PROPERTIES OF MICROCEMENT MORTAR WITH NANO PARTICLES

by

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Abstract

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WITH NANO PARTICLES

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Carbon nanotubes (CNT) and Carbon nanofibers (CNF) are one of the toughest and stiffest materials in the world presently with extreme properties yet to be discovered in terms of elastic modulus and tensile strength. Due to the advanced properties of these materials they are being used in almost all fields of science at nanolevel and are being used in construction industry recently for improvement of material properties. Microcement is fine ground cement which as half the particle size of ordinary Portland cement. In this research the behavior of cement mortar of micro cement with the addition of nanoparticles is studied.

Due to high aspect ratio and strong van der Waal forces between the particles of CNT and CNF, they agglomerate and form bundles when mixed with water, sonication method is used to mix nanoparticles with few drops of surfactant and super plasticizer. Mechanical properties such as compressive strength and flexural strength with CNT and CNF composites are examined and compared with control samples.

0.1% and 0.05 % of nanoparticles (both CNT and CNF) by the weight of cement are used in this research and 0.8% of super plasticizer by weight of cement was also used along with 0.4, 0.45 and 0.50 water cement ratios for making specimens for compression test. The compressive strength results are not satisfactory as there was no constant increase

in strength with all the composites, however strength of few nanocomposites increased by a good percentage. 0.5 water cement ratio cement mortar had compressive strength of 7.15 ksi (49.3 MPa), whereas sample with 0.1% CNT showed 8.38 ksi (57.8 MPa) with 17% increase in strength after 28 days. Same trend was followed by 0.4 water cement ratio as the compressive strength of control sample was 8.89 ksi (61.3 MPa), with 0.05% of CNT strength increased to 10.90 ksi (75.2 MPa) with 23% increase in strength. 0.4 water cement ratio was used for flexural tests including 0.1%, 0.05% of CNT and 0.1%, 0.05% of CNF with 0.008 ratio of super plasticizer. Results showed that there was a significant increase in strength initially but gradually decreased as the time increase and showed decreased strength at 28 days when compared to control samples. Flow cone results are quite satisfying as the flow is significantly increased with the addition of nanoparticles. Time of efflux of control sample is 16.22 sec whereas for specimen with CNT had a time of efflux 12.67 sec and sample with CNF showed 13.65 seconds. Setting time test was carried on 0.4 water cement ratio. Composites with nanoparticles exhibited faster setting when compared to its control sample. Bleeding was not observed with the nanoparticles in the cement mortar. Shrinkage test was conducted on sample with 0.4 water cement ratio with 0.05% of CNT and CNF. Shrinkage was very small in the samples with nanoparticles.

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Chapter 1

Introduction

1.1 Introduction

Carbon nanotubes (CNT) and Carbon nanofibers (CNF) have a lot of significance in the field of science as they are the toughest, stiffest materials and possess extraordinary properties such as thermal conductivity and electric conductivity. CNT and CNF are valuable in electronics and other fields of materials science and nanotechnology. Particularly, owing to their extraordinary thermal conductivity, electrical and mechanical properties carbon nanotubes find applications as additives to various structural materials. Concrete, cement mortar had undergone many changes from the past from normal concrete to high strength concrete and high performance concrete. Recently carbon nanoparticles are been used in construction industry to increase the strength of cement mortar and to improve the material properties of cement. Mechanically, carbon nanoparticles show excellent elastic behavior, with Young's Modulus of approximately 145037.7 ksi (1 TPa) which is several times higher than steel in terms of strength and a density of about 0.0001789 lb/in^3 (1.33 gm/cm^3) which is several times lower than steel in terms of density. Carbon nanoparticles can also bear torsion and bending without breakage. Since carbon nanoparticles exhibit great mechanical properties along with extremely high aspect ratio ranging from 30 to more than several thousands and they are expected to produce significantly stronger and tougher cement composites than traditional reinforcing materials like glass fibers and carbon fibers. Since the size of nanoparticles range from 3.93×10^{-8} in (1 nm) to tenths of nm and large length to diameter ratio, these can be distributed in a finer scale than traditional fibers, resulting in more efficient crack bridging at very preliminary stage of crack propagation within the composites of cement mortar as shown in Figure 1-1. As the cement mortar is very good

at compression but weak in tension, for increasing tensile strength steel bars and other reinforcing materials are used in concrete cement. So to improve tensile properties of cement, CNT and CNF are added to the cement mortar as CNT and CNF are very good at bearing tension. So application of nanoparticles to the cement mortar is examined and the behavior of mortar with nanoparticles is investigated.

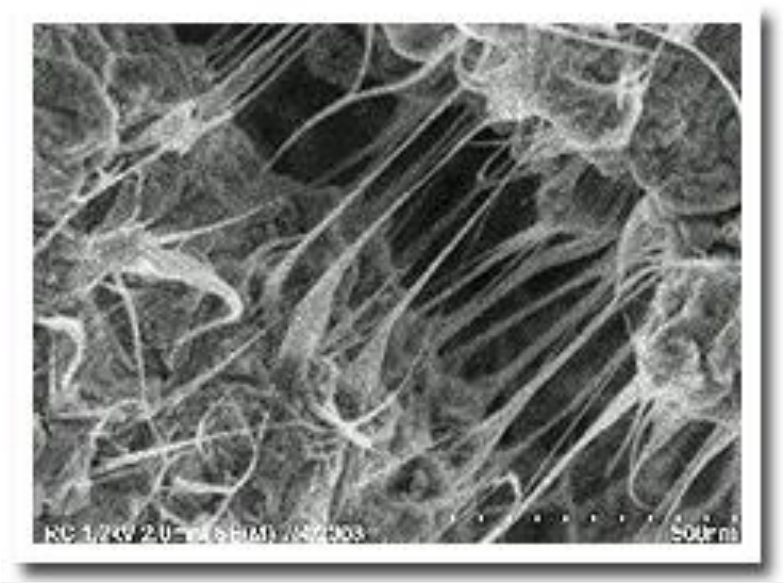

Figure 1-1 CNT bridging crack in a cement composite

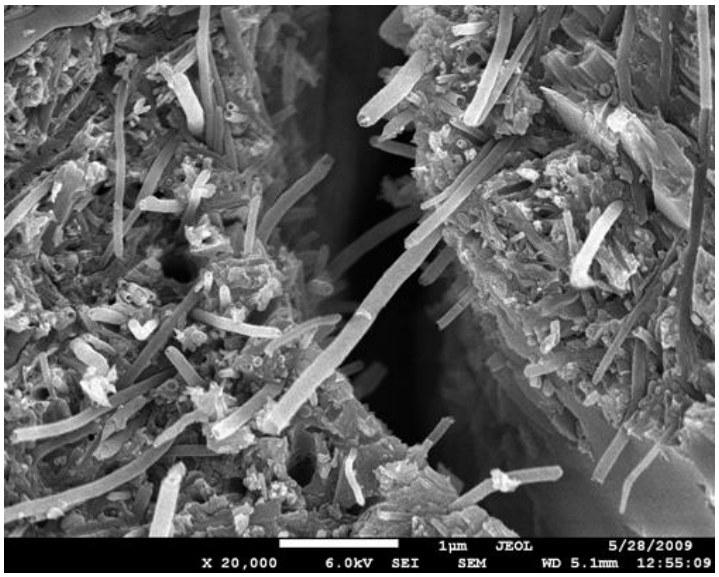

Figure 1-2 CNF bridging crack in cement composite

1.2 Research significance

Carbon nanoparticles had gained lot of importance in modern science in various fields such as automobile, biomedical, electrical, chemical, optics so on and lagged behind in construction sector when compared to all these sectors. The areas of importance of nanoparticles in construction industry include CNT, CNF composites made with existing construction materials, ropes made with CNT that are used as structural components and CNT heat transfer systems. CNT composite materials are the first application of nanoparticles in construction, as discussed earlier nanoparticles are excellent reinforcing materials because of their high aspect ratio, high strength and toughness. The properties that carbon nanoparticles impart to the cement composites are enhanced strength, stiffness and toughness without any addition of weight to cement composite, improved durability, increased functionality and reduced flammability. Cost of nanoparticles is very low when compared to other reinforcing materials.

1.3 Objective of research

As CNT and CNF possess extremely good properties, the study of nanocomposites is emerging as important research in the field of construction, moreover carbon nanoparticles brought many changes in other fields of science. Presently lot of research work is being done on nanocomposites of cement and carbon nanoparticles. Previous research concentrated more on dosage rate, percentage of nanoparticles used in cement mortar and mechanical properties of mortar. Past researches are done using ordinary Portland cement. Due to high aspect ratio and higher van der Waal forces nanoparticles form bundles when mixed with water, as a result there will be improper dispersion of nanoparticles. Proper dispersion of nanoparticles was not achieved by just mixing nanoparticles with a stirrer by hand, but by a complex process which uses sonication. Dispersion of nanoparticles into cement is done by various methods of sonication.

In this research we concentrate on tip sonication method for dispersion of nanoparticles into the aqueous medium using surfactant with the help of super plasticizer and syndicator and then introducing this aqueous solution in the cement mortar. Microcement was replaced with the ordinary cement as microcement is lot finer than ordinary cement and it has half the particle size of ordinary cement which allows to form smaller cement particles by which the bonding between cement particles and nanoparticles can be enhanced at micro level. 0.4, 0.45 and 0.50 water cement ratios are used in this research with 0.008 ratio of super plasticizer by the weight of cement. Two different ratios of nanoparticles are used in this research, 0.1% and 0.05% of both CNT and CNF are the ratios of nanoparticles used by the weight of cement.

The main objectives of this research is to study the behavior of cement mortar and compare the mechanical properties of cement composites with the control samples of cement.

The different processes followed to evaluate the improved properties of mortar is given below:

- Comparing the compressive strength of samples with the nanoparticles to the control samples with different water cement ratios.
- Comparing the flexural strength of the samples with CNT and CNF to that of control samples with 0.4 water cement ratio.
- Observing the increase in flow of the cement mortar with and without nanoparticles for specified water cement ratio.
- Finding out the setting time for cement composites with nanoparticles and without nanoparticles for 0.4 water cement ratio.
- Bleeding with samples that has CNT and CNF is investigated.
- Checked for shrinkage of the samples that has carbon nanoparticles.

Chapter 2

Literature Review

2.1 Introduction

Carbon nanotubes (CNT), Carbon nanofibers (CNF) and the properties of cement composites with these nanoparticles are studied in deep in this chapter. History of carbon nanoparticles, synthesis of these nanoparticles, structure and properties of CNT and CNF is further discussed in this section. A deep literature review is done on the research that has been done in the past with cement composites with nanoparticles.

Concrete is major part of all constructions, composed of coarse and fine aggregates held with hydrated cement binder. Concrete thus formed from hydrated cement is brittle and weak in tension. Various forms of reinforcements such steel bars, steel fibers, carbon fibers and so on are used to overcome this problem of weak tensile strength. The strength of concrete is dependent on various factors like water cement ratio, aggregates type of cement. Cement itself is a complex structure in a nanoscale and hydration process is a molecular process that which solidifies the concrete, so by introducing nanoparticles into cement they can impart strength to the concrete at nanolevel and form bridging between the micro cracks in the concrete. The properties of carbon nanoparticles when imparted to the formed concrete can greatly revolutionize the properties of concrete.

2.2 Carbon nanotubes

2.2.1 History

Carbon nanotubes (CNTs) were firstly observed and described in 1952 by Radushkevich and Lukyanovich, they published a paper in the Soviet Journal of Physical Chemistry showing images of hollow graphitic carbon fibers that are 50 nanometers in

diameter. Later in 1976 the single (or double) walled carbon nanotubes were observed by Oberlin. In more recent history the discovery of CNTs is attributed to Iijima, a Japanese scientist was the first scientist who described the multiwalled carbon nanotubes (MWNTs) preparation process after a random event during the test of a new arc evaporation method for C60 carbon molecule fabrication in 1991, from then CNT became popular around the world. In 1992 first theoretical predictions of the electronic properties of single-walled carbon nanotubes by groups at Naval Research Laboratory, USA. In 1993 another two separate works from Iijima and Bethune describing the growth process of single walled carbon nanotubes (SWNTs) were reported. Presently, carbon nanotubes is being used in every field of science like optics, electronics, automobiles, construction so on.

2.2.2 Synthesis of CNT

High temperature greater than 3092 ^{0}F (1700 ^{0}C) preparation techniques such as arc discharge or laser ablation were first used to produce CNTs but nowadays these methods have been replaced by low temperature chemical vapor deposition (CVD) techniques less than 1472 ^{0}F (800 ^{0}C), since the orientation, nanotube length, alignment, diameter, purity and density of CNTs can be later precisely controlled. Most of these methods require supporting gases and vacuum, but the growth at atmospheric pressure has been already reported. However, gas-phase methods are volumetric and hence they are suitable for applications such as composite materials that require large quantities of nanotubes and industrial-scale synthesis methods to make them economically feasible. Arc discharge belongs to the methods that use higher temperatures above 3092 ^{0}F (1700 ^{0}C) for CNT synthesis which usually causes the growth of CNTs with fewer structural defects in comparison with other techniques.

Figure 2-1 Methods of synthesis of CNT

2.2.3 Structure of CNT

Carbon nanotubes (CNTs) are allotropes of carbon with tube-shaped material made of carbon having diameter measuring on the nanometer scale. Carbon nanotubes have been constructed with length to diameter ratio of up to 132,000,000:1. The chemical bonding of nanotubes is composed entirely of sp^2 bond that are similar to those of graphite. These bonds are stronger than the sp^3 bonds found in alkanes and diamonds, which provide nanotubes with their unique strength. Nanotube consists of either one cylindrical graphene sheet called single walled nanotubes (SWNT) or several layered graphene sheets with a spacing of 13×10^{-9} to 14×10^{-9} inch (0.34 to 0.36 nm) with discrete angles and combinations of rolling angles and different radii called as multi

walled nanotube (MWNT). Figure 2-2 shows the structure of single walled carbon nanotube, whereas Figure 2-3 shows the structure of multi walled carbon nanotube.

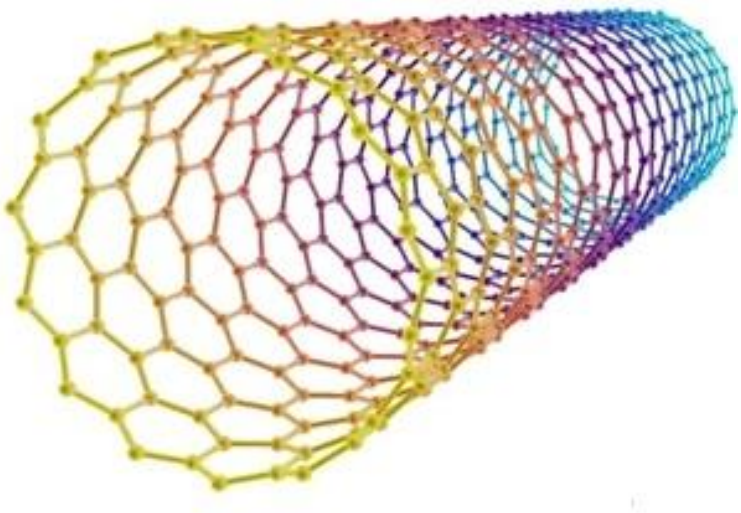

Figure 2-2 Single walled CNTs

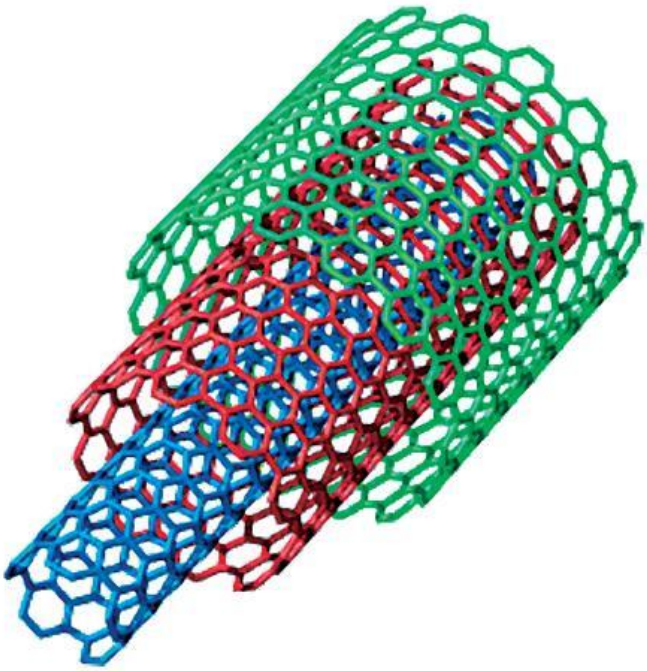

Figure 2-3 Mutliwalled CNTs

2.2.4 Properties of CNT

The intrinsic mechanical and transport properties of carbon nanotubes make them the ultimate carbon fibers. It has been shown that CNTs are very strong in the axial direction. Young's Modulus of the order 39160 to 137785 ksi (270 to 950 GPa) and tensile strength of 1595 to 9137 ksi (11 to 63 GPa) were obtained. It has a density of 0.0001789 lb/in^3 (1.33 gm/cm^3) making it very light material when compared to steel. Carbon nanotubes show a unique combination of strength, stiffness and tenacity compared to other fiber materials which usually lack one or more of these properties. CNT are expected to be very good thermal conductors along the tube, exhibiting a property known as ballistic conduction and these behave as good insulators laterally to the tube axis. SWCNT has a room-temperature thermal conductivity along its axis of about 3500 W·m^{-1}·K^{-1}, compared to copper which transmits 385 W·m^{-1}·K^{-1}. Because of

the symmetry and unique electronic structure of graphene, the structure of a nanotube shows extraordinary electrical properties. CNT also has good kinetic properties and optical properties.

2.2.5 Applications Of CNT

Carbon nanotubes can be used for a wide range of new and existing applications:

- Conductive plastics
- Structural composite materials
- Flat-panel displays
- Gas storage
- Antifouling paint
- Micro- and Nano-electronics
- Radar-absorbing coating
- Technical textiles
- Ultra-capacitors
- Atomic Force Microscope (AFM) tips
- Batteries with improved lifetime
- Biosensors for harmful gases
- Extra strong fibers

2.3 Use of CNT in past as cementations material

As CNT has its applications in various fields of science, due to its excellent properties various researchers are carrying their research on the effect of inclusion of carbon nanotubes on various mechanical properties of cement mortars.

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 poly acrylic acid polymer-treated MWCNTs compared to the control samples.

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 sulfuric 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.

In 2008 P. Balaguru and K. Chong made a study to analyze the behavior of cementations materials produced with the insertion of carbon nanotubes of multiple walls in different concentrations and compare their physical and mechanical properties with plain mortar. The examination of nanoscale cement products and the use of carbon nanotubes to increase the strength and durability of cementations composites was studied in this research. 0.20, 0.40 and 0.60% ratios of carbon nanotubes have been used in this research.

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. 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.

Yazdanbakhsh et al. (2011) inspected CNT for the enhancement of the mechanical properties of cementations 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.

2.4 Carbon nanofibers

2.4.1 History

In 1889 on synthesis of filamentous carbon by Hughes and Chambers found records concerning carbon nanofibers is the first patented data about carbon nanofibers.

In the early 1950's the first electron microscopy observations of carbon nanofibers were performed by the Soviet scientists Radushkevich and Lukyanovich, they published a paper in the Soviet Journal of Physical Chemistry showing hollow graphitic carbon fibers that are having a diameter of 50 nm.

In the 1970s, Japanese researchers Koyama and Endo succeeded in the manufacturing of vapor grown carbon fibers (VGCF) with a length of above 0.039 inch (1 mm) and diameter of 39×10^{-6} in (1 μm) and later Tibbetts in the USA and Benissad in France continued to perfect the VGCF fabrication process in early 1980s. Deeper studies

focusing on synthesis and properties of these materials are carried in USA for advanced applications were led by R. Terry and K. Baker.

Vapor Grown Carbon Fibers are attempted to commercialize firstly by the Japanese company Nikosso in 1991 under the trade name Grasker, the same year Sumio Iijima published his famous paper introducing the discovery of carbon nanotubes (CNTs).

Presently, several companies around the globe are actively involved in the commercial scale production of carbon nanofibers and new engineering applications are being developed for these materials intensively.

2.4.2 Synthesis of CNF

Carbon nanofibers are been known as a nuisance material for a long duration of time as this emerges during catalyst conversion of carbon containing gases. There are many methods of producing carbon nanofibers among which electric chemical vapor deposition (CVD), arc discharge, laser evaporation and plasma-enhanced CVD are important from all the methods. Among these, the CVD method seems to be the potential candidate for a commercial-scale process. Catalytic chemical vapor deposition (CCVD) or simply CVD with variants like thermal and plasma-assisted is the dominant commercial technique for the fabrication of vapor grown carbon nanofiber (VGCNF). Here, gas-phase molecules are decomposed at high temperatures and carbon is deposited in the presence of a transition metal catalyst on a substrate where subsequent growth of the fiber around the catalyst particles is observed. In general, this process involves separate stages such as fiber growth, carbon deposition, gas decomposition, fiber thickening, graphitization and purification, finally results in hollow nanofibers.

2.4.2 Configuration of CNF

Carbon nanofibers are the allotropes of carbon which are in the form of tabular microstructure called filament or fibers. Carbon atoms join each other in *sp*, sp^2 and sp^3 hybridized structures to form stable structures, carbon nanofibers come under this category. They are generally obtained in a very fine powder form. CNFs are available in diameters varying from 2.75×10^{-6} to 7.87×10^{-6} in (70 to 200 nm) and in lengths varying from 1.96×10^{-3} to 3.93×10^{-3} in (50 to 100μm).

2.4.3 Properties and Applications of CNF

CNFs have extra ordinary electrical conductivity, thermal conductivity and excellent chemical properties. CNFs possess exceptional mechanical properties like elastic modulus as high as 87022 ksi (600 GPa) and tensile strength as high as 1261 ksi (8.7 GPa). CNFs are highly adsorptive for organic materials. CNFs can withstand heat up to 5432 ^{0}F (3000 ^{0}C) due to which it has superior electrical properties.

CNF are used in various fields of science, few of them are

- Field electron emission sources
- Composite materials
- Scanning probe microscopy tips
- In petro chemistry as a carrier material for various catalysts
- In vertically-aligned arrays, a platform for gene delivery
- For electrode materials
- Oil spill remediation

2.5 Use of CNF in past

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.

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.

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.

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.

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.

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

Chapter 3

Materials

3.1 Microcement

Microcement is finely ground ordinary Portland cement that has a particle size of approximately one half of smaller magnitude when compared to the particle size of ordinary cement particles. The Blaine fineness of micro fine cement ranges from about 2929 ft^2/lb to 5858 ft^2/lb (6,000 to 12,000 cm^2/g) when compared to about 1464 ft^2/lb to 2441 ft^2/lb (3,000 to 5,000 cm^2/g) for ordinary Portland cement. When mixed with water, the smaller size particles react faster due to the significantly larger surface area that exposes more anhydrous material to the water as a result the hydration rate increases. Microcement sets fast as finer particles hydrate relatively fast compared to coarser particles and increasing particle fineness tends to decrease the viscosity and yield stress. Micro cement is used basically for grouting in rocks and for soil injections.

3.1.2 Microcement used in research

MasterRoc MP 650 micro fine Portland cement is replaced by ordinary Portland for making specimens in this research. MasterRoc MP 650 has a small particle size making it particularly well-suited for penetration into tight joints, fissures and pore spaces. Superior penetration provides a water-tight grouted rock or soil mass much more effectively than ordinary Portland cement systems. The basic features of this micro cement are fast setting time, more durable, cost effective, fine particle size, non-hazardous. MasterRoc MP 650 is a well-graded cement milled from pure Portland cement clinker with a Blaine value of 3173 ft^2/lb (6,500 cm^2 /g). About 95% of particles are retained by 15 microns size sieve. Setting times for 1:1 water-cement ratio by weight

of micro cement and at 68 °F (20 °C) are 60 to 120 min for initial set measured by vicat needle 120 - 150 min for final set measured by vicat needle.

3.2 Carbon nanotubes

CNT used in this research are thin mutliwalled carbon nanotubes known as Nanocyl NC7000. The Nanocyl NC 7000 series was produced by the chemical vapor deposition. During their production, exclusive catalysts were used that make the Nanocyl NC7000 the most electrically conductive carbon nanotubes presently. NC7000 carbon nanotubes have one of the most perfect chemical surfaces enabling high efficiency in the matrix in which they are embedded. Scanning electron microscope (SEM) image of NC 7000 was given by the Figure 3.1. Powdered form of CNT was used and was shown in Figure 3.2. Properties of CNT are given below in the Table 3-1.

Table 3-1 Properties of CNT

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	m^2 /g	250-300	BET

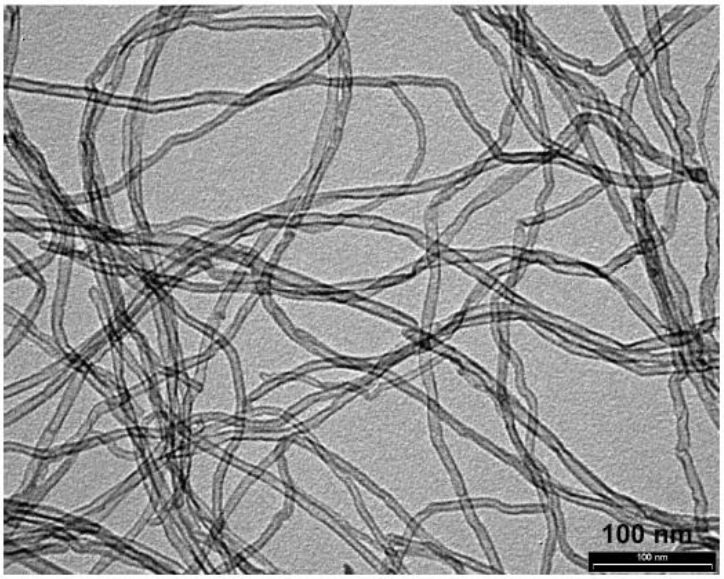

Figure 3-1 SEM image of CNT

Figure 3-2 Powdered form of CNT

3.3 Carbon nanofibers

PR-24-XT-LHT, CNF from Pyrograf are the nanofibers that are used in this experiment. The LHT grade was produced by heat-treating the fiber at 2732 ^{0}F (1500 ^{0}C). This converts any chemically vapor deposited carbon present on the surface of the fiber to a short range ordered structure. Transmission electron micrograph showing catalytic layer is given by the Figure 3.3. The properties of carbon nanofibers is given by the below Table 3-2.

Table 3-2 Properties of CNF

Properties	Unit	Value
Fiber diameter	nm(average)	100
CVD carbon coat on fiber	-	No
Surface area	m^2/gm	41
Dispersive surface energy	mJ/m^2	135
Moisture	Wt %	<5
Iron	ppm	<100
Polyaromatic hydrocarbon	mg PAH/gm	<1

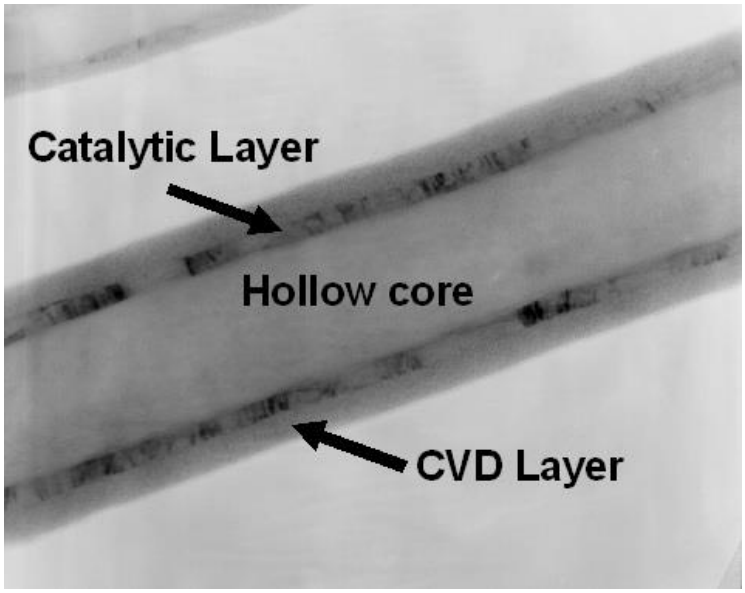

Figure 3-3 Catalytic layer of CNF

Figure 3-4 Powdered form of CNF

3.4 Surfactant and Super plasticizer

Nanosperse AQ was used as dispersing agent to disperse nanoparticles into water uniformly. Nanosperse AQ was a specially formulated dispersant package for creating aqueous dispersions of multi-walled carbon nanotubes and carbon nanofibers. Surfactant plays an active role in dispersion of nanoparticles into the water, it is used along with super plasticizer for better dispersion. MaterGlenium 7700 was used as super plasticizer, it is a high range water reducing admixture. Superior slump retention, excellent early strength development, high ultimate strengths, optimum setting time, consistent air entrainment and dosage flexibility are few important features of this super plasticizer.

Chapter 4

CNT And CNF Composites

4.1 Introduction

In this chapter, mixing techniques used in this research are discussed in detailed. Experimental setup and test procedures used are described. Micro cement was used for preparing cement composites with the combination of CNT and CNF. Dispersion of CNT and CNF by achieved by tip ultra-sonication method with the aid of super plasticizer and surfactant. Testing procedures are according to ASTM standards. Compression tests are carried out on 0.4, 0.45 and 0.5 water cement ratio with 0.05% and 0.1% of CNT and CNF. Flexural tests are performed with 0.4 water cement ratio with nanoparticles. Flow value was examined, setting time was determined, bleeding was checked and Shrinkage test is performed.

4.2 Mixing techniques

Mixing mainly focused on dispersion of CNT and CNF into water, as it is very complicated and tough to achieve well dispersed solution. Sonication process is used for achieving proper dispersion of nanoparticles in water. In this section, various methods of sonication are discussed, the reason for usage of tip sonicator in this research was explained further.

4.2.1 Sonication

4.2.1.1 Introduction

The process of applying sound energy to agitate particles in a sample for various purposes is known as sonication. Sonication process is carried by an equipment termed as sonicator. The disruptions produced by sonicator are used to mix solutions and speed

the dissolution of a solid into a liquid (like sugar into water), it also removes dissolved gas from liquids. The desired effects from the ultra-sonication of liquids including homogenization, deagglomeration, dispersing, milling, extraction, emulsification, disintegration and sonochemical effects that are caused by cavitation. The introduction of high power ultrasound into a liquid medium allows the sound waves to transmit in the fluid and create alternating high-pressure (compression) and low-pressure (tension) cycles, with rates depending on the frequency. High-intensity ultrasonic waves are created during low pressure cycles which produce small vacuum bubbles or voids in the liquid. As the bubbles attain a certain volume at which they can no longer absorb energy, they collapse impulsively during a high-pressure cycle. This phenomenon is known as cavitation. Locally very high temperatures of approximately 8540 ^{0}F (4726 ^{0}C) and pressures of approximately 2,000 atm equal to 29.4 ksi (202.6 MPa) are reached during the implosion, it is a phenomena in which objects are destroyed by collapsing on themselves. The implosion of the cavitation bubble also results in liquid jets of up to 280 m/s (918 ft/sec) velocity.

Sonicators either produce sound waves into a water bath, where samples are placed in bath and sonicated or can be probes that are put directly into the sample to be sonicated. Both process produce sound waves for dispersion of particles into the aqueous medium. However these methods vary slightly in their working process.

Probe type sonication versus Ultrasonic bath:

Sonication processes can be carried out by the use of a probe-type ultrasonic homogenizer or an ultrasonic bath. However, both techniques apply ultrasound to the sample, there are significant differences in efficiency, effectiveness, and process capabilities.

4.2.1.2 Ultrasonic bath

In an ultrasonic bath, cavitation occurs non-conformable and uncontrollably distributed throughout the tank. The effect of sonication is of low intensity and unevenly spread. The scalability and repeatability of the process is very low. Figure 4.1 below shows the results of a foil testing in an ultrasonic tank conducted by Kiani et al in the year 2011. A thin aluminum foil is placed at the bottom of ultrasonic tank filled with water. After sonication, single erosion marks are observed. Those single perforated spots and holes in the foil indicate the cavitational hot spots. The erosion marks occur only spot-wise due to the very low energy and the uneven distribution of the ultrasound within the tank. Hence, ultrasonic baths are mostly used for applications of cleaning.

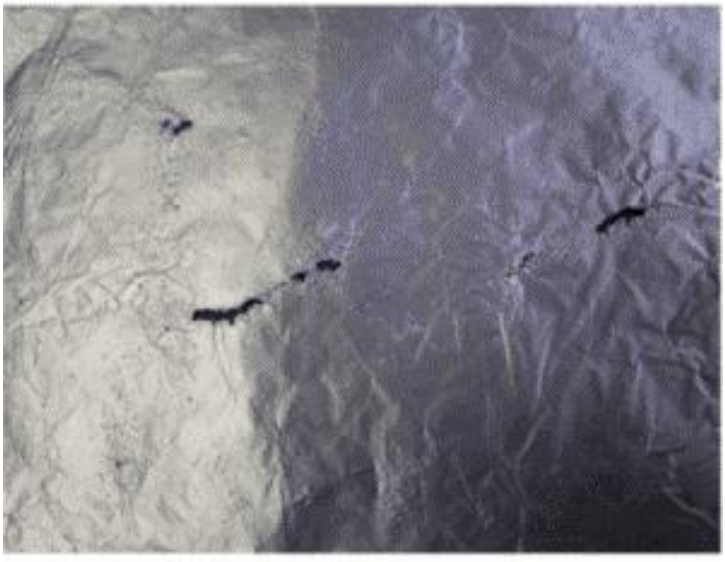

Figure 4-1 Foil test using bath sonication

4.2.1.3 Probe-type ultrasonic

When samples are sonicated using an ultrasonic probe device, intensity is very high and the intensity of sonication zone is directly concentrated beneath the sonotrode probe. The concentration of ultrasonic irradiation is limited to a certain area near the tip of sonotrode. Tip ultra-sonication process in an open beakers are mostly used for feasibility testing and for sample preparation of smaller volumes. Probe sonication is highly effective for processing nanomaterial (carbon nanotubes, inks, graphene, metal oxides, etc.). Probe sonicators are many times more powerful and effective than ultrasonic baths. Sonication bath technique takes many hours to accomplish what a ultra sonicator probe can do in minutes. Figure 4-2 shows the tip sonication in a beaker with liquid.

Figure 4-2 Probe sonication

4.2.1.3 Sonicator used in experiments

Ultrasonic tip sonicator named as Misonix 4000 from Misonix Company was used for sonication in this research. It had a titanium tip, which was effective in dispersing the carbon nanomaterial 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 4.7×10^{-3} in (120 μm). It has a frequency varied from 1 to 100 that can be changed manually on the digital screen shown in Figure 4-3. Figure 4-4 shows the setup of sonicator used in this research.

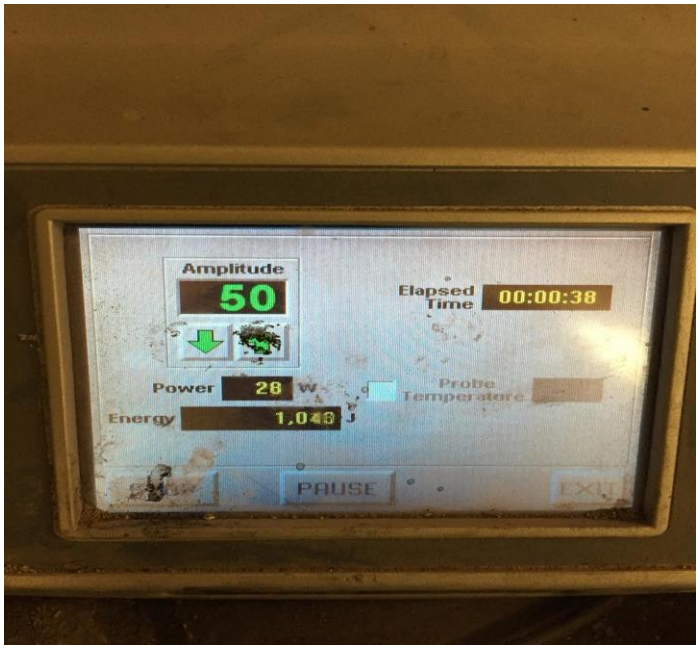

Figure 4-3 Digital screen

Figure 4-4 Sonicator setup

4.2.2 Mortar mixing procedure

The dispersion of CNT and CNF into aqueous medium is very much difficult, as they agglomerate and form bundles when mixed with water, sonication process is used to disperse nanoparticles into water. Further mixing the water with nanoparticles into the cement is also very crucial. Figure 4-6 shows the sonicator tip inserted in the jar with water and nanoparticles that are being sonicated. Figures 4-5 shows aqueous medium with nanoparticles without proper dispersion and Figure 4-7 shows well dispersed aqueous solution with nanoparticles that is obtained through sonication process.

From previous research sonication of water with nanoparticles was not successful to disperse nanoparticles into water uniformly, water is mixed with 0.8% of super plasticizer,

then stirred well with the stirrer, few drops of surfactant is added to the aqueous solution, then the solution is sonicated for 2 minutes with 50% amplitude for obtaining a proper mixed aqueous solution. Later CNT or CNF is measured accordingly based on the weight of cement. CNT and CNF were added in a sequence and was sonicated for 5 minutes for each addition, total sonication time was approximately 40 minutes. The amplitude was varied between 50% and 75%. Thus well sonicated aqueous solution is added to cement and mixed for few minutes in a mixer with flat beater.

Figure 4-5 Agglomeration of CNT

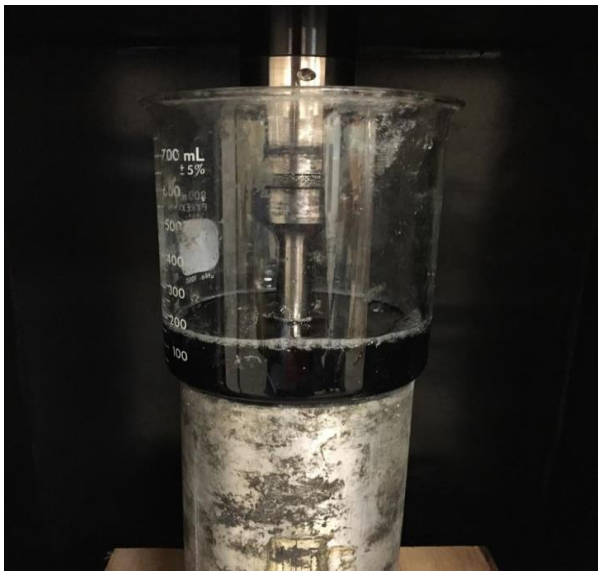

Figure 4-6 Sonication of CNT in water

Figure 4-7 Well dispersed CNT after sonication

Different water cement ratios are used for making specimens as there is no clear evidence of water cement ratio in previous researches. Water cement ratios used for making specimens are 0.4, 0.45 and 0.50 with different ratios of nanoparticles. 0.1% and 0.05% of mutliwalled carbon nanotubes (MWCNT) are used and 0.1% and 0.05% of carbon nanofibers are used for preparing samples.

4.3 Experimental setup and test procedure

Preparation and curing of specimens is discussed in this part, different test procedures and test setups used in this research are detailed in this section.

4.3.1 Compressive strength test

The ASTM C109 test procedure was used to determine the compressive strength of a hydraulic cement mortar using 2 inch (50 mm) cube. All the testing materials were kept at ambient temperature i.e., 73 ± 5.5 ^{0}F (20 ± 5.5 ^{0}C). The mortar consists of micro cement grout with 0.4, 0.45 and 0.5 water cement ratios. Mixer with flat beater was used to mix the mortar.

A thin coating of release agent is applied to the interior faces of the mold and non-absorptive base plates. Oil is applied using an impregnated cloth and mold faces and the base plate are wiped with a cloth as necessary to remove any excess release agent, to achieve a thin and even coating on the interior surfaces.

Sonicated aqueous solution is mixed with micro cement in the mixer for few minutes until a uniform grout is formed. After mixing, the grout is put into the mold in two layers 1 in (25 mm) each of each layer and tamped well for two layers with the help of a tamping rod.

Immediately upon completion of molding, test specimens are placed in the moist closet or moist room. After 24 hours the specimens are unmolded and placed in saturated lime

water in storage tanks constructed of noncorroding materials. Before testing specimens at 7, 14 and 28 days, specimens are removed from storage tank and wiped well with a cloth so that the surface is dried. Apply the load to specimen faces that were in contact with the true plane surfaces of the mold. Load is applied at the rate of 300 lb/s (1334 N/s) uniformly until the specimen is failed. Peak load at the failure of specimen is noted. The compressive strength is calculated by the Eq. 1.

$$f_m = \frac{P}{A} \qquad \text{Eq. 1}$$

Where,

f_m = compressive strength of specimen psi (Pa)

P = maximum peak load at failure of specimen in lbf (N)

A= area of cross section in in^2 (mm^2)

Figure 4-8 Specimens in lime saturated water

Figure 4-9 Compressive strength test setup

Figure 4-10 Compression test on specimen

4.3.2 Flexural strength test

The ASTM C348 test procedure was used to evaluate the flexural strength of the hydraulic cement mortar using a mold of size of 1.574 by 1.574 by 6.299 in (40 by 40 by 160 mm). 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 0.787 in (20 mm) in thickness. Then the mortar was compacted in 2 layers by 12 strokes in 4 rounds. After 24 hours the molds were unmolded and stored in a lime saturated water tank as shown in Figure 4-11. The flexural strength of the sample was determined by using a center point loading test. The loading rate of 593 ± 24.7 lb (2640 ± 110 N) was applied on the sample, and the maximum load to break the sample was recorded.

The flexural strength S_f in MPa of the specimen is computed by the Eq. 2

$$S_f = 0.0028P \qquad \text{Eq. 2}$$

Where,

S_f – flexural strength, ksi (MPa)

P –total maximum load, lbf (N)

Figure 4-11 Specimens in lime saturated water

Figure 4-12 Flexural strength test setup

Figure 4-13 Flexure test setup

Figure 4-14 Flexure test

4.3.3 Flow cone test

ASTM C939-10 method is used for measuring flow of the micro cement mortar. Flow cone is used for measuring the flow, time of efflux was calculated using this flow cone which is in conical shape with 0.5 inch (12.5 mm) diameter nozzle outlet for grout flow. The time taken by water or cement grout to pass through the nozzle outlet of flow cone when it is released to flow from the flow cone is called as time of efflux. Cement mixing procedure is same as mentioned in compression test. Figure 4-15 and Figure 4-16 shows the flow cone setup and flow of cement grout from the flow cone respectively. Stop watch is used to calculate time of efflux. 0.5 water cement and 0.008 ratio of super plasticizer was used with 0.05% of CNT and 0.05% of CNF and compared with control samples without nanoparticles.

Figure 4-15 Flow cone test setup

Figure 4-16 Flow cone test

4.3.4 Setting time test

Vicat apparatus was used for calculating setting time of cement mortar in this research. ASTM C191-13 test method was used in this research to determine the setting time of the cement mortar. Mix the cement mortar as described in compressive test, prepared cement paste is quickly transferred to vicat mold and tamped with a rod. Periodic penetration tests are performed on this paste by allowing a 0.039 in (1 mm) vicat needle to settle into this paste. Vicat initial time of setting is the time elapsed between the initial contact of cement and water and the time when the penetration is measured or calculated to be 1 in (25 mm). The vicat final time of setting is the time elapsed between initial contact of cement and water and the time when the needle does not leave a complete circular impression in the paste surface.

0.4 water cement ratio with 0.008 ratio of super plasticizer by the weight of microcement is considered as control sample. Specimens are made with 0.4 water cement ratio with 0.008 ratio of super plasticizer with 0.05% of CNT and CNF. Cement mixing procedure is same as described in compression test. The setting time of these samples are compared with control samples.

Setting time was calculated by using Eq. 3.

$$S = \frac{H - E}{C - D} \times (C - 25) + E \qquad \text{Eq. 3}$$

Where,

S = setting time

E = time in minutes of last penetration greater than 1 in (25 mm),

H = time in minutes of first penetration less than 1 in (25 mm),

C = penetration reading at time E

D = penetration reading at time H.

Determine the setting time test to the nearest of 5 min.

Figure 4-17 Setting time test

4.3.5 Shrinkage test

The term drying shrinkage is defined as the decrease in length of the test specimen, where the decrease is caused by any factor other than externally applied forces under stated conditions of temperature, relative humidity and evaporation rate in the environment; the term includes the net effect of a variety of phenomena tending to bring about both increases and decreases in length during the period in which the test specimens under consideration are stored in the environment and in which a number of processes, including hydration of the cement, are taking place at a variety of rates.

ASTM C596-09 method is used for making and storing of samples in this research for calculating drying shrinkage of the mortar. Micrometer is used to measure the length of specimen accurately. 1 in by 1 in by 5 in (25 mm × 25 mm × 125 mm) sized specimen was made with 0.4 water cement ratio with 0.05% of CNT and 0.05% of CNF. Two pins are inserted at the top face of the specimen, so that the length measurement can be done measuring the change in length between these pins. Initial length between these pins was noted as gauge length. The specimen is stored for 48 hours in lime saturated water, later they are wiped with a cloth and length is measured. Later the specimen is allowed to dry in air for 25 days and the length of the sample was calculated at different age periods. The length change of each specimen at each age of air drying is calculated by subtracting the initial reading, taken after removal from water storage, from the readings taken at each age of air drying and express as millionths and as the percent of the effective gage length.

The length change at any age x as a percent of the effective gauge length is calculated by using Eq. 4.

$$L = \frac{L_x - L_i}{G} \times 100$$ Eq. 4

Where,

L = change in length at x age, %,

L_x = Micrometer reading at age x, in (mm)

L_i = initial micrometer reading, in (mm)

G = Gauge length of the specimen

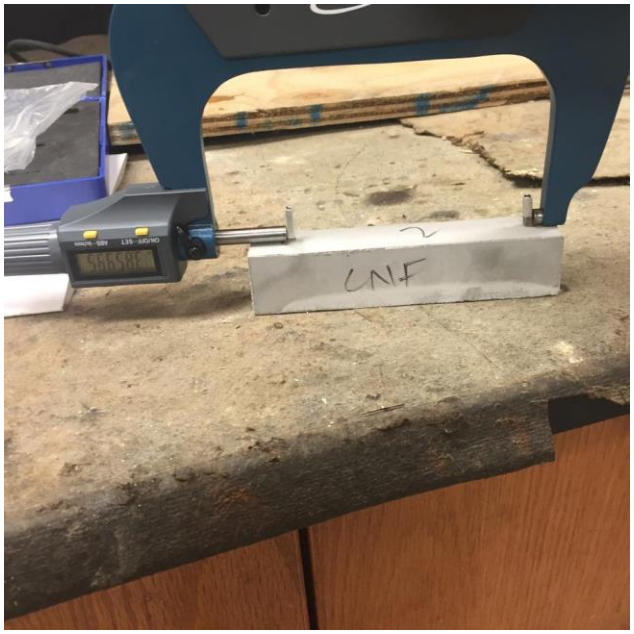

Figure 4-18 Shrinkage test

4.3.6 Bleeding test

ASTM 940-10a is used to determine expansion and bleeding of freshly mixed grouts in the laboratory and to calculate the accumulation of bleed water at the surface. Emergence of water from a newly placed cementations mixture caused by the settlement of the solid materials within the mass is termed as bleeding. Mixing procedure of cement mortar is same as earlier mentioned in the compressive test. Immediately after the completion of mixing, measure the temperature of the grout. The ambient temperature of the room in which the test is performed, the materials used is maintained at 73 ± 4 ^{0}F (23.0 ± 2 ^{0}C), then introduce the grout into a 33.81 oz. (1000 ml) graduated cylinder until the volume of the sample is 27 ± 0.33 oz. (800 ± 10 ml). Record the volume of the sample and the time at which the reading was made. Place the graduated cylinder on a level surface free of vibration. Cover to prevent evaporation of the bleed water. Take and record the readings, estimated to the nearest 0.0338 oz. (1 ml), of the upper surfaces of the grout and bleed water, if any, of the sample in the graduate at 5 minutes intervals. At the end of test, decant the bleed water into a 0.845 oz. (25 ml) graduate by tilting the specimen and drawing the water off with a pipet or large medicine dropper. Record the final volume of bleed water to the nearest 0.0169 oz. (0.5 ml). 0.4 water cement ratio with 0.8% of super plasticizer is used with 0.05% of CNT and CNF for this test.

The expansion of the grout, and its bleeding and the combined expansion of grout plus bleed water as percentages of the initial volume of the grout is calculated by Eq. 5, Eq. 6, Eq. 7, Eq. 8 given below

$$Expansion\ \% = \frac{V_g - V_1}{V_1} \times 100 \qquad \text{Eq. 5}$$

$$Bleeding\ \% = \frac{V_2 - V_g}{V_1} \times 100 \qquad \text{Eq. 6}$$

$$Combined\ Expansion\ \% = \frac{V_2 - V_1}{V_1} \times 100 \quad \text{Eq. 7}$$

$$Final\ Bleeding\ \% = \frac{V_w}{V_1} \times 100 \quad \text{Eq. 8}$$

Where,

V_1 = volume of sample at beginning of test, oz., ml,

V_2 = volume of sample at prescribed intervals, measured at upper surface of water layer, oz., ml,

V_g = volume of grout portion of sample at prescribed intervals, at upper surface of grout, oz., ml,

V_w = volume of decanted bleed water, oz., ml.

Figure 4-19 Bleeding test

Chapter 5

Test Results

5.1 Compressive strength of control samples

Three different types of water cement ratios are used for making control samples. 0.4, 0.45 and 0.50 water cement ratios with 0.8% of super plasticizer by weight of cement was used to make control samples. Samples are tested at 7, 14 and 28 days using compression testing machine. Results are shown by the Table 5-1.

Table 5-1 Compressive strength of control samples

Water cement ratio	7 Days	14 Days	28 Days
0.4	7.90 ksi (54.5 MPa)	8.47 ksi (58.4 MPa)	8.89 ksi (61.3 MPa)
0.45	8.25 ksi (56.9 MPa)	8.29 ksi (57.2 MPa)	8.47 ksi (58.4 MPa)
0.5	6.42 ksi (44.3 MPa)	6.57 ksi (45.3 MPa)	7.15 ksi (49.3 MPa)

5.2 Compressive strength of CNT composites

The compressive strength of CNT composites with three water cement ratios 0.4, 0.45 and 0.5 with 0.8% of super plasticizer and 0.1% of CNT by weight of cement tested at 7, 14 and 28 days are given by the Table 5-2.

Table 5-2 Compressive strength of samples with 0.1% of CNT

Water cement ratio	7 Days	14 Days	28 Days
0.4	6.00 ksi (41.4 MPa)	7.07 ksi (48.8 MPa)	6.65 ksi (45.9 MPa)
0.45	8.41 ksi (58 MPa)	8.28 ksi (57.1 MPa	9.32 ksi (64.2 MPa)
0.5	7.73 ksi (53.3 MPa)	7.68 ksi (53 MPa)	8.38 ksi (57.8 MPa)

The compressive strength of CNT composites with three water cement ratios 0.4, 0.45, 0.5 with 0.8% of super plasticizer and 0.05% of CNT by weight of cement was given by the Table 5-3.

Table 5-3 Compressive strength of samples with 0.05% CNT

Water cement ratio	7 Days	14 Days	28 Days
0.4	8.58 ksi (59.2 MPa)	11.34 ksi (78.2 MPa)	10.90 ksi (75.2 MPa)
0.45	5.33 ksi (36.8 MPa)	7.49 ksi (51.7 MPa)	9.10 ksi (62.8 MPa)
0.5	4.52 ksi (31.2 MPa)	6.84 ksi (47.2 MPa)	5.87 ksi (40.5 MPa)

5.3 Compressive strength of CNF composites

The compression test was conducted on CNF composites with three different water cement ratios of 0.4, 0.45 and 0.5 with 0.8% of super plasticizer and 0.1% of CNF by weight of cement. The strength results are given by the Table 5-4.

Table 5-4 Compressive strength of samples with 0.1% of CNF

Water cement ratio	7 Days	14 Days	28 Days
0.4	9.96 ksi (68.7 MPa)	7.52 ksi (51.9 MPa)	7.12 ksi (49.1 MPa)
0.45	8.26 ksi (57 MPa)	8.35 ksi (57.6 MPa)	8.87 ksi (61.2 MPa)
0.5	7.17 ksi (49.5 MPa)	7.06 ksi (48.7 MPa)	6.62 ksi (45.7 MPa)

The compressive strength results of CNF composites with three water cement ratios 0.4, 0.45, 0.5 with 0.8% of super plasticizer and 0.1% of CNF by weight of cement was given by the Table 5-5.

Table 5-5 Compressive strength of samples with 0.05% of CNF

Water cement ratio	7 Days	14 Days	28 Days
0.4	8.28 ksi (57.1 MPa)	8.09 ksi (55.8 MPa)	8.41 ksi (58 MPa)
0.45	6.77 ksi (46.7 MPa)	7.74 ksi (53.4 MPa)	8.15 ksi (56.2 MPa)
0.5	6.51 ksi (44.9 MPa)	5.55 ksi (38.3 MPa)	6.36 ksi (43.9 MPa)

5.4 Comparison of compressive strength

The compressive strength of cement mortars with different water cement ratio with the addition of 0.8% super plasticizer with the weight of cement and with the addition of nanoparticles with two different ratios, 0.1% and 0.05% CNT and with 0.1%, 0.05% of CNF are been compared with the control samples with same water cement ratio without nanoparticles. Figure 5-1 shows the bar graph with the compressive strengths of control samples and nanocomposites with different ratios of CNT at 7, 14 and 28 days. Figure 5-2 shows the bar graph with the compressive strengths of control samples and nanocomposites with different ratios of CNF at 7, 14 and 28 days.

5.4.1 Increase in strength of 0.1% CNT composite to control sample

The increase in the strength by its percentage when compared to control sample is given by the Table 5-6. From the table it can be seen that the strength was decreased for 0.4 and 0.45 water cement ratios with the addition of 0.1% CNT to the cement, however the strength of 0.5 water cement ratio was increased significantly with addition 0.1% CNT. The maximum strength at 28 days of sample with 0.5 water cement ratio and 0.1% CNT was 8.38 ksi (57.8 MPa) which was 17% higher than that of sample without CNT.

Table 5-6 Compressive strength increase in percent with 0.1% CNT

Water cement ratio	7 Days	14 Days	28 Days
0.4	-24%	-16%	-25%
0.45	2%	0	10%
0.5	20%	17%	17%

5.4.2 Increase in strength of 0.05% CNT composite to control sample

The comparison of strength results by percentage increase with 0.05% of CNT with the control samples was given by the Table 5-7. The strength values was decreased with the addition of 0.05% CNT with 0.45, 0.5 water cement ratios with cement. Although the specimens with 0.4 water cement showed slightly higher strengths compared to that of control samples. The specimen with 0.4 water cement ratio and with 0.05% of CNT showed 23% increase in strength by its control sample.

Table 5-7 Compressive strength increase in percent with 0.05% CNT

Water cement ratio	7 Days	14 Days	28 Days
0.4	9%	34%	23%
0.45	-35%	0	0
0.5	-29%	4%	-17%

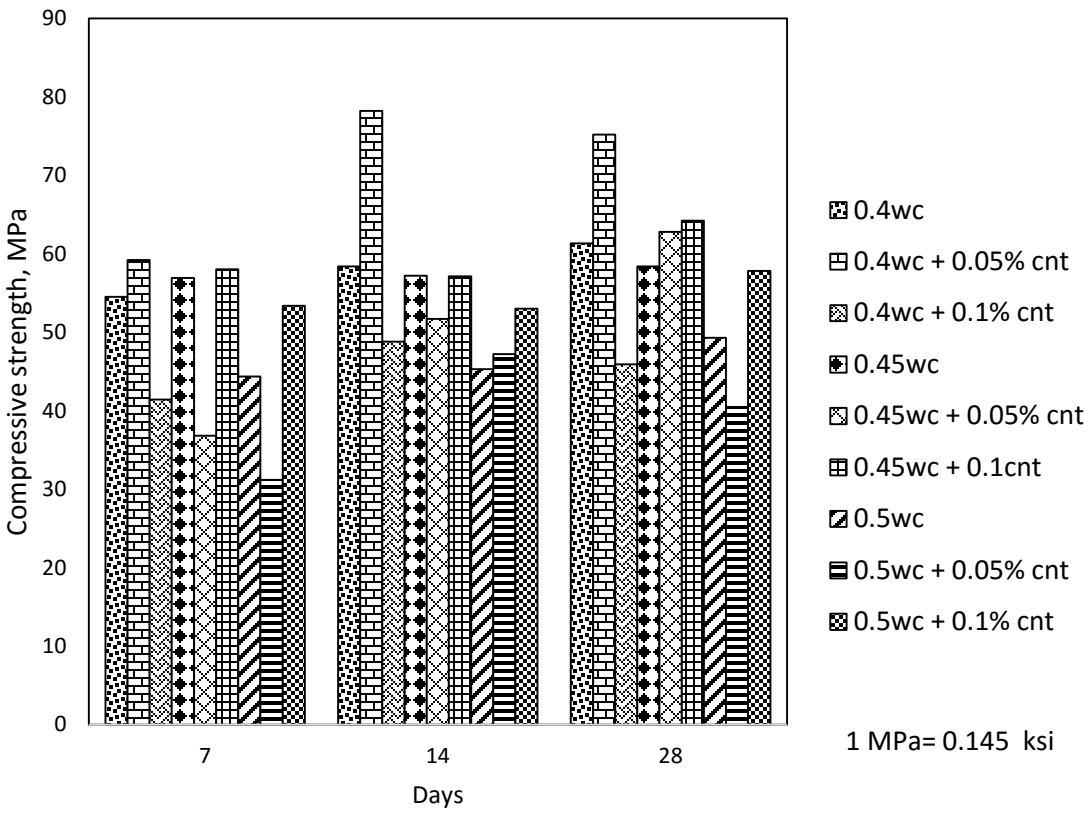

Figure 5-1 Comparison of compressive strengths of CNT composites with control samples

5.4.3 Increase in strength of 0.1% CNF composite to control sample

In this section the strength between CNF composites and control samples is analyzed. From Table 5-8, it is clearly evident that there was no significant increase in strength with 0.1% of CNF when compared to control samples. However there was good initial strength but as the time increase the strength is decreased.

Table 5-8 Compressive strength increase in percent with 0.1% CNF

Water cement ratio	7 Days	14 Days	28 Days
0.4	26%	-11%	-19%
0.45	0	0	5%
0.5	12%	8%	-7%

5.4.4 Increase in strength of 0.05% CNF composite to control sample

In this section the strength between CNF composites and control samples is analyzed. From Table 5-9, it is clearly evident that there was no significant increase in strength with 0.05% of CNF when compared to control samples. However there was good initial strength but as the time increase the strength is decreased.

Table 5-9 Compressive strength increase in percent with 0.05% CNF

Water cement ratio	7 Days	14 Days	28 Days
0.4	5%	-5%	-6%
0.45	-17%	-6%	-3%
0.5	0	-15%	-11%

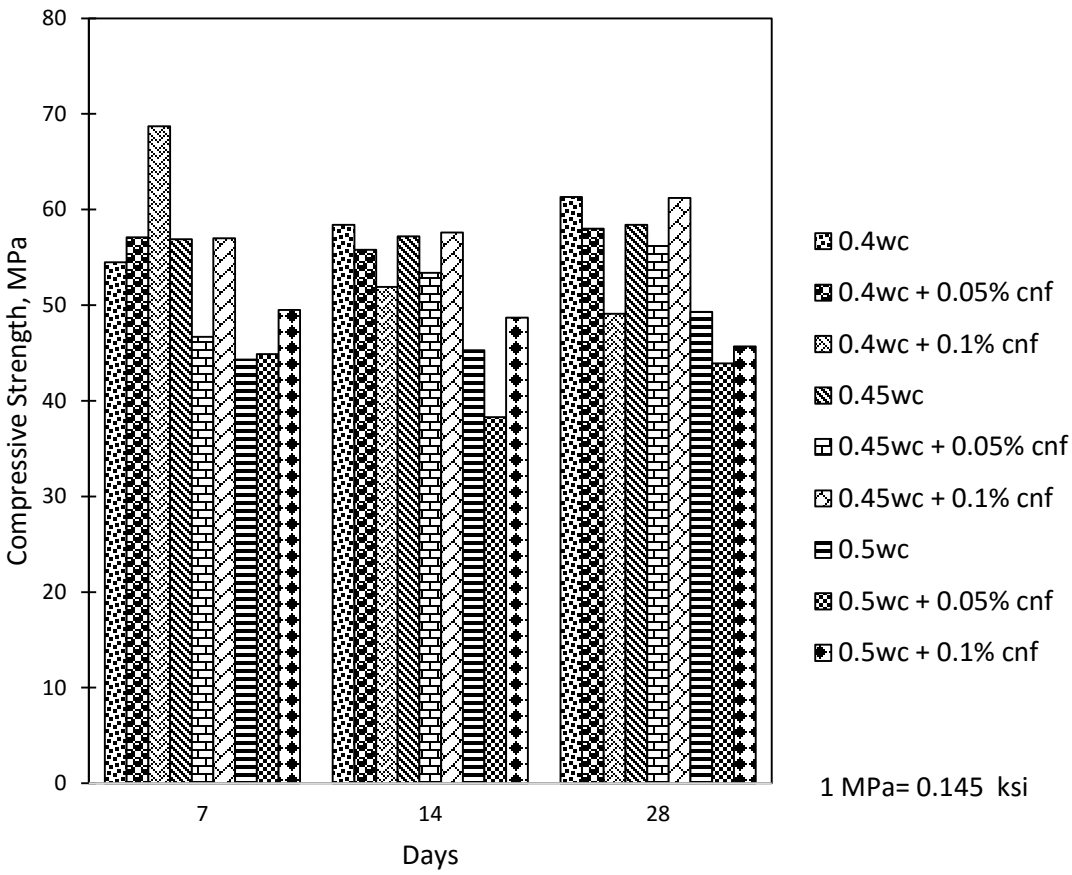

Figure 5-2 Comparison of compressive strengths with CNF composites to control samples

5.5 Flexural strength of control samples

The flexural strength of control samples made with 0.4 water cement ratio, 0.8% of super plasticizer by weight of cement is given by the Table 5-10. 0.1% and 0.05% of nanoparticles are used for preparing flexural specimens.

Table 5-10 Flexural strength of control sample

Water cement ratio	7 Days	14 Days	28 Days
0.4	0.81 ksi (5.6 MPa)	1.11 ksi (7.7 MPa)	1.21 ksi (8.4 MPa)

5.6 Flexural strength of CNT composites

The flexural strength of specimens with 0.4 water cement ratio, 0.8% of super plasticizer and nanoparticles with 0.1%, 0.05% of CNT by weight of cement at 7, 14, 28 days is given by the Table 5-11.

Table 5-11 Flexural strength of CNT composite

Composite	7 Days	14 Days	28 Days
0.1% CNT	1.07 ksi (7.4 MPa)	1.01 ksi (7.0 MPa)	1.13 ksi (7.8 MPa)
0.05% CNT	0.92 ksi (6.4 MPa)	1.27 ksi (8.8 MPa)	1.20 ksi (8.3 MPa)

5.7 Flexural strength of CNF composites

The flexural strength of specimens with 0.4 water cement ratio, 0.8% of super plasticizer and nanoparticles with 0.1%, 0.05% of CNF by weight of cement at 7, 14, 28 days is given by the Table 5-12.

Table 5-12 Flexural strength of CNF composite

Composite	7 Days	14 Days	28 Days
0.1% CNF	1.18 ksi (8.2 MPa)	1.21 ksi (8.4 MPa)	1.14 ksi (7.9 MPa)
0.05% CNF	0.95 ksi (6.6 MPa)	0.94 ksi (6.5 MPa)	1.11 ksi (7.7 MPa)

5.8 Comparison of flexural strength

In this section flexural strength of nanocomposite materials is compared with the control samples. Percentage increase of strength with addition of nanoparticles is determined.

5.8.1 Comparison of CNT composites

Percentage increase in strength of flexural samples with and without CNT is given by the Table 5-13. It can be observed that there is significant increase in the strength in the initial days, however the strength got reduced as the time increased.

Figure 5-3 shows bar graph comparing the flexural strengths of control samples with 0.4 water cement ratio and 0.8% of super plasticizer to that of specimens with 0.1% and 0.05% of CNT.

Table 5-13 Flexural strength increase in percentage with CNT

Composite	7 Days	14 Days	28 Days
0.1% CNT	32%	-9%	-7%
0.05% CNT	14%	14%	-1%

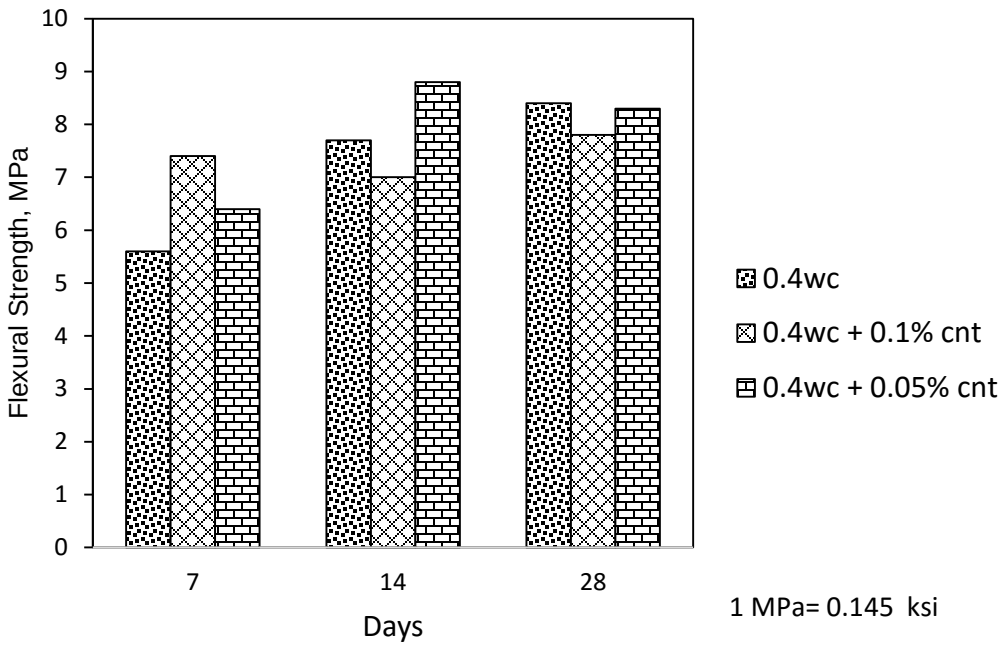

Figure 5-3 Comparison of flexural strengths with CNT composites to control samples

5.8.2 Comparison of CNF composites

Percentage increase in strength of flexural samples with and without CNF composites is given by the Table 5-14. It can be seen that there is a good increase in the strength in the initial days, however the strength got decreased as the time increased.

Figure 5-4 shows bar graph comparing the flexural strengths of control samples with 0.4 water cement ratio and 0.8% of super plasticizer to that of specimens with 0.1% and 0.05% of CNF.

Table 5-14 Flexural strength increase in percentage with CNF

Composite	7 Days	14 Days	28 Days
0.1% CNF	46%	10%	-6%
0.05% CNF	17%	-15%	-8%

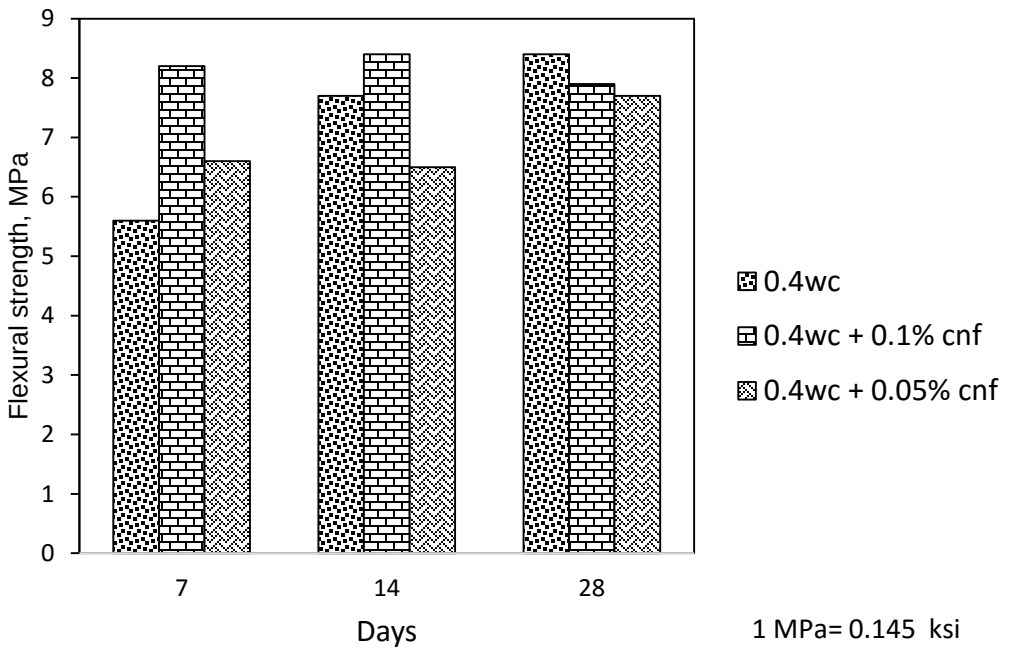

Figure 5-4 Comparison of flexural strengths with CNF composites to control samples

5.9 Flow cone test

0.5 water cement ratio was used for observing the flow by flow cone method. 0.5 water cement ratio with 0.8% of super plasticizer was used as control sample. 0.5 water cement ratio and 0.05% nanoparticles with super plasticizer is compared with the control sample. The flow is compared by observing the time of efflux value given by the Table 5-15. Control sample with 0.8% super plasticizer and 0.5water cement ratio has a time of efflux of 16.22 seconds, the mortar with 0.05% of CNT has a time of efflux of 12.67 sec and specimen with 0.05% of CNF has 13.65 sec. The flow value is significantly increased with the addition of nanoparticles to the mortar, especially CNT showed better results when compared to CNF. Figure 5-5 shows the graph between time of efflux in sec and cement composites.

Table 5-15 Time of efflux values

Specimen	Time of efflux (sec)
control	16.22
CNT	12.67
CNF	13.65

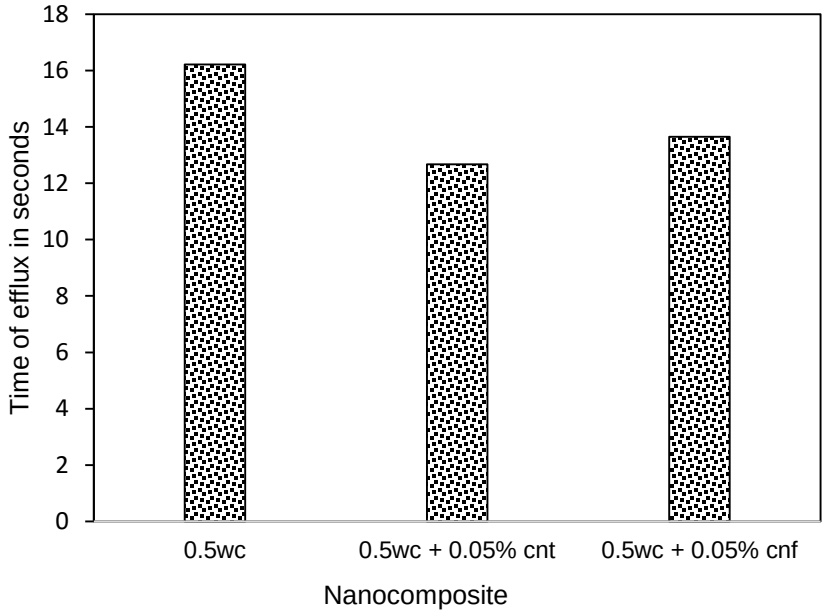

Figure 5-5 Time of efflux graph

5.10 Setting time test

0.4 water cement ratio mortar with super plasticizer included is taken as control sample and the setting time results are compared with the nanocomposite materials that has 0.05% of CNT, 0.05% of CNF. Control sample with 0.4 water cement ratio and 0.8% of super plasticizer had final setting time of 27 minutes whereas sample with 0.05% of CNT

included showed final setting time of 20 minutes, further sample with 0.05% of CNF showed 18 minutes. The setting of cement mortar is greatly influenced by nanoparticles. Figure 5-6 shows the graph between setting time in minutes and cement mortar composition.

Table 5-16 Final setting time

Specimen	Setting Time (min)
control	27
CNT	20
CNF	18

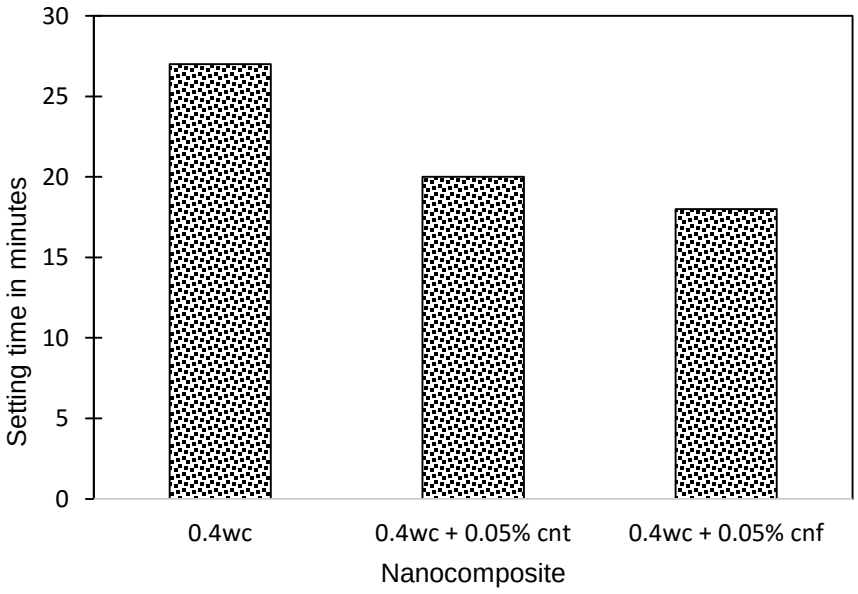

Figure 5-6 Setting time graph

5.11 Bleeding test

Bleeding test was carried on composite materials with 0.05% of CNT and 0.05% of CNF and 0.8% of super plasticizer with 0.4 water cement ratio. Bleeding was negligible in the test. No volume of cement mortar was increased in the test. Water quantity collected when the glass jar is bent is almost zero with nanocomposite materials.

5.12 Shrinkage test

0.4 water cement ratio and 0.8% super plasticizer with nanoparticles 0.05% CNT and 0.05% of CNF was used for this test. The change in length of the specimen expressed as percent of its gauge length measured by the micrometer at different ages is determined. Initial lengths of the sample are noted for both specimens. Shrinkage per unit length observed at different ages for specimen with 0.05% of CNT and 0.05% of CNF with 0.4 water cement ratio given by Table 5-16 below.

Table 5-16 Shrinkage per unit gauge length

Number of weeks	Shrinkage in CNT	Shrinkage in CNF
1	0.01%	0.02%
2	0.03%	0.06%
4	0.06%	0.08%
8	0.07%	0.09%

It was observed that the shrinkage gradually got reduced and was not significantly increased by 8^{th} week.

Shrinkage of CNT specimen was 0.07% per unit gauge length at 8 weeks of age and 0.08% for the specimen with CNF.

Chapter 6

Conclusions

6.1 Conclusions

Different properties of micro cement mortar are studied and analyzed with the addition nanoparticles. The following conclusions are made

1. Cement Mortar with 0.5 water cement ratio and with 0.1% CNT showed higher compressive strength values when compared to control samples at 28 days. Compressive strength of control sample with 0.5 water cement ratio was 7.15 ksi (49.3 MPa) and the strength of specimen with 0.1% of CNT with 0.5 water cement ratio is 8.38 ksi (57.8 MPa) with 17% increase in strength at 28 days.
2. Specimens with 0.4 water cement ratio and 0.05% of CNT showed higher compressive strength values at 28 days. 8.89 ksi (61.3 MPa) was the maximum compressive load applied on the control sample with 0.4 water cement ratio and 10.90 ksi (75.2 MPa) was the maximum compressive load applied on the specimen with 0.05% of CNT. An increase in strength by 23% was observed at 28 days.
3. CNF composites showed significantly reduced compressive strength when compared to its control samples at 28 days.
4. The flexural strengths of the specimens with nanoparticles was well increased at initial days and was decreased in strength by 28 days.
5. Flow values greatly influenced by the addition of nanoparticles. The time of efflux value for specimen with 0.5 water cement ratio without nanoparticles, with 0.05% CNT and 0.05% CNF is 16.22, 12.67, 13.65 seconds respectively.
6. Final setting time value is greatly improved with addition of nanoparticles when compared to its control samples. Specimen with 0.4 water cement was taken as

control sample had a setting value of 27 minutes, specimen with 0.05% of CNT had a value of 20 minutes whereas sample with 0.05% of CNF set more faster within 18 minutes when compared to earlier specimens.

7. Shrinkage was very small for specimen with 0.4 water cement ratio with 0.8% of super plasticizer, 0.07% and 0.09% shrinkage per unit gauge length are observed for CNT and CNF specimens respectively when measured at 8 week.
8. There is no clear evidence of constant variation of compressive and flexural strength with addition of nanoparticles into cement as the dispersion of CNT and CNF into the cement is not known perfectly, it is extremely difficult to analyze the reinforcement between cement particles and nanoparticles.

6.2 Future Recommendations

1. Now-a-days different varieties of CNT and CNF are been produced based on the usage, nanoparticles which can be easily dispersed in aqueous solution should be should so that dispersion process can be simplified and good dispersion can be achieved in cement mortar which can enhance the strength properties of cement mortar.
2. Chemical Analysis can be done to study the structure of cement composites for various compositions of nanoparticles. Varying the compositions based on structure can be done to achieve better strength results.
3. Microscopic studies should be conducted on various samples to understand the structure of composite material with various combinations of water cement ratio, super plasticizer through which reinforcement can be enhanced.

4. Behavior of concrete with nanocomposites can be studied as the crack bridging criteria may increase bond between cement particles and aggregates.
5. Microcement mortar with nanoparticles as a repair material for grouting into beam and girder cracks can be studied as flow and setting are increased.
6. Grout material with nanoparticles can be studied and analyzed more as soil injection material as flow of mortar with nanoparticles is significantly increased when compared to plain mortar.

Appendix A

Percentage Increase In Strength Calculations

Consider Table 5-6 where 0.1% of CNT was used with different water cement ratios for making specimens, 0.5 water cement ratio showed increase in compressive strength when compared to its control sample on 7, 14 and 28 days.

Compressive strength of control sample with 0.5 water cement ratio specimen at 7 day = 6.42 ksi (44.3 MPa) (from Table 5-1)

Compressive strength of specimen with 0.5 water cement ratio specimen with 0.1% of CNT at 7 day = 7.73 ksi (53.3 MPa) (from Table 5-2)

Increase in percentage of compressive strength at 7 day =

$$\frac{Compressive\ strength\ of\ specimen\ at\ 7\ day\ with\ 0.1\%\ CNT - Compressive\ strength\ of\ control\ sample\ at\ 7day}{compressive\ strength\ of\ control\ sample\ at\ 7\ day} \times 100$$

$$= \frac{7.73\ ksi - 6.42ksi}{6.42\ ksi} \times 100$$

= 20%

Compressive strength of control sample with 0.5 water cement ratio specimen at 14 days = 6.57 ksi (45.3 MPa) (from Table 5-1)

Compressive strength of specimen with 0.5 water cement ratio specimen with 0.1% of CNT at 14 days = 7.68 ksi (53 MPa) (from Table 5-2)

Increase in percentage of compressive strength at 14 day =

$$\frac{Compressive\ strength\ of\ specimen\ at\ 14\ day\ with\ 0.1\%\ CNT - Compressive\ strength\ of\ control\ sample\ at\ 14\ day}{compressive\ strength\ of\ control\ sample\ at\ 14\ day} \times 100$$

$$= \frac{7.68\ ksi - 6.57ksi}{6.57\ ksi} \times 100$$

= 17%

Compressive strength of control sample with 0.5 water cement ratio specimen at 28 days = 7.15 ksi (49.3 MPa) (from Table 5-1)

Compressive strength of specimen with 0.5 water cement ratio specimen with 0.1% of CNT at 28 days = 8.38 ksi (57.8 MPa) (from Table 5-2)

Increase in percentage of compressive strength at 28 day =

$$\frac{Compressive\ strength\ of\ specimen\ at\ 28\ day\ with\ 0.1\%\ CNT - Compressive\ strength\ of\ control\ sample\ at\ 28\ day}{compressive\ strength\ of\ control\ sample\ at\ 28\ day} \times 100$$

$$= \frac{8.38\ ksi - 7.15 ksi}{7.15\ ksi} \times 100$$

= 17%

Similarly percentage increase in strength is calculated for different water cement ratios and different composites.

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