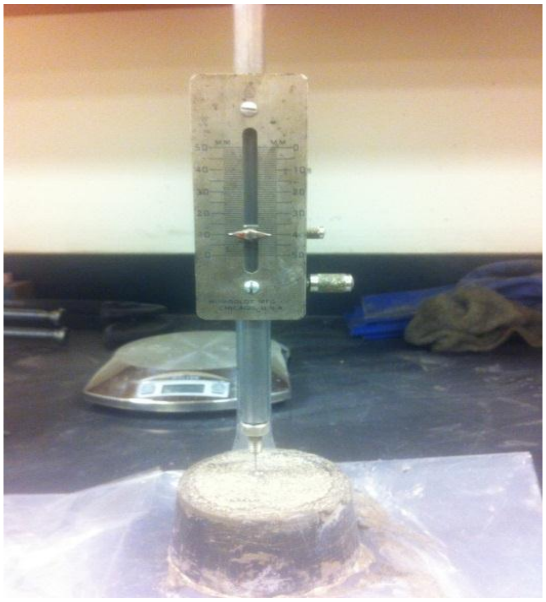


Figure 4.9: Setting time test - Vicat's needle touching the bottom of the sample

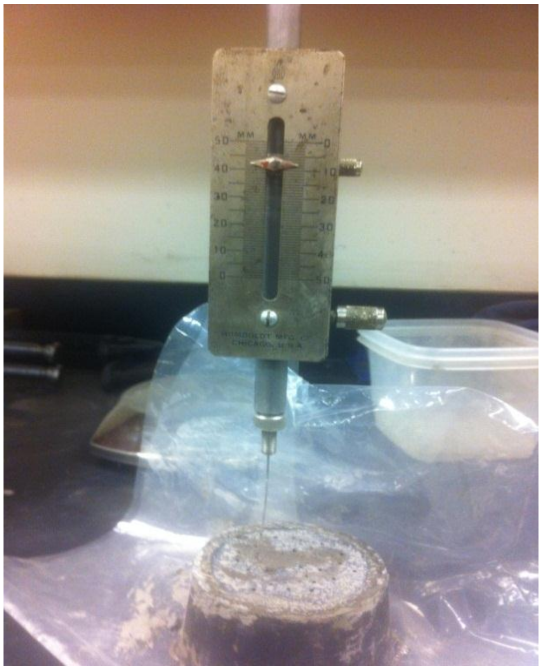


Figure 4.10: Setting time test - Penetration of needle less than 10 mm

Figure 4.11: Setting time test - Reading scale of Vicat’s apparatus

Control sample with w/c ratio of 0.45, 0.1% of CNF and CNT with w/c ratio of 0.45 and control sample with w/c ratio of 0.45 having plasticizer were prepared for setting time test. The setting time test results are tabulated in Table 4.3.

Setting time was calculated using the formula

$$T = \{((H - E)\big|(C - D)) * (C - 10)\} + E \qquad \text{[Eq. 4.1]}$$

Where

E - Time in minutes of last penetration greater than 10 minutes.

H - Time in minutes of first penetration less than 10 mm.

C - Penetration reading at time E.

D - Penetration reading at time H.

Table 4.3: Setting time test results

Mix Proportion	No of sets	Amount of Plasticizer	Setting Time min
0.45 W/C	S1	NA	183
	S2		186
0.45 W/C + 0.008 SP	S1	0.008	303
	S2		295
0.1% CNT -0.45 W/C + 0.008 SP	S1	0.008	264
	S2		278
0.1% CNF -0.45 W/C + 0.008 SP	S1	0.008	272
	S2		283

S1 – set1 and S2 – set2

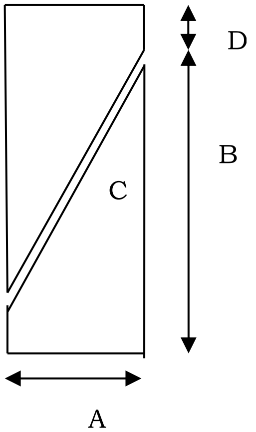
From the test result it was seen that the CNF and CNT composites reached the initial setting much faster than the control sample having super plasticizer. This phenomenon was anticipated as the CNF and CNT accelerates the hydration process quicker. Control samples without super plasticizer had attained their setting time prior to the CNF and CNT composites.

4.5 Slant Shear Test

Slant shear test is the effective testing method widely followed for evaluating the bond strength of old concrete substrate and the repair material. ASTM standard C882 test procedure was used to determine the bond strength of epoxy resins normally used for Portland cement [38]. The bond strength was calculated by joining two equal halves of the cylinder with epoxy resins.

In this study, w/c ratio of 0.45 having 0.1% CNF and 0.1% CNT cement composite mortar was used as a repair material for bond strength. Cylinders (75 mm by 150 mm) were used as per ASTM standard and were cut in to two equal halves at an angle of 30° from vertical. Then the concrete cylinder was placed in the storage tank for 24 hours. After 24 hours, the cylinders were cleaned and surfaced dried before applying the nanocomposites mortar. The schematic diagram of the cut is shown in Figure 4.12. Three mm of CNT and CNF mortar was placed to join the two equal halves of the old concrete substrate. Similarly 0.5 mm thickness of epoxy resin was used for joining the two equal halves for comparing the bond strength with the nanocomposite cement mortar.

Pro-Poxy 300 Fast, an epoxy recommended by TXDOT for the quick repair of cracks for bridges, was used for the study. After sandwiching the old concrete substrate with the epoxy and CNF and CNT mortar, the specimens were kept in a moist room. The specimen was tested for compressive strength at 3, 7 and 28 days. The maximum failure load was recorded. Bond Strength of epoxy resin and CNT and CNF mortar was calculated by dividing the maximum failure load by the bonded surface area. Slant shear test were carried out for 3, 7 and 28 days. Casting and testing images are shown in Figures 4.13 to 4.16. The slant shear test results are tabulated in Table 4.4.



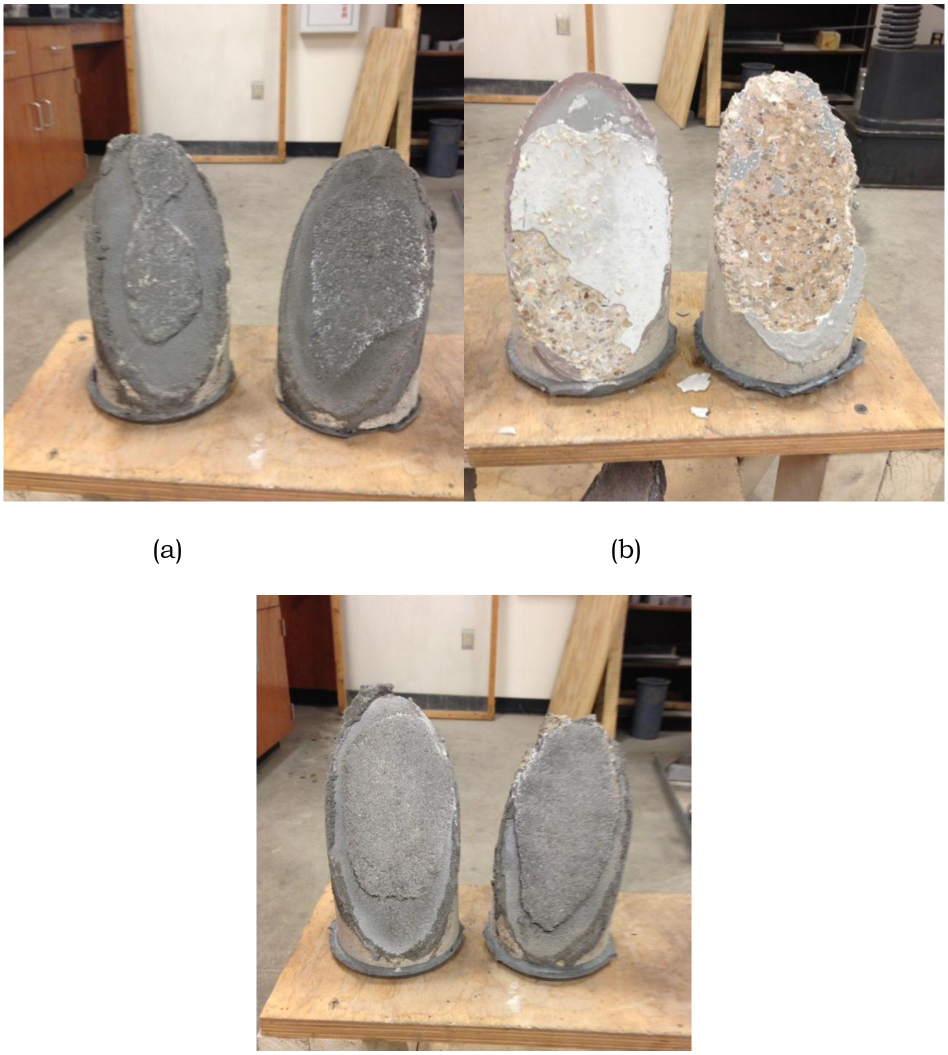
A – Diameter	75 ± 2 mm
B – Height	140 ± 2 mm
C – Slant Height	150 ± 2 mm
D – Base Height	10 ± 2 mm

Figure 4.12: Dimensions of cylinder for slant shear test

Figure 4.13: Concrete cylindrical specimens in two equal halves at 30° with vertical

(a) (b)

Figure 4.14 Concrete cylinder bonded by (a) CNF and CNT composites (b) epoxy resin



(a) (b)

(c)

Figure 4.15 Bonded concrete cylinders after testing (a) CNT cement composites (b) epoxy resin and (c) CNF cement composites

Table 4.4 Slant shear test results

Mix Proportions	3 Days MPa	7 Days MPa	28 Days MPa
0.1% CNF -0.45 W/C + 0.008 SP	6.20	8.35	9.70
0.1% CNT -0.45 W/C + 0.008 SP	6.80	10.10	11.56
Pro Poxy 300 Fast - Epoxy Resin	14.10	14.80	15.30

From the slant shear test results, 3 day bond strength of CNT and CNF composites were low compared to the epoxy resin. The bond strength of epoxy resin samples was almost double the bond strength of CNF and CNT composites. The CNT composites showed better result than the CNF composites. Similar effect of bond strength was observed at 14 days. At 28 days, epoxy resin performed 30% higher strength than the CNT composites and 58% higher than the CNF composites. The decrease in strength of CNT and CNF composites was due to either poor dispersion or agglomeration effect when mixed with the cement matrix. Epoxy (PRO POXY 300 Fast) attained high strength at 3 days and has no major improvements in strengths as expected of a chemical repair material. If the dispersion of the CNF and CNT composites is improved, the bond strength could be improved or close to the epoxy resin.

4.6 Discussion

From the SEM images of CNF and CNT composites, it is apparent that the dispersion of CNF and CNT in the cement matrix was not very uniform. Some re-agglomeration took place when the CNF and CNT were mixed with the cement to form cement paste. Both CNT and CNF samples and control samples showed no marks of bleeding. CNF and CNT cement composites exhibited faster setting time than the control samples with super plasticizer. Bond strength of both CNT and CNF composites was low compared to epoxy.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The following conclusions may be made based on the study reported herein:

[1] The major difficulty in using the nanoparticles within the cement matrices was the rate of dispersion. The nanoparticles attract each other forming either bundles or ropes due to van der Waal's force. Therefore Ultrasonication, a method used to disperse the nanoparticles in the aqueous medium was pursued.

[2] From the test results, an effective w/c ratio of 0.45, which produced higher compressive and flexural strength, was obtained. CNT percentage of 0.1 cement composites attained 54% and 14% higher in compressive and flexural strength than plain cement paste. Similarly, 0.1% CNF cement composites achieved 67% and 8% higher in compressive and flexural strength compared to plain cement paste. These results indicate that the CNF and CNT cement composites will be promising material for the repair material for the crack in bridges and pavements.

[3] The degree of dispersion was verified using SEM images, which revealed poor dispersion. SEM images of CNT and CNF cement composites showed bundles and clumps of CNF and CNT in the cement matrix. Ultrasonication images depicted more dark and thicker dispersion in the aqueous medium but the SEM images shows poor dispersion in the hardened cement paste. Poor dispersion may be due to re-agglomeration of CNF and CNT by absorption of water from the cement, when mixed to form the cement paste.

[4] The study shows no bleeding effect on CNF and CNT cement composites. Setting time for CNT and CNF composites was much faster than the plain cement containing super plasticizer. Bond strength of CNF and CNT composites were very low at 3 and 7 days compared to epoxy resin but the bond strength of CNT cement composites performed strength close to epoxy resin at 28 days. However CNF cement composites produced very low strength at 28 days.

The primary results from the compressive and flexural strength were promising in spite of poor dispersion observed in the hardened cement paste. Therefore it needs further investigations to study the dispersion of nanoparticles in the hardened state.

There are some limitations in this research work. There could be some possible deviation in the results since the samples are tested from two different batches for the same mix proportions. But this will not lead to a significant change in the mechanical properties such as compressive and flexural strength. Also, the rate of dispersion of CNT/CNF within the cement matrix is uncertain as there is no quantitative procedure for quantifying the dispersion.

5.2 Future Research Recommendation

In this research, untreated CNT and CNF were used to study the behavior of composites as reinforcement in cementitious material. To improve the dispersion rate and mechanical properties of the cementitious mortar, treated CNT and CNF has to be examined. The dispersion of CNT and CNF in water was facilitated by sonication with the help of plasticizer (Polycarboxylate ether group). A generalized chart or a table has to be developed for sonication time for a particular surface area of CNT and CNF, thereby producing a uniform dispersion.

Another emphasis on research should be on the grain size of cement. CNT and CNF somehow produces uniform dispersion in water with the help of sonicator but it re-agglomerates when it is mixed with cement. To eradicate this difficulty, micro cement could be used in place of ordinary cement.

In this study, application of nanocomposite cement mortar as a repair material has been investigated through setting time test; bleeding test and slant shear (bond strength). But in order to have a successful nanocomposite as a repair material, there are other tests which need to be examined. Durability test such as drying shrinkage, permeability, freezing-thaw resistance and sulfate resistance needs to be tested. If the repair material has to be used for spalling of concrete, the rebar pull out test has to be done to assess the bond strength between the rebar and the nanocomposite cement mortar.

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BIOGRAPHICAL INFORMATION

Vinoth Mohanam received his B.E in Civil Engineering from Anna University, India in 2006. He graduated M.Tech in Structural Engineering from VIT University, India in 2008. He received the annual scholarship for obtaining second rank with the GPA of 9.57 at the university level. His post-graduate project includes the optimum design of composite beams. Soon after this post-graduation he started his career as a structural engineer at M.N. Dastur & Co (p) Ltd, Consulting Engineers, India from 2008 to 2010. During this period he worked as a consultant for power plant and steel plant industries. His work mainly includes the design of super structure, sub structures and water retaining structures of both concrete and steel. He joined University of Texas at Arlington as a graduate student in the Civil Engineering Department in 2010. He started his master thesis under Dr. Nur Yazdani. His master thesis includes the application of Carbon nanotubes and Carbon nanofibers as cementitious composites.