NANO-MODIFIED CEMENT COMPOSITES AND ITS APPLICABILITY AS CONCRETE REPAIR MATERIAL

by

TANVIR MANZUR

Presented to the Faculty of the Graduate School of
The University of Texas at Arlington in Partial Fulfillment
of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

THE UNIVERSITY OF TEXAS AT ARLINGTON

August 2011

ACKNOWLEDGEMENTS

Thanks to Almighty, the Benevolent and the Kind, for His graciousness, unlimited kindness and with blessings of Whom the good deeds are fulfilled.

I want to take the great pleasure and proud privilege to express my deepest sense of gratitude and thankfulness to my erudite advisor Dr. Nur Yazdani for his constant guidance, support and frequent inspiration to perform the research work presented in the dissertation. His untiring efforts, great patience, valuable suggestions and keen interest were outstanding which made this work a reality. His contribution to materialize this work is ineffable.

I am indebted to the Department of Civil Engineering, UTA for its facilities that was enjoyed by me to accomplish the research work. I am grateful to my dissertation committee members Dr. John H. Mathys, Dr. Sahadat Hossain, Dr. Shih-Ho Chao and Dr. Samir Iqbal for their kind support and encouragement. I am especially thankful to Dr. Shih-Ho Chao and Dr. Samir Iqbal for providing support at CELB and NanoFab, respectively.

I would like to express my heartfelt appreciation to Mamidipally Chakravarthy for his valuable support in performing the experiments in connection with the dissertation. I also pay my deepest homage to my friends Sonnet, Zahid, Zafar, Tapu, Moshi, Shourav, Mamun, Rajib, Mahtab and Faisal for their indispensible assistance and mental support.

Yet none of these lines would have been written here without the affection, guidance, encouragement and moral support that were offered by my beloved parents and the only sister. A very special debt of deep gratitude is offered to them who are always a constant source of inspiration throughout my life.

July 11, 2011

ABSTRACT

NANO-MODIFIED CEMENT COMPOSITES AND ITS APPLICABILITY AS CONCRETE REPAIR MATERIAL

Tanvir Manzur, PhD

The University of Texas at Arlington, 2011

Supervising Professor: Nur Yazdani

Nanotechnology or Nano-science, considered to be the forth industrial revolution, has received considerable attention in the past decade. With the emerging nanotechnology, one can build material block atom by atom. Therefore, through nanotechnology it is possible to enhance and control the physical properties of materials to a great extent. Composites such as concrete materials have very high compressive strength and Young's modulus but relatively low toughness and ductility due to their covalent bonding between atoms and lacking of slip systems in the crystal structures. However, the strength and life of concrete structures are determined by the microstructure and mass transfer at nano scale. Cementitious composites are amenable to manipulation through nanotechnology due to the physical behavior and size of hydration products. Carbon nanotubes (CNT) are nearly ideal reinforcing agent due to extremely high aspect ratios and ultra high strengths. So there is a great potential to utilize CNT in producing new cement based composite materials.

In this work, an extensive parametric study has been conducted on cementitious composites reinforced by different types of treated and untreated multiwalled nanotubes (MWNT) and having different mix proportions. It is found that mixing of nanotubes within cement matrix is the key to develop composites with desirable mechanical properties. A mixing technique has been proposed to address the issues related to dispersion of nanotubes within cement matrix. Polycarboxylate based super plasticizer has been proposed to use as surfactant. It is evident that there exists an optimum concentration of MWNT and mix proportion to achieve proper reinforcement behavior and strength properties. The effect of size of MWNT on strengths (both compressive and flexure) of composites has also been investigated. Based on the parametric study and statistical analysis, a tentative optimum mix proportion has been proposed. Composites made by the proposed mixing technique and design mix obtained higher compressive and flexural strengths as compared to control samples at the age of 3, 7 and 28 days. It has also been suggested that application of MWNT reinforced cement mortar as concrete repair material has excellent potential since composites exhibited desirable behavior in setting time, bleeding and slant shear.

TABLE OF CONTENTS

LIST OF ILLUSTRATION

LIST OF TABLES

Table Page

CHAPTER 1

INTRODUCTION

1.1 Introduction

Utilization of nano-particles in improving material characteristics has already gained recognition and is being applied in many fields ranging from computer hard drives, cosmetics, sports goods to oil refining technology. The term nanotechnology usually means investigation of the behavior of a material at scales between 1 and 100 nm. Nano-materials exhibit distinctive chemical and physical properties that can result in the improvement of material effectiveness (Li et al, 2004). Nano-particles may yield favorable characteristics due to their extremely fine size. Application of nano-scale science to construction material has already begun. Strength and life of concrete structures are partly determined by the micro structure and by the mass transfer at nano-scale (Maile et al, 2006). Cement is the most widely used construction material in the world. However, cementitious materials are brittle in nature and have low tensile strength. The chemistry and physical behavior of hydration products are amenable to manipulation through nanotechnology (Makar et al, 2005). So there is a great potential to utilize nano-particle in producing new cement based composite materials.

1.2 Motivation

In the field of nanotechnology, Carbon nanotube (CNT) has the prime focus as one of the most major and significant areas of research. There is particular interest in developing nanotechnology for cement and concrete. Not only the chemistry that forms cement hydration products but also the physical behavior of those products are acquiescent to manipulation through nanotechnology. The mechanical properties of CNT depict their immense potential for use as reinforcements in composite materials. In addition to their high strength and elastic constant, CNTs have extremely high aspect ratios, with values typically higher than 1000:1 and reaching as high as 2,500,000:1 (Makar et al, 2005). The size and aspect ratios of CNT mean that they can be distributed on a much finer scale than commonly used reinforcing fibers (Makar et al, 2005). Cracks can be interrupted much more quickly during propagation in a CNT reinforced matrix. This bridge coupling effect of CNT in turn assures lower crack widths and eventually guarantees the load-transfer across voids and cracks. Addition of CNT may also greatly enhance the flexural and compressive strengths of cement, as well as decrease failure strain and overall density. These mechanical properties of CNT reflect its' prospect as reinforcement within the matrix of cementitious composites.

A potentially useful application of CNT in cement composites is in cement mortar that may be employed for concrete rehabilitation, such as surface restoration and crack repair. Several repair, retrofit and strengthening techniques are currently available to enhance the integrity and durability of concrete structures with cracks, spalling etc. In many instances, epoxy resins are used as repair materials for the maintenance of concrete infrastructure. Since epoxy resins are much more compliant than concrete substrates, interface failure caused by the mismatch in stiffness and strength between the repair material and concrete substrate may occur. A repair material is also expected to contribute to the mechanical strength of a concrete structure. A repair material is prone to differential movement and must have an elastic modulus close to that of the concrete substrate. Hence, a repair material with good fluidity and relatively high compressive and tensile strength compared to the concrete substrate is preferred. Spalling is the deterioration of concrete surface causing chunks of the concrete to separate from the structure. Epoxy repair is not suitable for repair of concrete spalling. An appropriate overlay repair is required in such cases. Rapid hardening cementitious repair materials are often used to minimize out of service time for pavements and bridge decks. Current available materials like epoxy for crack repair and cementitious grouts for spalling overlay are good solutions for concrete repair. However, the bond between epoxy and concrete substrate is a concern for the overall durability and performance of the repaired structure. Thermal aging may be accelerated when epoxy resins are exposed to relatively high temperature and humidity. In case of rapid hardening cementitious grout, repair depth and volume are usually kept small due to the high cost and rapid heat generation of the rapid-hardening materials. Therefore, there is always a need for innovative new high performing concrete repair materials with good mechanical, rheological and durability properties. Addition of CNT within cement matrix has great potential to produce a nano-modified cementitious repair mortar having the above mentioned desired properties.

In contrast to other composite materials, very few works have been done on the application of CNT to produce cementitious composites, with only very preliminary work being reported (Campilo et al, 2004).The majority of research on CNT composites has instead focused on polymer matrices, with ceramics and metals also being considered for this role. Recent results of CNT application in ceramic and polymer composites have been much more promising, with individual research showing significant improvements in fracture toughness, hardness and strength in both ceramic (Zhan et al, 2003) and polymer (Thostenson et al, 2002) matrices. Key factors that have contributed to these improvements include the process of distributing the CNT in the matrix material and the degree of bonding between the reinforcement and the matrix. Traditional reinforcing mechanisms such as crack bridging, fiber pull out and crack deflection have been identified in ceramic matrices, with additional, nanoscale reinforcement mechanisms also being demonstrated. Despite this high level of research activity, very little attention has been paid to potential CNT applications in the construction industry.

One of the barriers of utilization of CNT in the concrete construction industry is the high cost. The price of CNT is still too high to be applied on a large scale. The current obstacle of high cost is very much likely to decrease in the future (Scrivener et al, 2007). Multiwalled nanotubes (MWNT) are cheaper at present than other two types of CNTs i.e. single-walled nanotubes (SWNT) and dual-walled nanotubes (DWNT) that are commercially available. The cost of untreated MWNT is about $1000 per kg, and treated MWNT cost is around $3000 per kg, whereas the cost of SWNT is $20,000 per kg. Another difficulty of producing CNT-cement composites is the attainment of uniform dispersion of CNT. CNT has a tendency to agglomerate creating zones of weakness in composite materials. Past research has shown that it is possible to distribute CNT bundles across cement grains using a sonication technique (Makar et al, 2003, 2005; Li et al, 2004, 2007). It was also reported that CNT treated with HNO_3 and H_2SO_4 solution (Li et al, 2004, 2007) provide better reinforcement efficiency.

1.3 Objectives

An extensive literature review on current knowledge revealed only a few preliminary works on CNT applications in cement composites. It is apparent from the properties of CNTs that the application of CNT in concrete industry has a huge potential. There are various types of CNTs commercially available in the market. The past research on CNT-mortar or CNT-concrete was only based on the addition of a particular type and dosage of CNT. One major difficulty of producing CNT-cement composites is the attainment of uniform dispersion of CNT into cement but no standard procedures to mix CNTs within the cement is available. Due to high aspect ratio, CNTs attract more water to adhere to their surface which might result in less workability of the cement mix. All these issues need to be addressed before investigating the eventual application of CNT in cement composites. In light of this discussion, the objectives of the proposed study were divided into three phases.

First Phase

The cost of SWNT is quite high compared to that for MWNT. Due to the lower cost of MWNT, the current study was based on treated and untreated MWNT. The following objectives were selected for the first phase,

- To develop a suitable mixing technique for the uniform dispersion of MWNT within cement matrix.
- To explore the effect of untreated MWNT on the mechanical properties of cement mortar reinforced with MWNT.
- To determine the effect of various MWNT dosage rates on the strength properties of cement mortar reinforced with MWNT.
- To investigate the workability issues through the addition of plasticizer and various water-cement ratios on the strength characteristics of MWNT-cement mortar.
- To compare the compressive strength and flexural strength of plain cement mortar (control samples) and MWNT-cement mortar.

- To study the effect of treated MWNT addition and compare with untreated composites and control samples.
- To analyze the properties of MWNT composites and select a tentative optimum MWNT type and mix proportions for future research.

Second Phase

Based on the first phase test results, suitable mix proportions with a particular type of MWNT were chosen to carry out further investigation. Large number of samples were made to perform statistical calculations in order to make significant conclusion on the effect of MWNT addition to develop nano-modified composites. The following objectives were set for the second phase:

- To develop large numbers of MWNT reinforced composites using the selected mix proportion/proportions from Phase One and particular types of MWNT.
- To investigate comprehensively the workability issues and water content in terms of flow values (flow table test) on the strength properties of composites which was made possible by larger number of samples.
- To carry out hypothesis testing in terms of compressive strength and flexural strength to draw significant conclusions. Hypothesis testing is a decision making process to make significant statistical assessment based on experimental data. This method provides conclusion on whether an event occurred by chance or it is likely to occur. This testing is generally done at the data analysis stage of a comparative experiment.

Third Phase

The applicability of nanotubes reinforced composites in concrete repair works was investigated in the third phase. A high performance cementitious mortar intended for use in concrete repair should meet several performance criteria. High strength and good bonding with the existing concrete substrate are two important characteristics of a repair material. Setting times are important for fresh cement mortar to be used as repair material. The mortar should not suffer from bleeding since bleeding may adversely affect the durability of repair material. The bond between the repair material and the concrete base often presents a weak link in the repaired structure. This was evaluated through slant shear test. Based on the above discussion the following objectives were set for the third phase,

- To investigate the effect of MWNT addition on setting time.
- To examine the effect of MWNT addition on bleeding
- To investigate the bond strength between the repair materials (MWNT-cement composite, normal-cement mortar and epoxy resin) and concrete substrate through slant shear tests.

1.4 Scope of the Study

The obtained results from the current study have some boundaries,thus the limitations of the experimental program should be carefully understood. The MWNT used in the experiments were collected from a single source that manufactured nanotubes commercially. The properties of MWNT may vary with the production process. Surface treatment of MWNT was conducted by the manufacturer. Ordinary Type II Portland cement was used as cementitious material. Mechanical properties of cement largely depend on its type. Therefore, results found from the current study may not be used to compare with nanotubes reinforced cementitious composites made by different type of cement. Polycarboxylate based Type I plasticizing agent ADVA Cast 575 was used both as surfactant to disperse MWNT and to increase the workability of cement mix. Every research work has its own boundary and the extent of the present experimental program should be clearly understood during utilization of the outcome of the study. Statistical properties of various obtained results are provided for better visualization of the range of some variables of the current study.

1.5 Organization of the Study

The organization of the rest of the thesis is as follows. Previous work on application of carbon nanotubes in construction industry and related literature are reviewed in Chapter 2. Various test methods followed in the study are also highlighted. The first phase of the study are presented in Chapter 3 which include types of material used, experimental set ups and detailed description of the obtained results. Chapter 4 deals with the second phase of the study. Importance of flow values in assessing dispersion quality of nanotubes within cement mixes and using plasticizer as surfactant are presented in this chapter. Strength results obtained from large number of samples are described in details. Finally, results of hypothesis testing are provided in this chapter. In Chapter 5, applicability of nanotubes reinforced cementitious composites as concrete repair material is portrayed. Results of setting time, bleeding and slant shear strength tests are presented and discussed. The summary of the research is provided in Chapter 6. The major contributions of the research and the future research recommendations are also described in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The review of literature related to previous research on application of CNT in construction industry and practical issues associated with development of CNT reinforced cementitious composites are presented in this Chapter. This chapter also contains a brief description of ASTM (American Society for Testing and Materials) tests that were followed in the study.

Cement is the most widely used construction material in the world. However, cementitious materials are characterized by low tensile strength. In order to control growth of cracks in the cementitious material, researchers have been using various types of macro and micro fibers. Some notable researches regarding application of fibers within cement matrix are Altoubat et al. 2009, Wang et al. 2008, Fihcher et al. 2007, Savastano et al. 2005, Li et al. 1996, Mangat et al. 1984 etc. In recent times, various nano fibers have raised the interest of researchers due to their exceptional mechanical properties and high potential to be used as reinforcement within cement matrix. Carbon nanotube (CNT) is one of the most important areas of research in the field of nanotechnology. CNTs have already proven their reinforcing performance in polymer based materials (Marrs et al. 2007, Coleman et al. 2006, Wang et al.

2006 etc.). The size and exceptional mechanical properties of CNT show their high potential to be used to produce high performance next generation cementitious composites.

2.2 Carbon Nanotubes

Discovered in 1991, carbon nanotube (CNT) is a unique form of carbon that has desirable mechanical, thermal and electronic properties. They can be easily visualized by considering a single graphene sheet, a lattice of carbon atoms distributed in a hexagonal (honeycomb) pattern. Many layers of carbon atoms are bonded together to form the grapehene sheet. Weak bonds exist between the sheets and strong bonds exist within them. A single walled CNT (SWNT) looks like a single sheet rolled up into a tube, while multi-walled CNT (MWNT) looks like multiple sheets rolled into a series of tubes, one inside the other. A single walled CNT is typically 1-3 nm in diameter and a micrometer or more long. Multi-walled CNT typically ranges in diameter from 10 to 40 nm, but has the same length as the single walled variety. Figure 2.1 shows the molecular structure of a typical SWNT and MWNT.

Carbon nanotubes have several distinctive properties. The electronic behavior of carbon nanotubes largely depends on the orientation of carbon atoms within the hexagonal formation with respect to the tube axis (Louie, 2001). Carbon nanotubes can be either metallic or semiconductor. The extent of conductivity of CNT is possible to alter by doping. For example, conductivity of CNT is considerably affected by the presence of oxygen (Collins et al. 2000).

Electronic properties of CNT can also be influenced by changing the size or mechanical deformation of nanotubes (Pablo et al. 2002). CNT also have high capability of field emission (Ajayan et al. 2001).

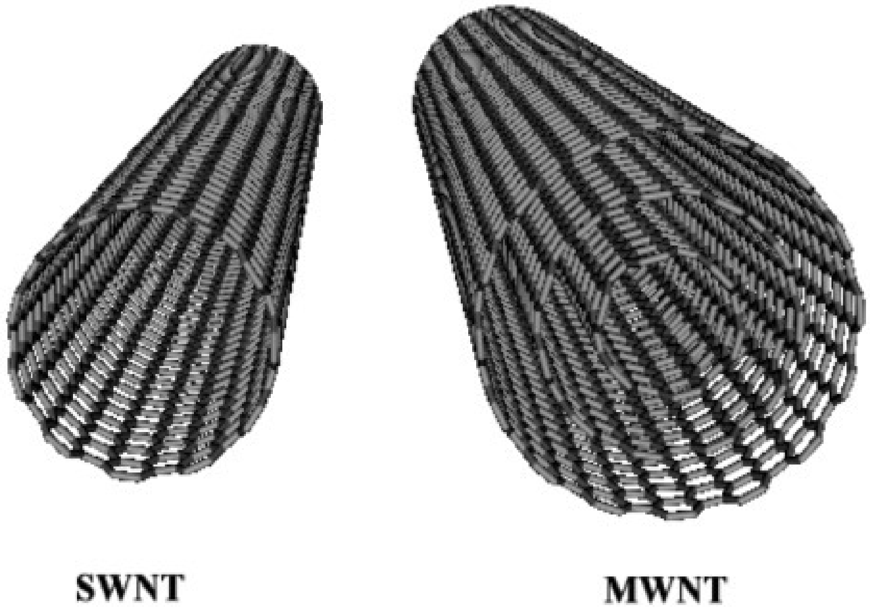


Figure 2.1: Molecular structure of a SWNT and a MWNT (Source: internet)

Mechanically, CNT appear to be the strongest material that has been discovered to date. Experimental results have shown that CNT has moduli of elasticity that exceed 1 TPa in value (Salvetat et al, 1999). CNT is highly flexible. They are capable of bending in circles or forming knots due to their high flexibility. Like macroscopic tubes, they can buckle or flatten under appropriate loadings. Tensile strengths of SWNT ranging from 13-52 GPa were reported (Yu et al. 2000). Tensile strengths corresponding to MWNT were ranged between 11-63 GPa (Yu et al. 2000). Compressive strength of 100-150 GPa and compressive strain of 5% for MWNT were reported (Lourie et al. 1998). Lourie et al. (1998) measured compressive response of CNT using micro-Raman spectroscopy and reported Young's modulus of 2.8-3.6 TPa and 1.7-2.4 TPa for SWNT and MWNT, respectively. Under tensile loading, Young's modulus of SWNT and MWNT were obtained as 320-1470 GPa and 270-950 GPa, respectively (Yu et al. 2000).

Carbon nanotubes have already proven their potential application in electronics, sensors, filler and storage material. One of the most successful and highly developed commercial applications of carbon nanotubes is application of MWNT as filler material in paints and plastic material (Baughman et al. 2002). This market has already been identified as having a multibillion dollar value (Makar et al, 2003). Application of CNT in various types of transistors and logic gates have already been verified (Javey et al. 2002) due to their ability to act as both metalic and semiconductor. Various research attempts were also made to develop CNT-metal (Kuzumaki et al. 2002) and CNT-ceramic composites (Wu et al. 1998). Application of CNT in the fields of polymer matrices, ceramics and metals also demonstrated promising results in terms of fracture toughness, hardness and strength (Zhan et al, 2003 and Thostenson et al, 2002). The main contributing factors that yielded better performance in metal and ceramic field were the dispersion method of CNT within the matrix material and the reinforcement between CNT and the matrix. Fiber pull out and crack bridging have been observed in those cases. In addition, the composites exhibited nano scale reinforcement.

2.3 Potential of Carbon Nanotubes in Construction Industry

The physical structure of cement hydration products is such that flaws within cementitious composite exist at nanoscale. Therefore, research at nano scale has huge potential to contribute to resolve these flaws. Application of fibers at nanoscale can significantly control cracks of cement matrix at nanoscale and eventually result in stronger and tougher composites. Carbon nanotubes can be considered as an exceptional reinforcing material due to their extremely high aspect ratios (Zheng et al. 2004), ultra high strength (Yu et al. 2000), modulus (Salvetat et al. 1999) and elasticity (Walters et al. 1999). The dimensions of nanotubes are at nanoscale which means that they can be distributed within the cement matrix at much more finer scale as compared to traditional reinforcing fibers since reinforcement of cement is typically done at millimeter scale. The application of carbon nanotubes to reinforce cementitious composites is therefore intended to enhance the reinforcing behavior at nano level instead of macro level. Cracks can be interrupted much more quickly and eventually hinder growth of crack at early stage and prevent propagation of cracks to micro scale. In addition, nanotubes have the potential to act as filler within the cement grains, thus producing denser composites. Therefore, CNT reinforcements have the ability to produce significantly stronger and tougher composites as compared to traditional reinforcing fibers.

2.4 Prior Research Works on Application of CNT in Construction Industry

Despite high potential of CNT to be applied as nano scale reinforcement to produce cementitious composites, little work has been done on the use of cements to produce CNT-cement composites. Although few studies have been found related to this issue, the outcomes are extremely encouraging. Recently, several research works have been initiated to explore the behavior and mechanical properties of CNT reinforced cement composites. The notable investigations and their outcome in the field of carbon nanotubes application to produce cementitious composites are discussed in brief in the following sections.

A study by Makar et al. (Makar et al. 2005) shows that addition of SWNT accelerates the hydration process at early age. Hardness of composites were also measured since the Vickers hardness measurement can be directly correlated to the elastic modulus of cement paste (Beaudoin et al. 1975). It was statistically proven that addition of nanotubes resulted in improvements of Vicker's hardness of up to six times the values measured in pure ordinary portland cement samples hydrated for the same time at the same ratio of water to cement. Figure 2.2 shows the hardness measurement done by the study. The composites were prepared with CNT/cement ratio of 0.02 by weight. Ultrasonic vibration was utilized to disperse nanotubes within cement matrix. Crack bridging and fiber pull out mechanisms were also evidenced through SEM images. Therefore, the outcome of the study suggested that nanotubes not only act as a reinforcement but also affect the hydration behavior of the cement paste.

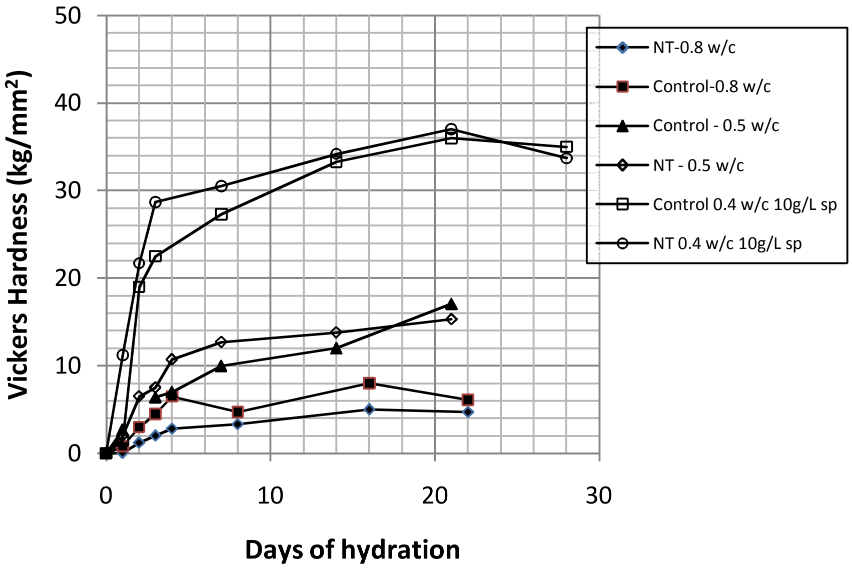


Figure 2.2: Vickers Hardness Comparisons between control and composite samples (after Makar et al. 2005)

The effect of CNT addition on cement hydration process is explained in details in another study by Makar et al. (Makar et al. 2009). It was found that the presence of nanotubes affected the morphology of cement hydration products, both the initial C_3A and the C_3S hydration products. It was observed that CNT accelerated the rate of hydration process by acting as a matrix for the development of C-S-H and $Ca(OH)_2$ produced during the hydration. CNT act as nucleating agent during cement hydration by providing more sites for the reaction to occur and encourage the formation of reaction products. In CNT reinforced cement composites, the nucleation of the C-S-H on nanotubes slowed the development of C-S-H coating on the surface of cement grains and eventually accelerated the dissolution and nucleation and growth of hydration products as compared to normal cement paste. The performance of nanotubes as nucleating agent have also been observed for other materials like nanodiamonds grown on SWNT (Terranova et al. 2005), zirconium oxide grown on MWNT (Lupo et al. 2004), silicon nitride grown on MWNT (Balázsi et al. 2006), calcium carbonate grown on MWNT (Tasis et al. 2007) etc. Fiber pull out mechanism of nanotubes was also observed in 22 of the 24 samples examined in the study.

Li et al. (Li et al. 2005) found that an addition of 0.5% MWNT increased both the 28-day cement mortar compressive and flexural strength as compared to Portland cement composite. Three mixes of cement mortar were prepared and tested. The mixes were ordinary Portland cement mortar, cement mortar reinforced by untreated carbon fibers and cement mortar reinforced by treated MWNT. The results obtained from this study are provided in Table 2.1. The typical compressive stress-strain curves of the composites are shown in Figure 2.3. It was observed that the deformation ability of cement composites was improved by the addition of nanotubes. Another study by Li et al. (Li et al. 2007) reported that CNT, treated with HNO_3 and H_2SO_4 solution, provide better reinforcement efficiency.

An increase in compressive strengths at early age was obtained by Agullo et al. (Agullo et al. 2009) through the addition of low concentration of MWNT. However, no significant increment was found in 28 day compressive strength. Composites with medium concentration of MWNT obtained less compressive strength than that of normal cement samples at the age of 28 day. Figure 2.4 shows the compressive strength of different mixes obtained by the study. For mortar with low concentration of MWNT (Figure 2.5), higher flexural strengths were achieved, both at early and later ages. According to the study, the strong fibrilar structure of MWNT ensures permanent reinforcement and therefore, improves the flexural behavior of composites. For high concentration of MWNT, similar behavior was observed in flexure as in the case of compressive strengths.

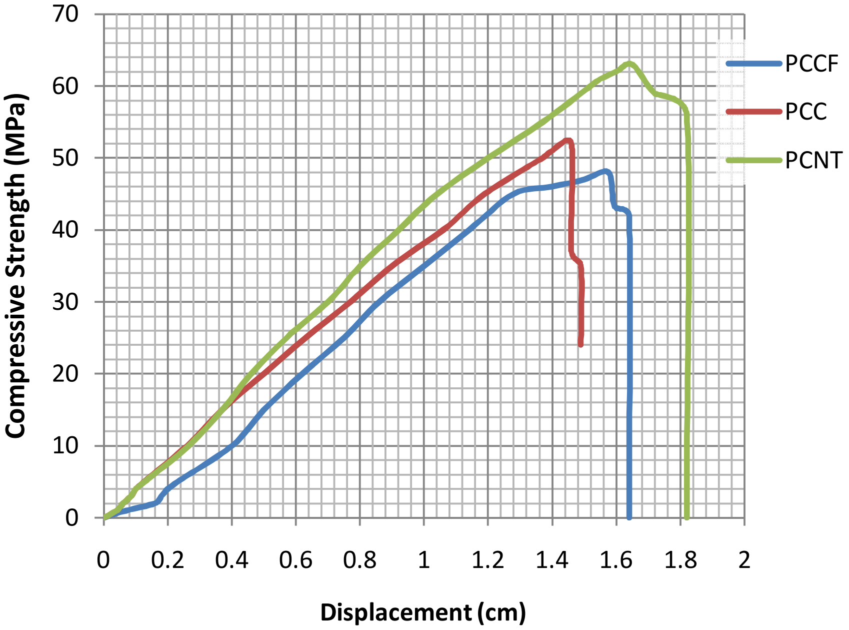


Figure 2.3: Load displacement curves of different mixes (after Li et al. 2005)

A study by Yazdanbakhsh et al. (Yazdanbakhsh et al. 2010) found that using polycarboxylate based superplasticizer as surfactant to distribute nanotubes within cement paste can achieve stable dispersion. Similar dispersion method also yielded better performance to disperse carbon nanofibers within cement matrix by Gay et al. (Gay et al. 2010). Cwirzen et al. (Cwirzen et al. 2008) obtained an increase of 10% in flexural strength of MWNT reinforced composites in comparison with plain cement mortar. The CNT to cement proportion was used as 0.042. The results of the experimental study conducted by Konsta et al. (Konsta et al. 2010) shows that cement composites reinforced with short and long MWNT exhibited better performance in flexure and Young's modulus as compared to plain cement paste (Figure 2.6).

Table 2.1: Strength of Different Mixes at 28 day (after Li et al. 2005)

Mix	Compressive Strength (MPa)	Flexural Strength (MPa)
PCC (Portland cement composite)	52.27	6.69
PCCF (cement mortar with untreated carbon fiber)	47.51	8.14
PCNT (cement mortar with treated carbon nanotubes)	62.13	8.37

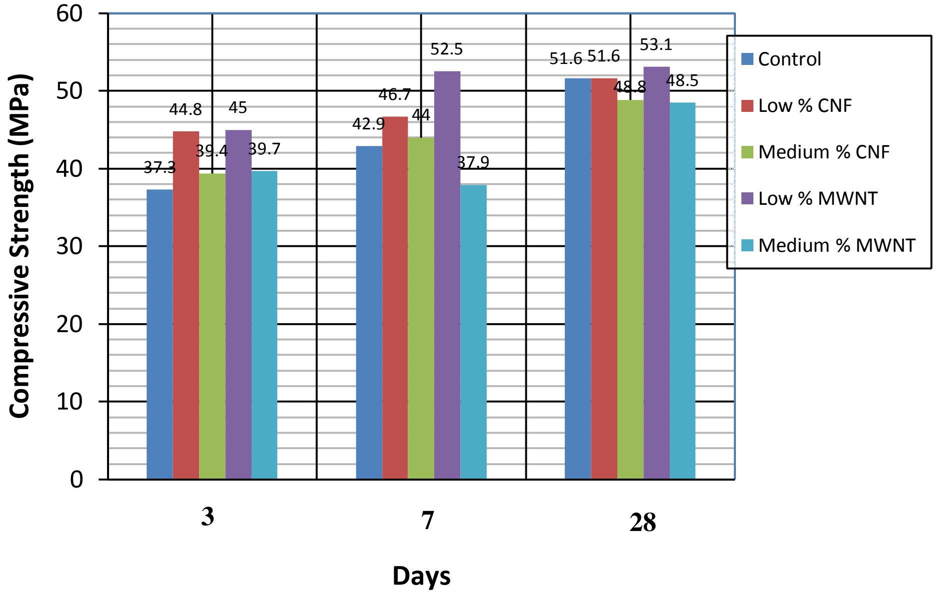


Figure 2.4: Compressive strengths of mortars reinforced with carbon nanofilaments (after Agullo et al. 2009)

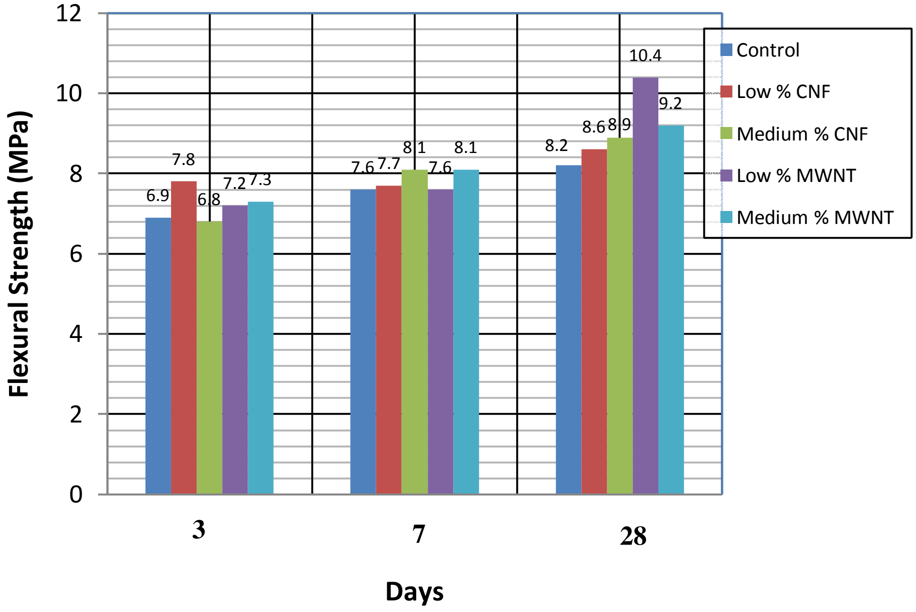
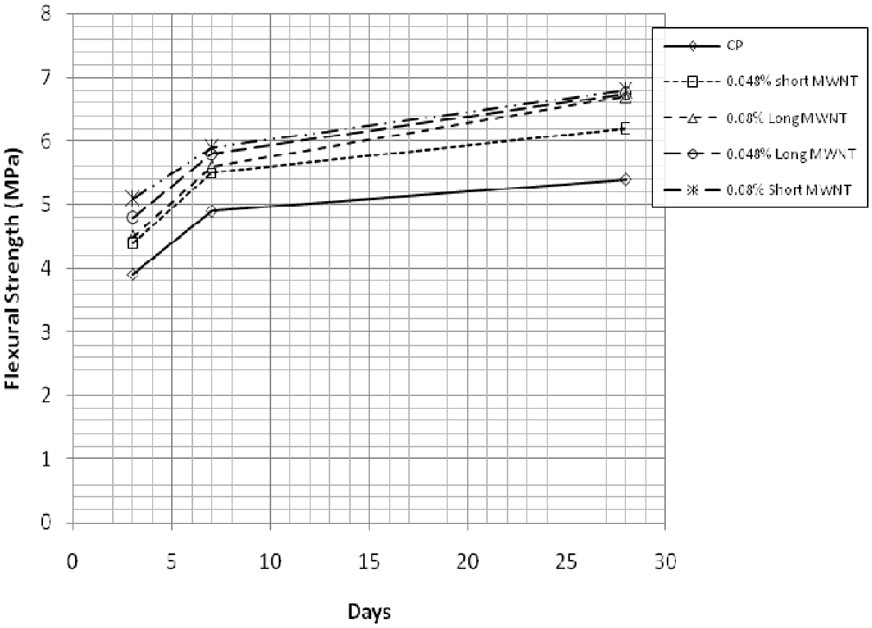
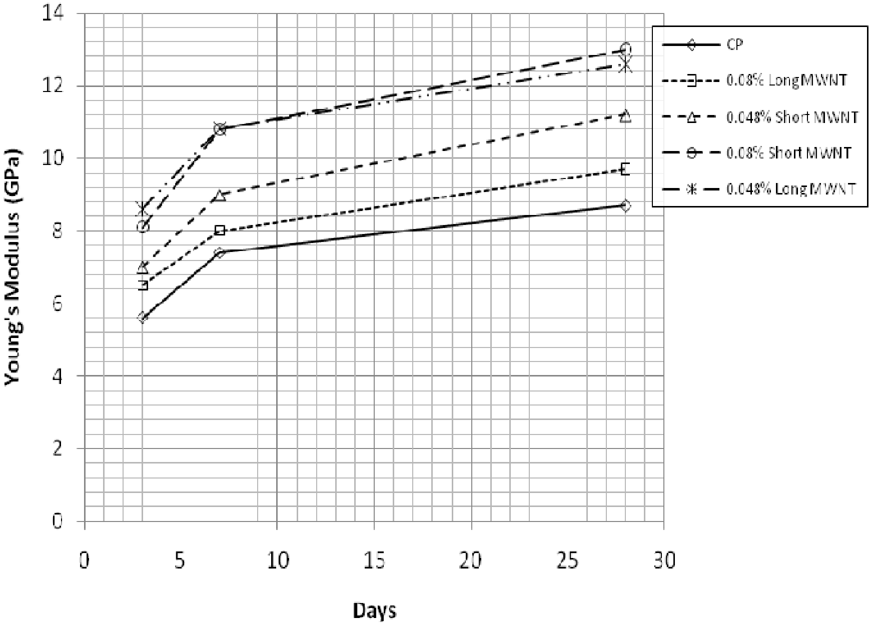


Figure 2.5: Flexural strengths of mortars reinforced with carbon nanofilaments (after Agullo et al. 2009)



(a)



(b)

Figure 2.6: Flexural strength (a) and Young's modulus (b) of plain and MWNT reinforced cement paste (after Konsta et al. 2010)

2.5 ASTM Tests

The procedure and significance of ASTM tests conducted in the present study to evaluate and compare mechanical properties of MWNT reinforced cementitious composites are briefly described in the following sections.

2.5.1 Compressive Strength Test (ASTM C109/C 109M)

Compressive strengths of the samples were evaluated according to ASTM C109/C109M (ASTM C109/C109M, 2008). Rotary mixture with flat beater was used for mixing as per ASTM specification. Cube specimens of 50 mm length were prepared with 1 part of cement and 2.75 parts of sand by mass. All the cube specimens were kept in the mold for 1 day in the moisture room and then were demolded and immersed in lime water until tested. The loads were applied at a rate of 1400 N/s.

2.5.2 Flexural Strength Test (ASTM C348-02)

ASTM C348-02 (ASTM C348-02, 2008) test procedure was followed for flexural strength evaluation of both plain and composite samples. The test procedure involved a central point loading of mortar beam specimen having a span approximately four times its depth. The standard beam size used for flexural strength test was 40 mm (1.6 in) by 40 mm (1.6 in) by 160 mm (6.3 in). . Specimens were kept in the mold in the moisture room for 1 day and then were removed from the mold and immersed in lime water until tested. The load was applied at a rate between 900 to 1800 N/s (200 to 400 lb/s). The failure load was estimated to the closest of 22 N.

2.5.3 Flow Table Test (ASTM C1437-07*)*

Flow of the plain and nanotubes reinforced composites was measured following ASTM C137-01(ASTM C1437-07, 2008). Mold was filled up in three layers with each layer having thickness of 25 mm. Each layer was tamped 20 times with the tamper. Flow values were determined to the nearest 1%. Flow values are important for evaluating the workability of the mix. Through the flow values, the affect of MWNT addition on workability of the composites was evaluated.

2.5.4 Setting Time Test (ASTM C807-08*)*

The setting times of mixes were determined using the modified Vicat apparatus described in ASTM C807-08 (ASTM C807-08, 2009). After mixing, mold was first filled with a layer of mortar with about 20 mm in thickness and then tamped with the tamper. A total of 14 strokes were applied around the outside of the mold and 4 strokes were applied to the center of the samples. Then the rest of the mold was filled and same procedure was followed. The setting time represents the beginning of the solidification phase at which fresh grout can no longer be properly handled or injected. This test is significant for evaluating the affect of nanotubes addition on setting time of cementitious mortar. Setting time values were reported in minutes to the nearest 1 minute. Setting time of two samples having the same mix proportions should not differ by more than 43 minutes.

2.5.5 Bleeding Test (ASTM C940-98a*)*

Bleeding of the freshly mixed mortar samples was measured following the procedure given in ASTM C940-98a (ASTM C940-98a, 2008). The amount of expansion and accumulation of bleed water at the surface of fresh mixes is measured by this test method. In each case, an 800 ml quantity of fresh mix was made and poured into a 1000 ml glass graduated cylinder and covered. The height of free water was noted after complete sedimentation to the nearest 1 mm. The height was expressed as a percent of the original height of the mix. Final bleeding was calculated by expressing volume of decanted bleed water as percentage of the initial volume of the mix. Final bleeding was expressed to the nearest 0.2%.

2.5.6 Slant Shear Test (ASTM C882/C882 M and DMS 4655)

The bond strength between the cementitious mixes and concrete substrate was measured by slant shear test according to ASTM C882/C882 M (ASTM C882/C882, 2008) and DMS 4655 (DMS 4655, 2009). The efficiency of repair material used in concrete structures is ascertained through the bond strength. Bond strength was determined by joining two equal sections of concrete of 75 mm by 150 mm in size using epoxy resins and cementitious mixes. The concrete cylinders should have a minimum compressive strength of 34.5 MPa at the age of 28 day. The slant shear strengths for CNT-cement mixes, plain cement mixes and epoxy resin were obtained by conducting a series of compression tests.

2.6 Hypothesis Testing

Hypothesis testing is a statistical decision making tool about an event occurred within a population. The event is called statistically significant if it is not occurred by chance. Through hypothesis testing, it is possible to evaluate whether a result obtained from a random population is statistically significant based on pre-determined threshold probability. This pre-determined threshold probability is termed as the significance level. There are various methods of hypothesis testing to be applied depending on nature of population or data. One of these methods is the 't' distribution. The 't' distribution is utilized when the sample size is small and the variance of the population is not known. This method makes a reasonable assumption of underlying distribution as normal. Generally, concrete strengths are well approximated by the normal distribution. Moderate departure from normality of the population data has little effect on validity of the 't' distribution. Hence, 't' has wide applicability in hypothesis testing in many practical instances. The 't' distribution was utilized in the study to make statistical decision about performance of nanotubes reinforced cementitious composites.

2.7 Discussion

The results obtained from the testing of mechanical properties of nanotubes reinforced composites by past researches have been quite variable. It is evident that to improve the performance of CNT-cement composites, a particular combination of w/c ratio, admixture proportion and nanotubes content is required. For example, Cwirzen et al. (Cwirzen et al. 2008) studied 15 different combination of nanotubes concentration, water content and admixture amount and only one combination yielded significant improvement as compared to control samples. Therefore, developing an optimum mix proportion and suitable mixing technique for producing nanotubes reinforced cement composites are of immense importance.

CHAPTER 3

PHASE I STUDY: EFFECT OF VARIOUS MWNT AS REINFOREMENT IN CEMENT MORTAR

3.1 Introduction

One of the prime objectives of the study is to investigate the behavior of cement composites reinforced with different types and proportions of MWNT. In this section, results of the first phase of the study are presented and discussed. Due to the absence of any standard code practice on dispersion of MWNT within cement matrix, the type and dosage rate of MWNT to be used and a suitable design mix proportion to develop nanotubes reinforced composites with desired properties, an attempt has been made in this phase to explore the effect of addition of different types and amount of MWNT with different mix proportions on composite strength. Parametric studies on obtained strength data are carried out to find out the best performing MWNT type and amount with a tentative optimum mixing technique and design mix proportion. A suitable mixing technique and a tentative optimum type and dosage rate of MWNT with an appropriate mix proportion are of high importance to carry out further investigation on the composite behavior.

Seven types (based on outside diameter) of commercially available MWNT were used to reinforce the cement composites. Both compressive and flexural strength were determined and compared with the control samples. Different mixing methods to uniformly disperse the MWNT within cement matrix were explored and a suitable mixing technique was suggested. Surface treated MWNT by acid solution were also utilized as reinforcement and compared with the untreated MWNT reinforced composites. The various factors affecting the composite behavior are also identified and discussed.

3.2 Materials Used

Ordinary Type II Portland cement was used as cementitious material in this study. Special graded sand according to ASTM C109 (ASTM C109/C109M, 2008) test requirement was utilized. The specification of the sand is given in Table 3.1. The seven types of untreated MWNT and their properties and composition are shown in Table 3.2. Figures 3.1 through 3.7 show the TEM images of the different MWNT types used in the experimental program. ADVA Cast 575 was used as plasticizer in the experiments to improve the workability of the mix.

Table 3.1: Specification of sand

Specific Gravity	2.65
Bulk Density	1497 kg/m^3
Grading	No. 16 sieve retains 0%; No. 30 sieve retains 2%; No. 40 sieve retains 30%; No. 50 sieve retains 75%; No. 100 sieve retains 98%

Table 3.2: MWNT properties

Types of MWNT & Properties	M1	M2	M3	M4	M5	M6	M7
OD (outside diameter)	> 50 nm	20-30 nm	10-20 nm	< 8 nm	8-15 nm	20-40 nm	30-50 nm
Length	10-20 µm	10-30µm	10-30µm	10-30µm	10-30µm	10-30µm	10-20 µm
Purity	>95wt %	>95wt %	>95wt %	>95 wt%	>95 wt%	>95 wt%	>95 wt%
Ash	<1.5 wt%	<1.5 wt%	<1.5 wt%	<1.5 wt%	<1.5 wt%	<1.5 wt%	<1.5 wt%
SSA (Specific Surface Area)	>40 m^2/g	>110 m^2/g	>233 m^2/g	>500 m^2/g	>233 m^2/g	>110 m^2/g	>60 m^2/g
EC (Electrical Conductivity)	>10^{-2} s/cm	>10^{-2} s/cm	>10^{-2} s/cm	>10^{-2} s/cm	>10^{-2} s/cm	>10^{-2} s/cm	>10^{-2} s/cm

Figure 3.1: TEM image of M1 (Source: Cheap Tubes)

Figure 3.2: TEM image of M2 (Source: Cheap Tubes)

Figure 3.3: TEM image of M3 (Source: Cheap Tubes)

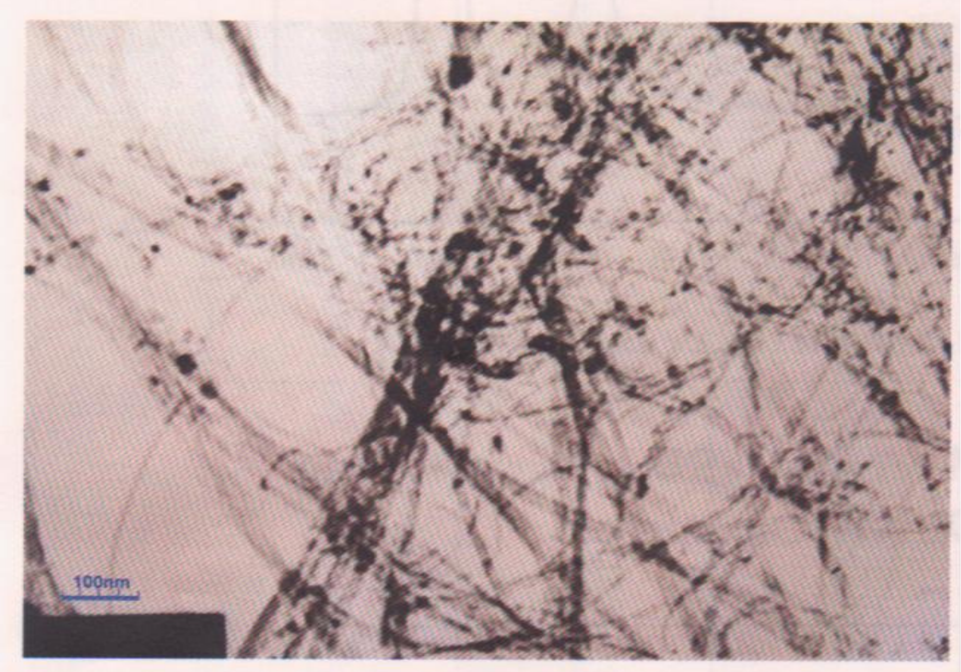


Figure 3.4: TEM image of M4 (Source: Cheap Tubes)

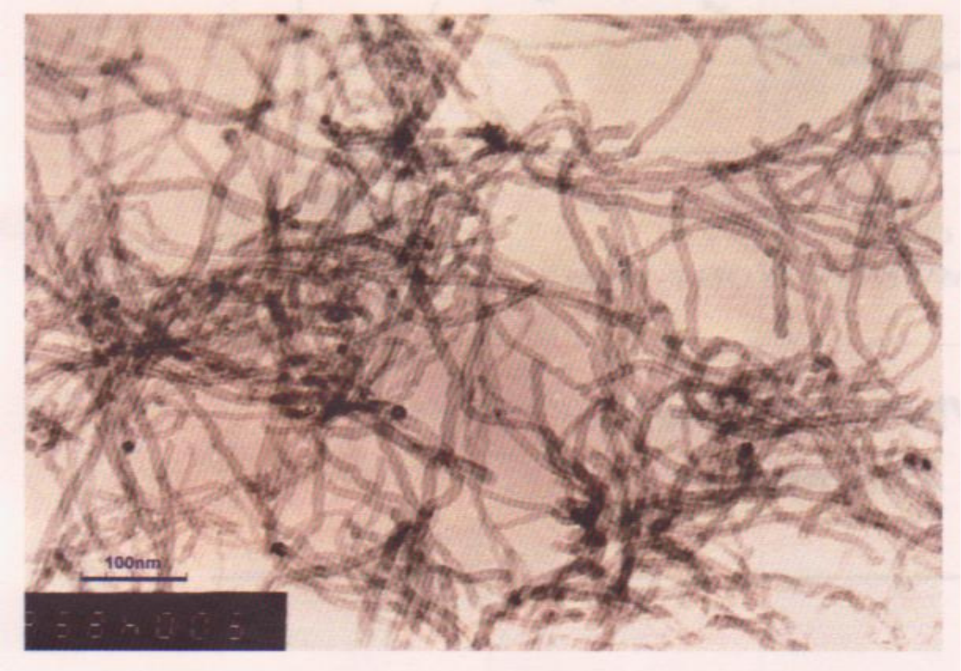


Figure 3.5: TEM image of M5 (Source: Cheap Tubes)

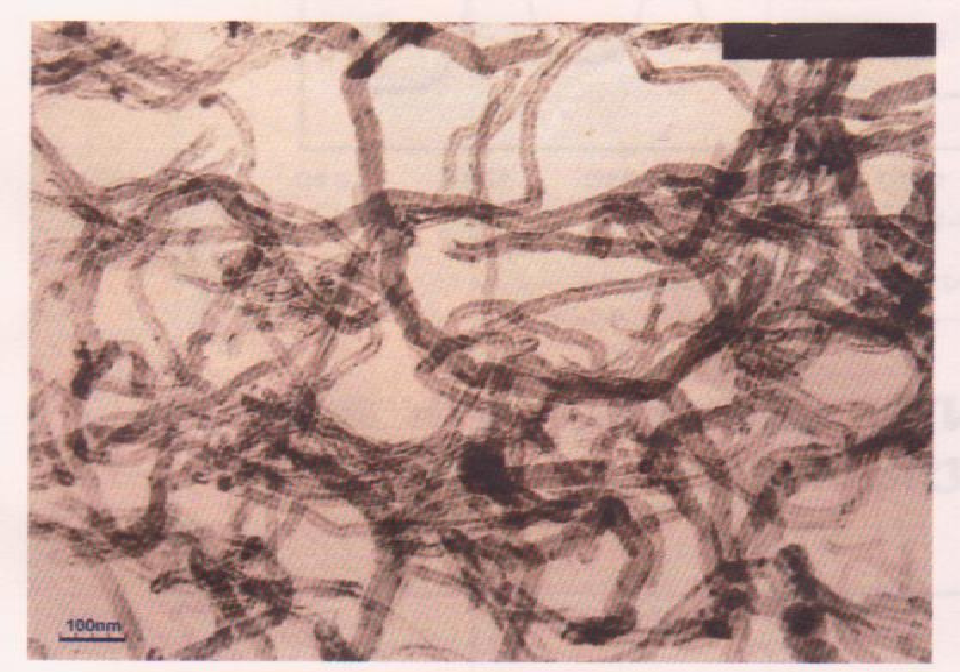


Figure 3.6: TEM image of M6 (Source: Cheap Tubes)

Figure 3.7: TEM image of M7 (Source: Cheap Tubes)

3.3 Mixing Technique

Commercially available MWNT were collected in powder form. The homogenous suspension of MWNT is of high importance to achieve the desired level of reinforcement within the composite. However, due to Van der Waals forces resulting from large surface area of MWNT, they tend to adhere together and is extremely difficult to separate. Manual stirring of MWNT within water is not suitable to suspend nanotubes as this process is not capable of producing required energy to break the agglomeration of MWNT which in turn produce an unstable mix (Figure 3.8). Therefore ultrasonic vibration was utilized to exfoliate and distribute the MWNT bundles across the cement grains.

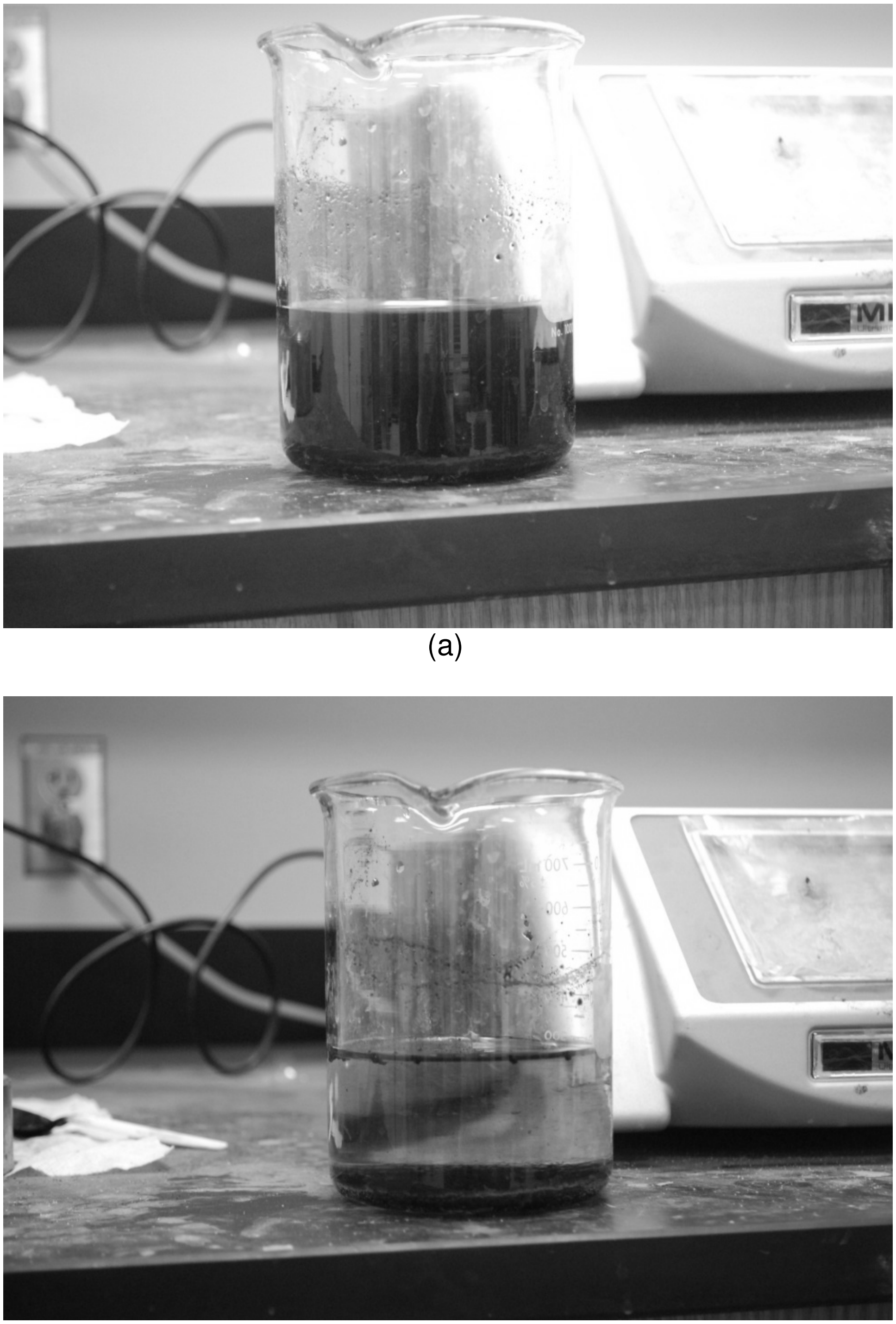
A MISONIX 4000 sonicator was used herein for mixing the MWNT within cement matrix. Ultrasonic waves were transmitted from a probe into water producing alternate expansion and compression. Microscopic bubbles were created by this pressure fluctuation. These bubbles increased in volume during negative pressure excursions and imploded viciously during the positive excursion. The collapses of bubbles give rise to huge number of shock waves, acoustic streaming, high pressure and extreme temperature. The total energy produced by the cumulative effect of this process is extremely high and capable of breaking agglomeration of MWNT. In a typical procedure of this phase of study, MWNT suspension was prepared by sonicating them into water. This water was then used as mixing agent to prepare the composite mortar.

A parametric study was carried out to find a suitable mixing technique in the absence of a standard procedure. For the base study, 0.3% of M1 by weight of cement was added through the sonication process. Three mixing techniques were utilized with different sonication timing and steps.

In Method 1, the whole amount of M1 was added to the water and then sonicated for 5 minutes at amplitude of 50%. After completing the sonication cement was added into the MWNT dispersed water. A water cement ratio of 0.485 was used. A rotary mixer with flat beater was used for this mixing process. After mixing the cement and water for 30 seconds the sand was added keeping the mixer rotating and mixed for 3.5 minutes. ASTM C 109 procedure was followed for the entire mixing process (ASTM C109/C109M, 2008).

For Method 2, sonication was done for 15 minutes after adding all required amount of M1. The amplitude was varied between 50% and 70%. The mixing sequence was kept similar to Method 1.

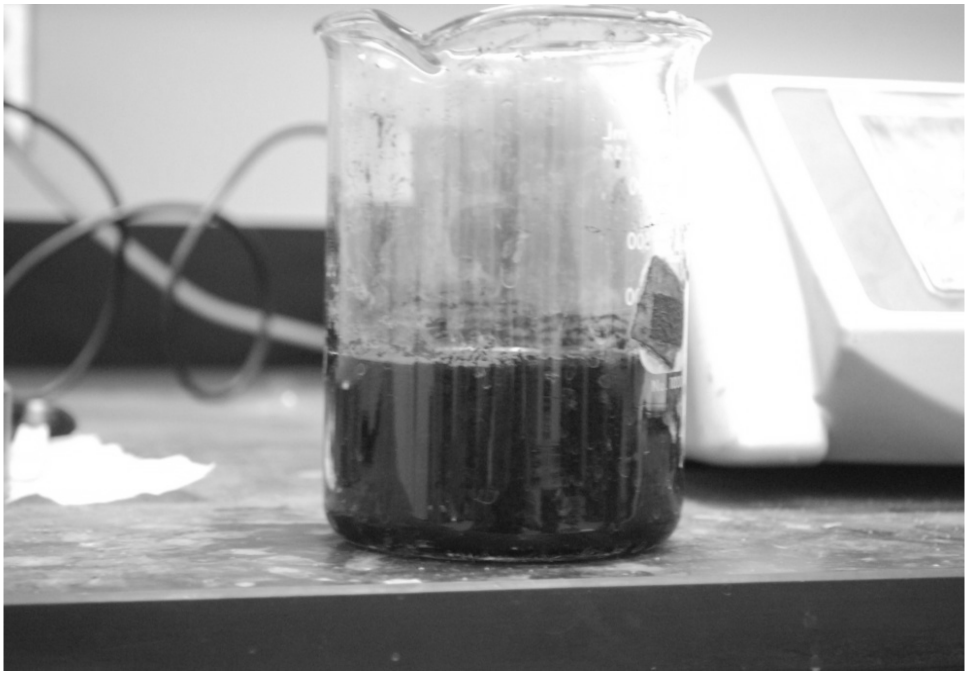
In Method 3, M1 was added in sequence and was sonicated for 5 minutes for each addition. Total sonication time was 40 minutes for this method. The amplitude was varied between 50% and 75%. Figure 3.9 shows the MWNT dispersion into the water using the 3rd mixing method. It is apparent that the mix remains stable even after few hours of sonication.


(a)

(b)

Figure 3.8: Manual mixing of MWNT (a) Just after Mixing and (b) 15 minutes after mixing

(a)



(b)

Figure 3.9: Mixing of MWNT through 40 minutes sonication(a) Just after Mixing and (b) 120 minutes after mixing

Figure 3.10 shows the compressive strengths of MWNT reinforced cement composites prepared by three mixing methods at 7 and 28 day. Method 3 mixing technique yielded the highest compressive strength in both cases. About 70% variation was found in the 7 day compressive strength, and 30% in 28 day strength (Figure 3.10) between Method 1 and Method 3 sonication process. For 7 day compressive strength both Method 2 and Method 3 resulted in similar strengths, but Method 3 produced 16% higher strength than Method 2 at the age of 28 day. The difference between 28 day compressive strength of Method 2 and Method 1 was 13%.

Therefore, proper sonication mixing method is important to generate CNT reinforced cement composite with more efficient particle packing. If the sonication is not appropriate, the agglomeration of the MWNT cannot be overcome; this eventually results in inadequate reinforcement of nanotubes within the cement matrix. In addition, if the nanotube bundles remain intact, they no longer remain in the nano scale range. As a result, instead of filling the nano void spaces within the cement grains, they take place between cement hydration products creating zones of weakness through the cement matrix. At the same time, lack of proper dispersion of MWNT make the paste more viscous affecting workability of the mix adversely. The cumulative outcomes of these effects reflect on the strength of the composite, which is much less than the strength of normal cement mortar. Method 3, the best performing technique, was then utilized for the subsequent mixing in the first phase of study. More variation is found in the 7 day strength. SEM images were taken of the crushed samples at 28 day. These SEM images show that MWNT can be distributed fairly uniformly through the sonication process (Figures 3.11 and 3.12).

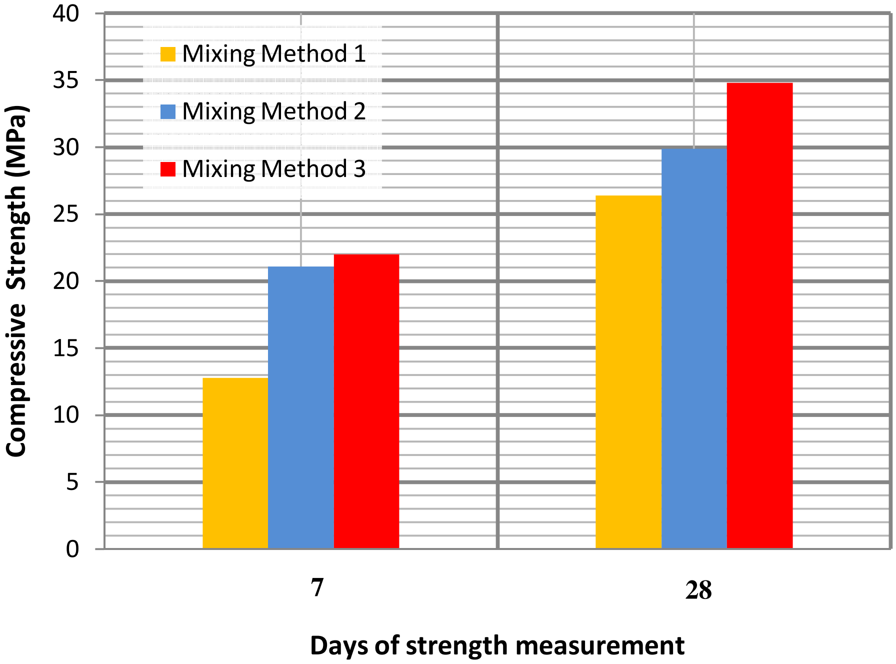
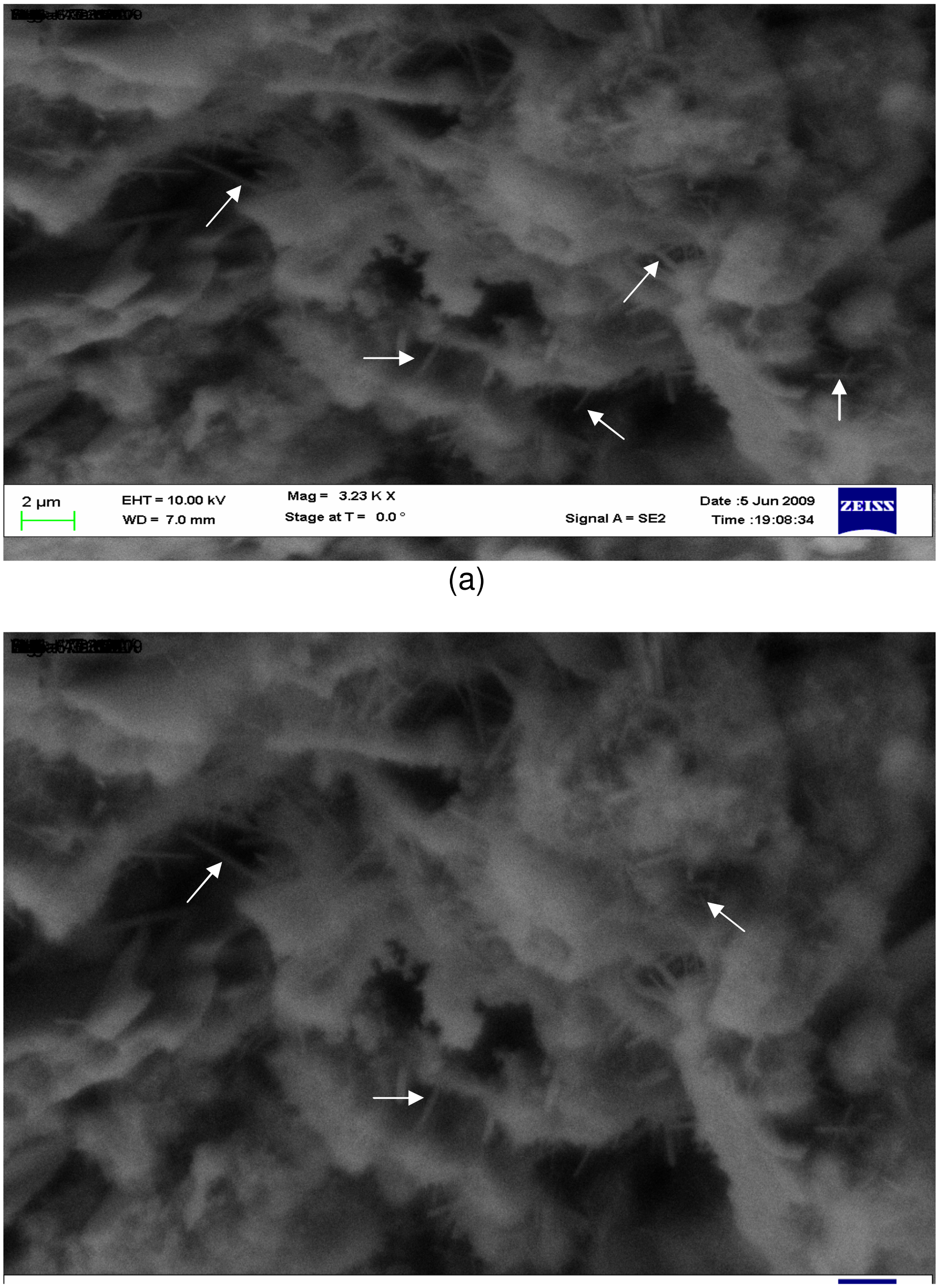


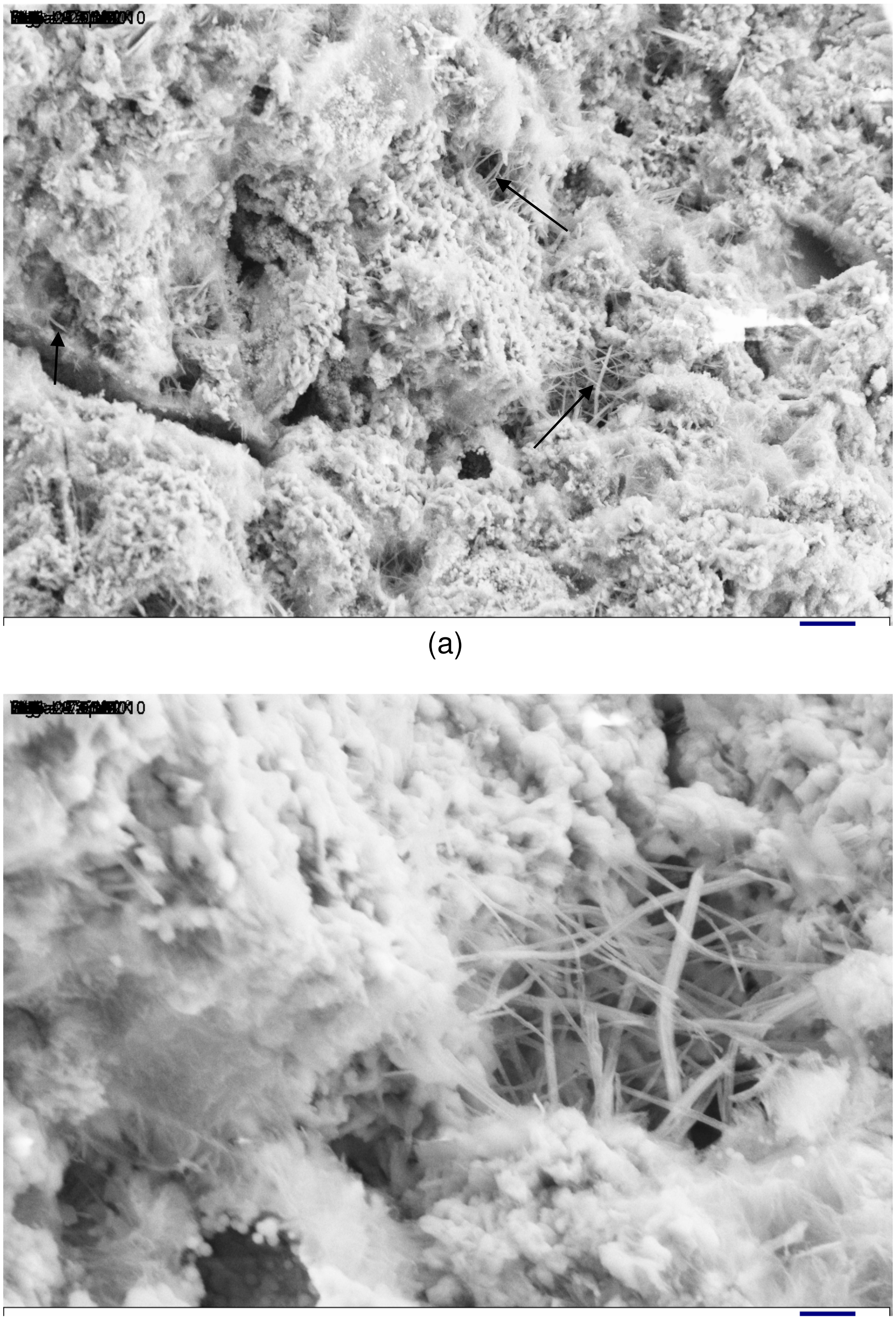
Figure 3.10: Mortar compressive strength for various mixing techniques



(a)

(b)

Figure 3.11: Distribution of CNTs through sonication within cement matrix in (a) Sample 1 and (b) Sample 2



(a)

(b)

Figure 3.12: SEM images of 28 day crushed cement (a) Sample 1 and (b) Sample 2

3.4 Experimental Setup and Testing Procedure

Compressive strengths of the samples was determined according to ASTM C109 (ASTM C109/C109M, 2008). Cube specimens of 50 mm size were prepared with 1 part cement and 2.75 parts of sand by mass. A rotary mixer with flat beater was used for mixing as already mentioned. MWNT were first mixed with water and stirred by hand. Afterwards, sonication was done for 40 minutes in sequence. Cement, sand and nanotubes were then mixed in the mixer for about 6 minutes as per ASTM C109 requirements. After pouring the mixes into oiled molds (50x50x50 mm), the specimens were surface-smoothed and covered with wet clothes. All the cubes were then kept in the mold for one day in the moisture room and then were demolded and immersed in the lime water until tested. Compressive strength tests were conducted at the ages of 7 and 28 day. An MTS machine was used to apply compressive load on the specimens. The load was applied at a rate of 1400 N/sec and the results were obtained through a data acquisition system. The experimental setup for compressive strength test is shown in Figures 3.13, 3.14 and 3.15.

Both control samples (no MWNT) and composite samples were prepared for testing and comparison purposes. A w/c ratio of 0.485 was initially used. Due to the strong capillary forces of the nano-tubes, water was drawn into them, effectively sequestering them from the rest of the mixture and causing workability to decrease. This in turn prevented the fluid cement from completely filling the mold, resulting in large bubbles being trapped in the cement. These bubbles and corresponding voids produced samples with uneven sides and surfaces (Figure 3.16) that significantly reduced the compressive and tensile strengths. To avoid this problem, a super-plasticizer was used to increase the workability in some cases. Also w/c ratio was increased in other cases. Figures 3.17 and 3.18 show the composite samples with higher w/c ratio and plasticizer addition, respectively.

Flow values were measured using the flow table as per ASTM C1437-07 (ASTM C1437-07) Flow values are important for evaluating the workability of the mix. Through the flow values, the effect of MWNT addition on workability of the composites was assessed. Flow values of control samples were also determined and compared with the composites. As mentioned earlier, to overcome the workability issue, w/c ratio was increased or plasticizer was added. The effect of such measures was directly reflected by the corresponding flow values. As workability increased, compressive strength of composites also increased in all cases. All these phenomena are presented and discussed in the following sections.

Figure 3.13: Compressive strength test using MTS and data acquisition system

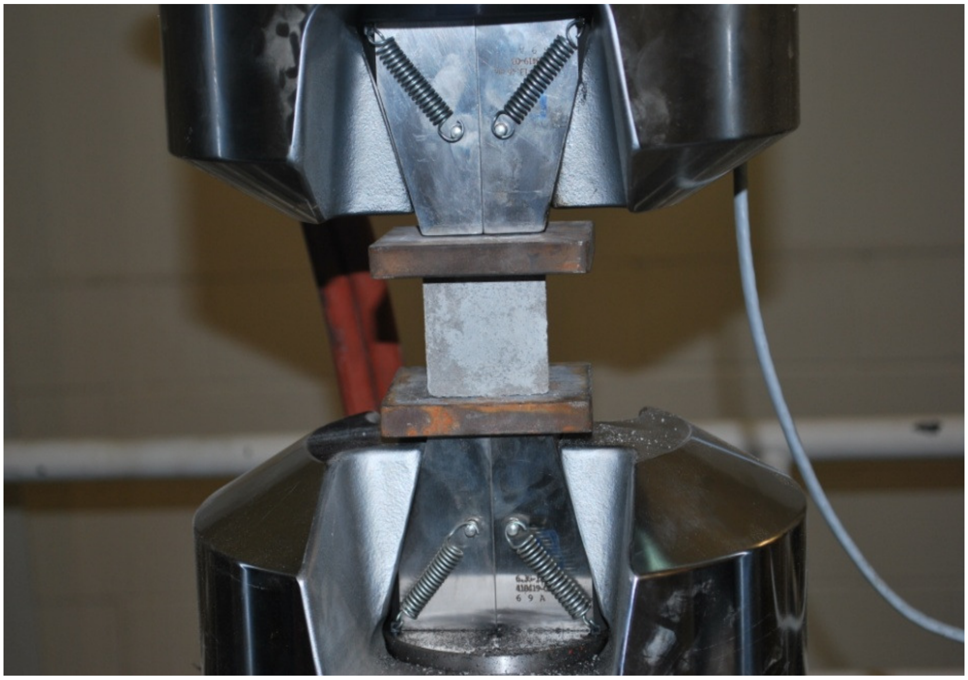


Figure 3.14: Compressive strength test of mortar cube using MTS

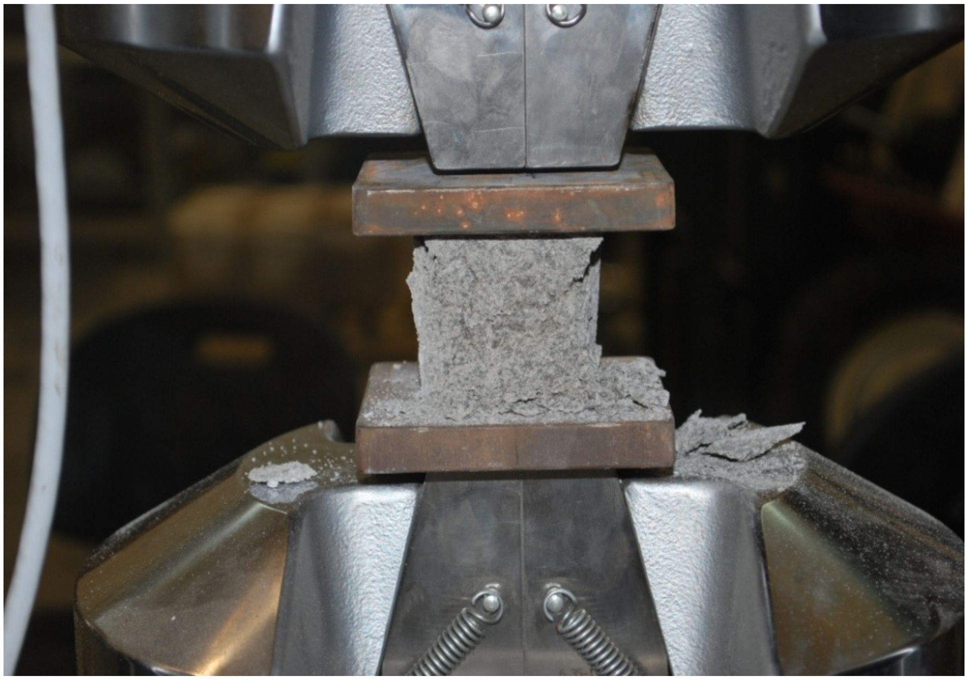


Figure 3.15: Crushed mortar cube after testing using MTS

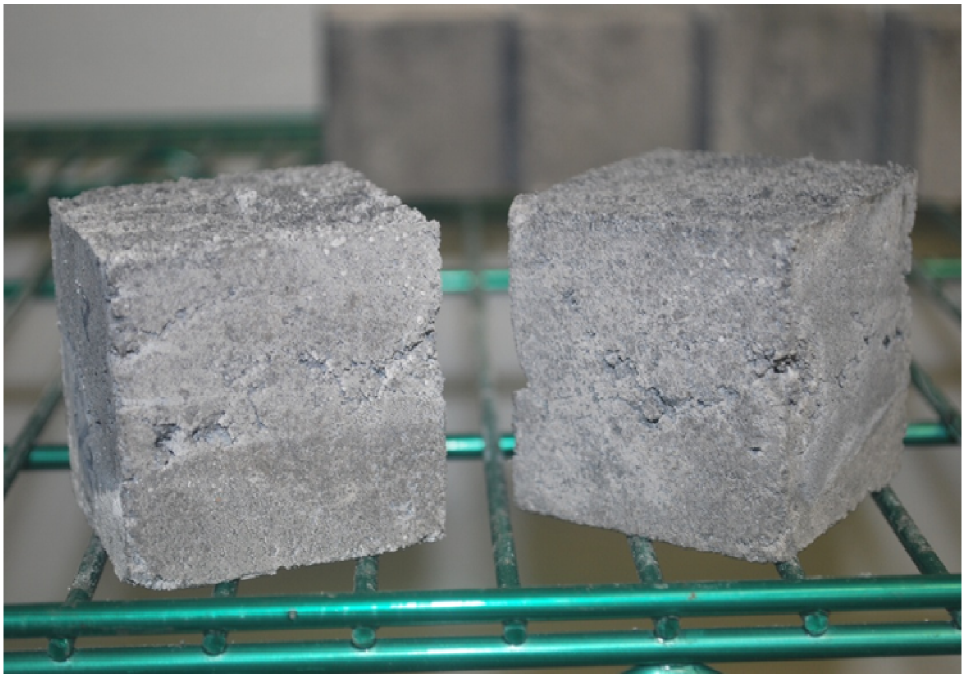


Figure 3.16: Composite with 0.5% M1 and w/c ratio of 0.485

Figure 3.17: Composite with 0.5% M1 and w/c ratio of 0.60

Figure 3.18: Composite with 0.5% M1 and w/c ratio of 0.485 and plasticizer proportion of 0.005

ASTM C348-02 (ASTM C348-02, 2008) test procedure was followed for determining flexural strengths of MWNT-cement samples. The test procedure involved a central point loading of a beam specimen having a span approximately four times its depth. The standard beam size used for flexural strength test was 40 mm (1.6 in) by 40 mm (1.6 in) by 160 mm (6.3 in). The load was applied at a rate between 900 to 1800 N/s (200 to 400 lb/s) through MTS. The flexural test was carried out for both composite samples having different types of MWNT with different dosage rates and control samples containing no nanotubes. Figures 3.19 through 3.21 show the experimental setup for flexural test.

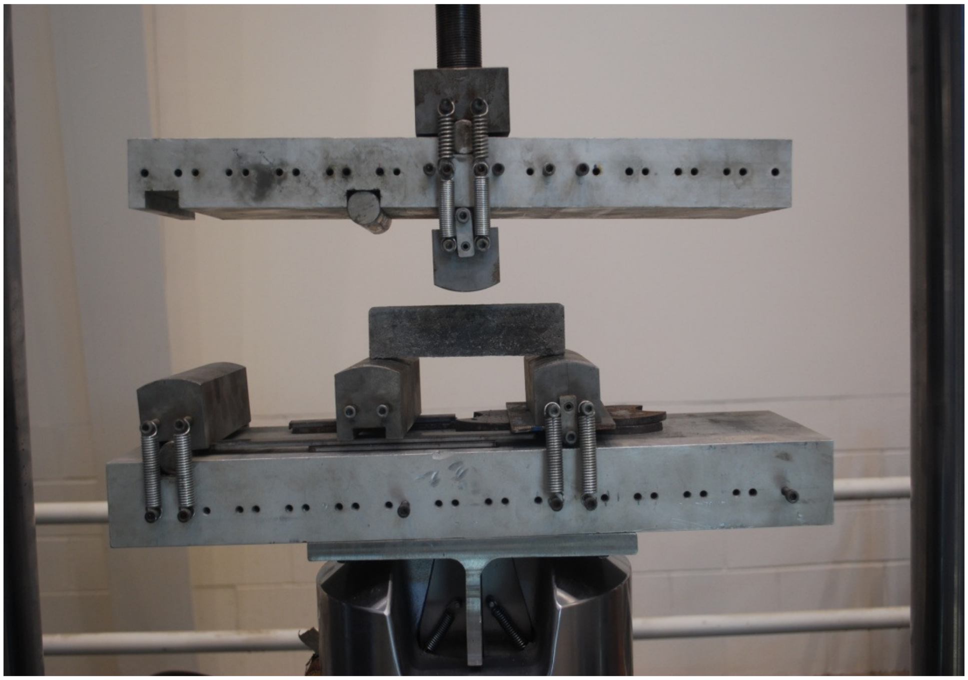


Figure 3.19: Flexural strength test setup using MTS

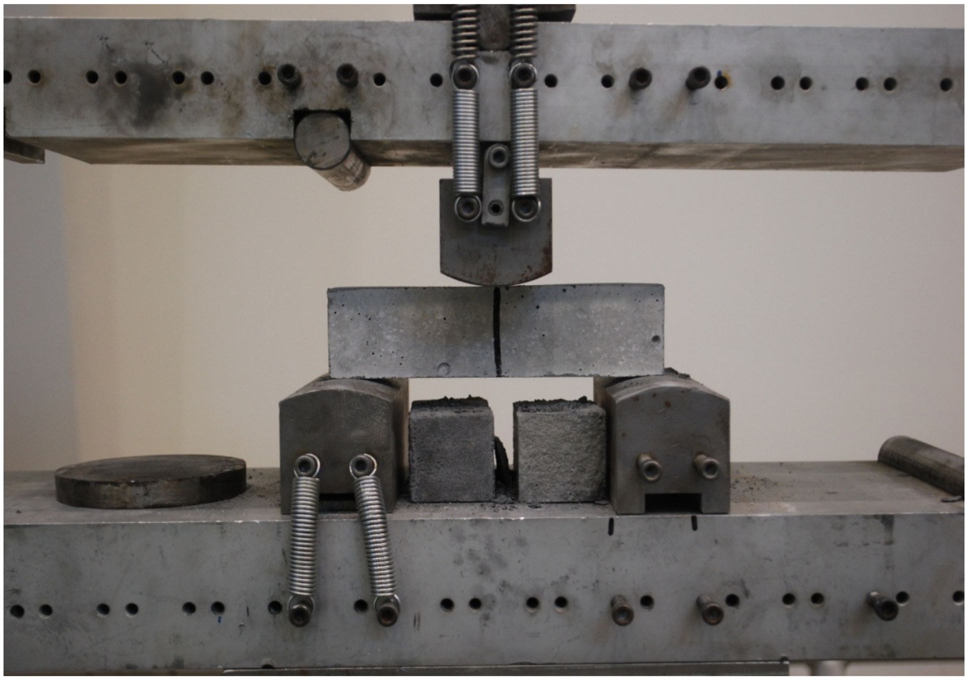


Figure 3.20: Loading applied on a flexural specimen using MTS

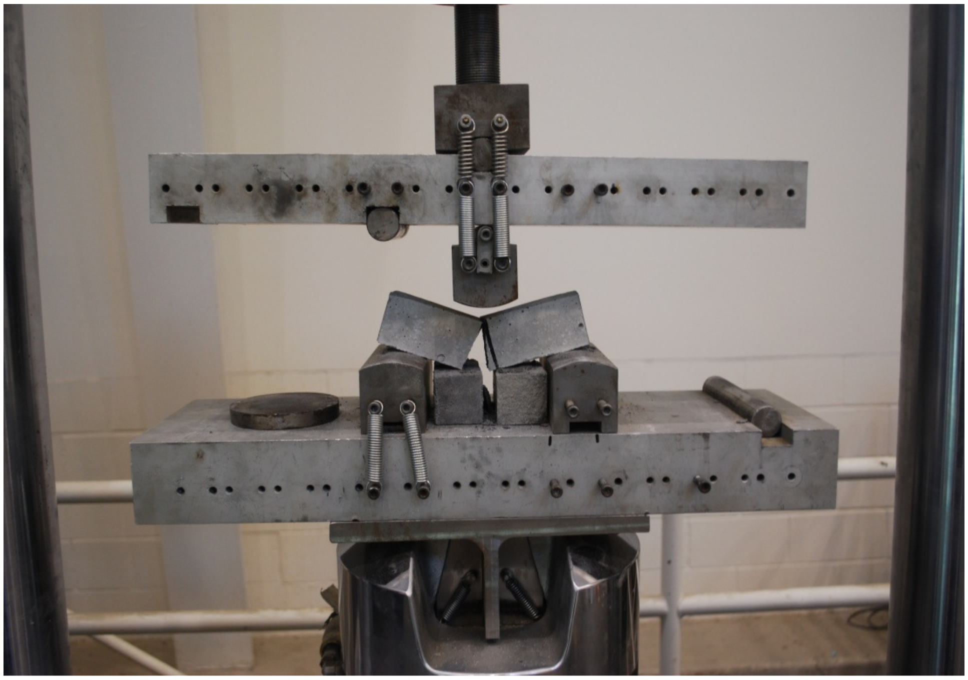


Figure 3.21: Broken flexural specimen after testing

3.5 Effect of MWNT Addition on Compressive Strength of Composite Mortar

In this section, effects of seven different types of MWNT addition on compressive strength of MWNT reinforced cementitious composite are presented. The composites were prepared using different mix proportions having different w/c ratio, different dosage rates and types of MWNT. Plasticizers were used in some mix proportions to increase the workability of the mix. The amount of plasticizer was also varied to explore the effect of different amount of plasticizer addition on the overall workability and strength of the composites. The w/c ratios were kept between 0.485 and 0.65. The dosage rates of MWNT were varied between 0.10% and 0.80% by weight of cement. Proportions of plasticizer to cement were ranged from 0.004 to 0.006. Control samples with no MWNT were also made. The compressive strengths of the samples were measured at 7 and 28 days. The obtained test data are presented and discussed in the sections through 3.5.1 to 3.5.7.

3.5.1 M1 Addition

Compressive strengths of 0.50% M1 reinforced composite with different mix proportions are shown in Figure 3.22. For samples with plasticizer, w/c ratio was kept as 0.485. Maximum 28 day compressive strength was found for composites with w/c ratio of 0.60. This strength was about 1.5% higher than the control sample. Composite with w/c ratio of 0.485 resulted in lowest strength at both 7 and 28 day, which were about 14% and 27% less than that of control samples, respectively. For 0.5% M1 reinforced composites, when w/c ratio was changed from 0.485 to 0.60, the 7 day and 28 day compressive strengths increased by about 19% and 38%, respectively. Although composites with plasticizer proportions of 0.004 and 0.005 yielded relatively higher 7 day strength, their 28 day strengths were quite lower than the control samples. In Table 3.3, total number of samples for each mix proportion and corresponding flow values and mean strengths with standard deviations are provided.

Variation in compressive strengths of 0.3% M1 reinforced composites at the age of 7 and 28 day, due to different w/c ratios and amount of plasticizers are presented in Figure 3.23. The maximum compressive strengths (both at 7 and 28 day) were obtained for w/c ratio of 0.60, as found in the previous case. Though the 7 day compressive strengths for samples with plasticizer proportion of 0.005 were higher than composites with w/c ratio of 0.60, the 28 day strength is about 6% higher for composite with w/c ratio of 0.60. The w/c ratio of 0.485 resulted in the lowest composite strength both at 7 and 28 days. The 7 day compressive strength for composite samples with w/c ratio of 0.485 was around 22% lower than that of composites with w/c ratio of 0.60. In case of 28 day compressive strength, this difference was about 13.5%. Use of plasticizer resulted in more workable mix which in turn resulted in increase in strength. The maximum increase was about 6% than that of control samples. Three different amounts of plasticizer were added and in all those three cases higher 7 day compressive strengths were obtained than the composites with 0.60 w/c ratio. However, the opposite phenomenon occurred at 28 day strength since plasticizer was not able to release entrapped water from the agglomerated nanotubes and less water remained available for hydration.

Composite samples were also made and tested by adding 0.8% of M1 for three different w/c ratios and plasticizer proportions. The composite strength for 0.8% addition of M1 is much less than that of 0.5% addition. The strength variations of composites with 0.80% M1 for different mixing proportions are presented in Figs. 3.24. For 0.8% M1 addition, the increases in 7 day and 28 day strengths were about 32% and 19% with the change in w/c ratio from 0.485 to 0.60. In this case, w/c ratio of 0.65 resulted in the highest compressive strength which was almost equal to the strength of control samples.

Addition of 0.5% M1 resulted in 1.5% increase in compressive strength as compared to control sample, whereas adding 0.8% M1 decreased the strength by about 16% for w/c ratio of 0.60. It was also observed that reduction in strength occurred with the increase in MWNT amount when plasticizer was used. In some cases of plasticizer addition, considerably high compressive strengths were achieved at 7 day (even higher than composites with w/c ratio of 0.6), though their 28 day compressive strengths were quite low. As amount of MWNT was increased, more aqueous solution was required for proper sonication and more water adhered to the MWNT surface due to greater surface area of nanotubes. This resulted in less strength due to less workability. Also higher dosage rate of MWNT has greater tendency to agglomerate and, therefore, uniform dispersion is difficult to achieve. In turn MWNT fail to fill nano space within cement grains which is very important for achieving proper reinforcement behavior. These are the reasons behind the higher strength of 0.80% M1 reinforced composites with w/c ratio of 0.65, though it was quite less than that of composites having lower dosage rate of MWNT. So there exists an optimum concentration of MWNT that could result in desired mechanical properties of composites.

Samples were also prepared by adding 0.1% and 0.2% M1 with w/c ratio of 0.6. Control samples were made (with no MWNT) for comparison purposes. For control sample the w/c ratio was taken as 0.485 as per ASTM C109 requirement. Control samples with w/c ratio of 0.60 were also prepared. The mean strength of control samples having w/c ratio of 0.60 was about 1.5% less than the samples with w/c ratio of 0.485. From Figure 3.25 it is apparent that 0.2 and 0.3% M1 reinforced composites produced almost equal compressive strengths. Addition of 0.3% M1 produced slightly higher strength (2.0% higher). As amount of M1 increased to 0.5% and 0.8%, reduction in strength was observed. Compressive strengths decreased by about 8% and 24% for 0.5% and 0.8% addition of M1, respectively, in comparison with 0.3% M1 addition. Composite with 0.3% MWNT resulted in the highest mean strength (both at 7 and 28 days) in case of M1 addition. 0.30% M1 added composites had 10 and 11% higher strengths than the control samples at 28 and 7 days, respectively. Composites with 0.8% of M1 yielded the minimum strengths (smaller than the control samples). Higher amount of MWNT not only decreases the workability but also has greater tendency of agglomeration, thus creating weaker zones.

Flow values for each sample set are also provided in Table 3.3. Composites with w/c ratio of 0.485 resulted in lowest flow values. It is apparent from Table 3.3 that for the same w/c ratio, the workability of mix decreases with the increase in MWNT concentration. The behavior was expected as more MWNT adhere to more water, causing workability to reduce. Addition of plasticizer increased the workability, but no increase in 28 day compressive strength as compared to control sample was found for higher dosage rates of MWNT. For 0.30% M1 reinforced composite addition of plasticizer yielded higher 28 day compressive strength than the normal cement mortar.

3.5.2 M2 Addition

Composites were also made and tested using M2 with different mix proportions. Since it was obvious that MWNT concentration higher than 0.3% resulted in weaker composites, the dosage rates used in this case were varied between 0.1% and 0.5%. It was found from M1 addition that composites with 0.1% and 0.2% MWNT also yielded higher compressive strength. However, in the previous case only one mix proportion (w/c ratio of 0.60) was used for these two dosage rates. Composites having 0.1% and 0.2% M2 were prepared with different mix proportions in this case.

Table 3.3: Test Information of M1 Reinforced Composites

Type of Sample	Amount of MWNT (%-)	w/c ratio	Amount of plasticizer (as part of cement by wt.)	No. of Samples *		Flow Values (%)	7 day mean compressive strength (MPa)	28 day mean compressive strength (MPa)
Control	NA	0.485	NA	S1*	3	25	24.3±2.30	35.7±2.40
				S2	3	32		
				S3	3	23		
				S4	3	37		
Composite	0.5	0.485	NA	S1	6	13	20.8±0.70	26.1±0.00
Composite	0.5	0.60	NA	S1	3	50	24.8±1.20	36.2±2.30
				S2	3	44		
				S3	3	45		
				S4	3	50		
Composite	0.5	0.65	NA	S1	6	82	24.8±0.97	35.4±1.60
Composite	0.5	0.485	0.005	S1	3	37	26.8±1.90	33.0±3.40
				S2	3	27		
Composite	0.5	0.485	0.004	S1	6	35	26.8±0.80	31.1±0.50
Composite	0.5	0.485	0.006	S1	6	52	21.1±1.20	25.7±1.10
Composite	0.3	0.485	NA	S1	6	25	22±0.30	34.8±0.70
Composite	0.3	0.60	NA	S1	3	40	27±1.10	39.5±1.80
				S2	3	53		
				S3	3	60		
Composite	0.3	0.485	0.005	S1	3	52	33.9±1.40	37.2±3.00
				S2	3	42		
Composite	0.3	0.485	0.004	S1	6	42	35.7±1.14	38±0.70
Composite	0.3	0.485	0.006	S1	6	60	34.1±1.50	37.7±2.60
Composite	0.8	0.485	NA	S1	6	3	18.0±0.40	25.3±1.60
Composite	0.8	0.60	NA	S1	6	25	23.9±1.40	30.1±1.60
Composite	0.8	0.65	NA	S1	6	37	23.2±1.20	35.7±1.30
Composite	0.8	0.485	0.005	S1	6	22	23.4±0.30	29.9±1.40
Composite	0.8	0.485	0.006	S1	6	37	22.8±0.20	33.2±0.80
Composite	0.1	0.60	NA	S1	6	62	21±0.50	38.2±0.60
Composite	0.2	0.60	NA	S1	6	55	26.3±0.60	38.7±1.70

*S1: Set 1, S2: Set2, S3: Set 3, S4: Set4

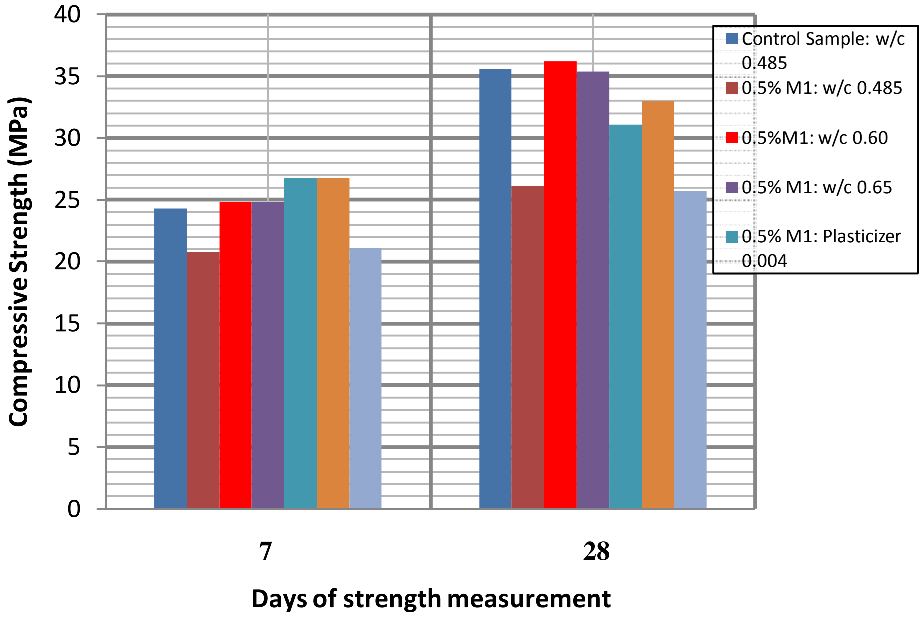


Figure 3.22: Compressive strength for different mix proportions of 0.5% M1 reinforced composites

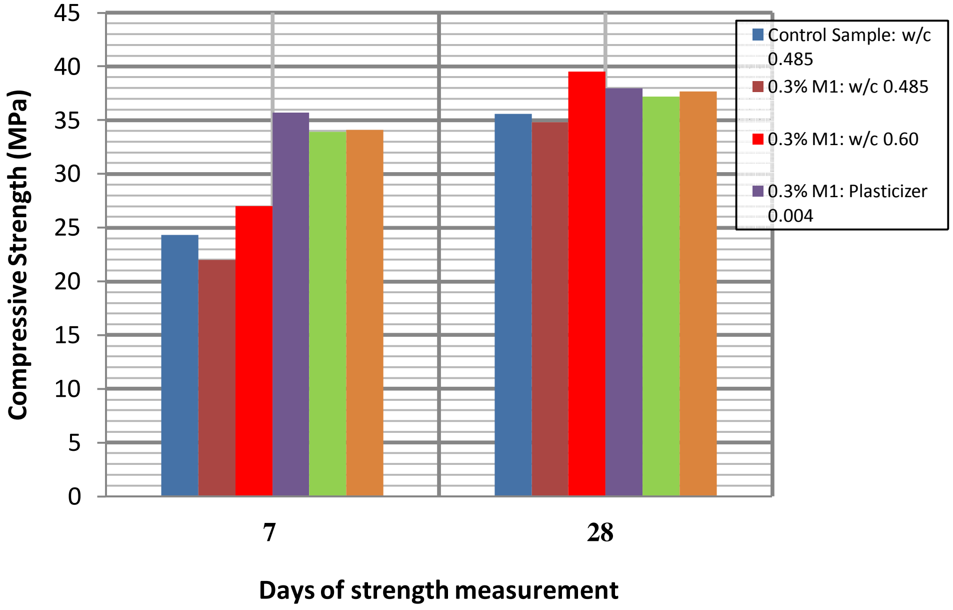


Figure 3.23: Compressive strength for different mix proportions of 0.3% M1 reinforced composites

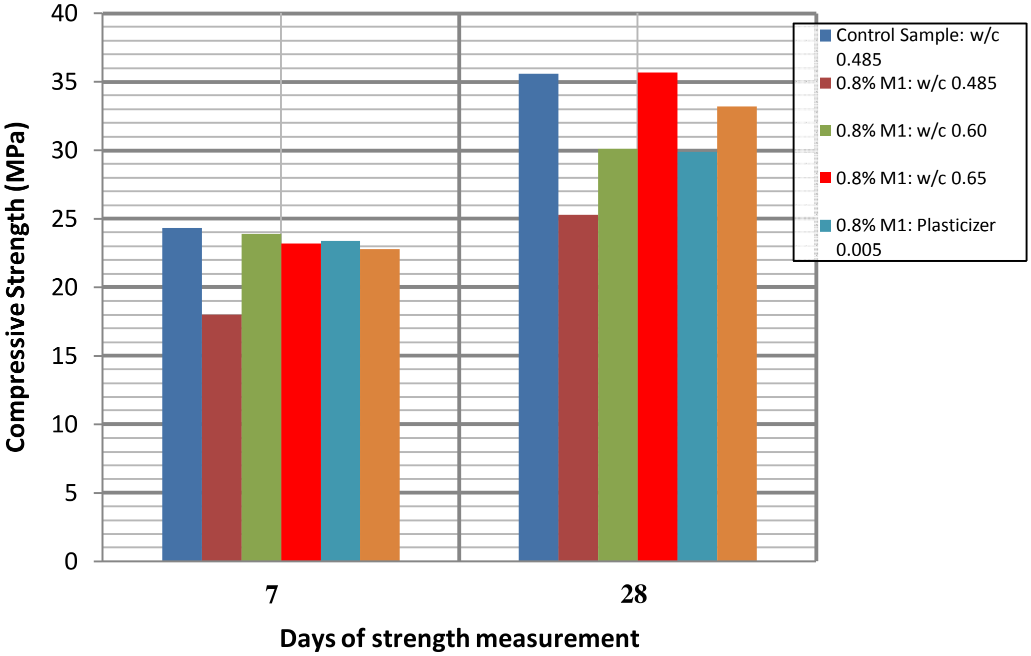


Figure 3.24: Compressive strength for different mix proportions of 0.8% M1 reinforced composites

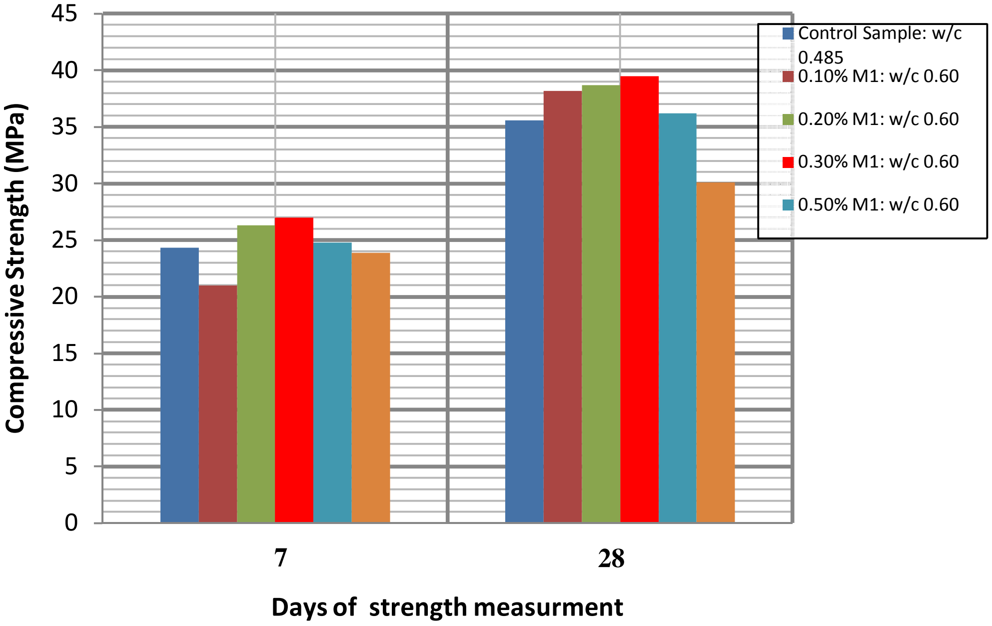


Figure 3.25: Compressive strength of control and M1 reinforced samples with w/c: 0.60

Figure 3.26 shows the compressive strengths of 0.3% M2 reinforced composites with different mix proportions. Seven day compressive strengths were higher for all the composites as compared to the control samples. The maximum compressive strength was achieved for composites with w/c ratio of 0.60 at both 7 and 28 days and these strengths were 28 and 11% higher than the strength of control samples, respectively. Composites were also prepared using w/c ratio of 0.55 that also resulted in higher strength. Seven day strength was 25% and 28 day strength was 8.5% higher than the control samples in this case. It was found that addition of plasticizer resulted in lesser 28 day compressive strength as also found in M1 addition. Composites with w/c ratio of 0.485 had lower (7%) 28 day compressive strength than the control samples though 7 day strength was about 15 % higher for the composite. This again proves the fact that presence of nanotubes accelerates the hydration process at early age of cement mortar.

Variations of compressive strengths for 0.2% addition of M2 are presented in Figure 3.27. Similar phenomena were also observed for these composites samples. The highest compressive strength was obtained for composites with w/c ratio of 0.60 at both 7 and 28 days. The 7 day strength was 31% and 28 day strength was 10% higher than the control samples. Composites with w/c ratio of 0.485 had the lowest strength both at 7 and 28 days, though 7 day strength was 12% higher as compared to control samples. The mix proportion having w/c ratio of 0.55 also achieved fairly high compressive strength in comparison with control samples at 28 day and it was about 4% greater. Addition of plasticizer again resulted in lower 28 day compressive strength than that of control samples.

Figure 3.28 presents the compressive strength variation in 0.1% M2 reinforced composites having different mix proportions. Composites having w/c ratio of 0.60 yielded about 26% higher 7 day strength and about 8.5% higher 28 day strength in comparison with control samples. The mix proportion with w/c ratio of 0.485 had 28 day compressive strength almost equal to the control samples (about 2% lower). This behavior was anticipated since lower concentration of nanotubes has lower water demand in terms of workability due to their lower surface area and should achieve similar amount of strength as achieved by control samples. Composites containing plasticizer produced higher 7 day strength (21% higher) but obtained 3% lower 28 day strength as compared to control samples.

A comparison of compressive strengths of different amounts of M2 reinforced composites having the w/c ratio of 0.60 is presented in Figure 3.29. The mix proportion with w/c ratio of 0.60 is chosen as it yielded the highest strength in all cases. Composites with 0.5% and 0.8% M2 were also made with w/c ratio of 0.60 to have more insight of the composite behavior. M2 dosage rates of 0.1, 0.2 and 0.3% obtained almost equal compressive strengths with 0.3% dosage rate obtained maximum compressive strength. Composites with 0.3% M2 had about 1.5% and 3% higher compressive strengths than 0.2% and

0.1% dosage rates of M2. M2 addition of 0.5% and 0.8% addition resulted in lower 28 day compressive strength with reference to the control samples, though they produced slightly higher 7 day strength. The 28 day strength of 0.5% M2-cement mortar was about 6% lower as compared to the control sample. For 0.8% M2 addition the percentage of strength reduction was about 8.5%. It is apparent from Figure 3.38 that an upward trend in the 28 day compressive strength occurred from dosage rate of 0.1% to 0.3% and after that the strength reduced quite sharply. In case of 7 day compressive strength, all the dosage rates produced higher compressive strengths relating to the control samples. Therefore, it can be concluded that the presence of nanotubes helps cement-mortar to achieve relatively greater strength at early stages. Table 3.4 provides the sample numbers, flow values, mean strengths and corresponding standard deviations.

3.5.3 M3 Addition

*C*ompressive strengths of M3 reinforced composites are discussed in this part of the study. Figure 3.30 shows the strength variations of 0.3% M3-cement composites with the variation in mix proportions. Similar to the earlier cases, three different w/c ratios of 0.485, 0.55 and 0.60 were used. Composites with w/c ratios of 0.55 and 0.60 produced equal 28 day compressive strengths which were 10% higher than the control samples. The seven day compressive strength of mix proportion having w/c ratio of 0.55 had 25% greater and composite containing w/c ratio of 0.60 had 23% greater strength as compared to control samples. In comparison with M1 and M2 reinforced composites having w/c ratio of 0.485, M3 reinforced composites having the same w/c ratio obtained relatively higher strength. The compressive strength was only 4% less than that of control samples in this case. Plasticizer addition increased the 7 day compressive strength by 26% and 28 day compressive strength by 7% as compared to control samples.

Compressive strengths of samples prepared with 0.2% M3 are presented in Figure 3.31. The maximum strength was obtained for mix proportion with 0.60 w/c ratio. The 7 and 28 day compressive strength was 24.5 and 11% higher than that of control samples, respectively. Composites having w/c ratio of 0.55 obtained higher compressive strength at 7 day but produced similar strength at 28 day as compared to control samples. Composites with w/c ratio of 0.485 produced slightly higher 7 day strength (1.0%) and 3% lower 28 day strength as compared to the control samples. Concerning control samples, composites made with plasticizer addition had 25% higher 7 day and 1.3% higher 28 day compressive strengths.

In Figure 3.32, compressive strengths of 0.1% M3 reinforced composites are shown. The highest compressive strength was obtained by mix proportion with w/c ratio of 0.60. The increase was 23.5 and 8.5% at 7 and 28 day than that of control samples, respectively. The increment in compressive strength for w/c ratio of 0.55 was 20% for 7 day and 8% for 28 day compressive strengths.

The plasticizer addition increased the 7 day compressive strength by 23.5%, but decreased the 28 day compressive strength by 0.50%.

Since for all dosage rates, the mix proportion having w/c ratio of 0.60 yielded maximum compressive strengths both at 7 and 28 day (except for 7 day compressive strength of 0.3% M3 composites which was only 2% lower than the maximum), a comparison between compressive strengths of composites for different M3 dosage rate with w/c ratio of 0.60 is shown in Figure 3.33. Composites with dosage rate of 0.2 and 0.3% had almost equal 7 and 28 day compressive strengths, which were about 23 and 11% higher than the control samples, respectively. The 0.1% M3 reinforced composites produced similar 7 and 28 day compressive strengths as obtained by 0.2 and 0.3% M3 added composites (28 day compressive strength was only 1.5% lower than the other two dosage rates). For comparison, samples with 0.5% dosage rate of M3 were also made. Like the previous two cases, 0.5% dosage rate resulted in lower 28 day compressive strength than the control samples and strength was reduced by 1.6%. However, the 7 day compressive strength was higher than the control samples (about 12% higher).

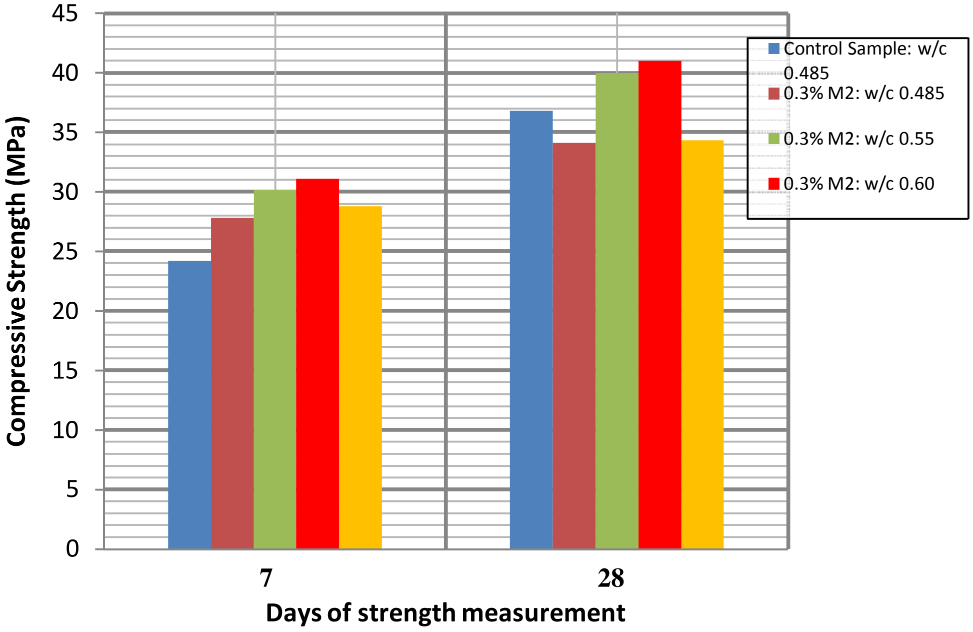


Figure 3.26: Compressive strength for different mix proportions of 0.3% M2 reinforced composites

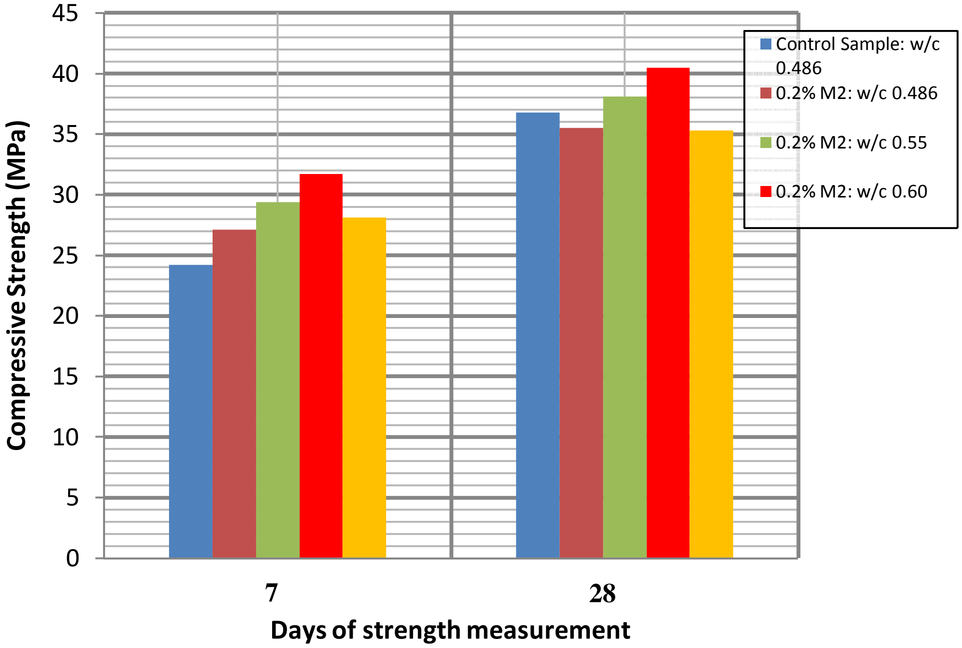


Figure 3.27: Compressive strength for different mix proportions of 0.2% M2 reinforced composites

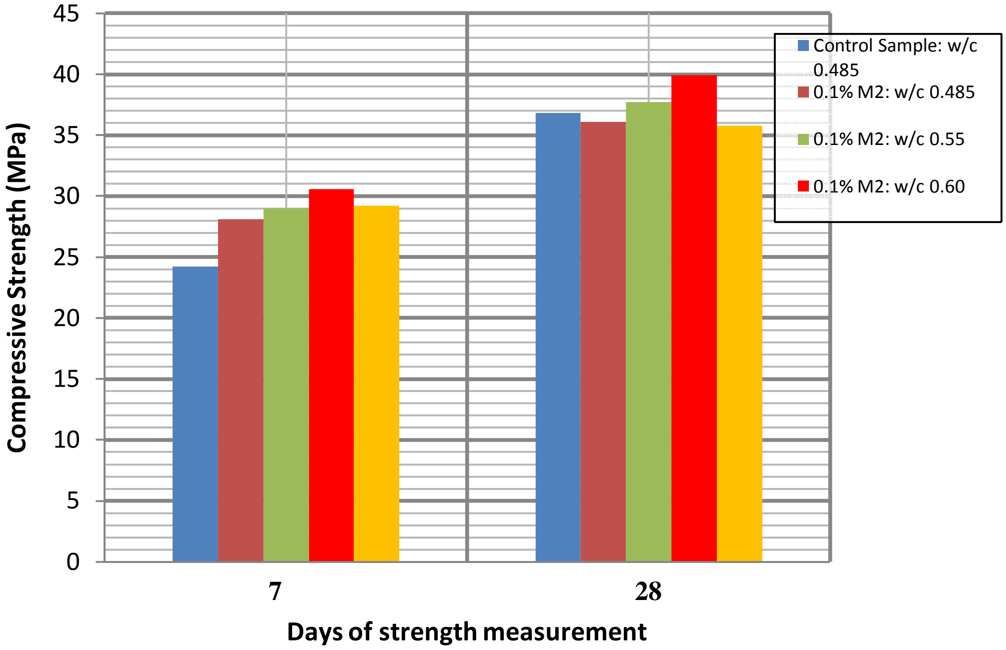


Figure 3.28: Compressive strength for different mix proportions of 0.1% M2 reinforced composites

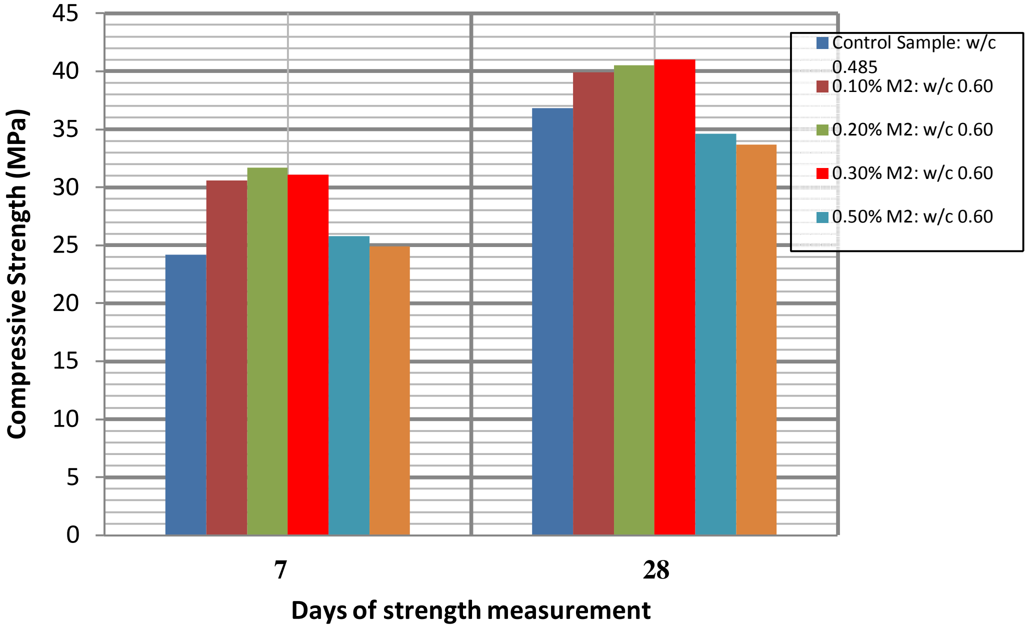


Figure 3.29: Compressive strength of control and M2 reinforced samples with w/c: 0.60

Table 3.4: Test Information of M2 Reinforced Composites

Type of Sample	Amount of MWNT (%)	w/c ratio	Amount of plasticizer (as part of cement by wt.)	No. of Samples *		Flow Values (%)	7 day mean compressive strength (MPa)	28 day mean compressive strength (MPa)
Control	NA	0.485	NA	S1*	3	32	24.2±2.30	36.8±2.10
				S2	3	23		
				S3	3	37		
Composite	0.3	0.485	NA	S1	6	15	27.8±1.00	34.1±3.00
Composite	0.3	0.60	NA	S1	3	48	31.1±1.70	41.0±1.45
				S2	3	37		
				S3	3	35		
				S4	3	35		
Composite	0.3	0.55	NA	S1	6	30	30.2±1.40	40±1.45
Composite	0.3	0.485	0.005	S1	6	37	28.8±0.21	34.3±2.10
Composite	0.2	0.485	NA	S1	6	18	27.1±0.90	35.5±1.60
Composite	0.2	0.60	NA	S1	6	47	31.7±0.20	40.5±1.90
Composite	0.2	0.55	NA	S1	6	42	29.4±1.10	38.1±1.30
Composite	0.2	0.485	0.005	S1	6	40	28.1±1.20	35.3±1.70
Composite	0.1	0.485	NA	S1	6	25	28.1±0.80	36.1±1.20
Composite	0.1	0.60	NA	S1	6	55	30.6±0.50	39.9±0.30
Composite	0.1	0.55	NA	S1	6	52	29.0±1.20	37.7±0.60
Composite	0.1	0.485	0.005	S1	6	46	29.2±0.30	35.8±1.40
Composite	0.5	0.60	NA	S1	6	40	25.8±1.80	34.6±1.20
Composite	0.8	0.60	NA	S1	6	25	24.9±1.20	33.7±0.10

*S1: Set 1, S2: Set 2, S3: Set 3, S4: Set 4

3.5.4 M4 Addition

Samples were made by adding 0.3% M4 having w/c ratio of 0.485, 0.60 and 0.55. Plasticizer proportion of 0.005 was also used in one mix proportion. The compressive strengths of these composites are shown in Figure 3.34. At 7 day, the compressive strengths of composites with w/c ratio of 0.485, 0.55 and 0.60 were 11, 23.5 and 26.5% greater than the control sample strength, respectively. The 28 day compressive strengths for these cases were 3% lower, 4.5% and 12.5% higher as compared to the control samples, respectively.

Samples with plasticizer resulted in 4% less 28 day compressive strength relating to the control samples, though they obtained higher strengths at 7 day.

Figure 3.35 presents compressive strengths of various 0.2% M4 reinforced composites. The mix proportion with w/c ratio of 0.60 yielded the maximum compressive strength both at 7 and 28 day. This increment was 24 and 13.8% at 7 and 28 day, respectively, in comparison with the control samples. As compared to the control samples, composites with plasticizer also obtained higher compressive strength at 7 day and 28 day.

The changes in compressive strengths of 0.1% M4-cement composites with change in mix proportions are provided in Figure 3.36. Similar trend was found, with composites having w/c ratio of 0.60 producing the highest strengths both at 7 and 28 days. In respect to the control samples, the 7 day strength was 29% and 28 day strength was 9% higher for these composites. Plasticizer addition also yielded greater strengths than the control samples as found in lower concentration of MWNT addition in previous cases. The mix proportion containing w/c ratio of 0.485 produced 8.5% higher and 2% lower compressive strengths at 7 day and 28 day, respectively.

In Figure 3.37, compressive strengths of M4 reinforced composites having w/c ratio of 0.60 with different dosage rates are presented. Composites with 0.2% dosage rate produced slightly higher compressive strengths than the 0.3% dosage rate at 28 day. In comparison with the control samples, M4 reinforced composites with dosage rates of 0.2% and 0.3% had 13.8% and

12.5% higher compressive strengths at 28 day, respectively. The 7 day compressive strength for 0.2% M4 addition was 24% greater and for 0.3% M4 addition was 26.5% greater than that of control samples. Composites with 0.5% and 0.8% dosage rates were not prepared, as these higher concentrations resulted in quite lower compressive strengths in reference to the control samples, particularly at 28 day in earlier cases. The M4 reinforced composites with 0.1% dosage rate obtained 29% higher 7 day and 9% higher 28 day compressive strengths relating to the control samples.

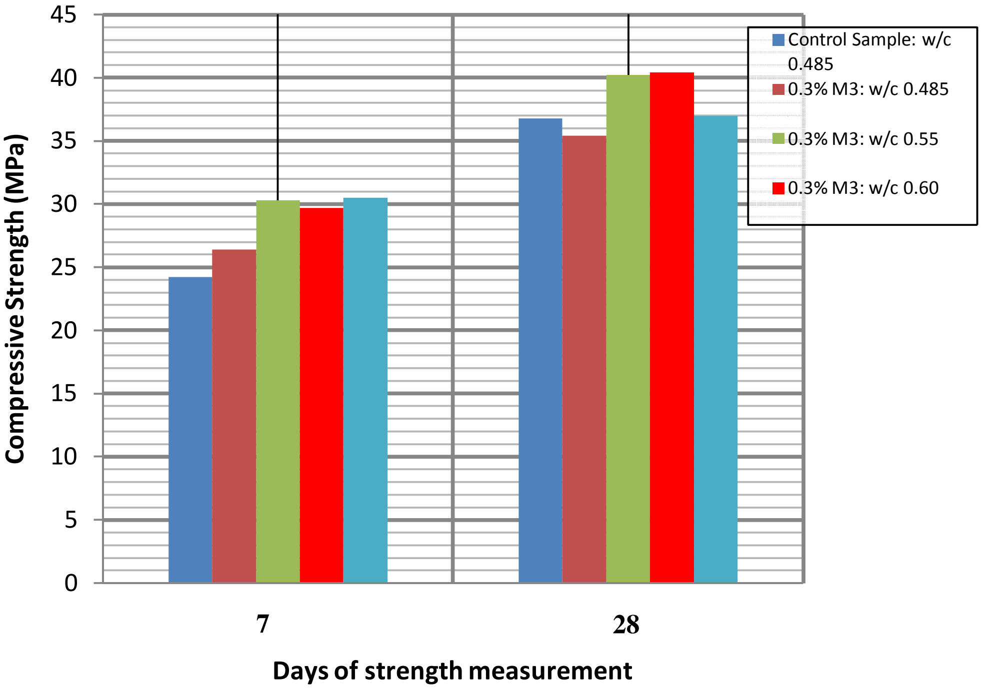


Figure 3.30: Compressive strength for different mix proportions of 0.3% M3 reinforced composites

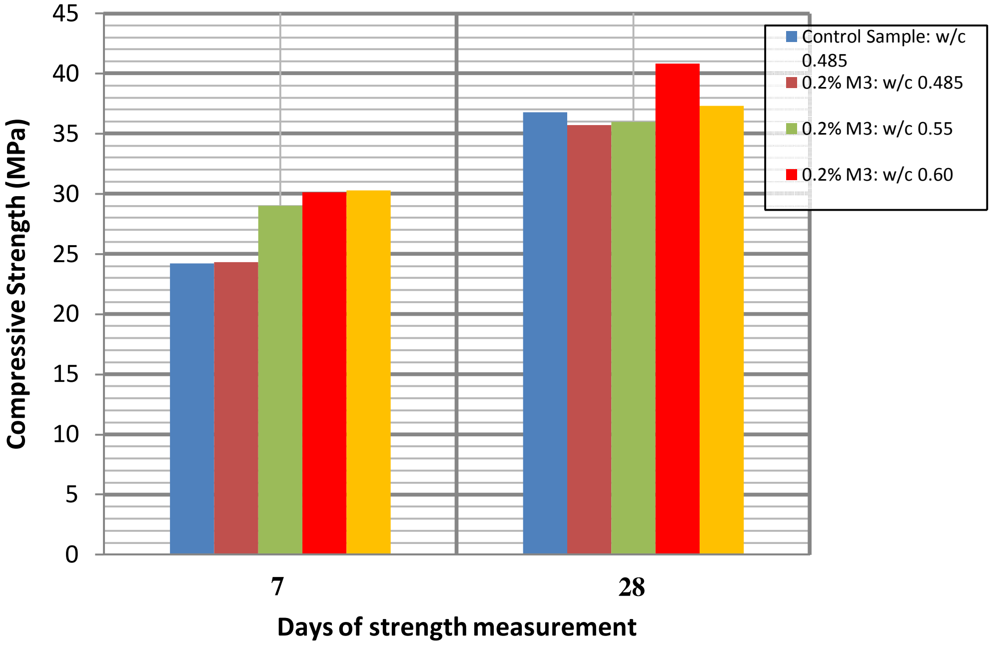


Figure 3.31: Compressive strength for different mix proportions of 0.2% M3 reinforced composites

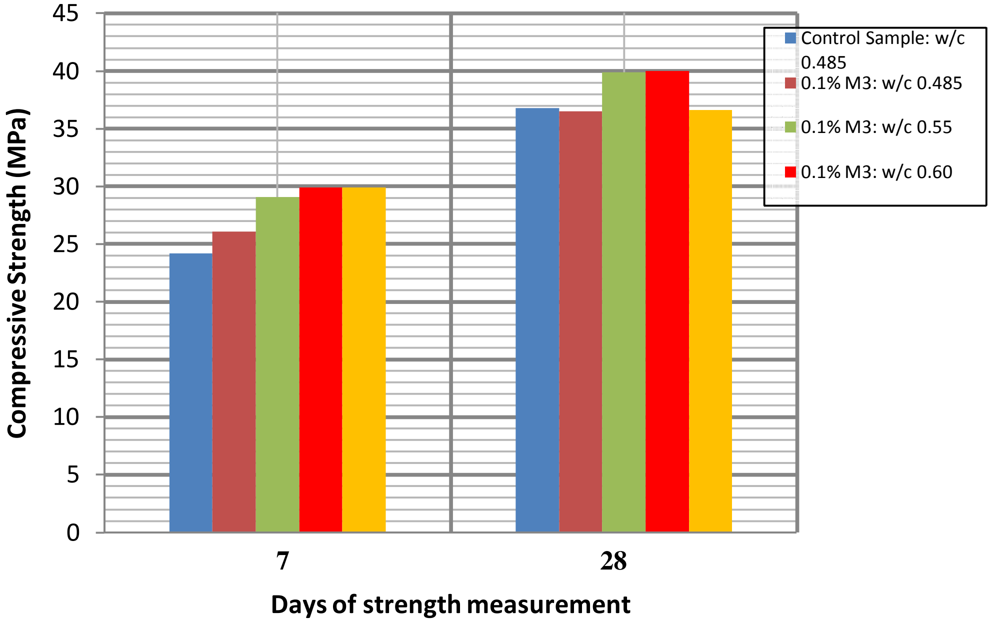


Figure 3.32: Compressive strength for different mix proportions of 0.1% M3 reinforced composites

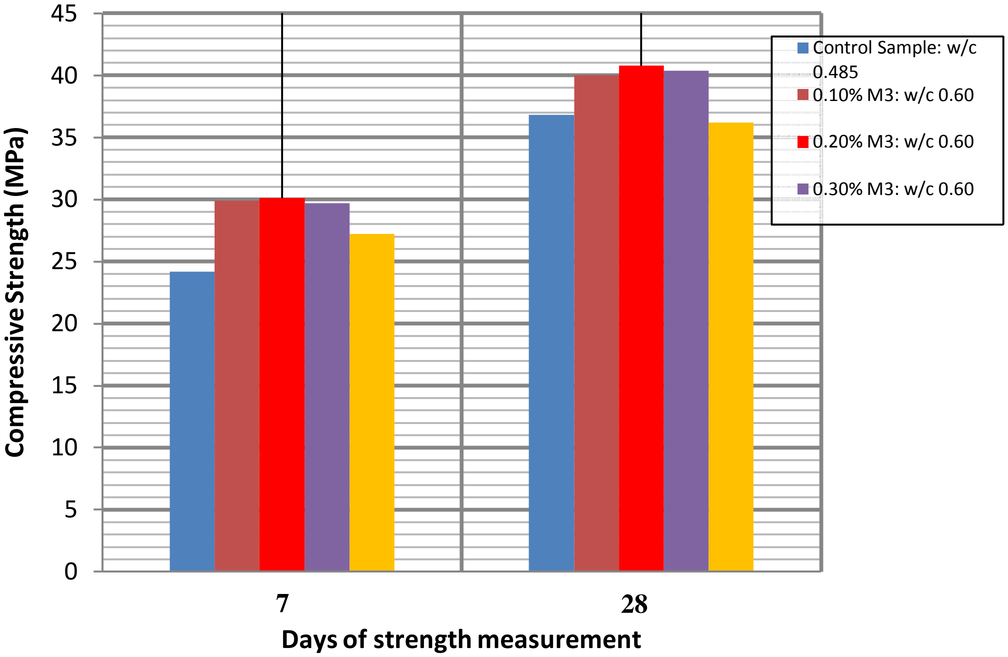


Figure 3.33: Compressive strength of control and M3 reinforced samples with w/c: 0.60

3.5.5 M5 Addition

In this section, the compressive strengths of M5-cement composites having various dosage rates and mix proportions are provided and discussed. Variation of strengths at both 7 day and 28 day for 0.3% dosage of M5 is given in Figure 3.38. The mix proportion having w/c ratio of 0.60 produced the maximum compressive strength. The 7 day and 28 day strengths were 17% and 1% higher than that of control samples. As compared to other nanotubes reinforced composites, a deviation was found in the increment of the 28 day compressive strength in this case. It was also found that composites with w/c ratio of 0.55 obtained 0.5% greater strength at 28 day as compared to control samples. This may be due to improper sonication and inadequate attainment of reinforcement through MWNT. Later it was found that for other two MWNT (M6 and M7), the 28 day compressive strength for mix proportion having w/c ratio of 0.60 was comparable to compressive strengths of M1- M4 reinforced composites. Therefore, the only exception was found for M5 addition and this issue was eventually addressed in the second phase of the study with larger number of samples. The mix proportion with plasticizer addition gained 18% higher 7 day strength, but had 2.5% lesser strength as compared to the control samples.

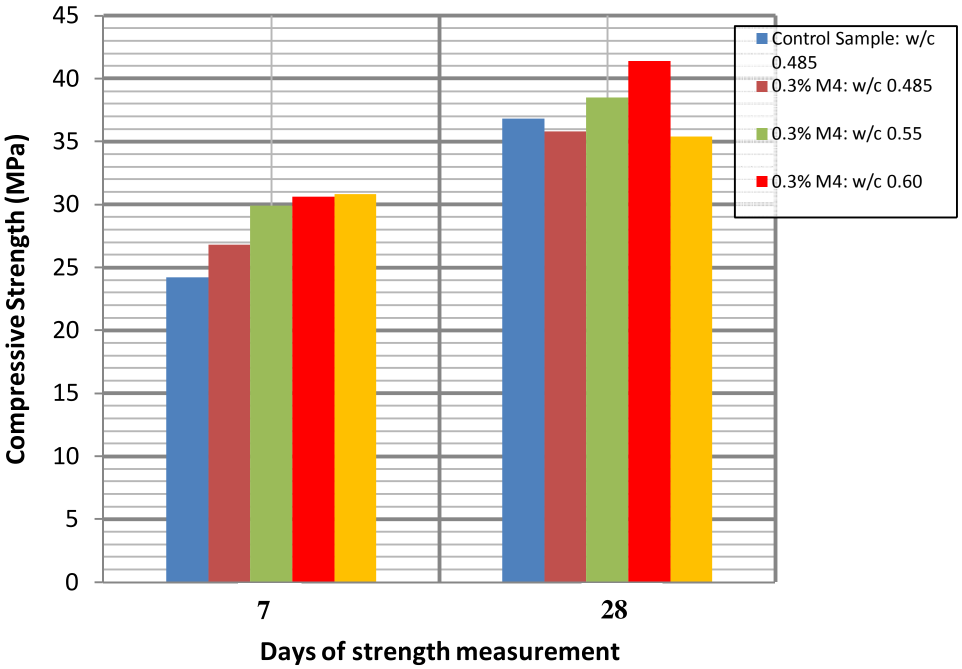


Figure 3.34: Compressive strength for different mix proportions of 0.3% M4 reinforced composites

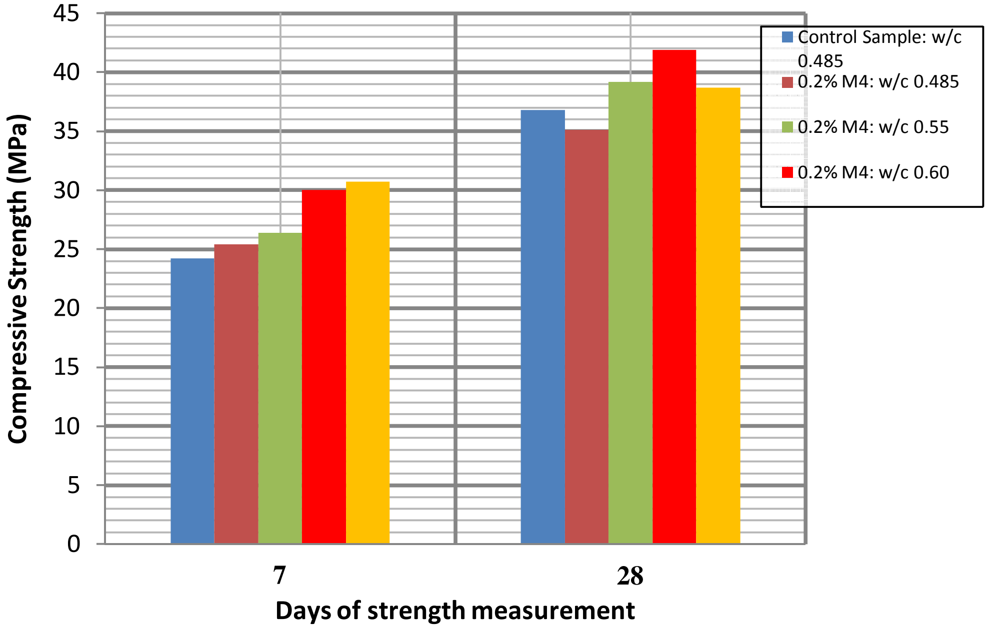


Figure 3.35: Compressive strength for different mix proportions of 0.2% M4 reinforced composites

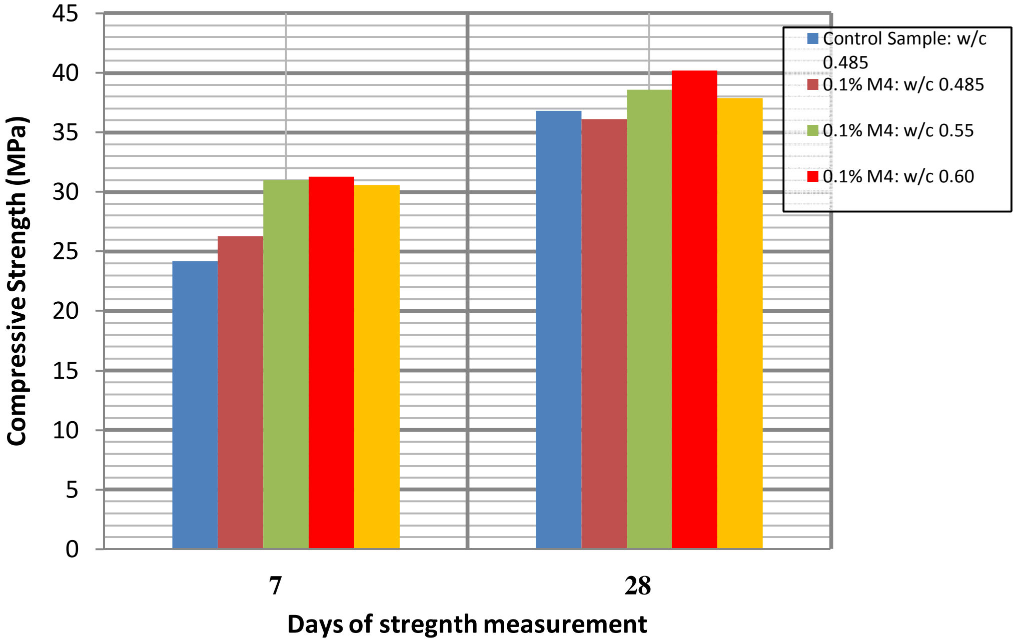


Figure 3.36: Compressive strength for different mix proportions of 0.1% M4 reinforced composites

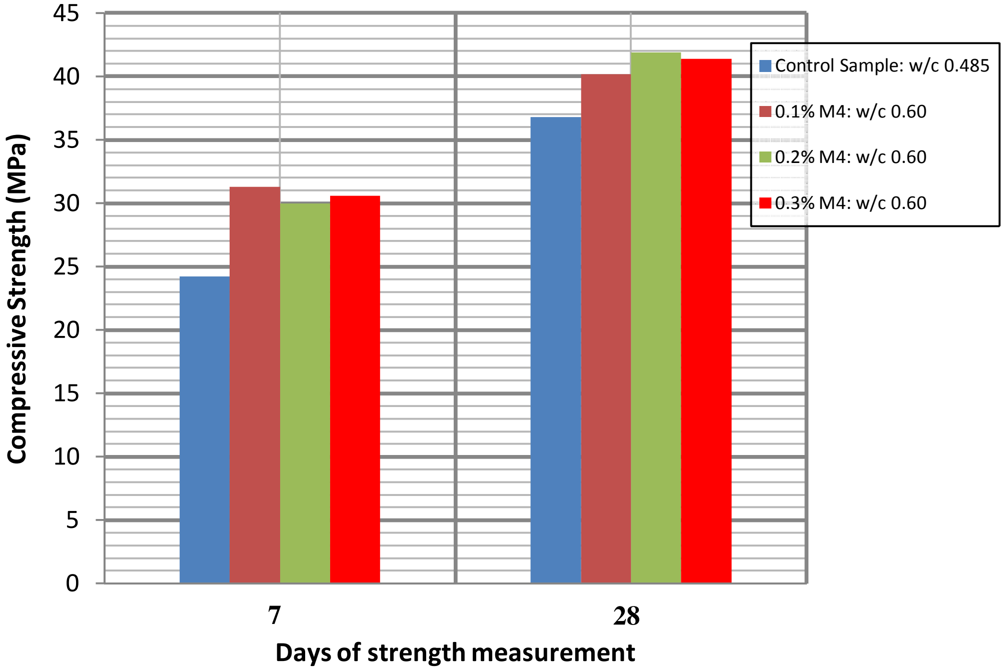


Figure 3.37: Compressive strength of control and M4 reinforced samples with w/c: 0.60

Figure 3.39 shows compressive strengths of 0.2% M5-cement composites. Yet again, composites with w/c ratio of 0.60 obtained maximum strengths both at 7 and 28 days. The increase in strength at 7 day was 8% and at 28 day was 9.5% as compared to control samples. In Figure 3.40, the change in compressive strengths with the change in dosage rates are shown for M5 reinforced composites with w/c ratio of 0.60. Composites with 0.2% M5 yielded the highest compressive strength at 28 day, which was 9.5% higher than the controls samples. The peak 7 day compressive strength (28.5% higher relating to control samples) was produced by 0.1% amount of M5. Composites with 0.5% M5 produced about 8.5% lower strength as compared to control samples at 28 day, though the 7 day compressive strength was 11% more than that of control samples.

Table 3.5: Test Information of M3 Reinforced Composites

Type of Sample	Amount of MWNT (%)	w/c ratio	Amount of plasticizer (as part of cement by wt.)	No. of Sam--ples *		Flow Values (%)	7 day mean comp-ressive strength (MPa)	28 day mean comp-ressive strength (MPa)
Control	NA	0.485	NA	S1*	3	32	24.2±2.30	36.8±2.10
				S2	3	23		
				S3	3	37		
Composite	0.3	0.485	NA	S1	6	13	26.4±0.97	35.4±1.50
Composite	0.3	0.60	NA	S1	3	32	29.7±0.14	40.4±3.10
				S2	3	48		
				S3	3	48		
Composite	0.3	0.55	NA	S1	3	40	30.3±1.00	40.2±1.00
				S2	3	42		
Composite	0.3	0.485	0.005	S1	6	42	30.5±0.60	37.0±1.17
Composite	0.2	0.485	NA	S1	6	8	24.3±0.41	35.7±0.85
Composite	0.2	0.60	NA	S1	6	52	30.1±0.90	40.8±1.66
Composite	0.2	0.55	NA	S1	6	42	29.0±1.45	36.0±2.00
Composite	0.2	0.485	0.005	S1	6	35	30.3±0.66	37.3±1.20
Composite	0.1	0.485	NA	S1	6	15	26.1±1.20	36.5±1.66
Composite	0.1	0.60	NA	S1	6	55	29.9±1.00	40.0±1.45
Composite	0.1	0.55	NA	S1	6	45	29.1±0.83	39.9±1.50
Composite	0.1	0.485	0.005	S1	6	53	29.9±0.90	36.6±1.35
Composite	0.5	0.60	NA	S1	6	37	27.2±0.55	36.2±1.45

*S1: Set 1, S2: Set 2, S3: Set 3

Table 3.6: Test Information of M4 Reinforced Composites

Type of Sample	Amount of MWNT (%)	w/c ratio	Amount of plasticizer (as part of cement by wt.)	No. of Samples *		Flow Values (%)	7 day mean compressive strength (MPa)	28 day mean compressive strength (MPa)
Composite	0.3	0.485	NA	S1*	6	15	26.8±0.76	35.8±1.00
Composite	0.3	0.60	NA	S1	6	52	30.6±0.83	41.4±1.00
Composite	0.3	0.55	NA	S1	6	42	29.9±0.70	38.5±2.00
Composite	0.3	0.485	0.005	S1	6	40	30.8±1.10	35.4±0.40
Composite	0.2	0.485	NA	S1	6	22	25.4±0.83	35.1±1.24
Composite	0.2	0.60	NA	S1	6	60	30.0±1.24	41.9±0.34
Composite	0.2	0.55	NA	S1	6	48	26.4±0.41	39.2±0.21
Composite	0.2	0.485	0.005	S1	6	40	30.7±1.10	38.7±1.66
Composite	0.1	0.485	NA	S1	6	27	26.3±0.76	36.1±1.45
Composite	0.1	0.60	NA	S1	6	65	31.3±1.20	40.2±0.50
Composite	0.1	0.55	NA	S1	6	52	31.0±0.30	38.6±1.24
Composite	0.1	0.485	0.005	S1	6	43	30.6±0.83	37.9±1.10

*S1: Set 1, S2: Set 2, S3: Set 3

Table 3.7: Test Information of M5 Reinforced Composites

Type of Sample	Amount of MWNT (%)	w/c ratio	Amount of plasticizer (as part of cement by wt.)	No. of Samples *		Flow Values (%)	7 day mean compressive strength (MPa)	28 day mean compressive strength (MPa)
Composite	0.3	0.485	NA	S1*	6	10	29.1±0.97	32.8±1.70
Composite	0.3	0.60	NA	S1	3	45	28.3±1.00	37.2±1.50
				S2	3	37		
Composite	0.3	0.55	NA	S1	6	30	30.2±0.83	37.0±1.45
Composite	0.3	0.485	0.005	S1	6	25	28.6±0.83	35.9±0.76
Composite	0.2	0.485	NA	S1	6	15	24.4±1.00	33.0±1.38
Composite	0.2	0.60	NA	S1	3	62	26.2±1.24	40.3±1.80
				S2	3	43		
Composite	0.2	0.55	NA	S1	6	37	25.5±1.10	36.8±1.50
Composite	0.2	0.485	0.005	S1	6	33	26.6±1.20	36.8±0.60
Composite	0.1	0.60	NA	S1	6	57	31.1±0.10	39.4±1.66
Composite	0.5	0.60	NA	S1	6	33	26.8±0.14	33.7±1.38

*S1: Set 1, S2: Set 2, S3: Set 3

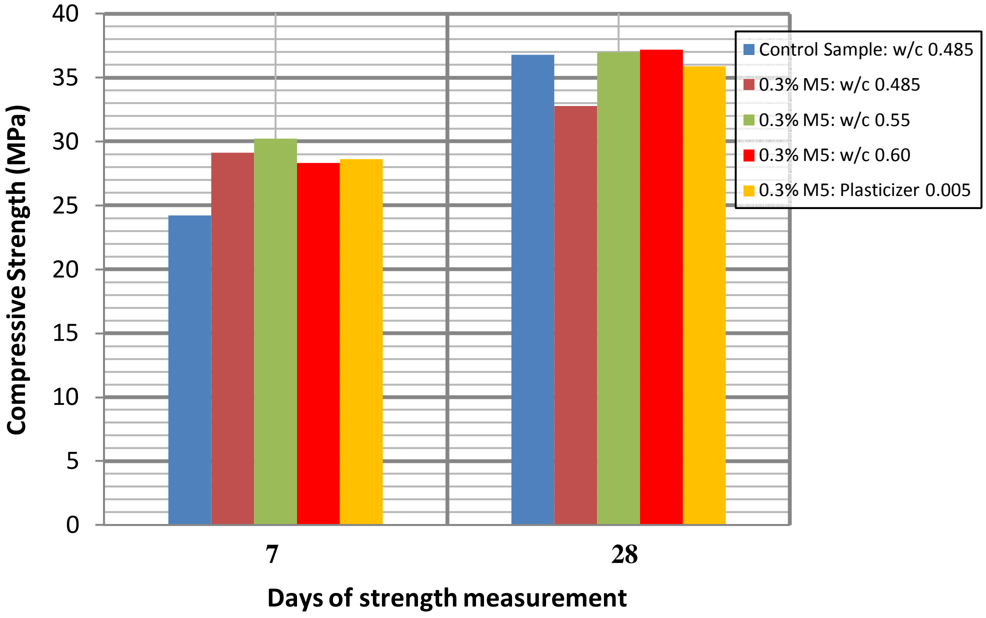


Figure 3.38: Compressive strength for different mix proportions of 0.3% M5 reinforced composites

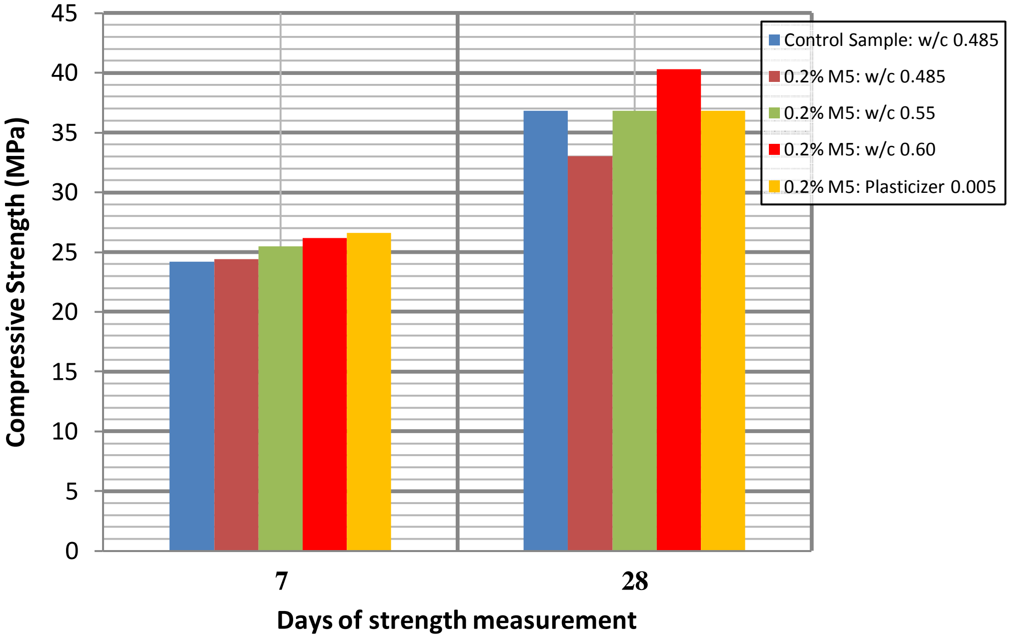


Figure 3.39: Compressive strength for different mix proportions of 0.2% M5 reinforced composites

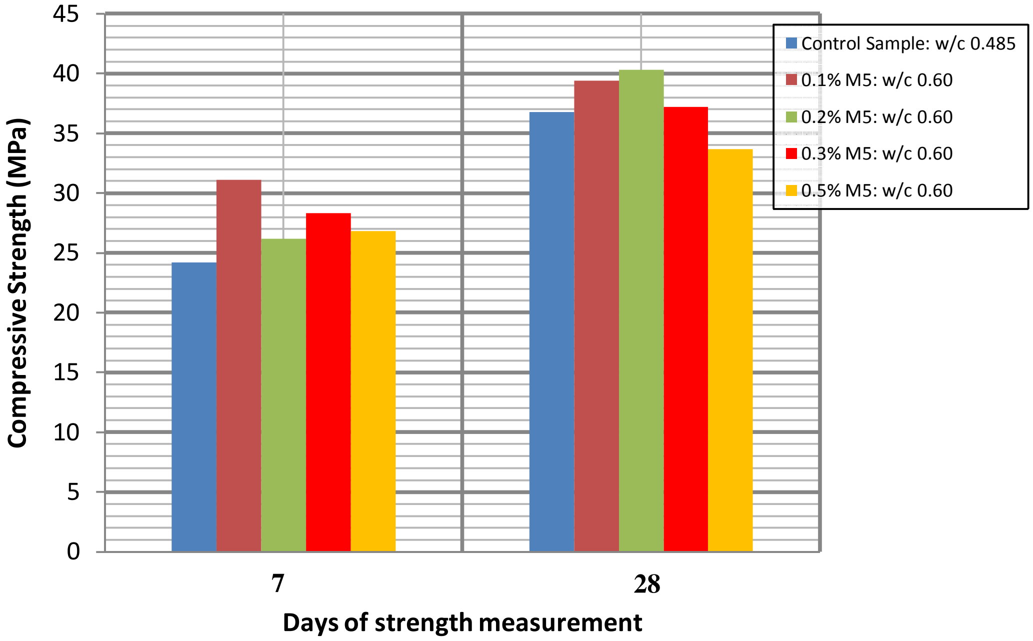


Figure 3.40: Compressive strength of control and M5 reinforced samples with w/c: 0.60

3.5.6 M6 Addition

Figure 3.41 shows compressive strengths of M6 reinforced composites with four different mix proportions. The peak compressive strength of 40.3 MPa at 28 day, 9.5% higher than that of control samples, was achieved by the mix proportion having w/c ratio of 0.60. The corresponding 7 day compressive strength was 31.4 MPa which was 30% greater relating to control samples. Composites prepared with w/c ratio of 0.55 also attained fairly higher compressive strength, both at 7 and 28 days, as compared to control samples. The corresponding 7 day compressive strength was 31.7 MPa and 28 day compressive strength was 40.1 MPa. The mix proportion having w/c ratio of 0.485 produced lesser compressive strength at 28 day, but obtained a little higher compressive strength at 7 day. Addition of plasticizer did not have significant effect on 28 day compressive strength, though these composites resulted in relatively high 7 day compressive strength.

In Figures 3.42 and 3.43, compressive strengths of 0.2% and 0.1% M6 reinforced composites are shown. For both cases, mix proportion with w/c ratio of 0.60 produced maximum compressive strength at 28 day. The addition of 0.2 and 0.1% M6 yielded 8.5 and 7.5% higher 28 day compressive strength as compared to control samples, respectively. The compressive strengths at 7 day for these cases were 28 and 22% higher, respectively. Composites with w/c ratio of 0.485 had the lowest compressive strengths both at 7 and 28 days for 0.2 and 0.1% dosage rates of M6. Like before, MWNT added composites with plasticizer addition produced considerably greater 7 day compressive strength, but 28 day compressive strengths were lower than or equal to the control samples.

A comparison of compressive strengths for different dosage rates having mix proportion with w/c ratio of 0.60 is shown in Figure 3.44. Dosage rates of 0.1, 0.2 and 0.3% yielded greater compressive strengths than that of control samples, both at 7 day and 28 day, with 0.3% concentration producing the maximum compressive strength. Addition of 0.5% M6 resulted in 3% lesser 28 day compressive strength as compared to control samples.

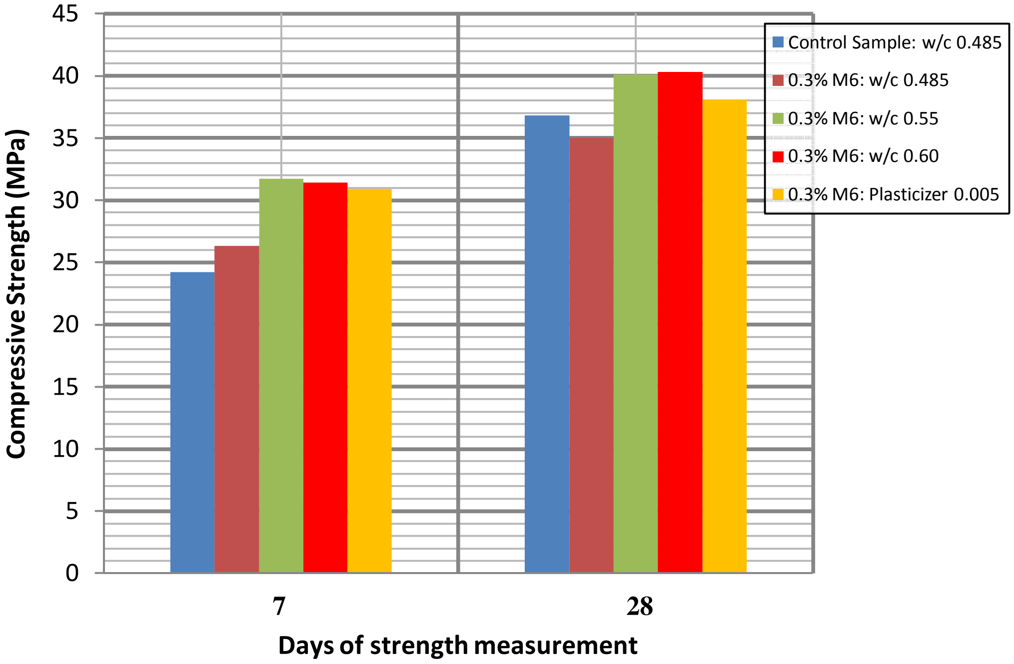


Figure 3.41: Compressive strength for different mix proportions of 0.3% M6 reinforced composites

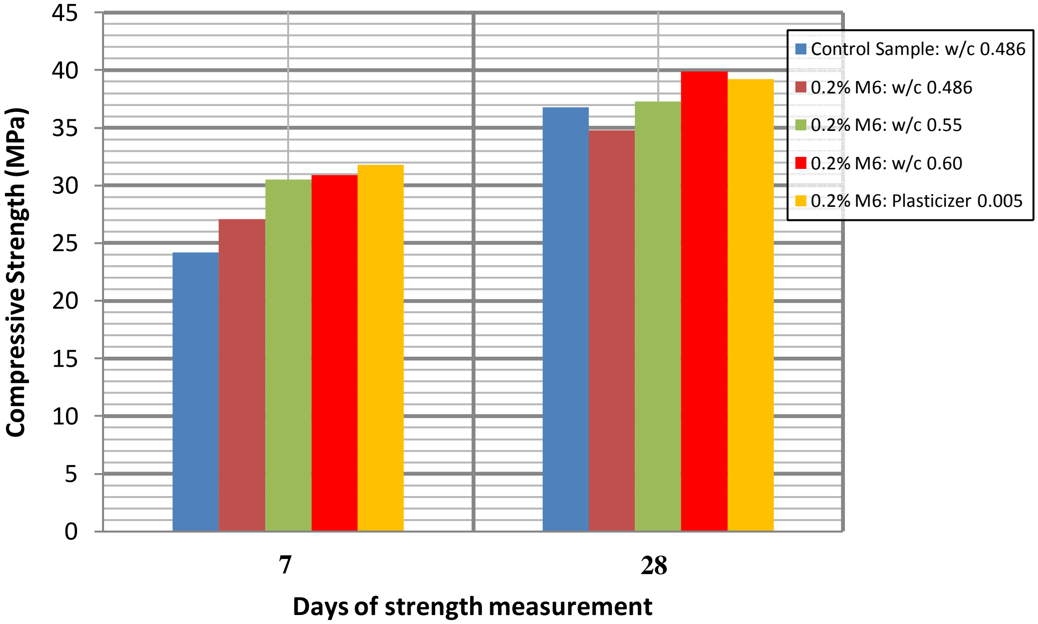


Figure 3.42: Compressive strength for different mix proportions of 0.2% M6 reinforced composites

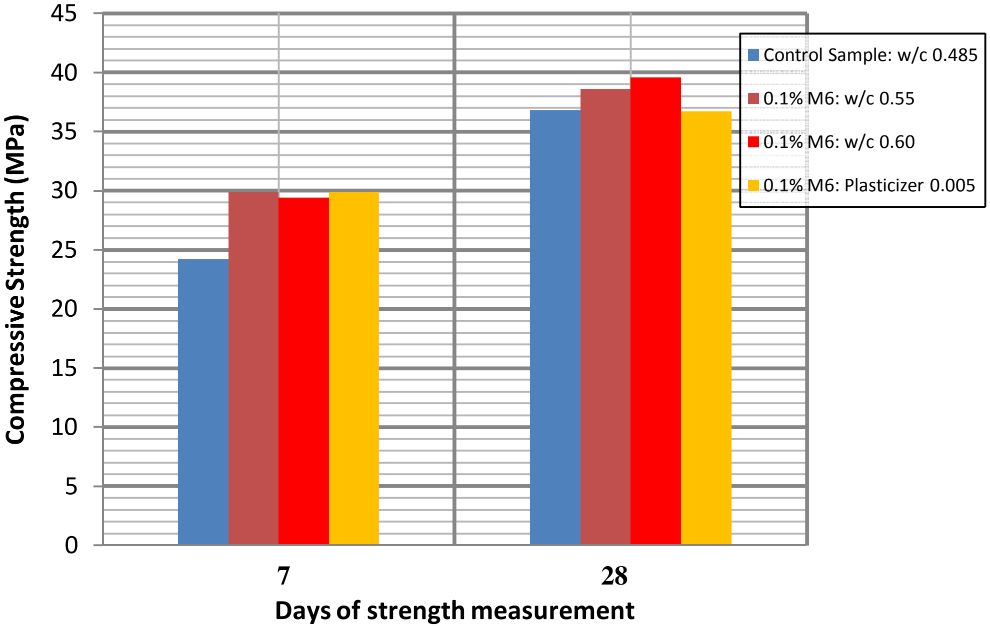


Figure 3.43: Compressive strength for different mix proportions of 0.1% M6 reinforced composites

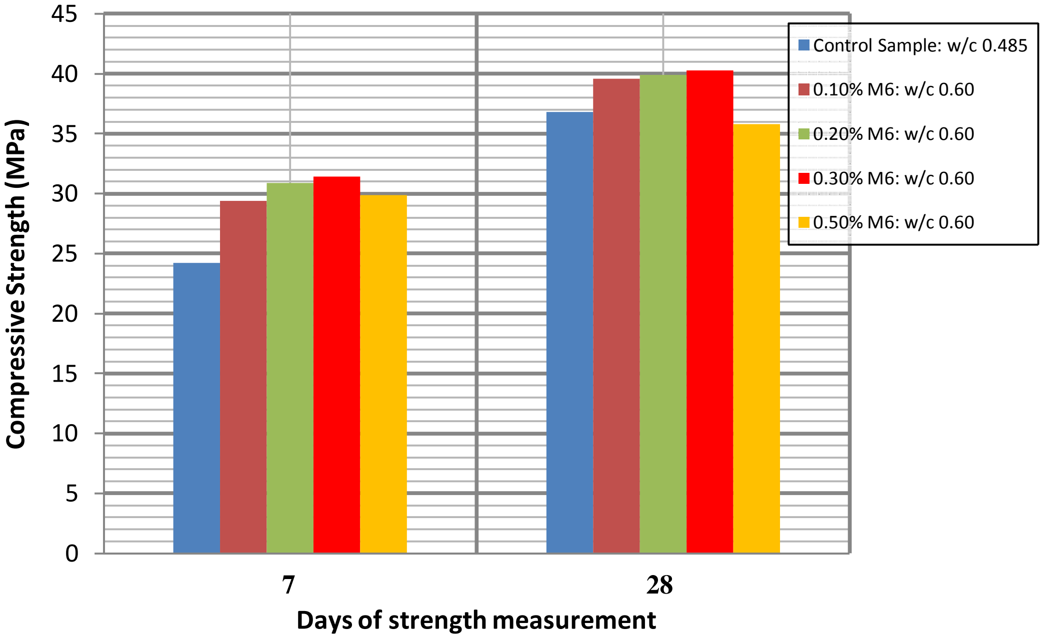


Figure 3.44: Compressive strength of control and M6 reinforced samples with w/c: 0.60

Table 3.8: Test Information of M6 Reinforced Composites

Type of Sample	Amount of MWNT (%)	w/c ratio	Amount of plasticizer (as part of cement by wt.)	No. of Samples *		Flow Values (%)	7 day mean compressive strength (MPa)	28 day mean compressive strength (MPa)
Control	NA	0.485	NA	S1*	3	32	24.2±2.30	36.8±2.10
				S2	3	23		
				S3	3	37		
Composite	0.3	0.485	NA	S1	6	15	26.3±0.83	35.0±0.76
Composite	0.3	0.60	NA	S1	6	60	31.4±1.31	40.3±1.66
Composite	0.3	0.55	NA	S1	6	55	31.7±0.70	40.1±2.00
Composite	0.3	0.485	0.005	S1	6	43	30.9±1.10	38.1±0.40
Composite	0.2	0.485	NA	S1	6	22	27.1±0.41	34.8±0.48
Composite	0.2	0.60	NA	S1	6	62	30.9±0.34	39.9±1.60
Composite	0.2	0.55	NA	S1	6	52	30.5±1.70	37.3±1.30
Composite	0.2	0.485	0.005	S1	6	38	31.8±1.60	39.2±0.62
Composite	0.1	0.60	NA	S1	6	67	29.4±0.40	39.6±1.70
Composite	0.1	0.55	NA	S1	6	57	29.9±0.35	38.6±1.10
Composite	0.1	0.485	0.005	S1	6	50	29.9±1.20	36.7±0.90
Composite	0.5	0.60	NA	S1	6	38	29.9±1.50	35.8±1.20

*S1: Set 1, S2: Set 2, S3: Set 3

3.5.7 M7 Addition

Composites were made and tested through addition of different dosage rates of M6 and different mix proportions. It is obvious from Figure 3.45 that the 7 day compressive strengths were higher for all the composites as compared to the control samples. The maximum strength was achieved for composites with w/c ratio of 0.60 at 7 day and 28 day and these strengths were 27% and 6.5% higher than the strength of control samples, respectively. Composites were also prepared using w/c ratio of 0.55 which also resulted in higher strength. The 7 day strength was 14% and the 28 day strength was 2.5% higher than the control samples in this case. It was found that the addition of plasticizer resulted in lesser 28 day compressive strength, as found in M1 addition also.

Composites with w/c ratio of 0.485 had lower (8%) 28 day compressive strength than the control samples, though the 7 day strength was about 6% higher for the composite.

Compressive strengths of 0.2% M3-cement mortar comprising of different mix proportions are presented in Figure 3.46. The maximum strength was obtained for mix proportion with 0.60 w/c ratio. The 7 day compressive strength was 38% and 28 day compressive strength was 8% greater relating to the strength of control samples. Composites having w/c ratio of 0.55 also achieved higher 7 day compressive strength than the control samples and this increment was 25.5%. The 28 day strength for this mix proportion was 3% more than that of control samples. Concerning control samples, composites made with plasticizer addition had 28% higher 7 day and 2.5% higher 28 day compressive strength.

The change in compressive strength of 0.1% M7-cement composites with change in mix proportions are provided in Figure 3.47. Composites having w/c ratio of 0.55 produced slightly higher compressive strengths at 28 day. In comparison with the control samples, the 7 day strength was 17% and 28 day strength was 7% more for these composites. Plasticizer addition also yielded greater strength than the control samples at 7 day. The mix proportion containing w/c ratio of 0.60 produced 19.5% and 3.5% higher compressive strength at 7 day and 28 day, respectively, as compared to the control samples.

In Figure 3.48, the change in compressive strengths with the change in dosage rates are shown for M7 reinforced composites with w/c ratio of 0.60. Composites with 0.2% M7 obtained the maximum compressive strengths at 7 and 28 days. These strengths were 38 % and 8% higher than the controls samples, respectively. Composites with 0.3% M7 produced about 6.5% higher strength, as compared to control samples at 28 day; the 7 day compressive strength was 27% more than that of control samples.

Table 3.9: Test Information of M7 Reinforced Composites

Type of Sample	Amount of MWNT (%)	w/c ratio	Amount of plasticizer (as part of cement by wt.)	No. of Samples *		Flow Values (%)	7 day mean compressive strength (MPa)	28 day mean compressive strength (MPa)
Control	NA	0.485	NA	S1*	3	32	24.2±2.30	36.8±2.10
				S2	3	23		
				S3	3	37		
Composite	0.3	0.485	NA	S1	6	8	25.7±0.90	33.9±1.24
Composite	0.3	0.60	NA	S1	6	55	30.8±0.97	39.2±1.18
Composite	0.3	0.55	NA	S1	6	45	27.5±0.90	37.7±0.70
Composite	0.3	0.485	0.005	S1	6	38	30.6±0.97	36.7±1.52
Composite	0.2	0.60	NA	S1	6	62	33.4±0.62	39.7±0.41
Composite	0.2	0.55	NA	S1	6	48	30.4±0.35	37.9±0.41
Composite	0.2	0.485	0.005	S1	6	42	31.0±0.83	37.7±0.69
Composite	0.1	0.60	NA	S1	6	72	28.9±1.03	38.1±0.76
Composite	0.1	0.55	NA	S1	6	60	28.4±0.69	38.7±1.24
Composite	0.1	0.485	0.005	S1	6	50	28.8±0.48	35.7±1.50

*S1: Set 1, S2: Set 2, S3: Set 3

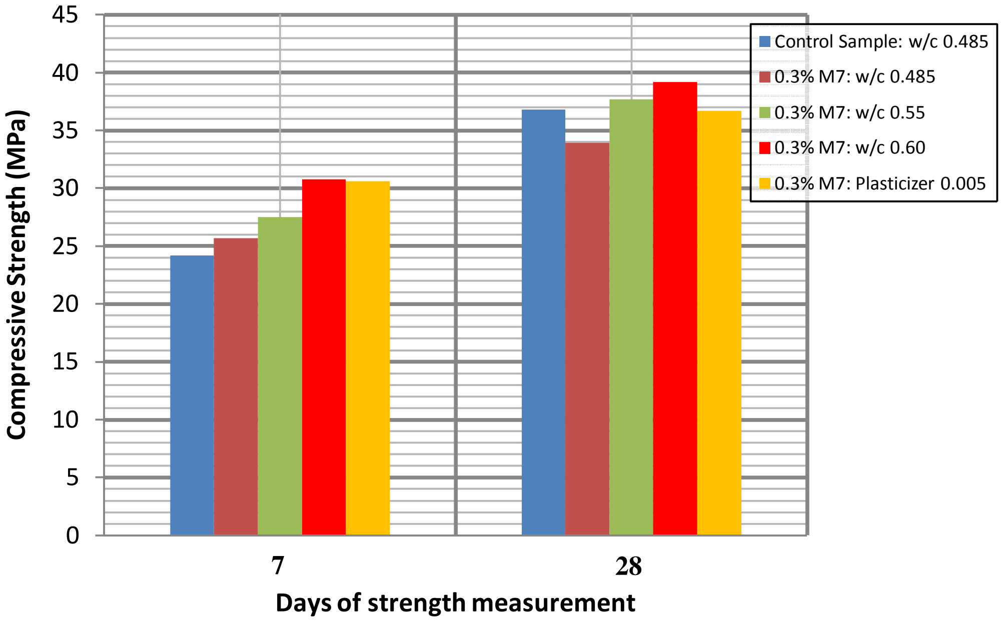


Figure 3.45: Compressive strength for different mix proportions of 0.3% M7 reinforced composites

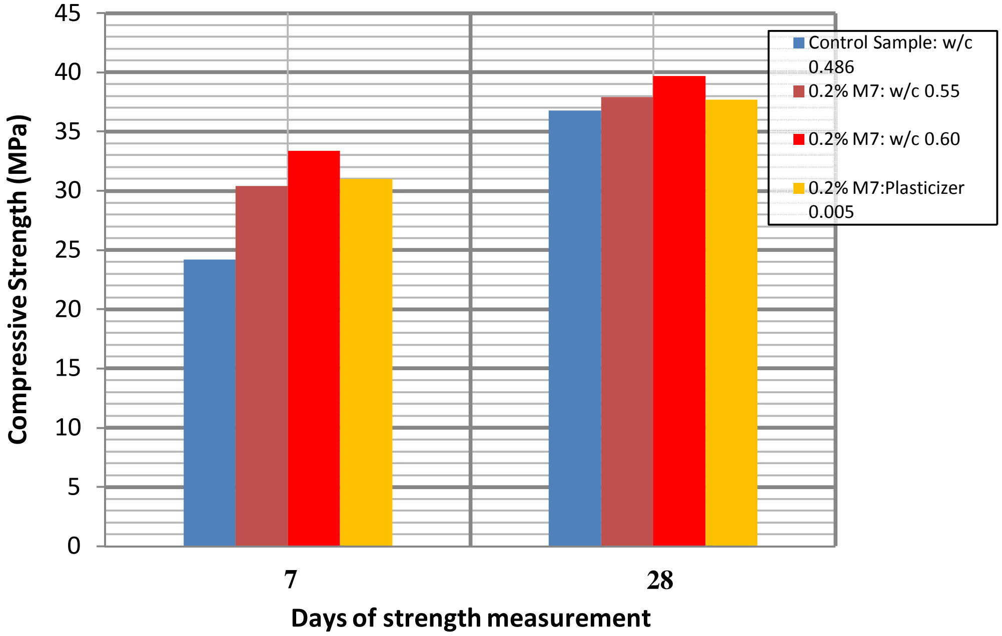


Figure 3.46: Compressive strength for different mix proportions of 0.2% M7 reinforced composites

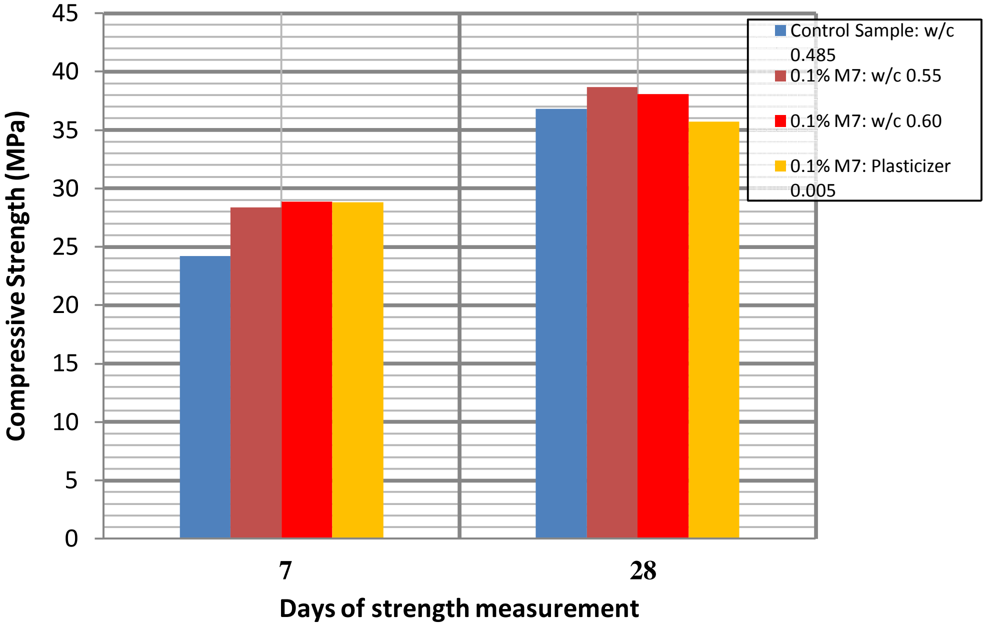


Figure 3.47: Compressive strength for different mix proportions of 0.1% M7 reinforced composites

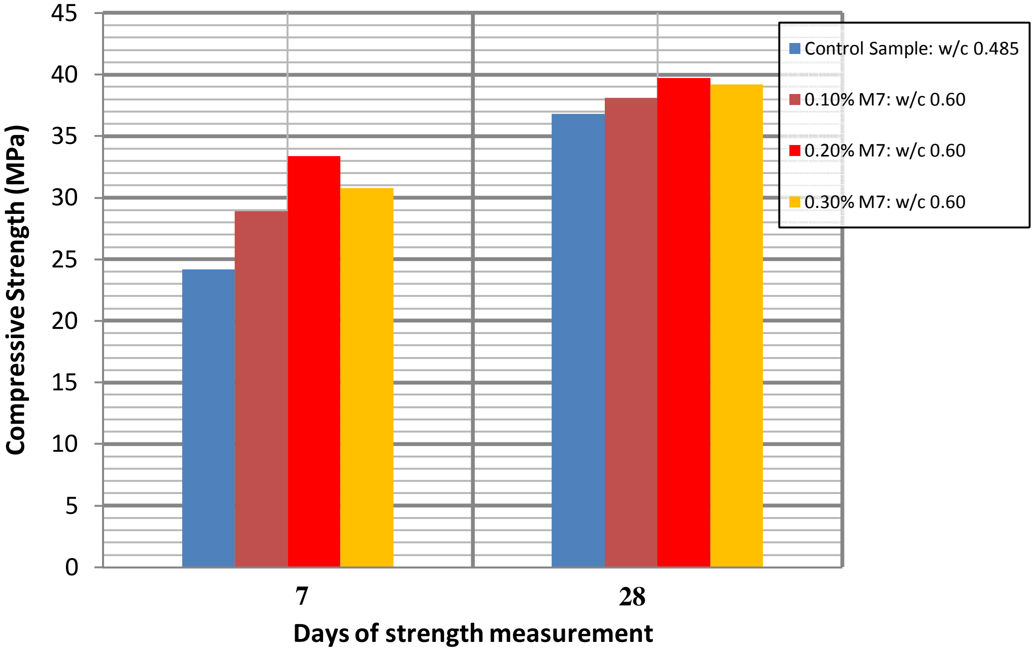


Figure 3.48: Compressive strength of control and M7 reinforced samples with w/c: 0.60

3.6 Size Effect of MWNT on Composite Compressive Strength

In this section, a comparison is made on the compressive strengths of MWNT reinforced composites based on size of nanotubes. Seven different types of MWNT based on outside diameter have been used in the experiment. It is already mentioned that the diameters ranged between 50 nm and 8 nm. Different mix proportions and dosage rates of MWNT were used to make the composites. These composites were then tested at 7 day and 28 day to measure the compressive strengths. The variations in compressive strengths with the change in MWNT size for different mix proportion and amount of MWNT are presented and discussed in the following section.

Figure 3.49 shows the compressive strengths at 7 day and 28 day in different MWNT reinforced composites having w/c ratio of 0.60 and 0.3% dosage rate of MWNT. It has already been shown that, in most cases, composites with w/c ratio of 0.60 produced the highest compressive strength. It is apparent from the results shown in Figure 3.48 that the size of nanotubes has considerable effect on the compressive strengths of composites. An upward trend in the compressive strength was found with the decrease in MWNT size. The maximum 28 day compressive strength was achieved by M4 addition which is the smallest in size. Both M1 and M7 produced the lowest compressive strengths at 28 day which was about 5% less than that of M4-composite. M1 and M7 have the larger outside diameter among the used MWNT. In case of 7 day compressive strength, a slight eccentricity was observed. M1 produced the lowest 7 day compressive strength as in the case of 28 day, but the highest compressive strength was gained by the addition of M2 and M6. However, the difference between compressive strengths of M2 and M4 added composites was only 1.5%.

Variations in compressive strengths at age of 7 and 28 day for seven different types of MWNT with dosage rates of 0.2%, 0.1% and 0.5% are provided in Figures 3.50 through 3.52 having w/c ratio of 0.60. It is observed that, with the decrease in MWNT size, an increase in compressive strength was achieved for both 0.2% and 0.1% amount of nanotubes addition. For 0.2% dosage rate, the highest compressive strength was gained by M4 and the minimum compressive strength was attained by M1 at the age of 28 day. The difference between these two extreme cases was around 8%. Identical phenomena occurred for 0.1% concentration of MWNT and the maximum compressive strength was 5% higher than the lowest one. Similar upward trends in compressive strengths were observed for 0.1% quantity of MWNT at the age of 7 day. In case of 0.2% dosage rate, the behavior analogues to 0.3% dosage rate were found. From the obtained test data, it can be inferred that for both 0.2% and 0.3% amount of MWNT addition besides the M1, the difference in compressive strength for other types of MWNT samples is minute. It is also observed that the composites producing the maximum 7 day compressive strengths did not always attain the peak strength at the age of 28 day, but was able to produce comparable strengths similar to the highest one.

Addition of 0.5% MWNT in all cases produced compressive strengths lower than that of control samples and no particular trend was evident. It was clear from Section 3.5 that any dosage rate greater than 0.3% yielded lower compressive strength at the age of 28 day. The reasons behind this type of behavior are inadequate dispersion of MWNT due to agglomeration of nanotubes and less workability. The compressive strength was lower for smaller size of MWNT at 28 day, with the high dosage rate of 0.5%. This is due to the greater surface area of smaller size MWNT which eventually cause more nanotubes to adhere to each other and also attract more water on their larger surface areas. This behavior clearly suggests that an optimum dosage rate exists to produce desirable composites for a given mixing technique and mix proportion.

In Figures 3.53 through 3.58, compressive strengths for samples reinforced with seven different types of MWNT for mix proportions with w/c ratio of 0.55 and 0.485 are shown. For composites containing w/c ratio of 0.55, a rising trend was found with decreasing size of MWNT having dosage rates of 0.2% and 0.1%. Addition of 0.3% MWNT yielded almost equal compressive strengths for M6, M2 and M3 addition at the age of both 7 and 28 day with addition of M4 produced a bit lower compressive strength in this case. Composites having w/c of 0.485 produced lesser compressive strengths than control samples for all dosage rates and, like 0.5% dosage rate with w/c ratio of

0.60, no definite pattern was apparent. These composites have extremely low workability and in turn fail to achieve sufficient strength.

Compressive strengths of MWNT reinforced cement composites made by plasticizer addition are presented in Figures 3.59, 3.60 and 3.61 with respect to size of nanotubes. It was observed that higher dosage rates of MWNT obtained lesser compressive strengths at 28 day in majority of cases. The compressive strength was greater than control samples only in two instances, but the increment was insignificant. For 0.2% and 0.1% addition of MWNT, the 28 day compressive strength increased somewhat in all seven instances, as compared to composites with 0.3% dosage rate. However, addition of plasticizer resulted in weaker composites, though workability of mixes was improved. This means that not only workability, but uniform dispersion of nanotubes is also essential for proper reinforcement within the composites.

It is obvious from the above discussion that the size of MWNT has significant influence on composite behavior. In general, an increasing trend in compressive strengths was found with smaller MWNT depending on proper dispersion of nanotubes within the cement mix. Uniform dispersion of MWNT can lead to higher compressive strength of composites, as compared to control samples. It was observed that MWNT having OD smaller than 30 nm produced similar compressive strengths at the age of 28 day. It was also found that M4 (OD<8 nm) reinforced composites performed better in majority of cases. Therefore, based on these results, it can be tentatively concluded that MWNT with OD smaller than 30 nm should be considered for reinforcement in producing carbon nanotubes-cement composites.

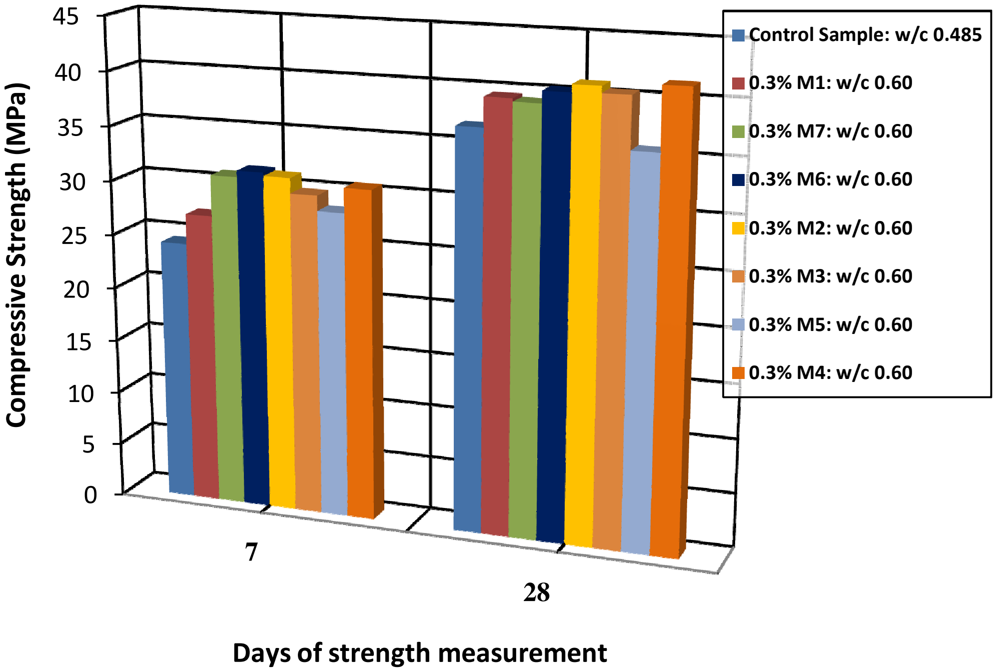


Figure 3.49: Compressive strength for different 0.3% MWNT-cement composites with w/c 0.60

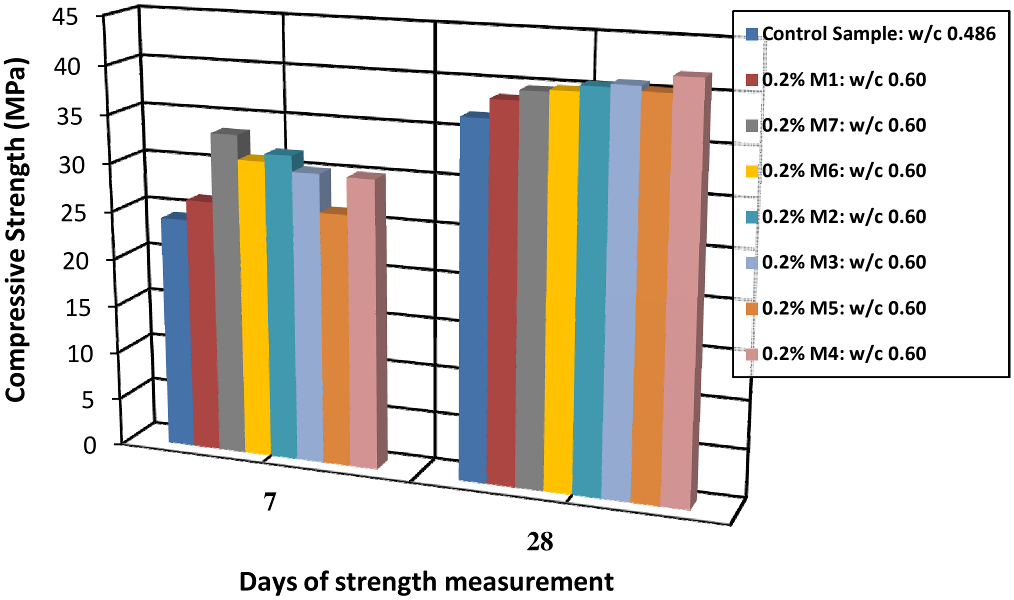


Figure 3.50: Compressive strength for different 0.2% MWNT-cement composites with w/c 0.6

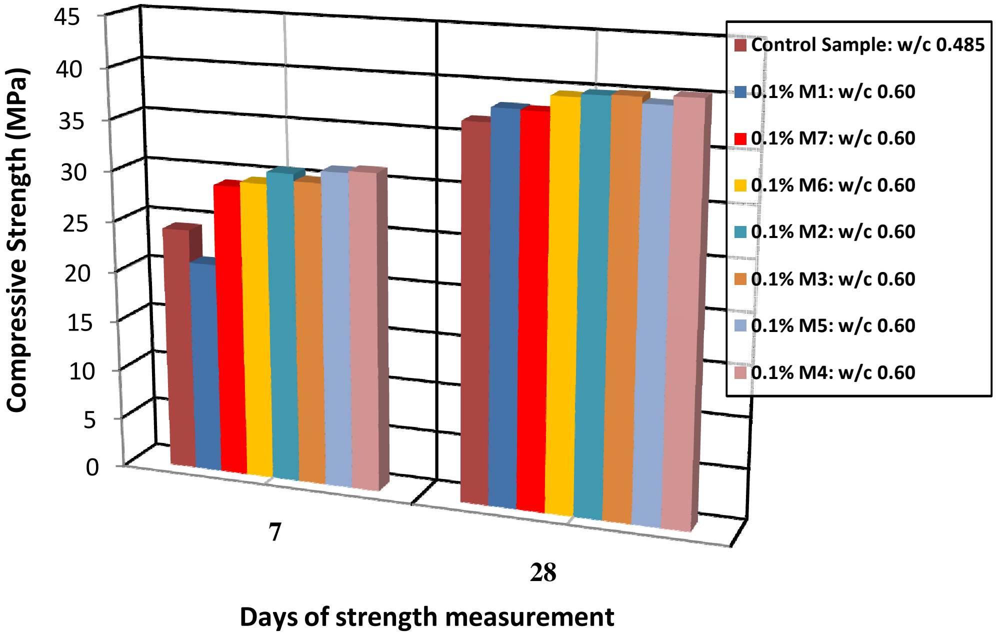


Figure 3.51: Compressive strength for different 0.1% MWNT-cement composites with w/c 0.60

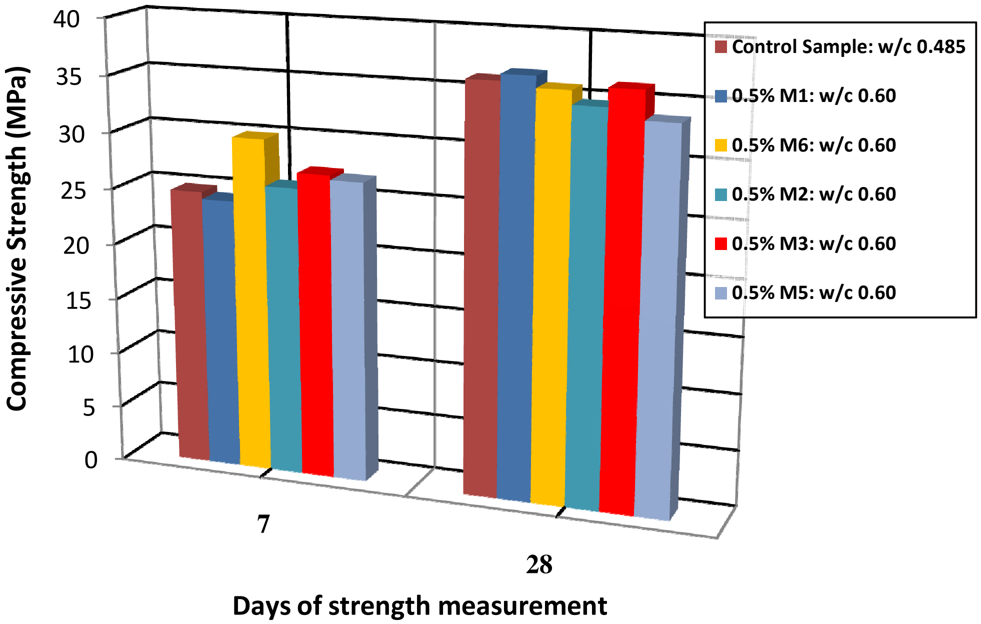


Figure 3.52: Compressive strength for different 0.5% MWNT-cement composites with w/c 0.60

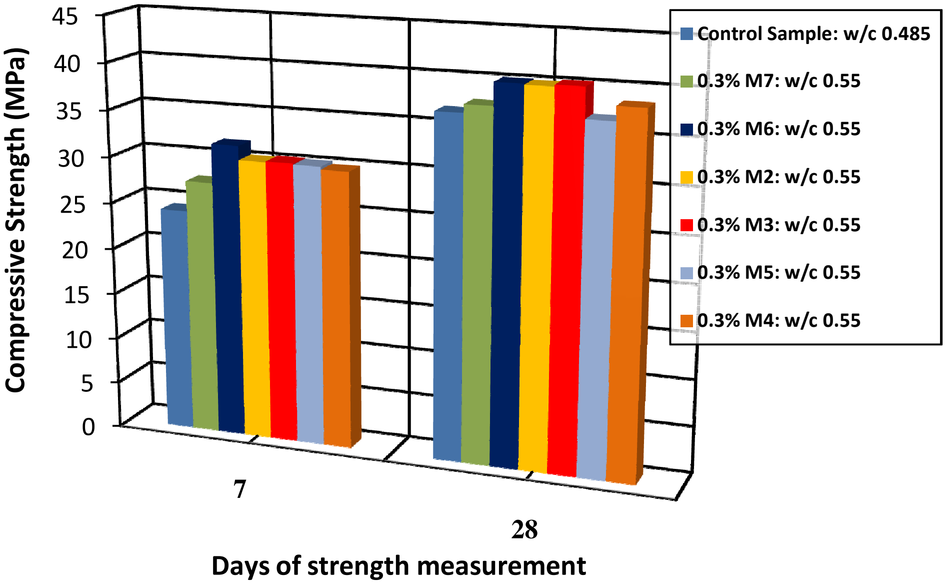


Figure 3.53: Compressive strength for different 0.3% MWNT-cement composites with w/c 0.55

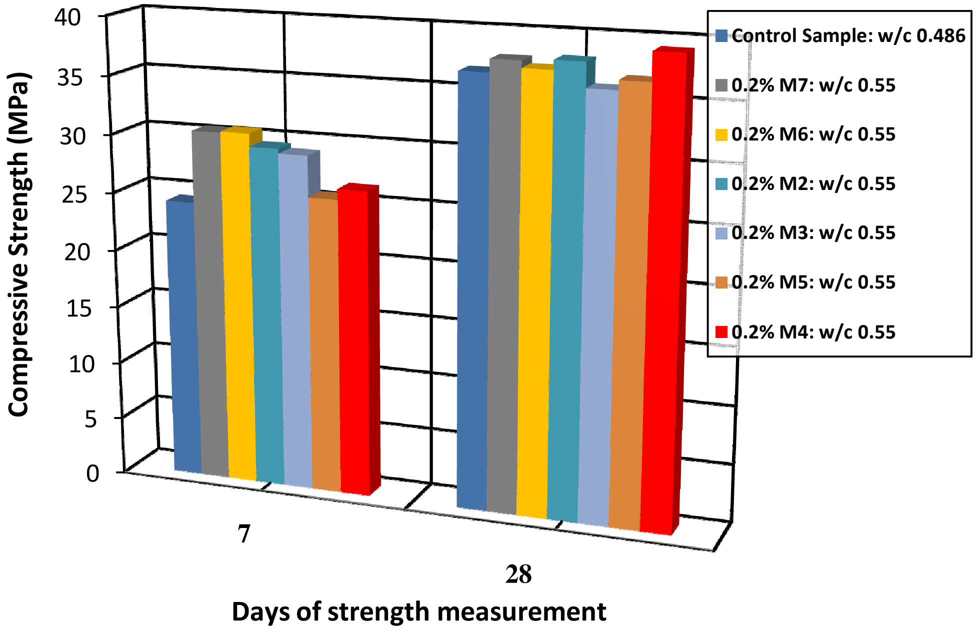


Figure 3.54: Compressive strength for different 0.2% MWNT-cement composites with w/c 0.55

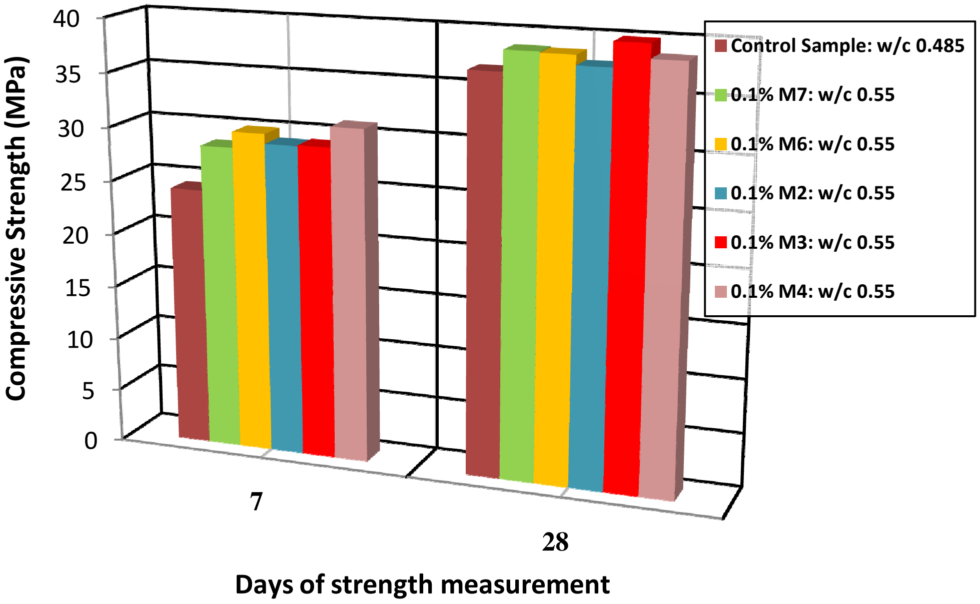


Figure 3.55: Compressive strength for different 0.1% MWNT-cement composites with w/c 0.55

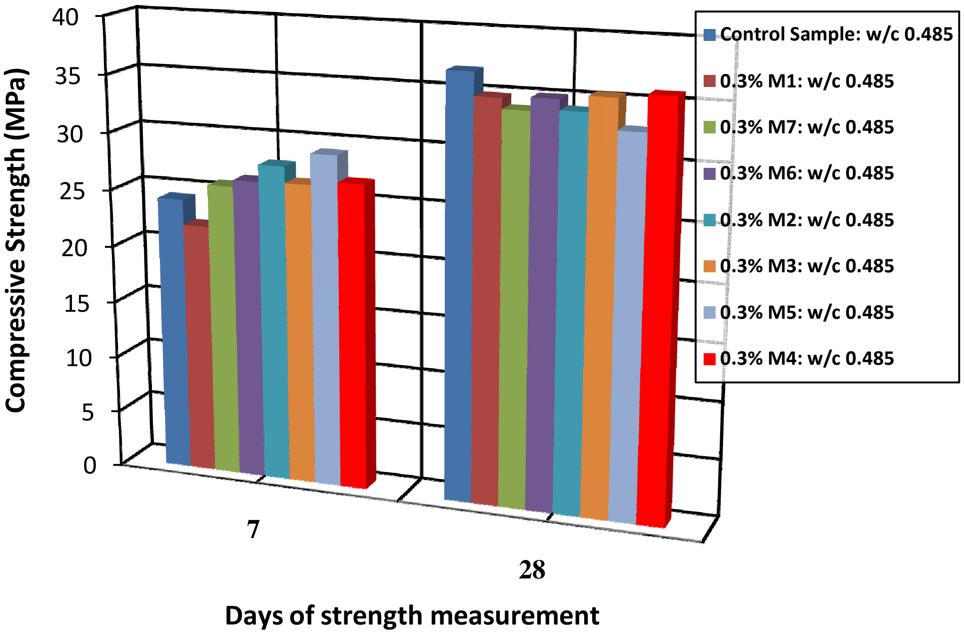


Figure 3.56: Compressive strength for different 0.3% MWNT-cement composites with w/c 0.485

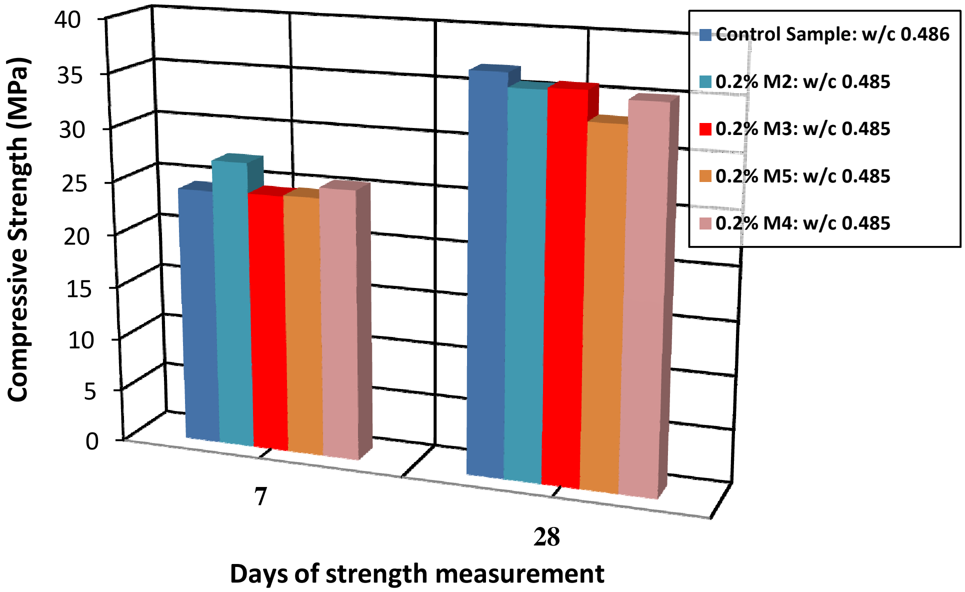


Figure 3.57: Compressive strength for different 0.2% MWNT-cement composites with w/c 0.485

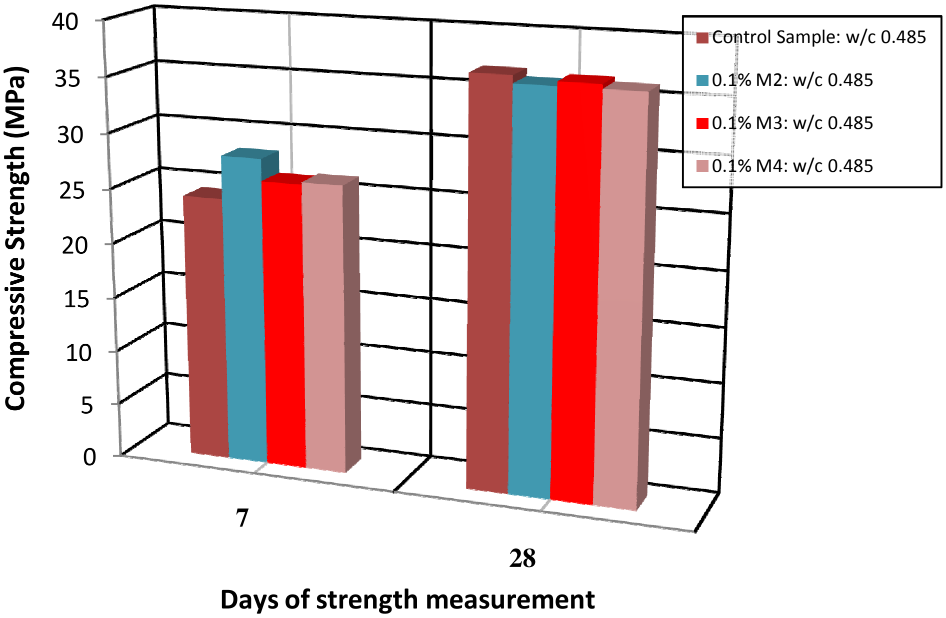


Figure 3.58: Compressive strength for different 0.1% MWNT-cement composites with w/c 0.485

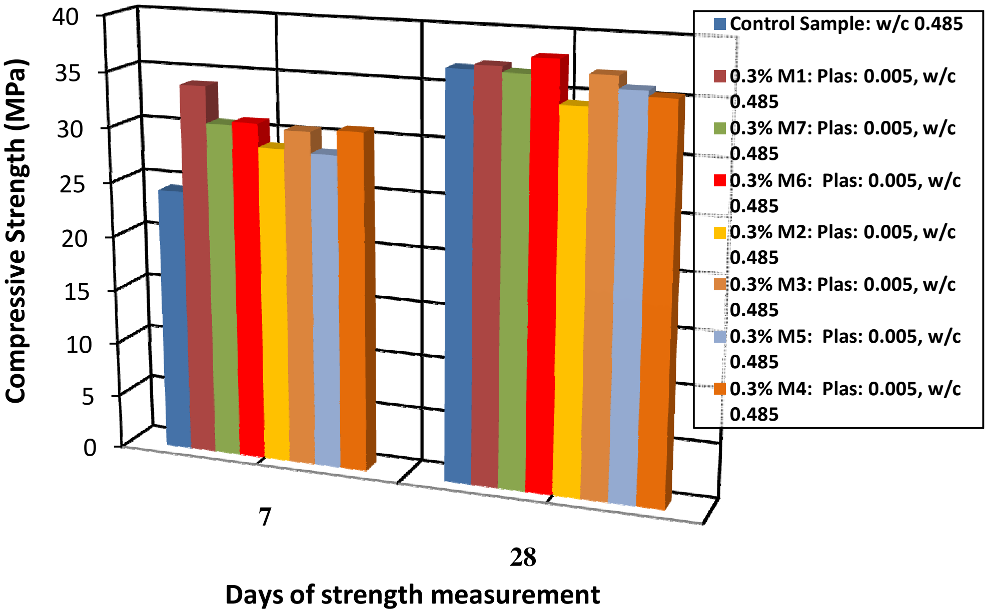


Figure 3.59: Compressive strength for different 0.3% MWNT-cement composites with 0.485 w/c and 0.005 plasticizer

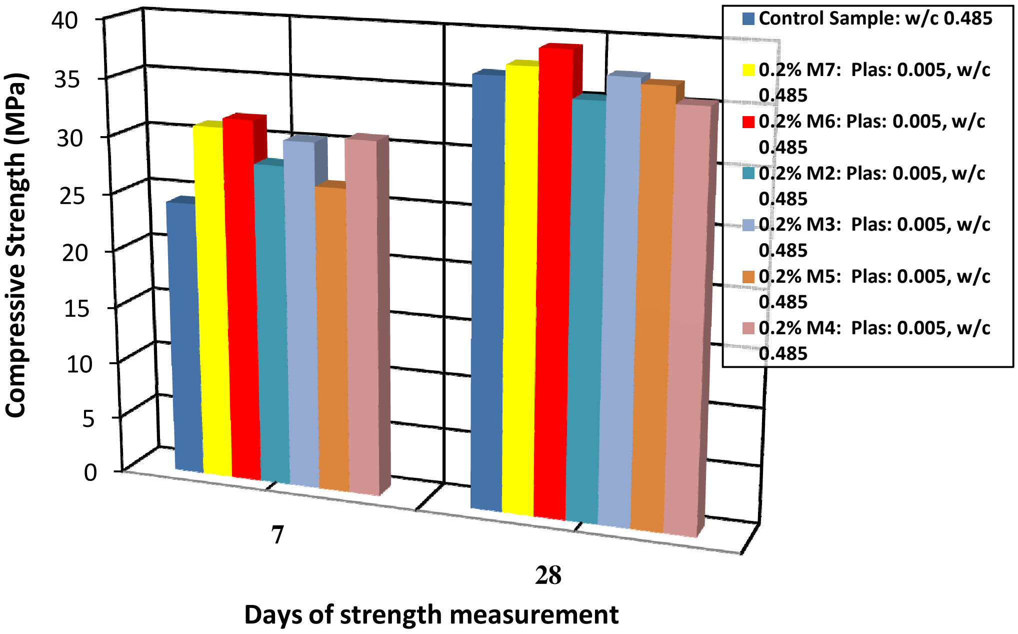


Figure 3.60: Compressive strength for different 0.2% MWNT-cement composites with 0.485 w/c and 0.005 plasticizer proportion

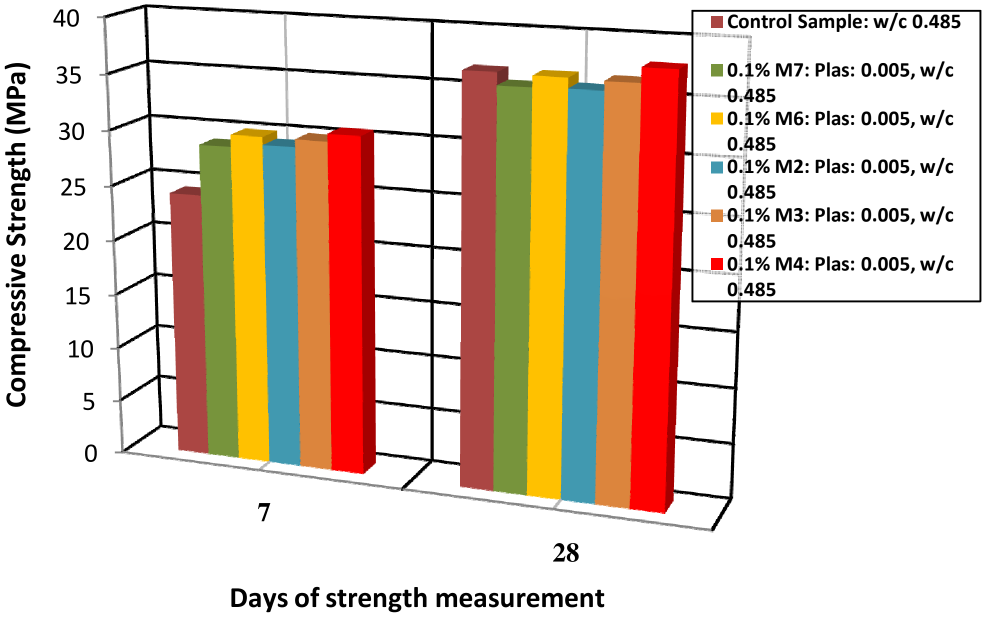


Figure 3.61: Compressive strength for different 0.1% MWNT-cement composites with 0.485 w/c and 0.005 plasticizer proportion

3.7 Effect of Treated MWNT on Composite Strength

An effective way to enhance dispersion is functionalization of nanotubes by adding polar impurities like hydroxyl or carboxyl end groups to the outer surface of MWNT. In this method of functionalization, the MWNT is oxidized in a mixture of nitric and sulfuric acids and then the acid treated MWNT is heated and sonicated. This acid treatment results in more soluble nanotubes than pristine CNT. Since behavior of MWNT reinforced cement composites is greatly influenced by uniform distribution of nanotubes across the cement grains, utilization of acid treated MWNT has potential to be used as reinforcing agent.

From the test data of untreated MWNT reinforced composites, it was obvious that MWNT with OD smaller than 30 nm resulted in higher compressive strength in comparison with composite reinforced by nanotubes having OD greater than 30 nm. Therefore, for this phase of the study, acid treated M2, M3, M4 and M5 were selected as reinforcing agents. TEM images of these treated MWNT are shown in Figures 3.62 to 3.65 and the properties are provided in Table 3.10. Mix proportion containing w/c ratio of 0.60 was selected as it yielded relatively higher compressive strength in majority of cases of untreated MWNT composites. Three dosage rates of 0.3%, 0.2% and 0.1% were utilized based on the previous results.

Table 3.10: Acid treated MWNT properties

Type of MWNT & Properties	M2	M3	M4	M5
OD (outside diameter)	20-30 nm	10-20 nm	< 8 nm	8-15 nm
Length	10-30 μm	10-30 μm	10-30 μm	10-30 μm
Purity	>95wt%	>95wt%	>95wt%	>95wt%
Ash	<1.5wt%	<1.5wt%	<1.5wt%	<1.5wt%
SSA (Specific Surface Area)	>110m^2/g	>233m^2/g	>500m^2/g	>233m^2/g
EC (Electrical Conductivity)	>10^{-2}s/cm	>10^{-2}s/cm	>10^{-2}s/cm	>10^{-2}s/cm
COOH Content (wt%)	1.23	2.00	3.86	2.56

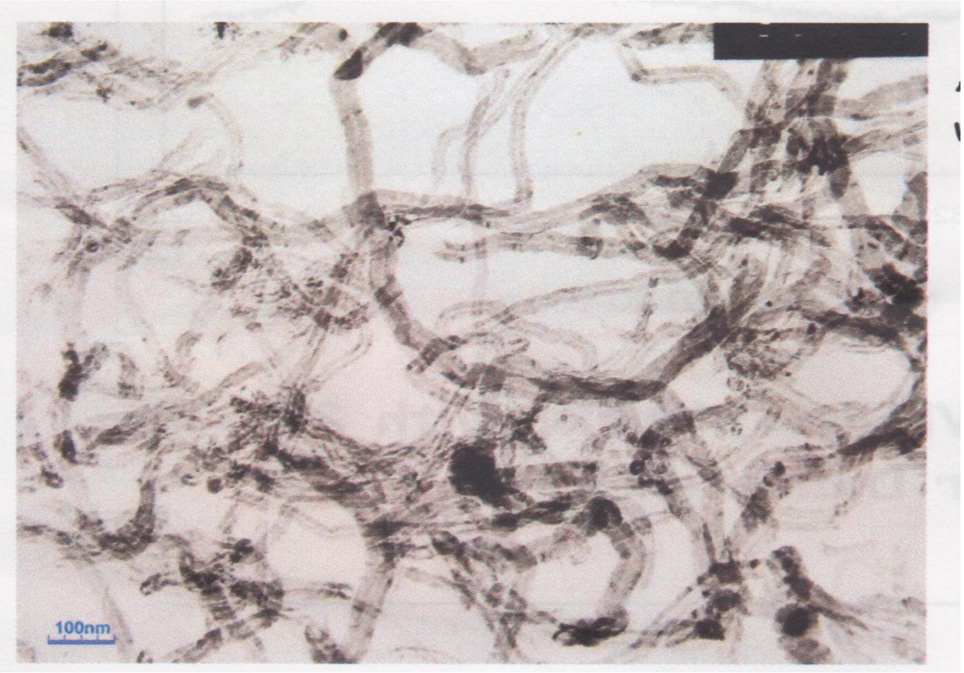


Figure 3.62: TEM image of treated M2 (Source: Cheap Tubes)

Figure 3.63: TEM image of treated M3 (Source: Cheap Tubes)

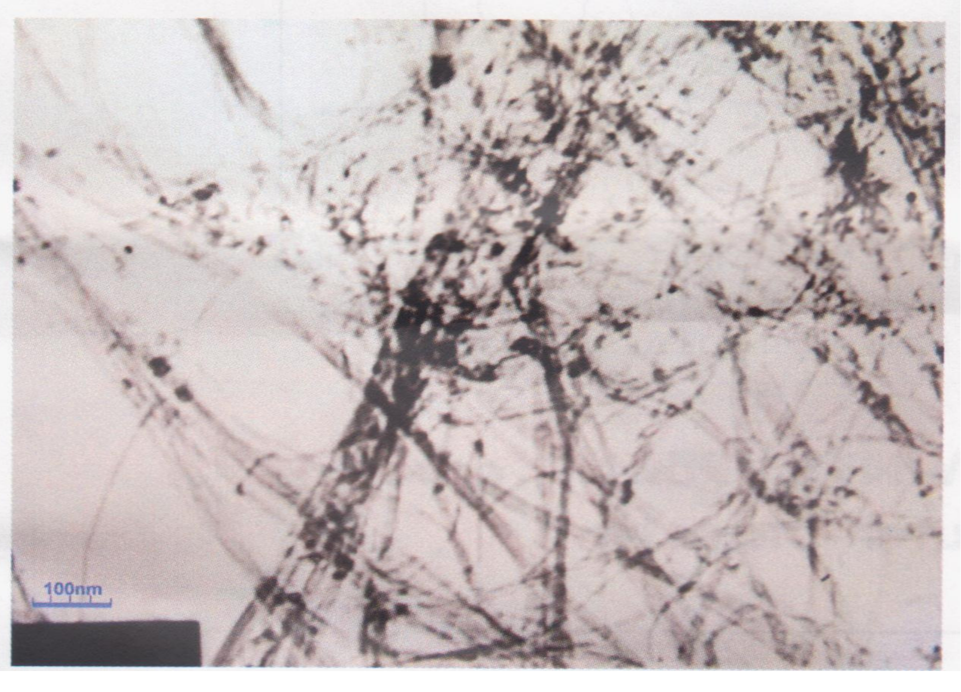


Figure 3.64: TEM image of treated M4 (Source: Cheap Tubes)

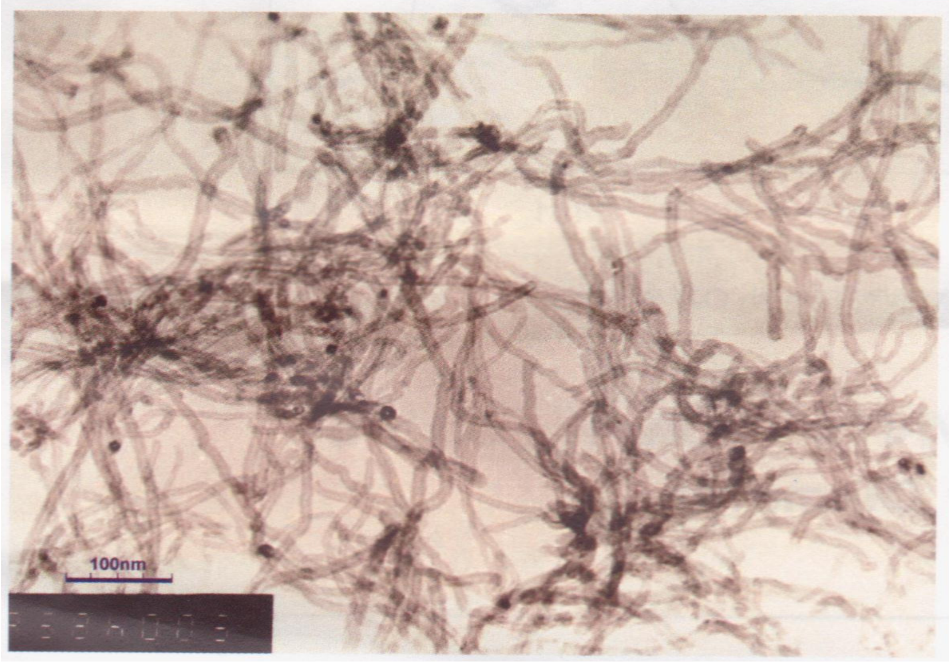


Figure 3.65: TEM image of treated M5 (Source: Cheap Tubes)

In Figure 3.66, the compressive strengths of 0.3% M2, M3, M4 and M5 reinforced composites at the age of 7 and 28 day are presented. In all cases, w/c ratio was kept at 0.60. At 28 day, all four MWNT added composites produced similar compressive strengths, though some deviations were observed at 7 day. The highest compressive strength was achieved by M4 reinforced composites at 28 day (about 13% higher than the control samples). For M3 addition, this increment was a little greater than 12%. At the age of 7 day, the highest compressive strength was achieved by M3 addition, which was about 40% higher than that of the control samples and around 2.5% greater than that of M4-composites. Compressive strengths of composites with 0.2 and 0.1% dosage rates of four different sizes of treated MWNT are shown in Figures 3.67 and 3.68. Relatively greater compressive strengths were achieved at 7 day than that of 28 day, as compared to control samples. Identical compressive strengths were obtained at 28 day for 0.2% addition of M2, M3 and M5 added composites, which was about 11.5% higher than that of control samples. M4 reinforced composites produced a little higher (13% more than that of control samples) 28 day compressive strengths in this case, and the strength difference between M3 and M4 reinforced composites was only about 1.5%. For 0.1% amount of MWNT addition, the maximum compressive strength obtained by the M3-cement composites. Those M3 reinforced composites produced 41 and 11.5% higher compressive strengths at the age of 7 and 28 day as compared to control samples, respectively.

It becomes clear from the compressive strength test data of treated MWNT reinforced composites that almost similar strength was obtained for all four types of nanotubes at 28 day. For dosage rates of 0.2 and 0.3%, M4 reinforced samples resulted in slightly higher compressive strengths. It was also found that, like untreated MWNT addition, composites achieved greater compressive strengths at early age. A comparison of compressive strengths of composites both at the age of 7 and 28 day are showed in Figures 3.69 through 3.74. The composites had same mix proportions but different types and dosage rates of treated and untreated MWNT. It was found that, in all cases, addition of treated MWNT resulted in greater compressive strength than the compressive strengths obtained by composites with untreated ones, both at early age of 7 day and at later age of 28 day. However, increases in compressive strengths varied with the variation in types of MWNT and dosage rates. Addition of treated MWNT resulted in higher gain in compressive strength at early age of 7 day in reference with the 28 day compressive strength. The average increase in 7 day compressive strength was about 12.5%, whereas at 28 day, the average raise of compressive strength was around 5% as compared to control samples. Similar trend was also found for 0.2% dosage rate of treated MWNT. At 7 day, the mean increase in compressive strength was around 15%, whereas at 28 day, this increase was about 1%. For 0.1% dosage rate, the mean increment was 9% and 2% at 7 and 28 day, respectively.

This pattern of behavior was predictable and matched with the hypothesis that the addition of MWNT accelerated early hydration process. Uniform dispersion of nanotubes ensures proper distribution of MWNT across cement paste. Acid treatment of MWNT increases its solubility and fills the nano void space within the cement grains more effectively. Eventually this accelerates the growth of hydration products around MWNT more effectively. Furthermore, it is apparent that as the amount of MWNT increases, the mean rise in compressive strength decreases. This is due to the fact that higher amounts of MWNT has higher tendency to agglomerate and it becomes difficult to separate and disperse the nanotubes properly. Since acid treatment hinders the tendency of agglomeration of nanotubes, the consequence of acid treatment will be more pronounced at higher concentration of MWNT.

3.8 Flexural Strength of Treated MWNT Reinforced Composites

Flexural samples were prepared using treated MWNT with w/c ratio of 0.60 according to ASTM C348-02 (ASTM C348-02, 2008). Samples were then prepared using a central point loading set up. Control samples were also made for comparison. Two dosage rates of 0.3% and 0.2% were utilized based on compressive strength test results. Samples were tested at 28 day. In all cases, composites reinforced with MWNT exhibited higher flexural strengths. It was evident from the increase in flexural strength that MWNT can effectively reinforce the cementitious matrix at nano scale and can help transfer load across the cracks. Figure 3.75 shows the flexural strength of control samples and composites reinforced with 0.2% dosage rate of treated MWNT at the age of 28 day. The addition of M4 gave the highest flexural strength and it was about 13% higher than that of control samples. Composites reinforced with M5 and M2 produced 12% and 10% more flexural strength, respectively. MWNT having OD smaller than 30 nm gave an average increase of 11.5% in flexural strength as compared to control samples, whereas MWNT larger than 30 nm obtained about 7% mean increase in flexural strength.

The 28 day flexural strengths of specimens reinforced with 0.3% addition of acid treated MWNT are shown in Figure 3.76. The maximum flexural strength was achieved for M3 and M4 addition which was about 15% more, as compared to control samples. It was found that samples with MWNT having OD less than 30 nm obtained 13.5% greater strength on an average, and samples with MWNT having OD greater than 30 nm obtained around 7% mean increase as compared to control samples. A comparison of flexural strength of specimens containing 0.3% and 0.2% surface treated MWNT are presented in Figure 3.77. It is clear from Figure 3.77 that 0.3% MWNT reinforced composites performed a little bit better, though in some cases, higher flexural strength was achieved by 0.2% addition. It was found that composites with 0.3% MWNT had 1% mean higher flexural strength than that of 0.2% reinforced composites at 28 day. Altogether, composite samples prepared by MWNT addition exhibited an improved mechanical performance over control samples.

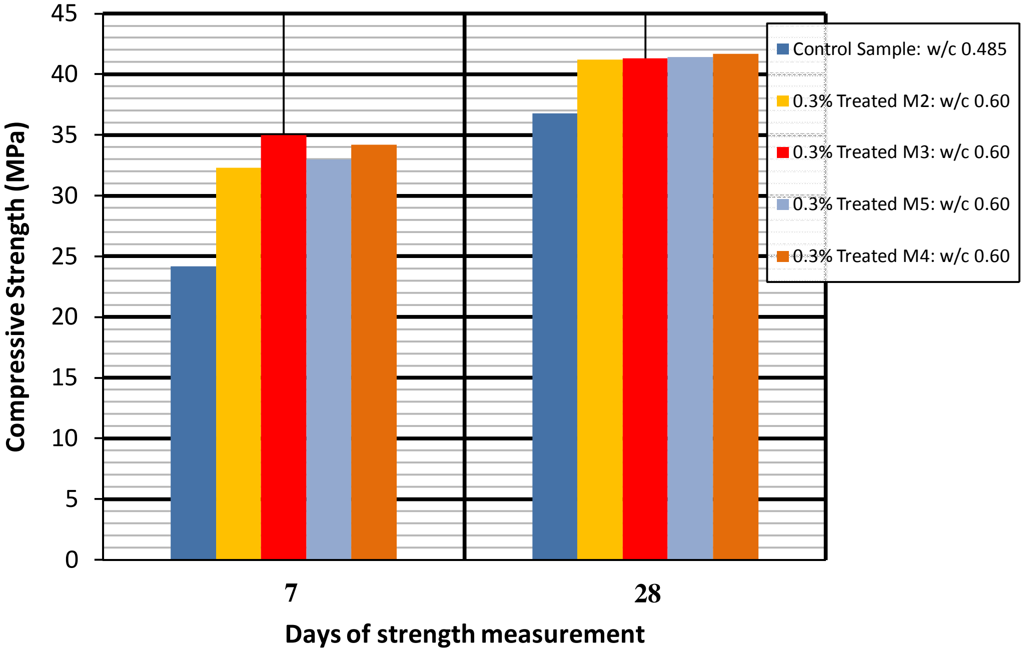


Figure 3.66: Compressive strength of different acid treated 0.3% MWNT reinforced composites with w/c ratio of 0.60

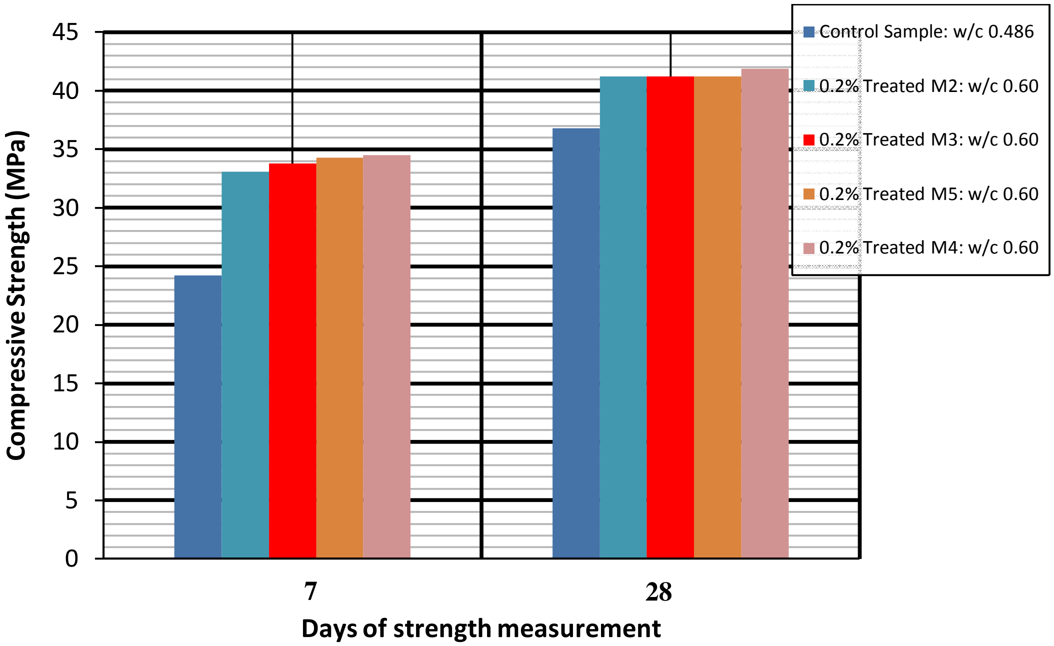


Figure 3.67: Compressive strength of different acid treated 0.2% MWNT reinforced composites with w/c ratio of 0.60

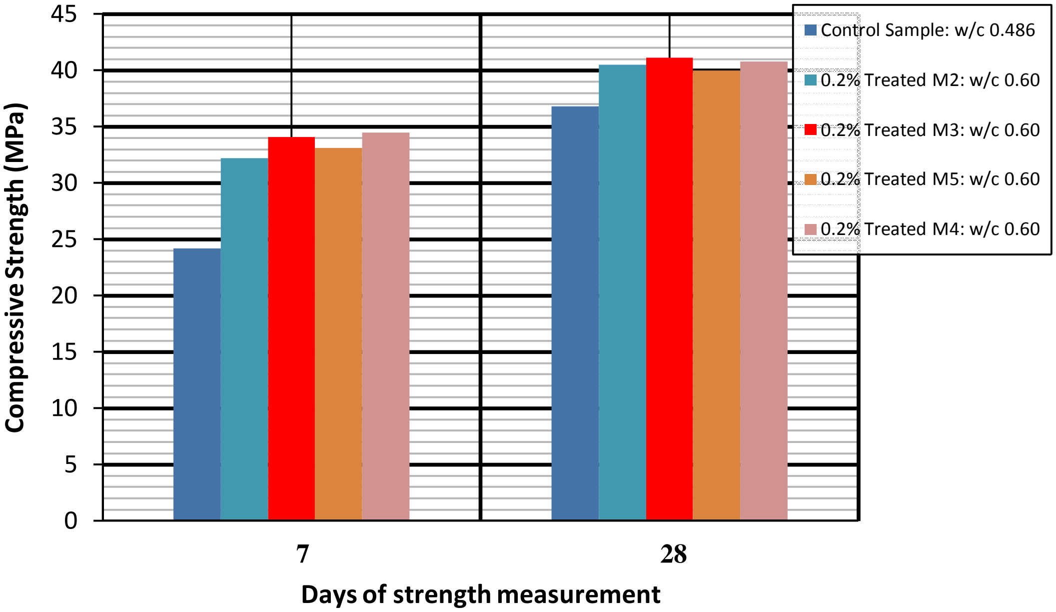


Figure 3.68: Compressive strength of different acid treated 0.1% MWNT reinforced composites with w/c ratio of 0.60

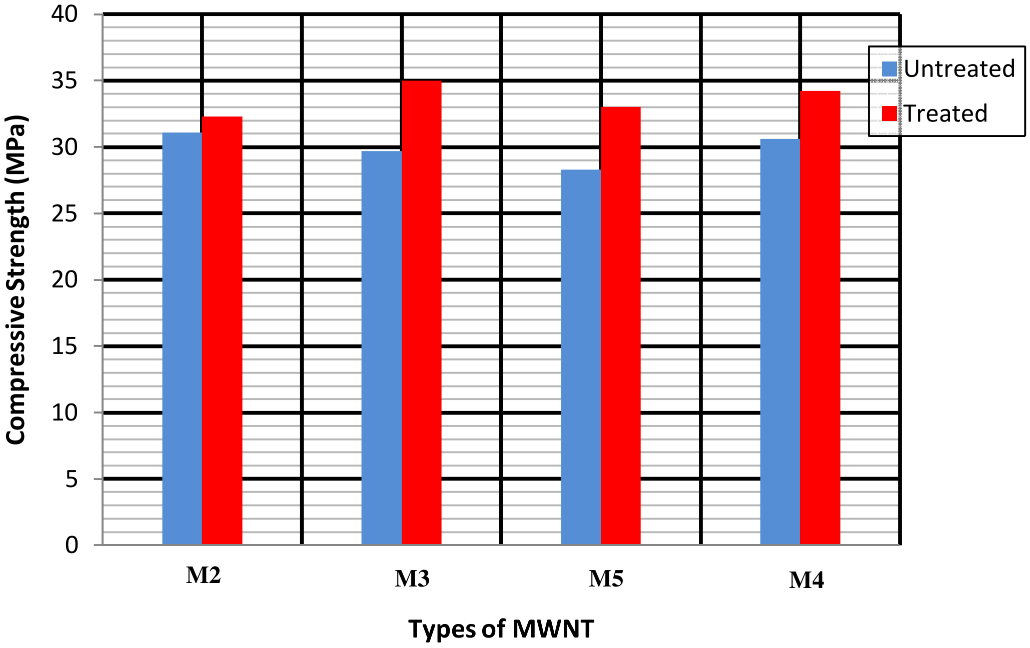


Figure 3.69: Comparison of compressive strength of different acid treated 0.3% MWNT reinforced composites at the age of 7 day

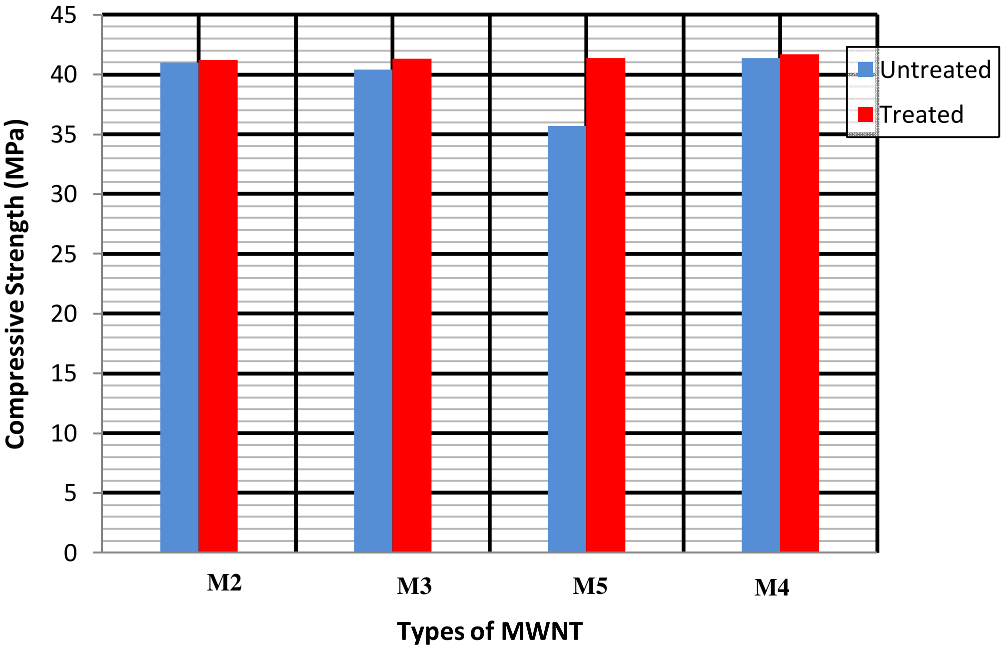


Figure 3.70: Comparison of compressive strength of different acid treated 0.3% MWNT reinforced composites at the age of 28 day

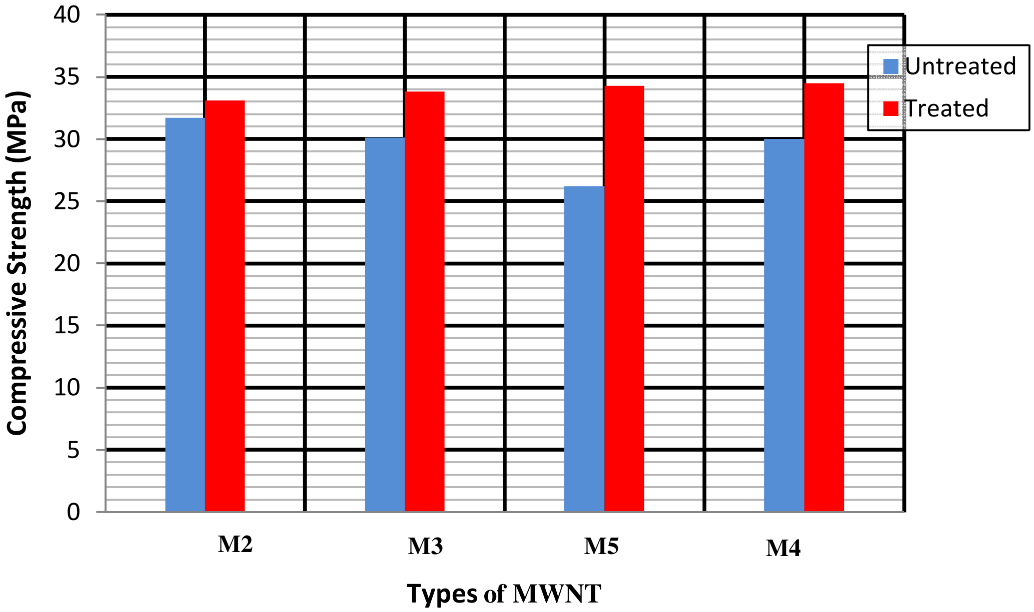


Figure 3.71: Comparison of compressive strength of different acid treated 0.2% MWNT reinforced composites at the age of 7 day

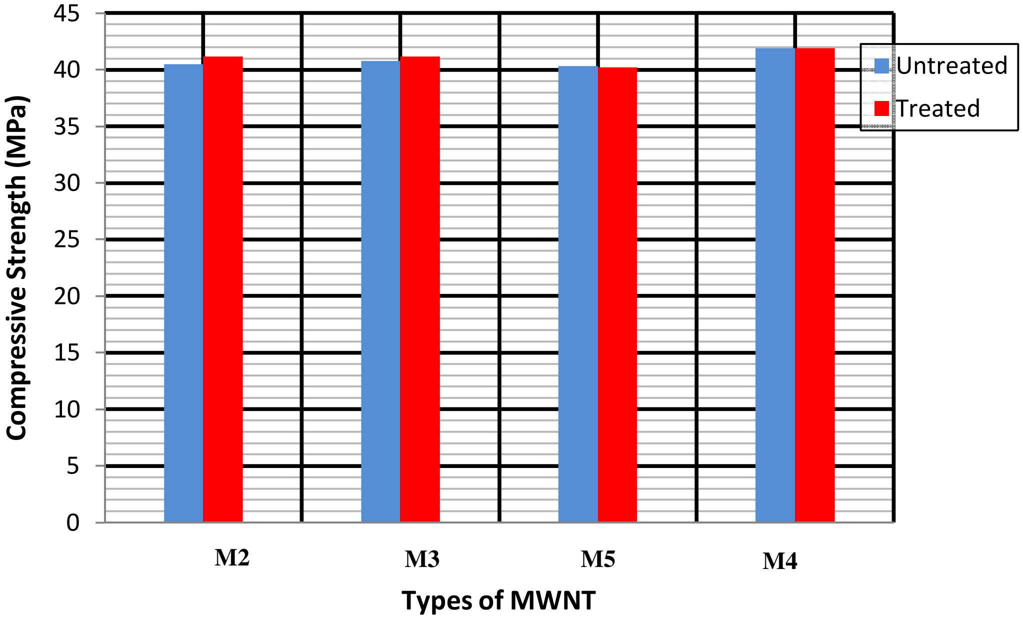


Figure 3.72: Comparison of compressive strength of different acid treated 0.2% MWNT reinforced composites at the age of 28 day

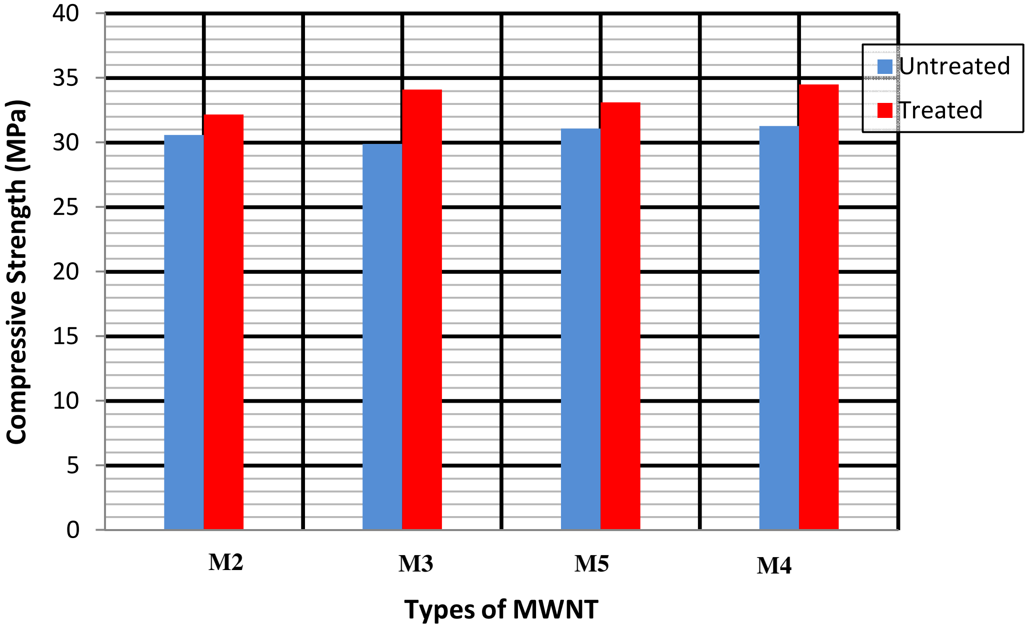


Figure 3.73: Comparison of compressive strength of different acid treated 0.1% MWNT reinforced composites at the age of 7 day

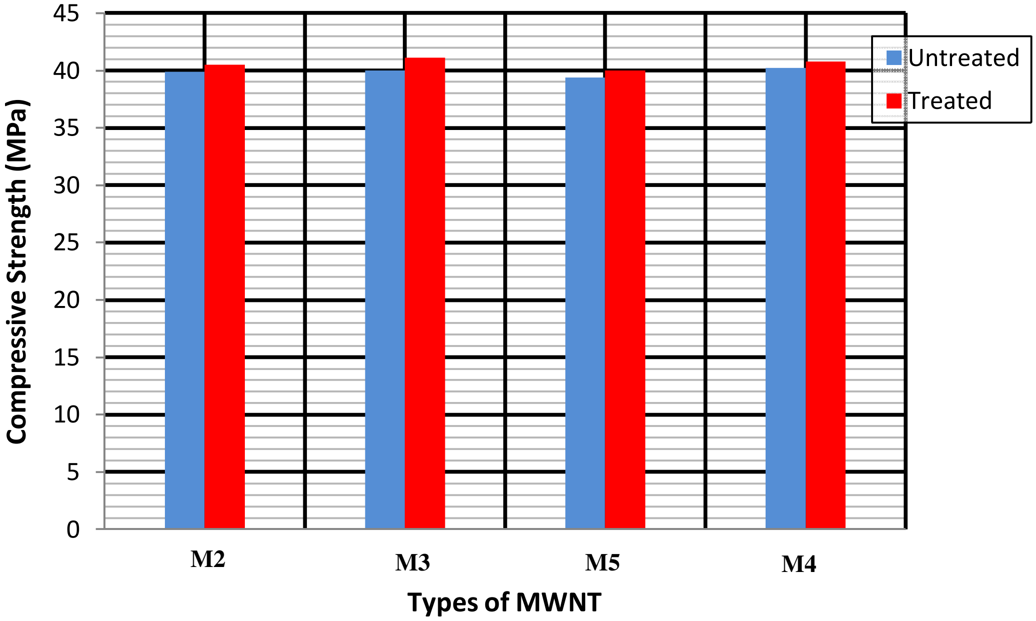


Figure 3.74: Comparison of compressive strength of different acid treated 0.1% MWNT reinforced composites at the age of 28 day

Table 3.11: Test Information of Treated MWNT Reinforced Composites

Type of Sample	Amount of MWNT (%)	w/c ratio	MWNT Types	No. of Samples *		Flow Values (%)	7 day mean comp-ressive strength (MPa)	28 day mean comp-ressive strength (MPa)
Control	NA	0.485	NA	S1*	3	32	24.2±2.30	36.8±2.10
				S2	3	23		
				S3	3	37		
Composite	0.3	0.60	M2	S1	6	48	32.3±3.00	41.2±1.00
Composite	0.2	0.60	M2	S1	6	53	33.1±1.20	41.2±1.60
Composite	0.1	0.60	M2	S1	6	55	32.2±1.80	40.5±1.50
Composite	0.3	0.60	M3	S1	6	38	35.0±0.80	41.3±0.80
Composite	0.2	0.60	M3	S1	6	40	33.8±1.70	41.2±1.80
Composite	0.1	0.60	M3	S1	6	50	34.1±0.70	41.1±0.80
Composite	0.3	0.60	M5	S1	6	44	33.0±1.20	41.4±0.90
Composite	0.2	0.60	M5	S1	6	48	34.3±0.90	41.2±1.80
Composite	0.1	0.60	M5	S1	6	55	33.1±1.20	40.0±0.35
Composite	0.3	0.60	M4	S1	6	38	34.2±0.70	41.7±1.00
Composite	0.2	0.60	M4	S1	6	38	34.5±1.20	41.9±0.90
Composite	0.1	0.60	M4	S1	6	50	34.5±0.90	40.8±1.30

*S1: Set 1, S2: Set 2, S3: Set 3

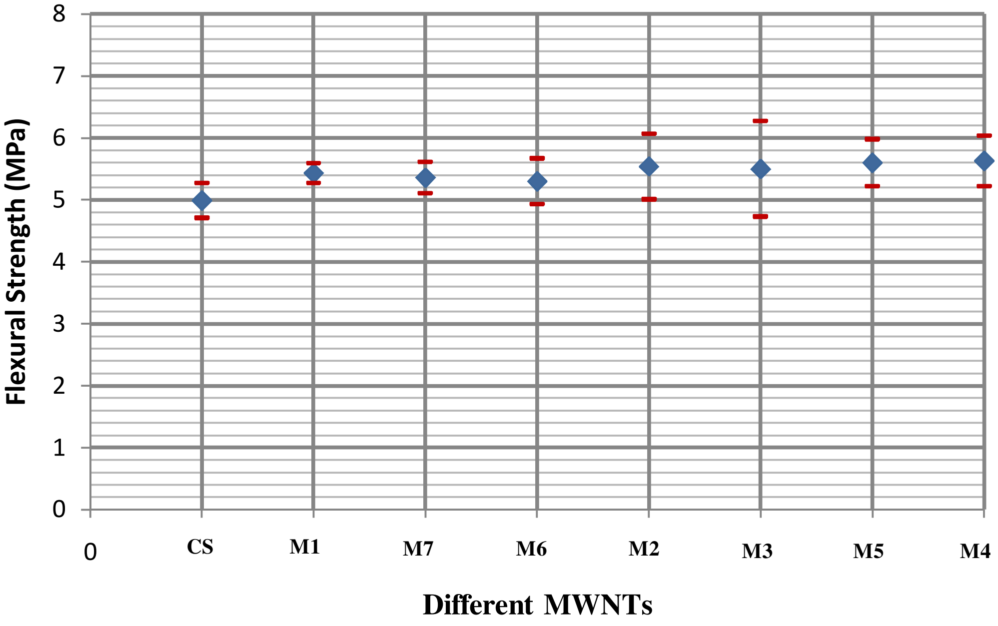


Figure 3.75: Flexural strength of control and 0.2% treated MWNT reinforced samples at 28 day

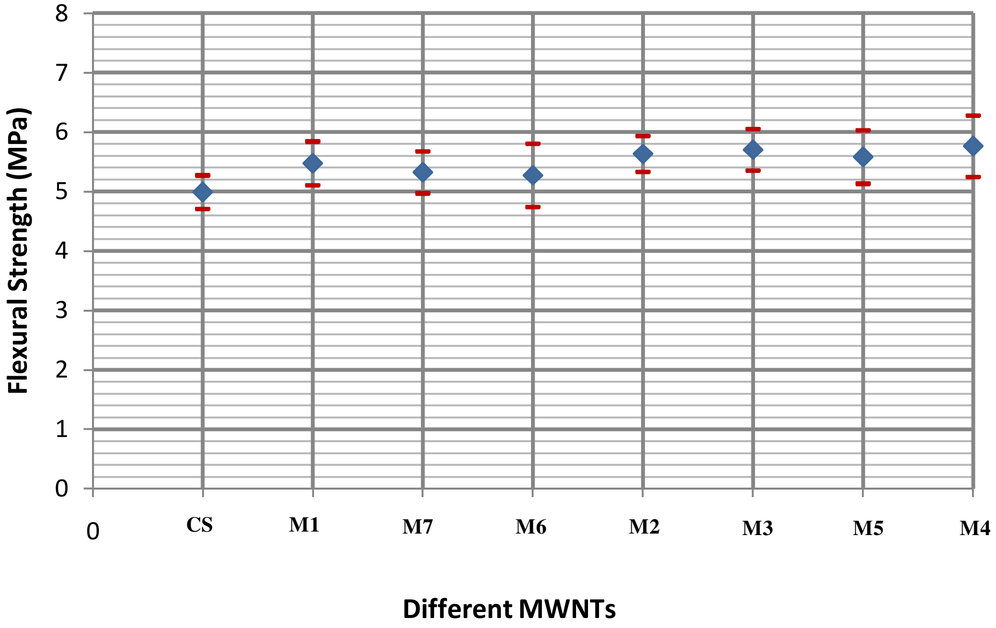


Figure 3.76: Flexural strength of control and treated 0.3% MWNT reinforced samples at 28 day

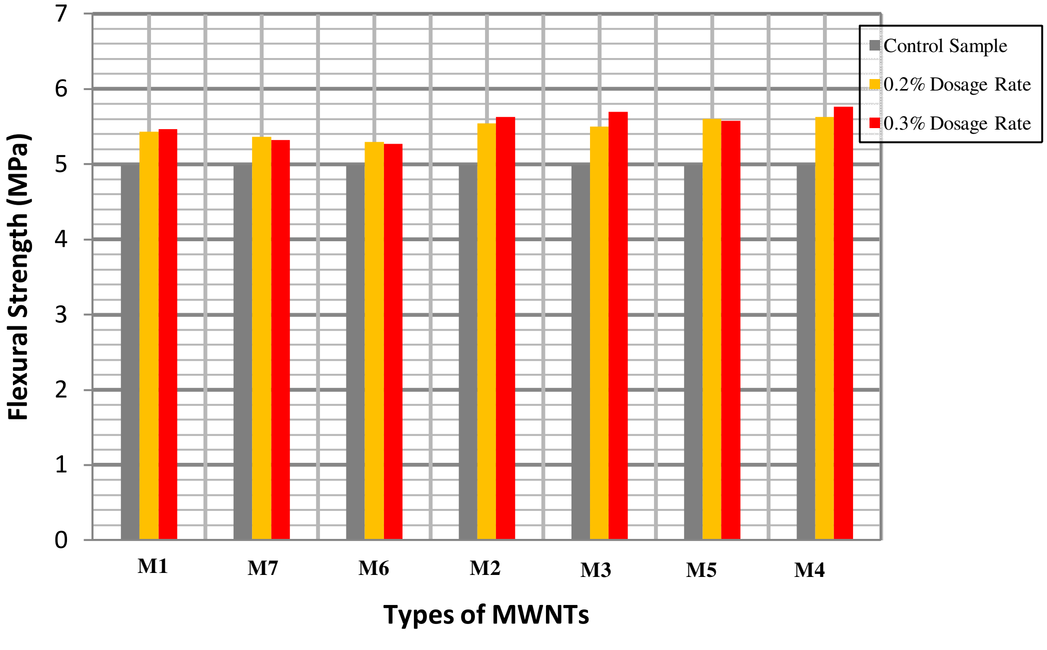


Figure 3.77: Flexural strength of control samples and 0.2% & 0.3% treated MWNT reinforced samples at 28 day

3.9 Discussion

The behavior and strength properties of seven different types of MWNT reinforced cement composites are discussed in this chapter. The effect of various mix proportions having different w/c ratios and plasticizer amount has also been explored. It was found that mixing of nanotubes plays an extremely important part to produce robust composites. It was also evident that there exists an optimum concentration of MWNT and mix proportion to produce strong composite under the process used in this study. In most cases composites with w/c ratio of 0.60 produced the highest compressive strengths. The 0.3% dosage rate of MWNT performed relatively better in terms of strength. However, for control samples the optimum w/c ratio was 0.485. Increases in compressive strengths were observed for all seven types of multiwalled nanotubes between 0.1 and 0.3% dosage rates of MWNT with w/c ratio of 0.60. It has been found that size of nanotubes has significant influence on strength of composites. Surface treated MWNT with sulfuric and nitric acid solution were also used as reinforcement as part of the experimental program. In all cases composites with treated MWNT yielded higher compressive strength than that of untreated ones. It was also observed that MWNT reinforced composites perform better in flexure than compression in terms of percentage increase in strength as compared to control samples. This is due to crack bridging and fiber pull out behavior of nanotubes are more pronounced in tension than compression. Finally it can be said that the initial results show some beneficial effect of utilizing MWNT in cement composites and demonstrate some of the challenges in terms of mixing techniques and workability issues that should be further investigated.

CHAPTER 4

PHASE II STUDY: COMPREHENSIVE EXPERIMENTAL ANALYSIS TO INVESTIGATE THE BEHAVIOUR OF MWNTS REINFORCED CEMENT COMPOSITES

4.1 Introduction

In this chapter, the second phase of the study is described. The surface treated M3 nano-tube was selected for this phase of experiments based on the first phase test results. The dosage rate of 0.3% was chosen since higher strengths were achieved by this amount of nanotubes in the majority of cases. Composite samples with large sample size were made using various mix proportions containing different amount of water and plasticizer in order to have a clear understanding on composite behavior. New mixing technique with plasticizer addition as surfactant was also explored. It was observed that using plasticizer as surfactant achieved more stable MWNT dispersion and eventually resulted in relatively robust composites. Hypothesis testing was also conducted on strength test data to compare composite strengths with control samples.

4.2 Compressive Strength of Composites

Composites reinforced with 0.3% dosage rate of treated M3 were prepared and tested to determine compressive strengths at 7 and 28 days. Treatment of M3 was made by a solution of nitric acid and sulfuric acid. Various properties of M3 are provided in Table 3.10. Ultrasonic vibration was used for dispersion of M3 within the cement matrix. Sonication and mixing of M3, cement, sand and water were done following the methods described in Sections 3.3 and 3.4. An MTS machine was used to break the samples for compressive strength measurement. Flow table was used to determine flow values of control and composite samples. Compressive strengths of control and composite samples are presented and discussed in the following sections. Comparisons of compressive strengths are also made between control samples and composite samples having different mix proportions.

4.2.1 Control Samples

Control samples containing no nanotubes were prepared using different w/c ratios, ranging from 0.485 to 0.60. Flow values were measured for each case and are provided in Table 4.1. It was found that the highest compressive strength was obtained for samples having w/c ratio of 0.50, both at 7 and 28 days. A total of 24 control samples were made with w/c ratio of 0.50 in four sets. The flow values ranged from 25-32%. The mean compressive strengths of 27.4 and 33 MPa at 7 and 28 days were obtained, respectively, for control samples with w/c ratio of 0.50. Figure 4.1 shows compressive strengths (both at the age of 7 and 28 days) from four different sets of control samples having w/c ratio of 0.50. Control samples with w/c ratio of 0.485 obtained mean compressive strengths of 26 MPa at 7 day and 32 MPa at 28 day. A total of three sets of samples were made in this case. Each set contained 6 samples. Compressive strengths of these control samples are presented in Figure 4.2. Control samples with w/c ratio of 0.60 resulted in the lowest compressive strengths. The average 7 and 28 day compressive strengths of 25.7 and 31.6 MPa were obtained, respectively, for w/c ratio of 0.60. A comparison of compressive strengths of control samples with different amount of water content is presented in Figure 4.3. Since control samples with w/c ratio of 0.50 yielded in maximum compressive strengths, both at 7 and 28 days, these strengths were used to compare with the strengths of composite samples containing M3 as reinforcement.

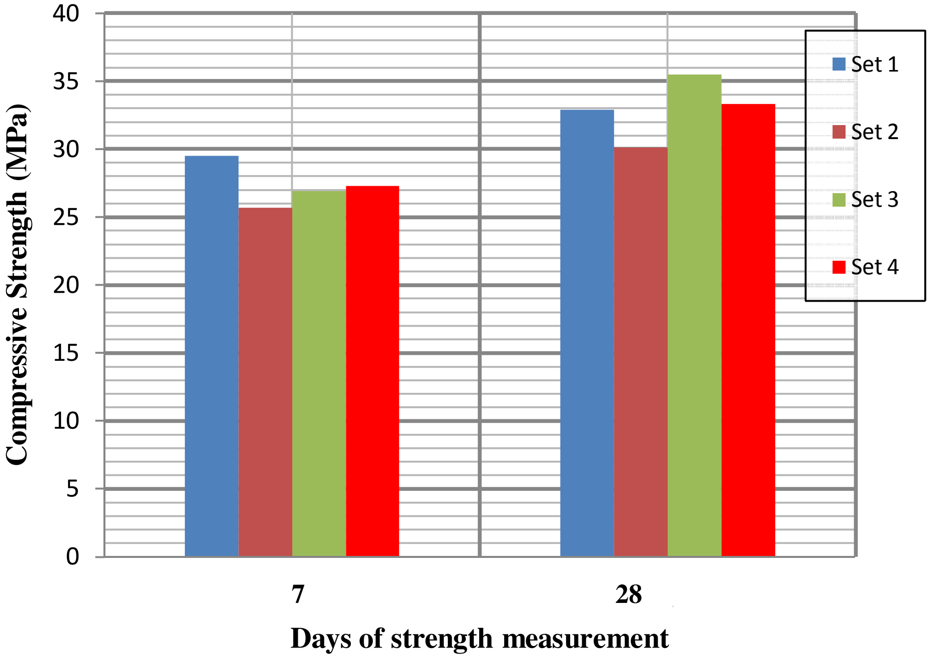


Figure 4.1: Compressive strength of control samples with w/c ratio of 0.50

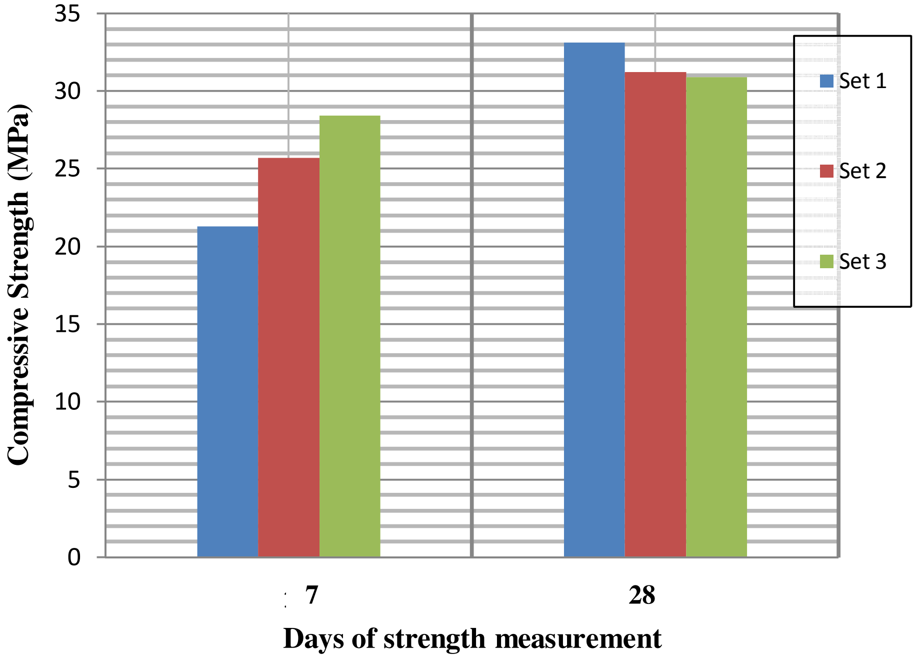


Figure 4.2: Compressive strength of control samples with w/c ratio of 0.485

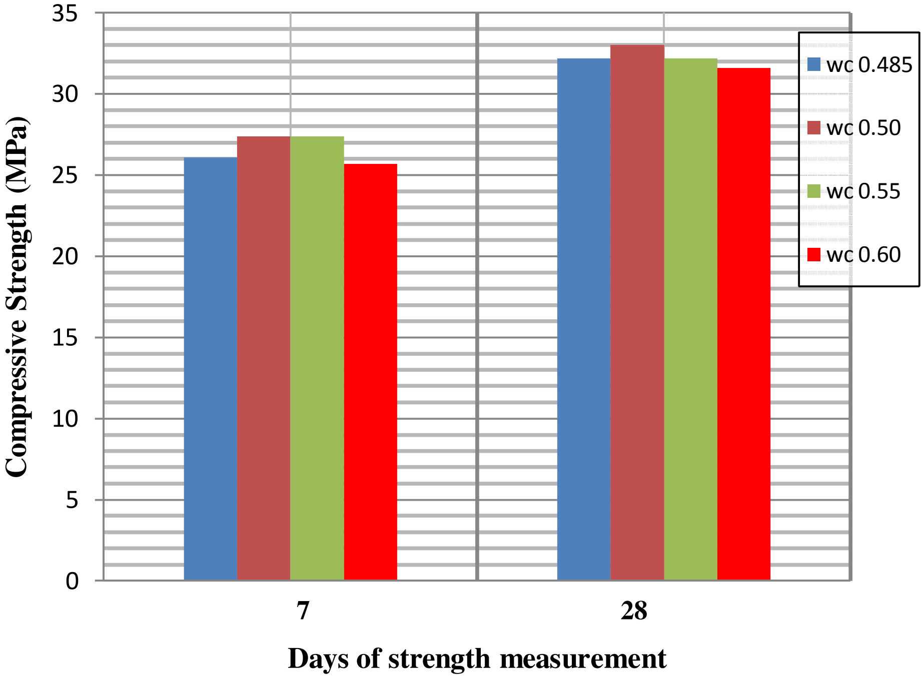


Figure 4.3: Compressive strength of control samples with different w/c ratio

Table 4.1: Test Information of Control Samples

Type of Sample	w/c ratio	No. of Samples*		Flow Values (%)	7 day mean compressive strength (MPa)	28 day mean compressive strength (MPa)
Control	0.485	S1*	6	18	26.0±3.38	32.2±1.72
		S2	6	25		
		S3	6	23		
Control	0.50	S1	6	32	27.4±1.66	33.0±2.00
		S2	6	25		
		S3	6	32		
		S4	6	30		
Control	0.55	S1	6	52	27.4±1.24	32.2±1.60
Control	0.60	S1	6	68	25.7±1.31	31.6±1.79

*S1: Set 1, S2: Set 2, S3: Set 3, S4: Set 4

4.2.2 Composites with Different Mix Proportions

Composite samples reinforced by 0.3% M3 were made with different mix proportions. Initially, composites having w/c ratio of 0.60 were used as this mix proportion obtained the maximum compressive strengths in the first phase. A total of eight sets of composite samples were made using this water content. There were six samples in each set. Figure 4.4 shows the compressive strengths of composites with w/c ratio of 0.60, both at the age of 7 and 28 days. The highest and lowest compressive strengths of 38.8 and 33.7 MPa at 28 day were obtained, respectively. These composites had mean compressive strengths of 31 MPa at 7 day and 36.1 MPa at 28 day. In Table 4.2, test information (total number of samples for each set and corresponding flow values and mean strengths with standard deviations) of these composites are provided.

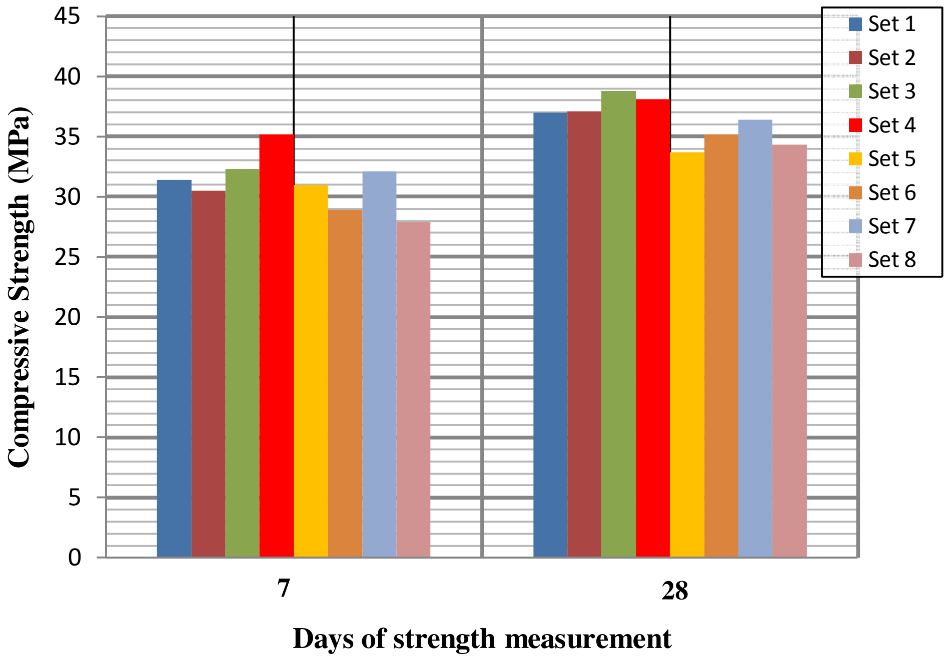


Figure 4.4: Compressive strength of composite samples with w/c ratio of 0.60

Table 4.2: Test Information of Composite Samples with w/c ratio of 0.60

Type of Sample	Amount of M3 (%)	w/c ratio	Amount of plasticizer (as part of cement by wt.)	No. of Samples *		Flow Values (%)	7 day mean compressive strength (MPa)	28 day mean compressive strength (MPa)
Composite	0.3	0.60	NA	S1*	6	52	31.0±2.41	36.1±1.93
				S2	6	54		
				S3	6	56		
				S4	6	49		
				S5	6	40		
				S6	6	42		
				S7	6	44		
				S8	6	33		

*S1: Set 1, S2: Set 2, S3: Set 3, S4: Set 4, S5: Set 5, S6: Set 6, S7: Set 7, S8: Set 8

Compressive strengths of composites with w/c ratio of 0.55 are shown in Figure 4.5. A total of 36 samples were made in six sets. Mean 7 and 28 day compressive strengths of 27.8 and 32.6 MPa were obtained, respectively. Test information of these six sets of composites is provided in Table 4.3.

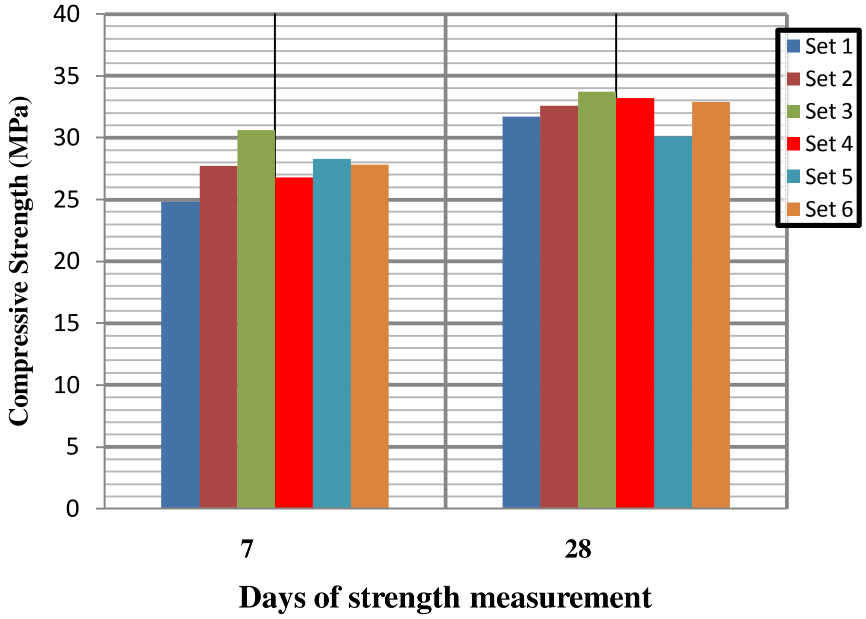


Figure 4.5: Compressive strength of composite samples with w/c ratio of 0.55

Table 4.3: Test Information of Composite Samples with w/c ratio of 0.55

Type of Sample	Amount of M3 (%)	w/c ratio	Plasticizer amount (as part of cement)	No. of Samples *		Flow Values (%)	7 day mean compressive strength (MPa)	28 day mean compressive strength (MPa)
Composite	0.3	0.55	NA	S1*	6	20	27.8±1.93	32.3±1.45
				S2	6	22		
				S3	6	22		
				S4	6	22		
				S5	6	11		
				S6	6	16		

*S1: Set 1, S2: Set 2, S3: Set 3, S4: Set 4, S5: Set 5, S6: Set 6

Composites were also made with w/c ratio of 0.62, 0.65 and 0.70. More variation in w/c ratio was utilized in this phase to have a detailed understanding on the effect of water content on composite strengths. A total of five sets of samples were prepared for w/c ratio of 0.62. In each set, there were 6 samples. Figure 4.6 shows 7 and 28 day compressive strengths of five different sets of composite samples with w/c ratio of 0.62. The maximum compressive strength of 37.6 MPa was obtained at 28 day. These composites had mean compressive strengths of 32.2 and 36.4 MPa at 7 and 28 day, respectively. Test information of these composites is given in Table 4.4. In Figure 4.7, compressive strengths of composites having w/c ratio of 0.65 are presented. A total of 24 samples were made. A mean compressive strength of 35.8 MPa was obtained at 28 day. The seven day mean compressive strength was 31.2 MPa. Table 4.5 contains the test information of composite samples with w/c ratio of 0.65. A total of 12 composite samples were prepared in 2 sets having w/c ratio of 0.70. Test information is provided in Table 4.6. Mean compressive strengths at 7 and 28 day were obtained as 27.0 and 31.0 MPa, respectively. Compressive strengths of composites having w/c ratio of 0.50 are shown in Figure 4.8. The sample size was 18 in this case. The mean compressive strengths at 7 and 28 day were obtained as 19.3 and 22.3 MPa, respectively. It was found that composites with w/c ratio of 0.50 had the lowest compressive strength, both at early age of 7 day and at 28 day. Flow values of these composites were the lowest, ranging between 5% and 7%. Composite samples were also made with plasticizer addition. Three different proportions of plasticizer were used with respect to the weight of cement. The w/c ratio was kept at 0.50 in all cases of plasticizer addition. A total of 24 samples were made with plasticizer proportion of 0.005 in 4 sets. Seven and twenty eight day compressive strengths of these composites are shown in Figure 4.9. These composites produced mean compressive strengths of 28.6 and 30.3 MPa at 7 and 28 day, respectively. In Figure 4.10, compressive strengths of composite samples with plasticizer proportion of 0.015 are showed. Test information of all the composite samples made with plasticizer addition is given in Table 4.7.

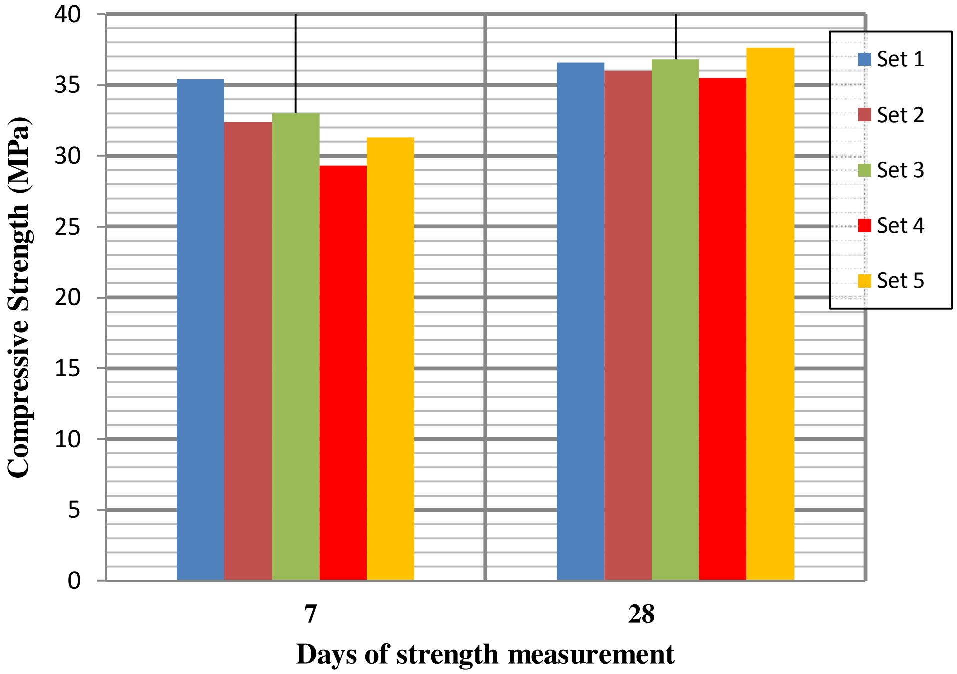


Figure 4.6: Compressive strength of composite samples with w/c ratio of 0.62

Table 4.4: Test Information of Composite Samples with w/c ratio of 0.62

Type of Sample	Amount of M3 (%)	w/c ratio	Amount of plasticizer (as part of cement by wt.)	No. of Samples *		Flow Values (%)	7 day mean compressive strength (MPa)	28 day mean compressive strength (MPa)
Composite	0.3	0.62	NA	S1*	6	47	32.2±2.10	36.4±1.31
				S2	6	42		
				S3	6	47		
				S4	6	49		
				S5	6	53		

*S1: Set 1, S2: Set 2, S3: Set 3, S4: Set 4, S5: Set 5

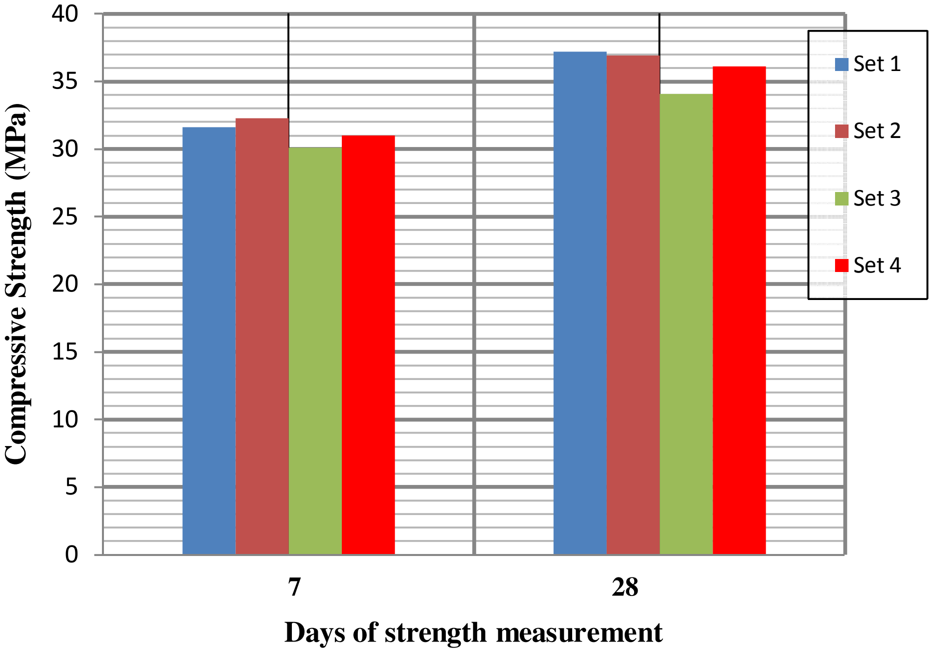


Figure 4.7: Compressive strength of composite samples with w/c ratio of 0.65

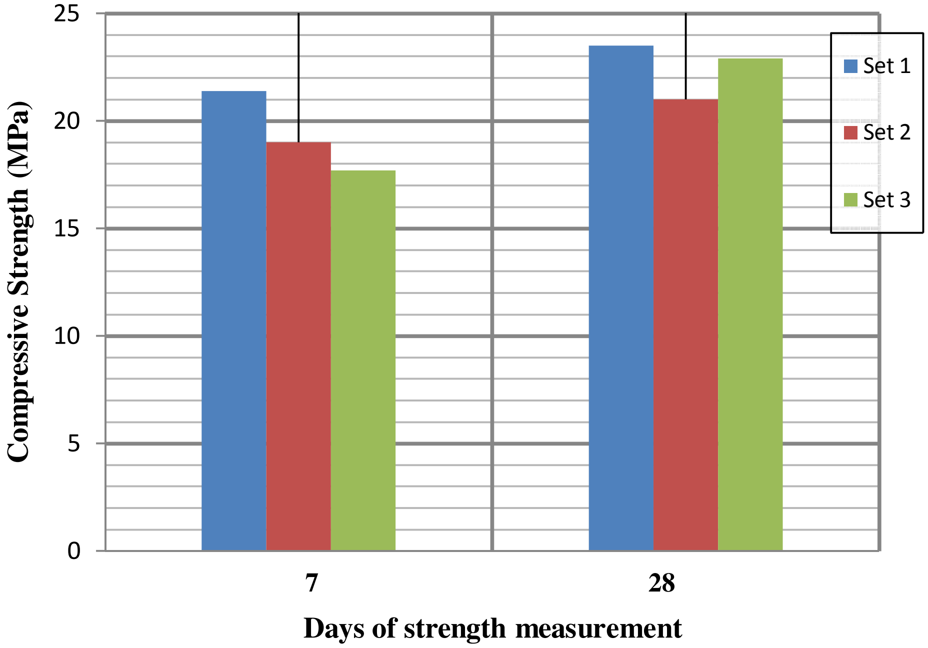


Figure 4.8: Compressive strength of composite samples with w/c ratio of 0.50

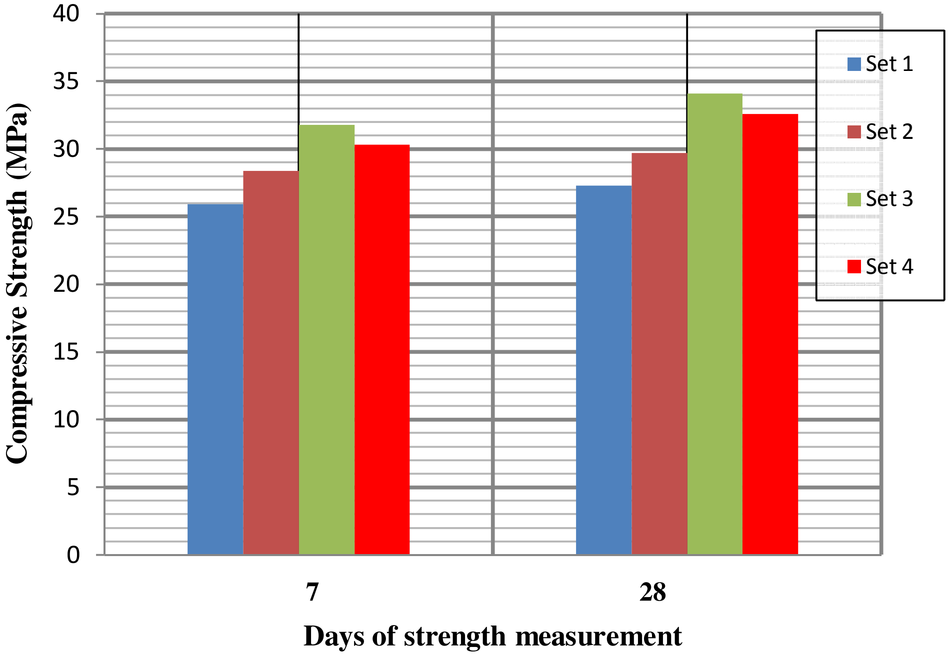


Figure 4.9: Compressive strength of composite samples with plasticizer proportion of 0.005

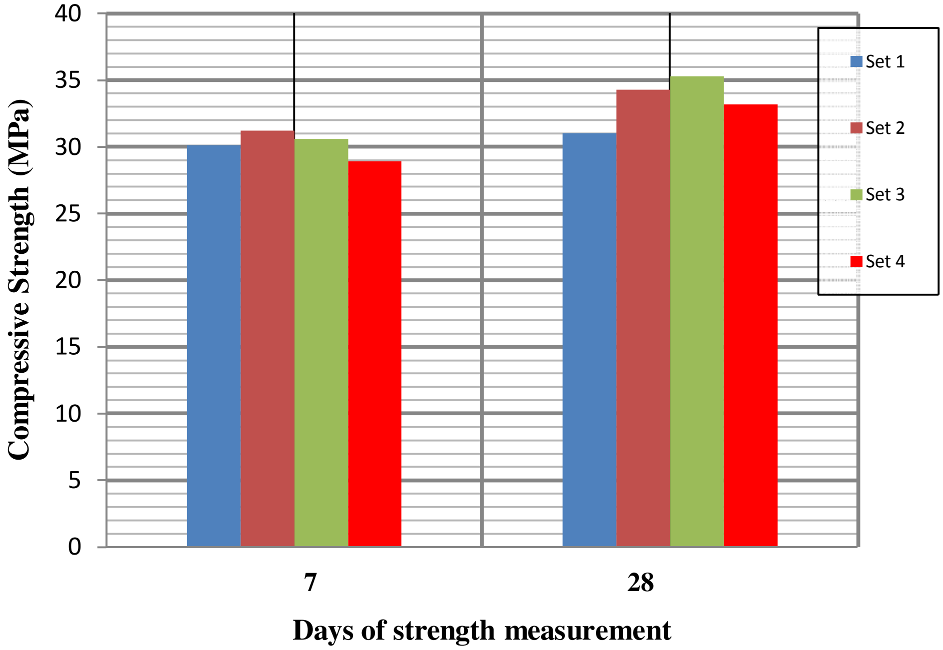


Figure 4.10: Compressive strength of composite samples with plasticizer proportion of 0.015

Table 4.5: Test Information of Composite Samples with w/c ratio of 0.65

Type of Sample	Amount of M3 (%)	w/c ratio	Amount of plasticizer (as part of cement by wt.)	No. of Samples *		Flow Values (%)	7 day mean compressive strength (MPa)	28 day mean compressive strength (MPa)
Composite	0.3	0.65	NA	S1*	6	60	31.2±0.97	35.9±1.79
				S2	6	58		
				S3	6	38		
				S4	6	56		

*S1: Set 1, S2: Set 2, S3: Set 3, S4: Set 4

Table 4.6: Test Information of Composite Samples with w/c ratio of 0.70

Type of Sample	Amount of M3 (%)	w/c ratio	Amount of plasticizer (as part of cement by wt.)	No. of Samples *		Flow Values (%)	7 day mean compressive strength (MPa)	28 day mean compressive strength (MPa)
Composite	0.3	0.70	NA	S1*	6	73	27.0±2.41	30.6±1.17
				S2	6	83		

*S1: Set 1, S2: Set 2

Table 4.7: Test Information of Composite Samples with Plasticizer

Type of Sample	Amount of M3 (%)	w/c ratio	Amount of plasticizer (as part of cement by wt.)	No. of Samples *		Flow Values (%)	7 day mean compressive strength (MPa)	28 day mean compressive strength (MPa)
Composite	0.3	0.50	0.005	S1*	6	5	28.6±2.62	30.3±3.17
				S2	6	13		
				S3	6	15		
				S4	6	13		
Composite	0.3	0.50	0.010	S1	6	11	30.6±1.93	31.9±1.31
				S2	6	27		
				S3	6	22		
Composite	0.3	0.50	0.015	S1	6	36	30.3±1.24	33.4±2.00
				S2	6	20		
				S3	6	29		
				S4	6	24		

*S1: Set 1, S2: Set 2, S3: Set 3, S4: Set 4

4.2.3 Comparison of Compressive Strengths

Comparisons between compressive strengths of control samples and composites at 7 and 28 day are made in this section. Comparisons are also made among the compressive strengths of composites having different mix proportions. Control samples with w/c ratio of 0.50 yielded the maximum compressive strengths among control samples having different w/c ratio (Figure

4.3). In Figure 4.11, compressive strengths of composites containing different amount of water are presented. Samples with w/c ratio of 0.62 produced the highest compressive strength, both at 7 and 28 days. Lowest compressive strengths were obtained for composite samples having w/c ratio of 0.50. The differences between these highest and lowest compressive strengths at 7 and 28 day were 51% and 63%, respectively. Composite sample with w/c ratio of 0.60 had slightly lower compressive strengths than that of samples with w/c ratio of 0.62, both at 7 and 28 days. Composites made with w/c ratio of 0.70 produced 8% and 19% less compressive strengths at 7 and 28 day than composites with w/c ratio of 0.62, respectively. Samples having w/c ratio of 0.55 had 10.6% and 12.6% lower compressive strengths at 7 and 28 days, as compared to composites with w/c ratio of 0.62. It is apparent from Figure 4.11 that composites having w/c ratio between 0.60 and 0.65 obtained almost similar compressive strengths particularly at the age of 28 day.

Figure 4.12 shows compressive strengths of control samples and composites made by addition of different amount of plasticizer to increase the workability. In most cases, 28 day compressive strengths of composites were less than that of control samples. However, the seven day compressive strengths of these composites were higher than the strengths of control samples. Similar phenomenon was also observed in the first phase of the study.

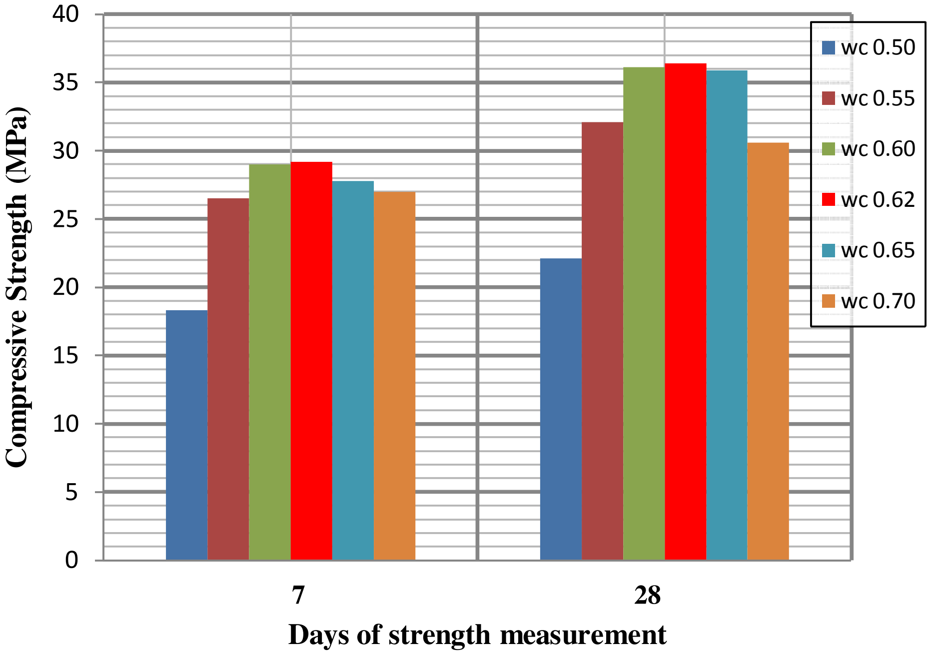


Figure 4.11: Compressive strengths of composite samples with various w/c ratio

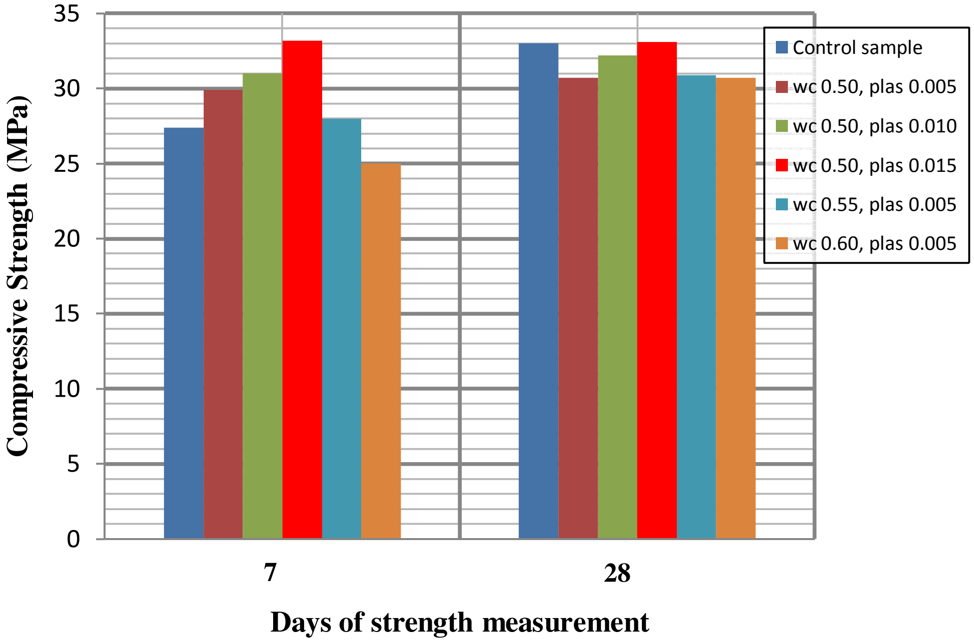


Figure 4.12: Compressive strengths of composite samples with plasticizer

Compressive strengths of control samples and composite samples having a variety of mix proportions are shown in Figure 4.13. Composites with w/c ratio of 0.50 had the lowest compressive strengths, both at 7 and 28 days. These composites had 22.6% and 32% less compressive strengths than that of control samples at 7 and 28 day, respectively. The highest compressive strengths at 28 day were achieved by composites with w/c ratio of 0.62. These composites had 17.5% and 10.3% higher compressive strengths at 7 and 28 day, as compared to control samples. Compressive strengths of composite samples having w/c ratio of 0.60 were 13.2% and 9.4% higher than the control sample's compressive strengths at the age of 7 and 28 day, respectively. Composites with w/c ratio of 0.65 also obtained higher compressive strengths than the control samples. The seven days compressive strength of these composites was about 14% greater than the control samples. The compressive strength at the age of 28 day was 8.8% higher in this case. Composites having w/c ration of 0.70 produced lower 7 and 28 day compressive strengths as compared to control samples. Composites with plasticizer and w/c ratio of 0.50 obtained higher compressive strengths at 7 day than control samples. The 28 day compressive strengths of these samples were lower with reference to the strengths of control samples in most cases. Only composites with plasticizer proportion of 0.015 and w/c ratio of 0.50 produced similar compressive strengths as control samples at 28 day. These composites with plasticizer proportion of 0.015 had 14.5% higher compressive strength at 7 day than that of control samples. Addition of plasticizer with higher amount of water resulted in lesser compressive strengths than that of control samples. In all instances composites with nanotubes achieved relatively higher compressive strengths 7 day than that of 28 day as compared to control samples. Similar trend was also observed in the first phase of the study in majority of cases. Therefore, it is evident that the presence of nanotubes accelerates the hydration process at early age of cement mortar.

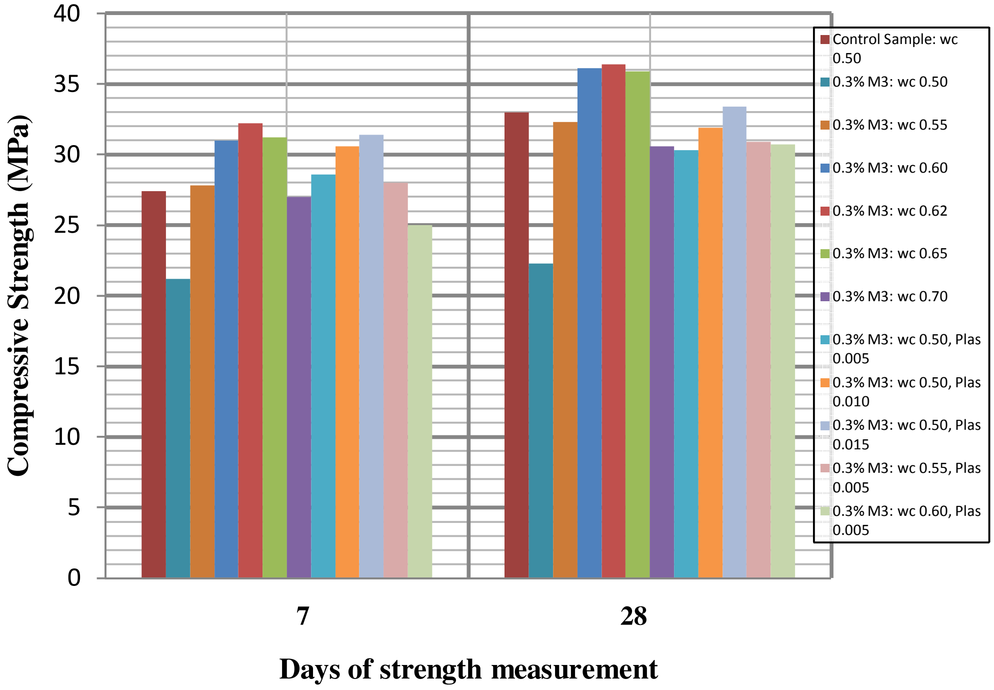


Figure 4.13: Compressive strengths of composite samples with different mix proportions

4.2.4 Importance of Flow Values

The compressive strengths of composites with w/c ratio of 0.60 were presented in Figure 4.4. It was obvious that compressive strengths had significant fluctuation both at 7 and 28 days. Similar variation was also observed for composites having other w/c ratios. Therefore, an attempt was made to establish a relation between compressive strengths and flow values for composites samples, both at the age of 7 and 28 day. Figures 4.14 and 4.15 show the relation between the average compressive strengths (with standard deviation) of different sets and corresponding flow values of composites having w/c ratio of 0.60 at the age of 7 and 28 day, respectively. A total of 48 samples were made in 8 sets. Flow values were measured for each set of the samples.

It is apparent that the effect of flow values on compressive strength was most pronounced at 28 day. Composites with higher flow values resulted in relatively higher compressive strengths at 28 day. The maximum 28 day compressive strength of 38.8 MPa was obtained for the highest flow value of 56%. It was also found that the mean compressive strength of these composites having flow values greater than 49% was 37.8 MPa. Composites having flow values less than 49% had mean compressive strength of 34.9 MPa at 28 day in this case. The lowest compressive strength was 33.7 MPa for a flow value of 40%. Similar trend was also found for 7 day compressive strengths but not as prominent as in the case of 28 day. In most cases, it was found that the 7 day compressive strengths of composites were higher than that of control samples even when the corresponding compressive strengths at 28 day were less as compared to control samples. Since the presence of nanotubes accelerates the early hydration process, it is understandable that there will be less influence of flow values on compressive strengths of nanotubes reinforced composites at early age. The relation between compressive strengths and flow values for composites with w/c ratio of 0.55 are shown in Figures 4.16 and 4.17. Both at 7 and 28 days, the maximum compressive strengths were obtained by the composite having the maximum flow values. Figures 4.18 through 4.21 present the relation between compressive strengths and flow values of composites having w/c ratio of 0.62 and 0.65. Similar phenomenon was also observed in these cases.

Relations between compressive strengths and flow values were also developed for composites made with plasticizer to increase the workability of mix. They are shown in Figures 4.22 through 4.25. The higher compressive strengths at 28 day were achieved by composites with higher flow values. However, the compressive strengths at 28 day were less than that of control samples in majority of cases. Therefore, it becomes clear that the higher compressive strengths particularly at 28 day were obtained for higher flow values for all composites irrespective of mix proportions.

It is obvious that the higher flow values represent better dispersion of nanotubes within the cement matrix. Inadequate distribution of nanotubes makes the mix viscous resulting in low flow values. As a result workability decreases, the cement paste fails to completely fill the molds and large bubbles get trapped in the cement. The corresponding voids created by these bubbles produce samples with uneven surfaces and sides. At the same time, inappropriate dispersion of nanotubes means more nanotubes remain adhere to each other. If the agglomeration of nanotubes is not broken properly, they create zones of weakness within the cement paste. The eventual outcome is the weaker composites with lesser compressive strengths. Therefore, flow values can be considered as a good measure of the quality of cement mix reinforced by nanotubes. A higher flow value of MWNT added composites, having same mix proportion, represents more uniform distribution of MWNT within the cement grains and more stable mix.

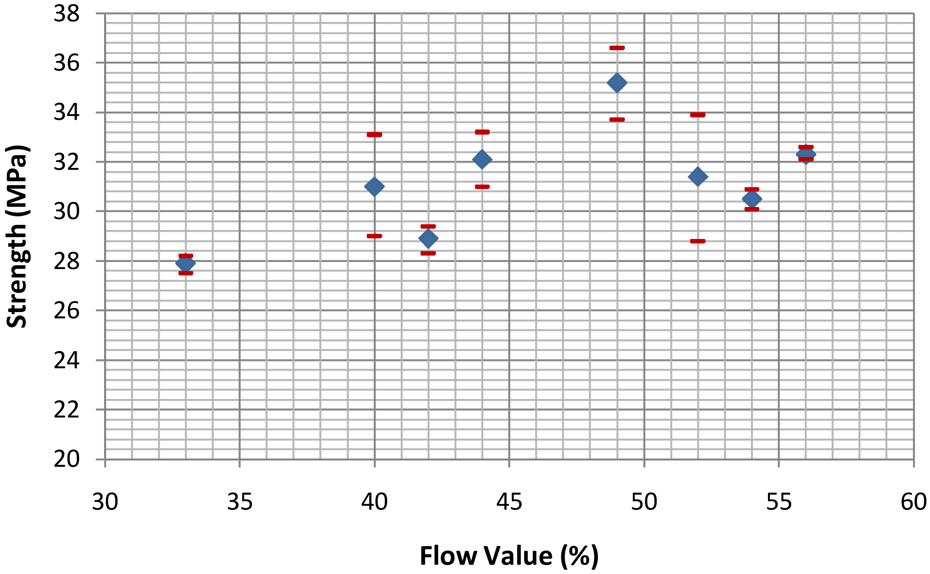


Figure 4.14: Compressive strengths vs flow values of composites with w/c ratio of 0.60 at 7 day

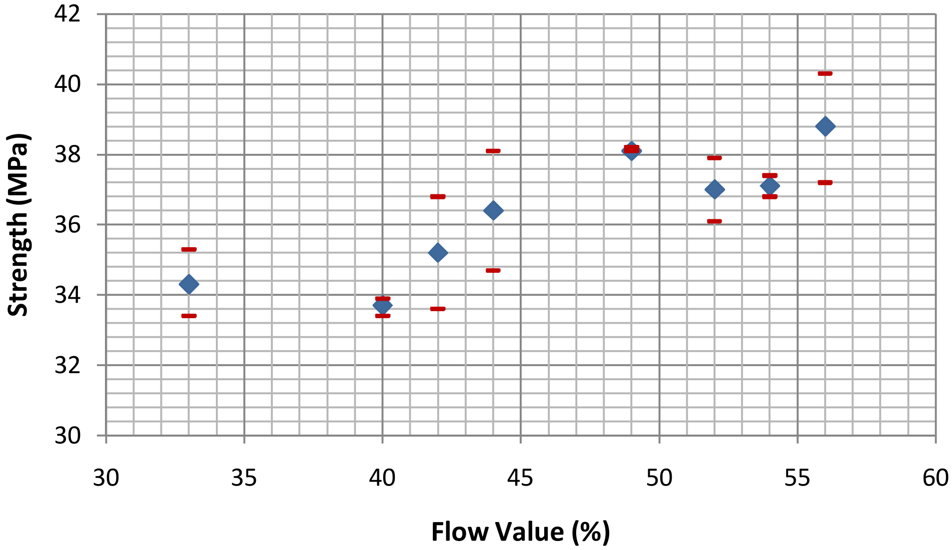


Figure 4.15: Compressive strengths vs flow values of composites with w/c ratio of 0.60 at 28 day

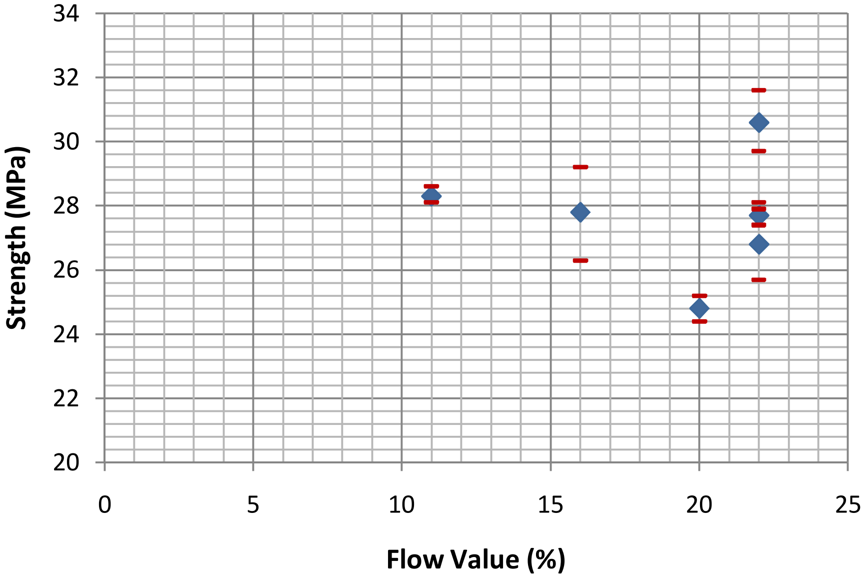


Figure 4.16: Compressive strengths vs flow values of composites with w/c ratio of 0.55 at 7 day

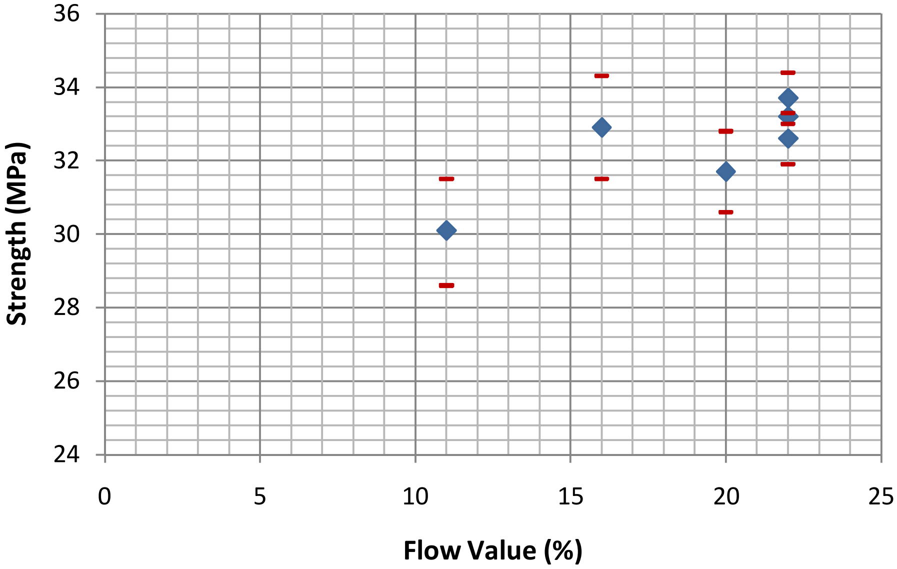


Figure 4.17: Compressive strengths vs flow values of composites with w/c ratio of 0.55 at 28 day

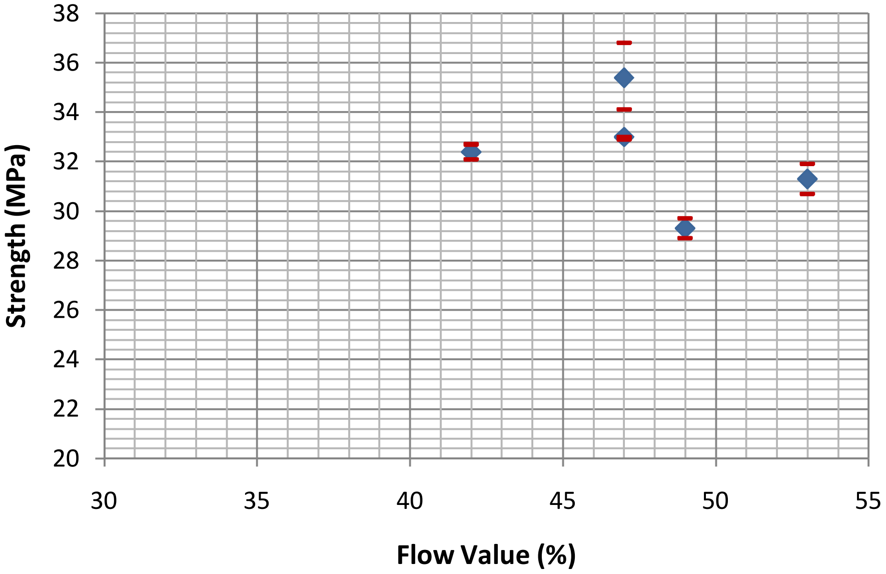


Figure 4.18: Compressive strengths vs flow values of composites with w/c ratio of 0.62 at 7 day

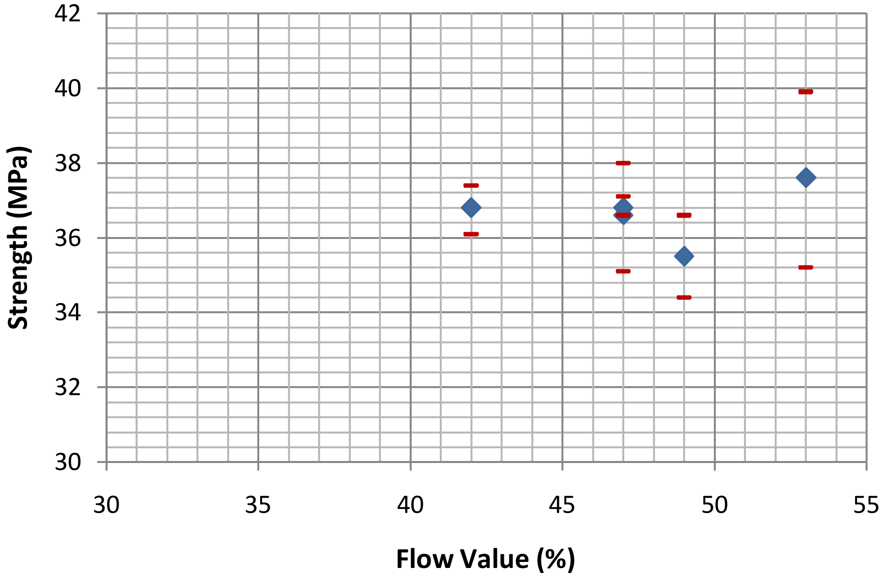


Figure 4.19: Compressive strengths vs flow values of composites with w/c ratio of 0.62 at 28 day

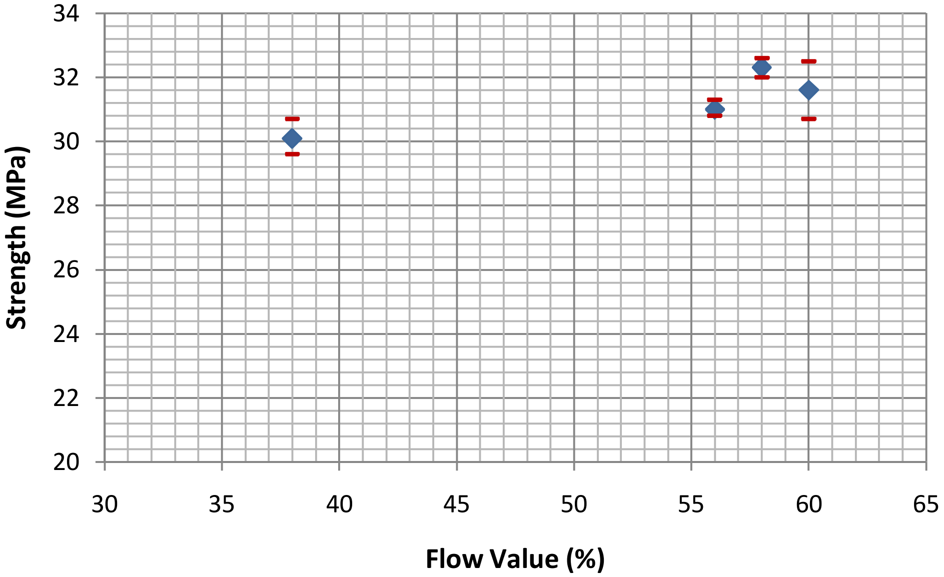


Figure 4.20: Compressive strengths vs flow values of composites with w/c ratio of 0.65 at 7 day

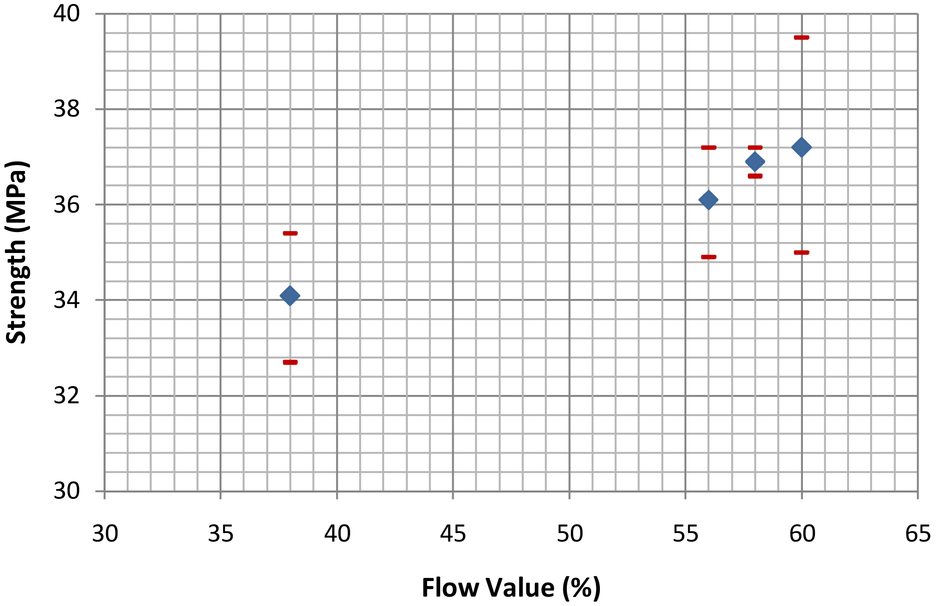


Figure 4.21: Compressive strengths vs flow values of composites with w/c ratio of 0.65 at 28 day

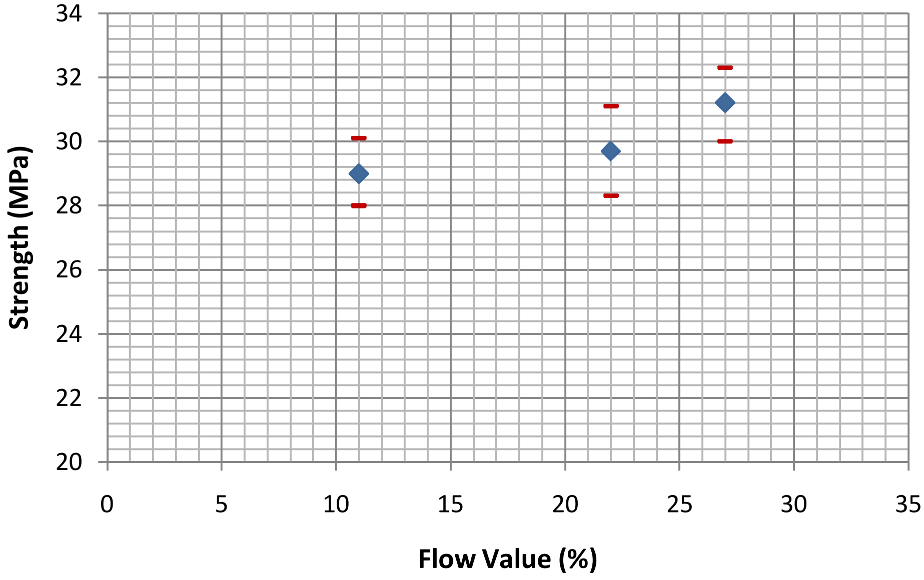


Figure 4.22: Compressive strengths vs flow values of composites with w/c ratio of 0.50 and plasticizer proportion of 0.010 at 7 day

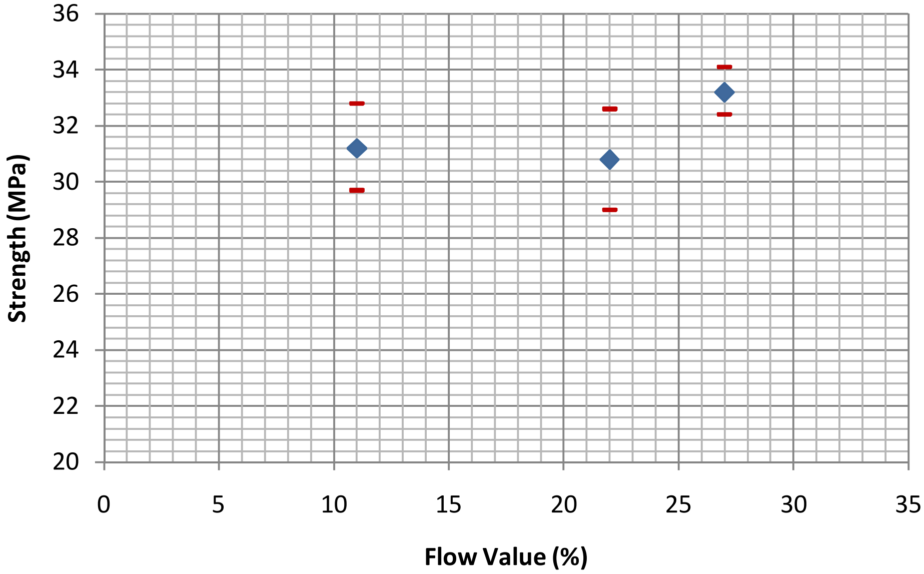


Figure 4.23: Compressive strengths vs flow values of composites with w/c ratio of 0.50 and plasticizer proportion of 0.010 at 28 day

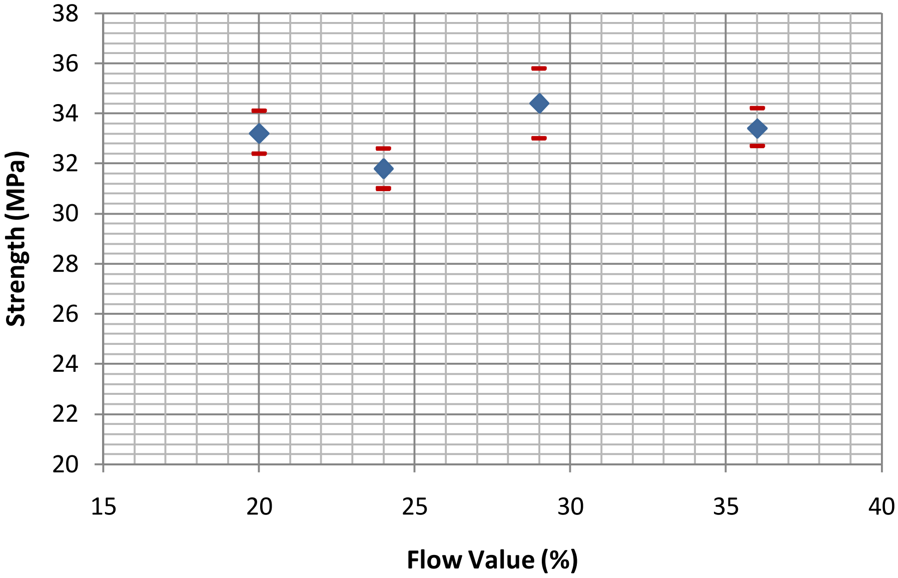


Figure 4.24: Compressive strengths vs flow values of composites with w/c ratio of 0.50 and plasticizer proportion of 0.015 at 7 day

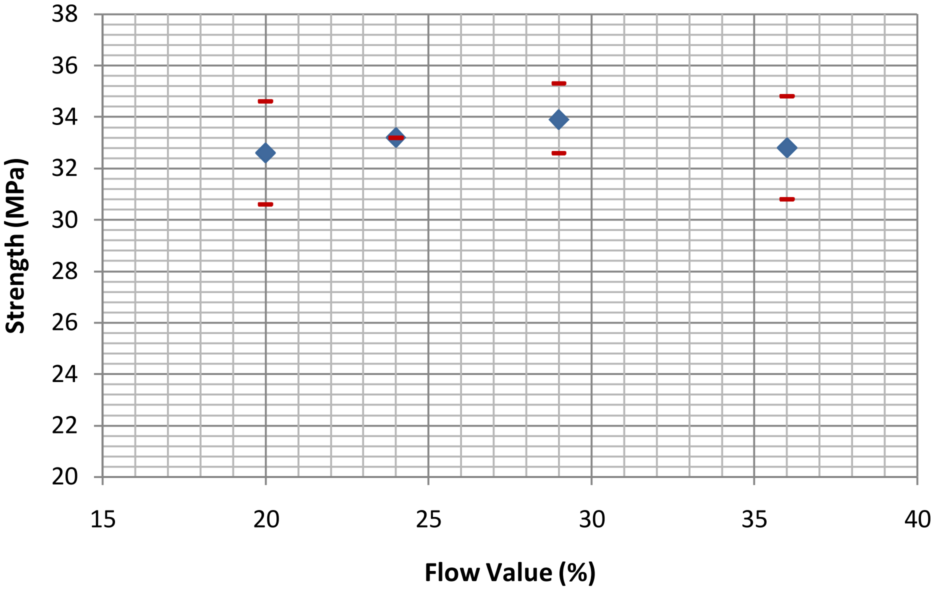


Figure 4.25: Compressive strengths vs flow values of composites with w/c ratio of 0.50 and plasticizer proportion of 0.015 at 28 day

4.3 Application of Plasticizer as Surfactant

It was observed in section 4.2.4 that the samples with higher flow values obtained higher compressive strengths. Higher flow values represent less viscous mixes produced from the uniform and proper dispersion of MWNT and eventually mean that adequate dispersion of MWNT ensures stronger composites. Sonication of MWNT in water only was not successful to produce stable mixes in all cases. Surfactants that are usually used to sonicate nanotubes in ceramic and other industry hinder the cement hydration process. Utilization of those surfactants resulted in extremely weak composites. Some recent studies (Gay et al, 2010 and Yazdanbaksh et al, 2010) showed that polycarboxylate based water reducing agent can be used as surfactant to disperse nanotubes within aqueous solution. Utilization of such super plasticizer as surfactant to distribute MWNT within cement matrix, not only ensure adequate dispersion of nanotubes but also increase workability of cement paste that is necessary to produce strong composites.

4.3.1 Mixing Technique

Composite samples were made using ADVA Cast 575 superplasticizer as surfactant. ADVA Cast 575 is a polycarboxylate based ASTM C494 (ASTM C494, 2010) Type F and ASTM C1017 (ASTM C1017, 2010) Type I plasticizing agent. Three different proportions of plasticizer, ranging from 0.005 to 0.010, were used in terms of weight of cement. Required amount of plasticizer was first mixed with water and sonicated for two minutes. Then the MWNT were added to that plasticizer mixed water and sonicated in sequence as described in sections 3.3 and 3.4. Compressive strengths of the samples were determined according to ASTM C109 (ASTM C109, 2008).

4.3.2 Compressive Strengths of Composites

Compressive strengths of composite samples with plasticizer proportion of 0.005 are shown in Figure 4.26. The w/c ratio was 0.50. A total of 24 samples in 4 sets were made. The mean compressive strength of 36.4 MPa was obtained at 7 day. The 28 day mean compressive strength was 40.8 MPa. The corresponding maximum compressive strengths of control samples were 27.2 and 36.2 MPa, respectively. Therefore, an 33.8% and 12.7% higher compressive strengths were obtained at 7 and 28 days, respectively, for these composites. Test information of these composites is provided in Table 4.8.

Relations between compressive strengths and flow values are presented in Figures 4.27 and 4.28. Closely spaced flow values were observed in both the cases. Flow values were ranged between 33 and 38%. It is also apparent from Figures 4.27 and 4.28 that the compressive strengths had less fluctuation, both at 7 and 28 days, as compared to composites prepared without using plasticizer as surfactant. Using plasticizer as surfactant hinders the agglomeration of nanotubes and ensures proper dispersion. The w/c ratio was kept as 0.50. This means that proper dispersion of nanotubes lessen the water demand as no water gets entrapped within the clumped nanotubes. At the same time, adequate dispersion ensures effective filling of nano space within the cement matrix by nanotubes that eventually results in more compact composite and ensures better reinforcement behavior.

In Figure 4.29, compressive strengths of composites with plasticizer proportion of 0.008 as surfactant, both at 7 and 28 days, are shown. The mean 7 and 28 day compressive strengths were obtained as 36.3 and 42.1 MPa, respectively. A total of 4 sets of samples were made and each set contained 6 samples. Relations between compressive strengths and flow values are presented in Figures 4.30 and 4.31. Less variation in compressive strengths was observed both at 7 and 28 days. The flow values were ranged from 34 to 42%. Closely spaced flow values and higher compressive strengths indicate more stable mix can be achieved through plasticizer addition as surfactant. Table 4.9 contains the test information of these composites.

Seven and twenty eight day compressive strengths of composite samples with plasticizer proportion of 0.010 as surfactant are shown in Figure 4.32. The total number of samples was 24 and they were made in 4 sets. Mean compressive strengths of 35.2 and 40.3 MPa were obtained at 7 and 28 days, respectively. Test information of these composites is provided in Table 4.10. Relations between compressive strengths and flow values for these composites are shown in Figures 4.33 and 4.34. The compressive strengths and flow values had less variation. Therefore, similar trend was observed in this case as previously observed for composites with plasticizer as surfactant.

Table 4.8: Test Information of Composite Samples with Plasticizer Proportion of 0.005 as Surfactant

Type of Sample	Amount of M3 (%)	w/c ratio	Amount of plasticizer (as part of cement by wt.)	No. of Samples *		Flow Values (%)	7 day mean compressive strength (MPa)	28 day mean compressive strength (MPa)
Composite	0.3	0.50	0.005	S1*	6	33	36.4±2.90	40.2±1.86
				S2	6	36		
				S3	6	38		
				S4	6	33		

*S1: Set 1, S2: Set 2, S3: Set 3, S4: Set 4

Table 4.9: Test Information of Composite Samples with Plasticizer Proportion of 0.008 as Surfactant

Type of Sample	Amount of M3 (%)	w/c ratio	Amount of plasticizer (as part of cement by wt.)	No. of Samples *		Flow Values (%)	7 day mean compressive strength (MPa)	28 day mean compressive strength (MPa)
Composite	0.3	0.50	0.008	S1*	6	34	36.3±1.10	42.1±2.40
				S2	6	42		
				S3	6	38		
				S4	6	40		

*S1: Set 1, S2: Set 2, S3: Set 3, S4: Set 4

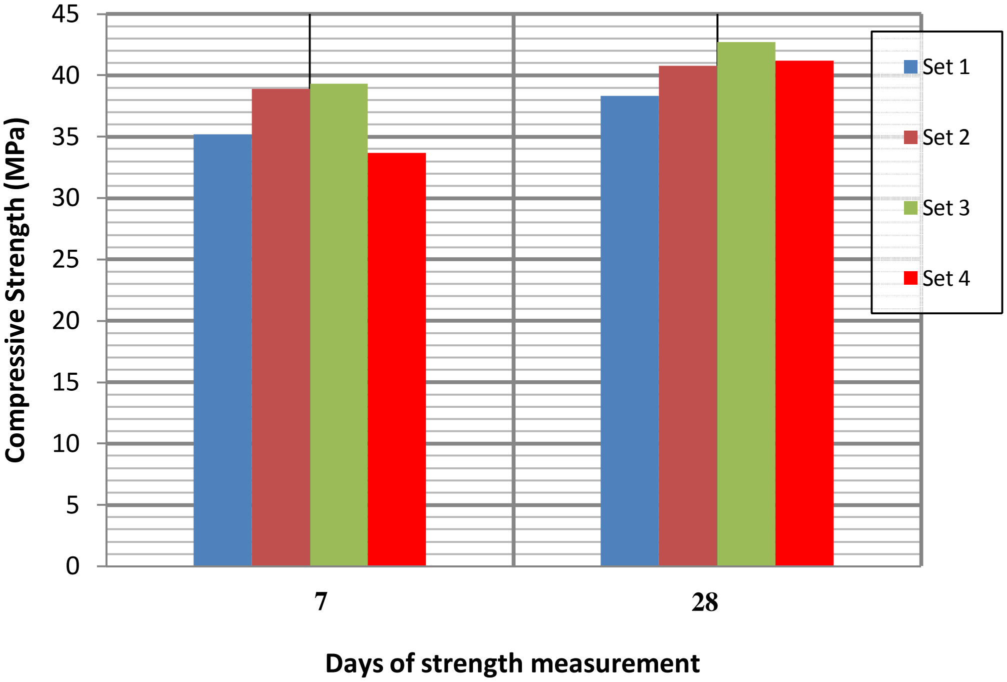


Figure 4.26: Compressive strengths of composite samples with plasticizer proportion of 0.005 as surfactant

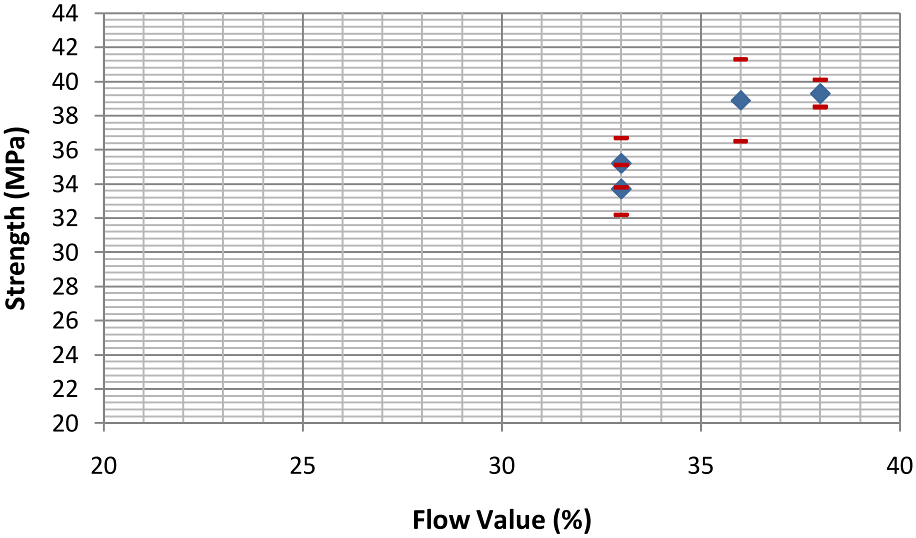


Figure 4.27: Compressive strengths vs flow values of composites with plasticizer proportion of 0.005 as surfactant at 7 day

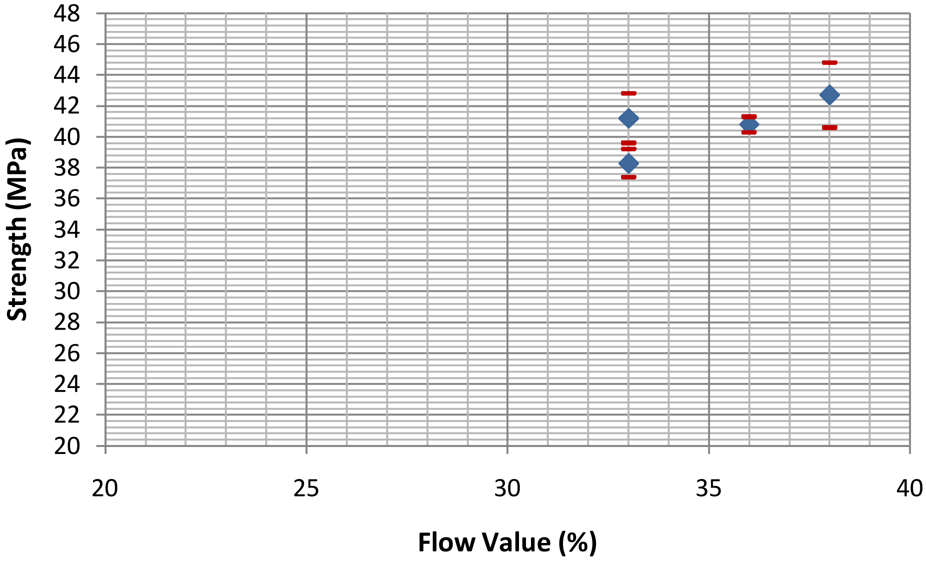


Figure 4.28: Compressive strengths vs flow values of composites with plasticizer proportion of 0.005 as surfactant at 28 day

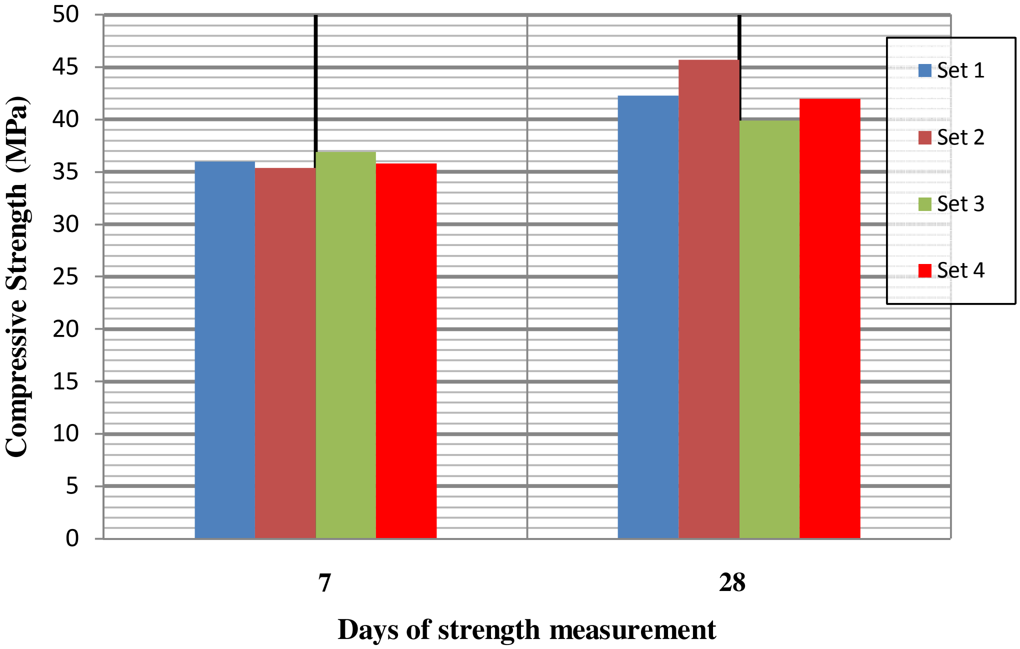


Figure 4.29: Compressive strengths of composite samples with plasticizer proportion of 0.008 as surfactant

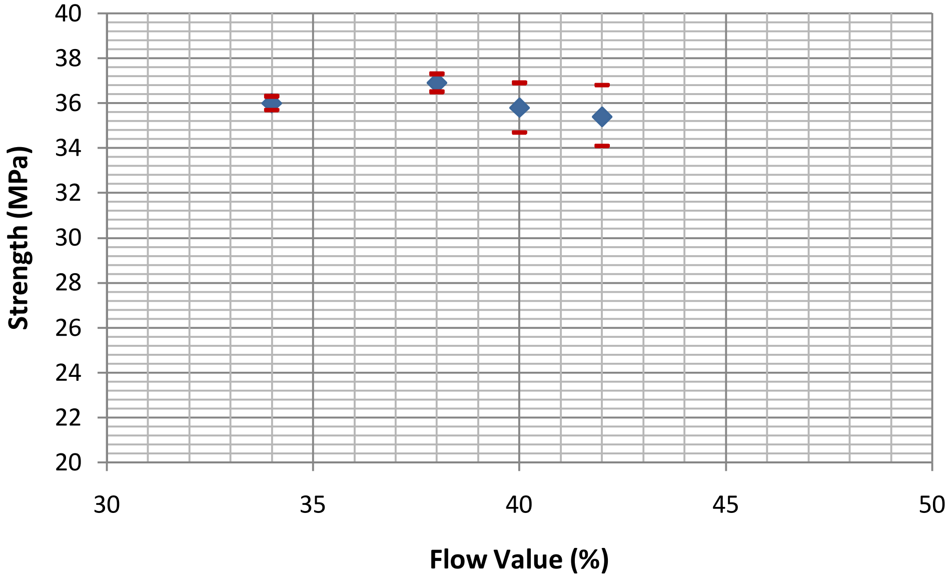


Figure 4.30: Compressive strengths vs flow values of composites with plasticizer proportion of 0.008 as surfactant at 7 day

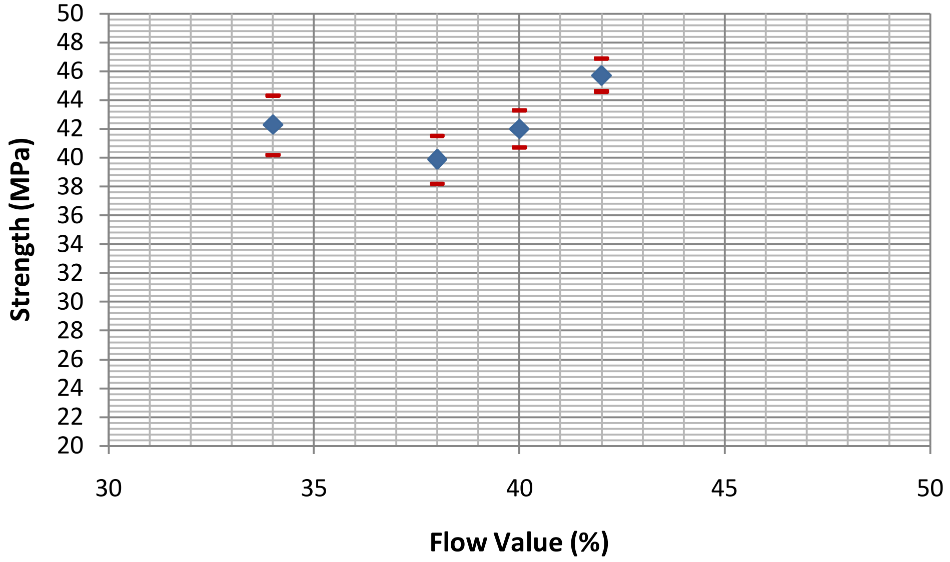


Figure 4.31: Compressive strengths vs flow values of composites with plasticizer proportion of 0.008 as surfactant at 28 day

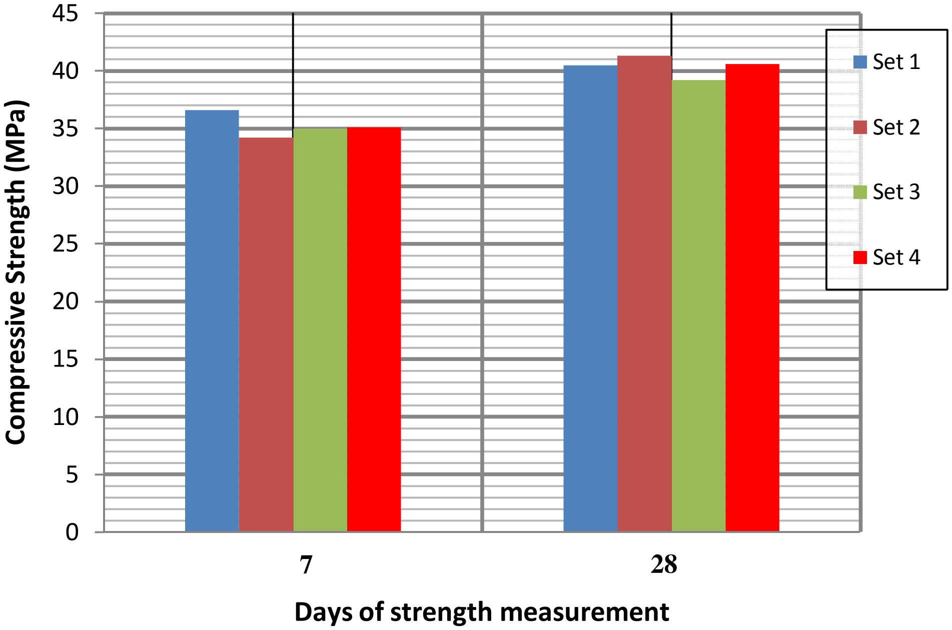


Figure 4.32: Compressive strengths of composite samples with plasticizer proportion of 0.010 as surfactant

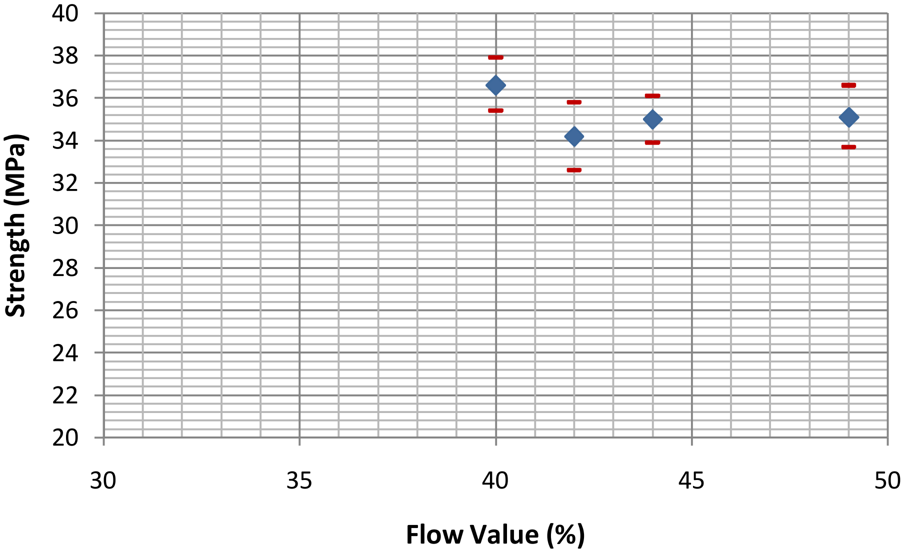


Figure 4.33: Compressive strengths vs flow values of composites with plasticizer proportion of 0.010 as surfactant at 7 day

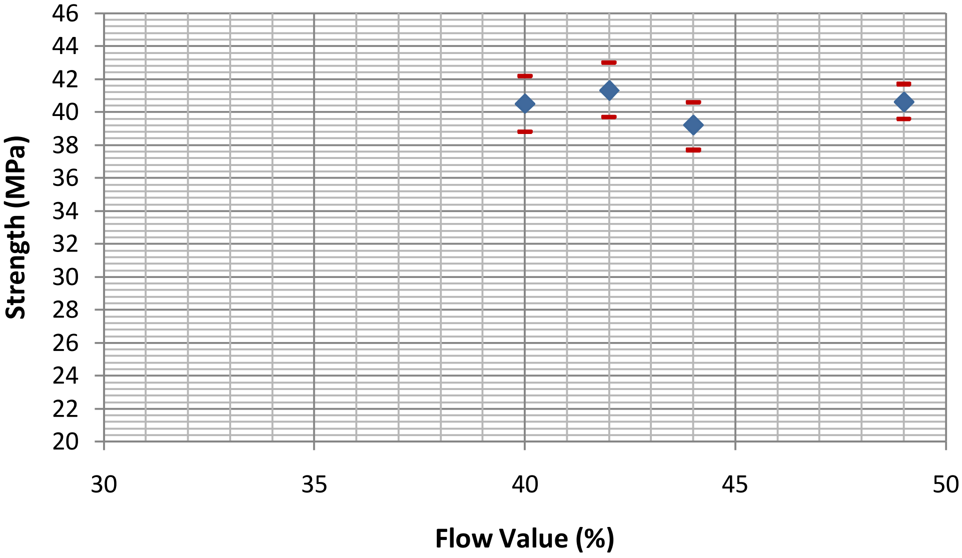


Figure 4.34: Compressive strengths vs flow values of composites with plasticizer proportion of 0.010 as surfactant at 28 day

Table 4.10: Test Information of Composite Samples with Plasticizer Proportion of 0.010 as Surfactant

Type of Sample	Amount of M3 (%)	w/c ratio	Amount of plasticizer (as part of cement by wt.)	No. of Samples *		Flow Values (%)	7 day mean compressive strength (MPa)	28 day mean compressive strength (MPa)
Composite	0.3	0.50	0.010	S1*	6	40	35.2±1.45	40.3±1.66
				S2	6	42		
				S3	6	44		
				S4	6	49		

*S1: Set 1, S2: Set 2, S3: Set 3, S4: Set 4

4.3.3 Comparison of Compressive Strengths

Composite samples having higher w/c ratio of 0.55 and 0.60 were also made with plasticizer as surfactant for comparison purpose. Control samples with plasticizer were also made. Figure 4.35 shows the compressive strengths of various control samples and composite samples at the age of 7 and 28 day.

The maximum 7 and 28 day compressive strengths were obtained by the plasticizer proportion of 0.008. These composites had 33.5 and 16.3% higher compressive strengths at 7 and 28 days, respectively, than that of control samples. Composites with plasticizer proportion of 0.005 produced 33.8% greater 7 day compressive strength as compared to control samples. The 28 day compressive strength of these composites was 12.7% higher. Compressive strengths of samples having 0.010 proportion of plasticizer had 29.4 and 11.3% higher compressive strengths as compared to control samples at 7 and 28 days, respectively. Composites made with higher water content and plasticizer as surfactant obtained lower compressive strengths both at 7 and 28 days. The 28 day compressive strength of composites with w/c ratio of 0.55 and plasticizer proportion of 0.003 was about 4% less than the control samples. Composite samples with no plasticizer and w/c ratio of 0.60, had 16.5 and 8% greater compressive strengths at 7 and 28 days, respectively, in comparison with control samples. Control samples with and without plasticizer addition had similar 28 day compressive strength though 7 day compressive strength of control samples with plasticizer was little bit higher.

It is obvious from test data that utilization of plasticizer as surfactant resulted in stronger composites in all cases. Composites with plasticizer proportion of 0.008 performed better. These composites had about 8% greater 28 day compressive strength as compared to composites with w/c ratio of 0.60 and no plasticizer. Therefore, it is clear that adequate dispersion of nanotubes is the key to produce properly reinforced nanotubes-composites. Application of polycarboxylate superplasticizer as surfactant makes the nanotubes more soluble and eventually results in uniform dispersion and more stable solution. As a result stronger and more compact composites are produced with higher compressive strengths both at 7 and 28 days.

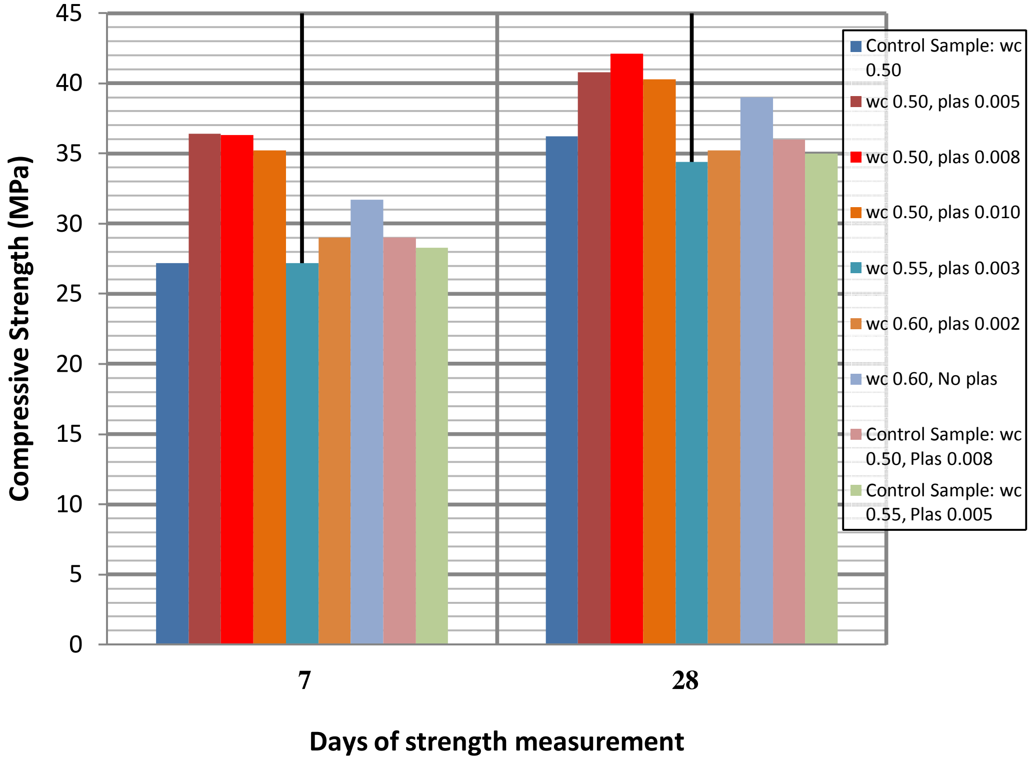


Figure 4.35: Compressive strengths of control samples and composite samples with different mix proportions

4.3.4 Hypothesis Testing

Hypothesis testing was carried out to compare composite samples with control samples. Hypothesis testing is a strong tool to make decision about a population. This method uses the information contained in random sample from the population. There are different methods of hypothesis testing based on data type. One of these methods is the 't' distribution which is applicable when variance (σ^2)of population is unknown and sample size is small. The distribution of population is assumed as normal by the t distribution. In practice, population of concrete strength are well approximated by the normal distribution. The 't' distribution has wide applicability as moderate departure from normality has little effect on validity. Therefore, the 't' distribution is utilized here to make statistical decision about the control and composite samples.

The P-value approach was used for hypothesis testing. The P-value is the weight of the evidence against null hypothesis. The smaller P-value represents higher evidence against the null hypothesis. The P-value is the smallest level of significance to reject the null hypothesis. Usually, if a P-value is smaller than 0.05, the null hypothesis is rejected. The test statistics used in the study are as follows,

$$T_0{}^* = \frac{\bar{X}_1 - \bar{X}_2 - \Delta_0}{\sqrt{\frac{S_1^2}{n_1} + \frac{S_2^2}{n_2}}} \qquad ----- 1$$

$$\upsilon = \frac{\left(\frac{S_1^2}{n_1} + \frac{S_2^2}{n_2}\right)^2}{\frac{\left(S_1^2 / n_1\right)^2}{n_1 - 1} + \frac{\left(S_2^2 / n_2\right)^2}{n_2 - 1}} \qquad ----- 2$$

where,

$\bar{\mathrm{X}}_1 = Mean\ of\ sample - 1$

$\bar{\mathrm{X}}_2 = Mean\ of\ sample - 2$

$n_1 = Sample\ size\ of\ sample - 1$

$n_2 = Sample\ size\ of\ sample - 2$

$S_1^2 = Variance\ of\ sample - 1$

$S_2^2 = Variance\ of\ sample - 2$

$\upsilon = Degrees\ of\ freedom$

The test statistics of hypothesis testing between different samples are provided in Table 4.11. The hypothesis testing was done on 28 day compressive strengths of control and composite samples.

A sample calculation of hypothesis testing between control samples and composites with w/c ratio of 0.60 is provided below.

$Null\ Hypothesis,\ H_0 : \mu_1 - \mu_2 = 0\ or\ H_0 : \mu_1 = \mu_2$

$Alternate\ Hypothesis,\ H_1 : \mu_1 > \mu_2$

$\bar{X}_1 = 36.1 Mpa$

$\bar{X}_2 = 33.0 MPa$

$n_1 = 48$

$n_2 = 24$

$S_1^2 = 3.72$

$S_2^2 = 4.00$

$$T_0{}^* = \frac{36.1 - 33.0 - 0}{\sqrt{\frac{3.72}{48} + \frac{4}{24}}} = 6.27$$

$$\upsilon = \frac{\left(\frac{3.72}{48} + \frac{4}{24}\right)^2}{\frac{\left(3.72/48\right)^2}{48-1} + \frac{\left(4/24\right)^2}{24-1}} = 44.63 \therefore \upsilon = 44$$

$From\ Table\ of\ Percentage\ Points\ t_{\alpha,\upsilon}\ of\ the\ t\ Distribution,$

$P < 0.005$

Since P – value is less than 0.05, *the null hypothesis can be rejected and the alternate hypothesis is true.*

$\therefore \mu_1 > \mu_2$

Therefore compressive strength of composite is greater than that of control samples.

Table 4.11: Information of Hypothesis testing

Sample 1	Sample 2	X_1	X_2	n_1	n_2	S_1	S_2	T_0^*	v	P-value	Comment
Composite w/ w/c ratio of 0.60	Control Sample	36.1	33.0	48	24	1.93	2.00	6.27	44	<0.005	Null hypothesis can be rejected
Composite w/ w/c ratio of 0.62	Control Sample	36.4	33.0	30	24	1.31	2.00	7.19	39	<0.005	Null hypothesis can be rejected
Composite w/ w/c ratio of 0.65	Control Sample	35.9	33.0	24	24	1.79	2.00	5.29	45	<0.005	Null hypothesis can be rejected
Composite w/ w/c ratio of 0.62	Composite w/ w/c ratio of 0.60	36.4	36.1	30	48	1.31	1.93	0.82	75	<0.25	Null hypothesis cannot be rejected
Composite w/ w/c ratio of 0.62	Composite w/ w/c ratio of 0.65	36.4	35.9	30	24	1.31	1.79	1.14	41	<0.25	Null hypothesis cannot be rejected
Composite with plas 0.005 as surfactant	Control Sample	40.8	36.2	24	24	1.86	1.93	8.4	46	<0.005	Null hypothesis can be rejected
Composite with plas 0.008 as surfactant	Control Sample	42.1	36.2	24	24	2.41	1.93	9.36	44	<0.005	Null hypothesis can be rejected

Table 4.11 – *Continued*

Composite with plas 0.010 as surfactant	Control Sample	40.3	36.2	24	24	1.66	1.93	7.89	45	<0.005	Null hypothesis can be rejected
Composite with plas 0.008 as surfactant	Composite with plas 0.005 as surfactant	42.1	40.8	24	24	2.41	1.86	2.1	43	<0.025	Null hypothesis can be rejected
Composite with plas 0.008 as surfactant	Composite with plas 0.010 as surfactant	42.1	40.3	24	24	2.41	1.66	3	40	<0.0025	Null hypothesis can be rejected
Composite with plas 0.008 as surfactant	Composite w/ w/c ratio of 0.60	42.1	39	24	18	2.41	2.62	3.92	35	<0.005	Null hypothesis can be rejected

From Table 4.11, it is found that composites with w/c ratio between 0.60 and 0.65 had higher compressive strengths than control samples at 28 day. The P-value was less than 0.05 in all three cases. Hypothesis testing was also done between composite samples with w/c ratio of 0.60 and 0.62. Since the corresponding P-value was greater than 0.05 (smaller than 0.25), the null hypothesis cannot be rejected. Therefore, though composites with w/c ratio of 0.62 had higher 28 day compressive strength as compared to composites with w/c ratio of 0.60, statistically these composites had similar compressive strengths at 28 day. It was also observed that all composites with plasticizer addition as surfactant had P-value much less than 0.05. The P-value of the composites having plasticizer proportion of 0.008 was the lowest. Therefore, it was statistically proved that compressive strengths of all these composites at 28 day were higher than control samples. Hypothesis testings were also carried out between composites with plasticizer proportion of 0.008 and composites having plasticizer proportion of 0.005, 0.010 and w/c ratio of 0.60 with no plasticizer, respectively. In all three instances, the P-values were found to be less than 0.05 which meant that composites with plasticizer proportion of 0.008 performed best among all composites. Therefore, it can be concluded that utilization of plasticizer as surfactant to disperse nanotubes produces relatively stronger nanotubes reinforced composites. The tentative optimum proportion of plasticizer is found to be 0.008 in terms of weight of cement.

4.3.5 Parametric Study

A parametric study was carried out between composites with different dosage rates of M3 and plasticizer proportion of 0.008 as surfactant. The dosage rates were ranged between 0.05 and 0.5%. Control samples were also made using plasticizer proportion of 0.008 for comparison purpose. A total of 12 samples were prepared in each case. The compressive strengths were measured at 3, 7, 28 and 100 days. Figure 4.36 shows the compressive strengths of controls samples and composite samples with different dosage rates of M3 at different ages. It was found that the dosage rate of 0.1 to 0.3%

obtained similar compressive strengths at the age of 3, 7, 28 and 100 day. Composites with 0.1% M3 had about 26% higher compressive strength than control samples at 3 day. The compressive strengths of 0.2 and 0.3% M3 added composites at 3 day were about 22 and 20% greater as compared to control samples, respectively. The 7 day compressive strengths of 0.1, 0.2 and 0.3% M3 reinforced composites were 21, 22 and 27.5% higher than that of control samples, respectively. At the age of 28 day, composites had about 15, 13.5 and 16% higher compressive strengths in comparison with control samples for 0.1, 0.2 and 0.3% dosage rates of M3, respectively. Similar increasing trend was also observed for 100 day compressive strengths. Though composites with 0.05% M3 had higher compressive strengths than control samples at all ages of 3, 7, 28 and 100 day, these composites had significantly less compressive strengths than that of 0.1, 0.2 and 0.3% dosage rates at all ages. Composites with 0.5% M3 obtained a little bit higher compressive strengths at early age of 3 and 7 day but had less compressive strengths at 28 and 100 day as compared to control samples. Similar phenomenon was also observed in the first phase of study. This is due to the fact that presence of nanotubes accelerate the hydration process of cement paste at early stage. It is evident from Figure 4.36 that an optimum range of concentrations of MWNT exists that produce the stronger nanotubes reinforced composites. Therefore, it can be concluded that the tentative optimum dosage rate of MWNT ranges between 0.1 and 0.3% in terms of weight of cementitious material.

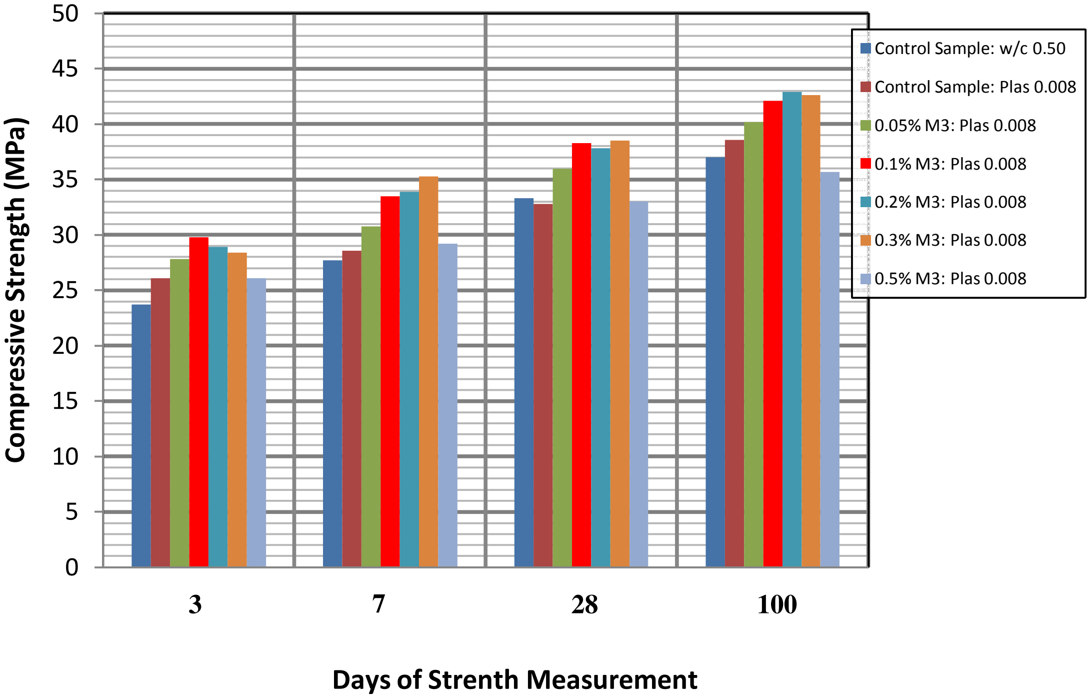


Figure 4.36: Compressive strengths of control samples and composite samples with different dosage rate of M3 at different ages

4.4 Flexural Strength

Flexural samples were prepared, both with and without nanotubes, and tested. Initially, 0.3% dosage rate of M3 was utilized to produce composites. Plasticizer proportions of 0.005 to 0.010 were used as surfactant and the w/c ratio was 0.50. Composites were also made with w/c ratio of 0.60. The flexural strengths of control samples with w/c ratio of 0.50 at 28 day are shown in Figure 4.37. A total of 30 samples were made in 5 sets. The highest flexural strength was obtained as 5.12 MPa by control samples. The mean flexural strength was 4.67 MPa. Figure 4.38 shows the 28 day flexural strengths of composites having plasticizer proportion of 0.005 as surfactant. A total of 5 sets of samples were made. Each set contained 6 samples. The mean flexural strength of 5.09 MPa was obtained in this case. Composites with plasticizer proportion of 0.008 had mean flexural strength of 5.42 MPa at 28 day. Total number of samples were 36 for these composites. These samples were made in 6 sets. The flexural strengths of these 6 sets of samples are presented in Figure 4.39. The 28 day flexural strengths of composites with 0.010 proportion of plasticizer are shown in Figure 4.40. A total of 24 samples in 4 sets were made. The highest, mean and the lowest flexural strengths of 5.37, 5.21 and 4.94 MPa were obtained, respectively, at 28 day in this case. Composite samples made with w/c ratio of 0.60 obtained mean flexural strength of 5.10 MPa at 28 day. The total number of samples was 24 for these composites. Test information of all the flexural samples is provided in Tables 4.12 through 4.14.

A comparison of the flexural strengths between control samples and composite samples at 28 day is shown in Figure 4.42. Composite samples with w/c ratio of 0.50 were also prepared for comparison purpose. The highest flexural strength was obtained by the composites with plasticizer proportion of 0.008. The flexural strength of this composite was 16% higher than that of control samples. Similar trend was also observed in case of compressive strengths. Except composites with w/c ratio 0.50, all other composites obtained higher flexural strength as compared to control samples. Composite samples with plasticizer proportion of 0.005 and 0.010 had 9 and 11.5% greater flexural strength than that of control samples, respectively. Composites with w/c ratio of

0.50 obtained about 8% less flexural strength relating to control samples. The flexural strength of composite samples with w/c ratio of 0.60 was 9.2% higher than flexural strength of control samples.

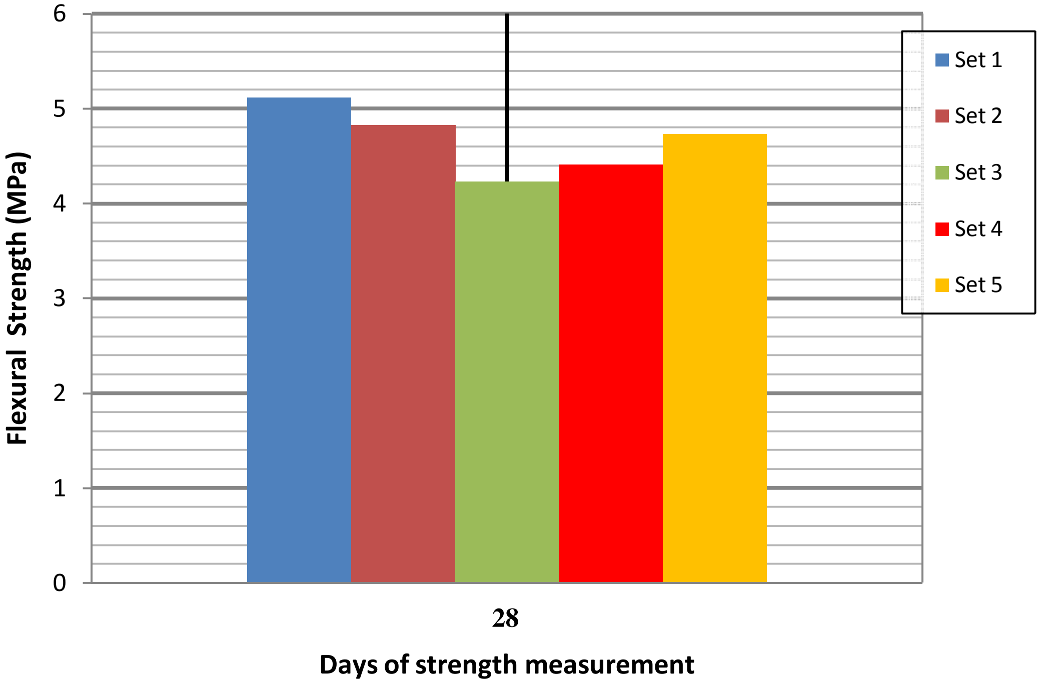


Figure 4.37: Flexural strengths of control samples at 28 day

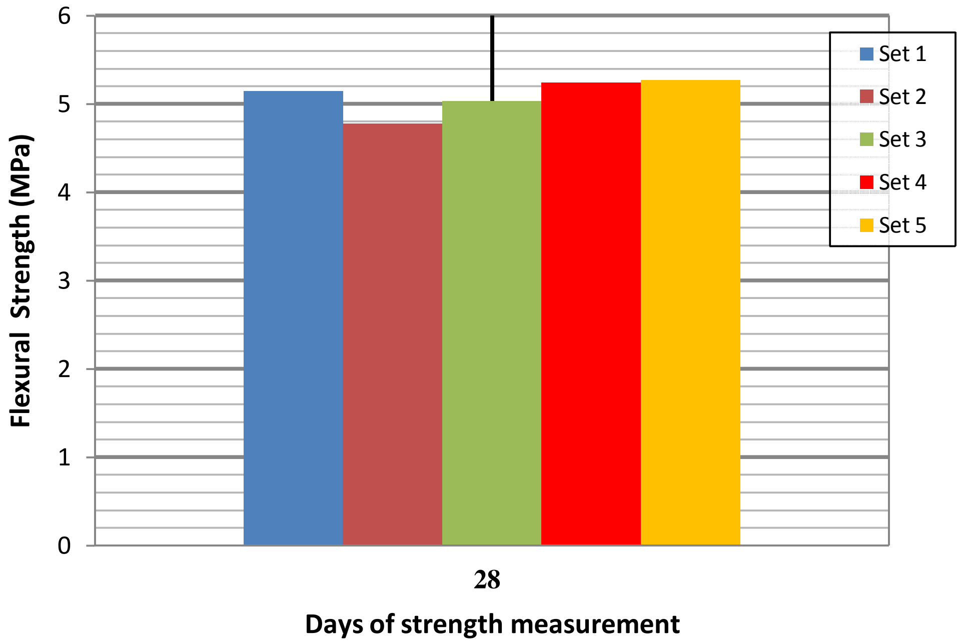


Figure 4.38: Flexural strengths of composite samples with plasticizer proportion of 0.005 as surfactant at 28 day

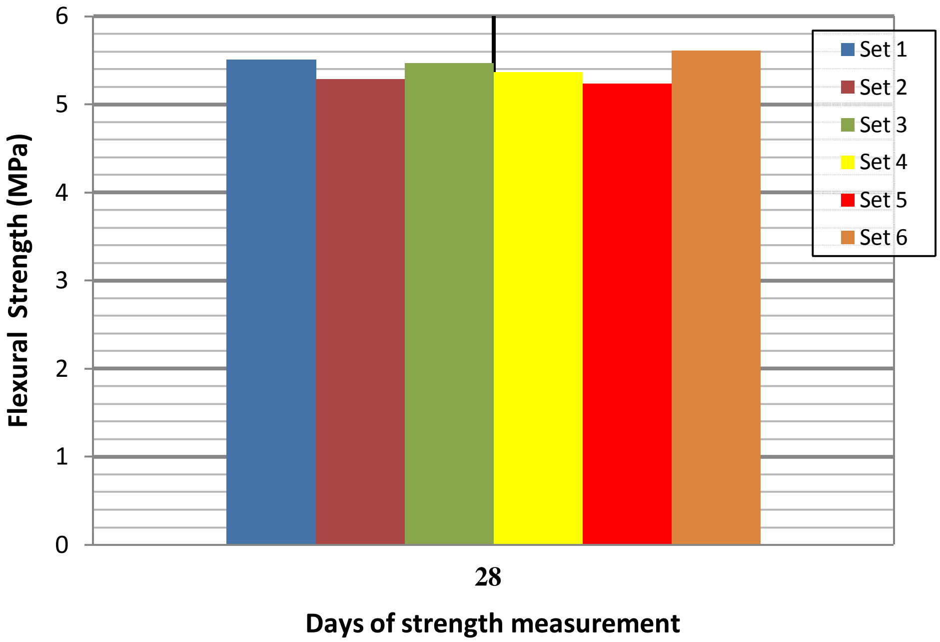


Figure 4.39: Flexural strengths of composite samples with plasticizer proportion of 0.008 as surfactant at 28 day

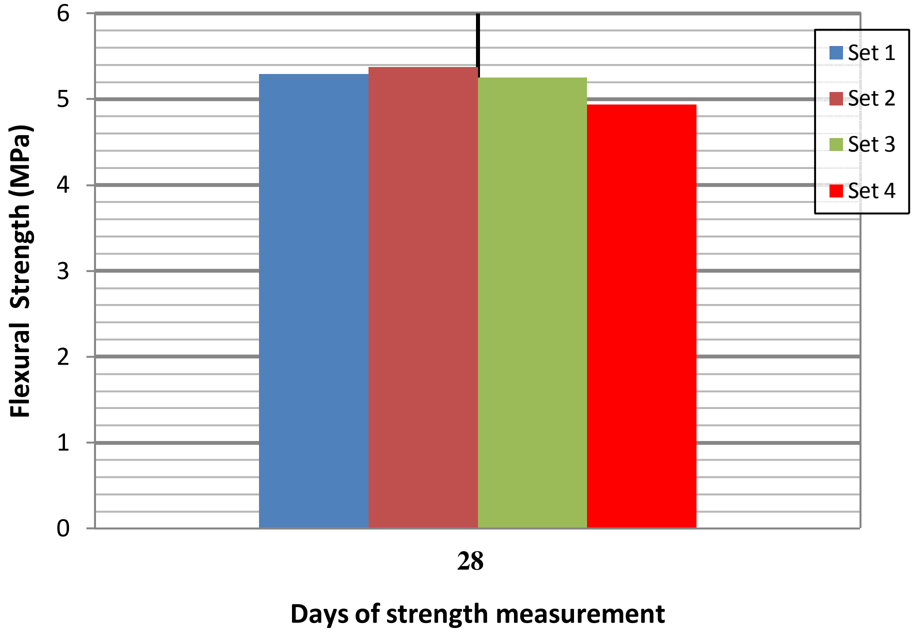


Figure 4.40: Flexural strengths of composite samples with plasticizer proportion of 0.010 as surfactant at 28 day

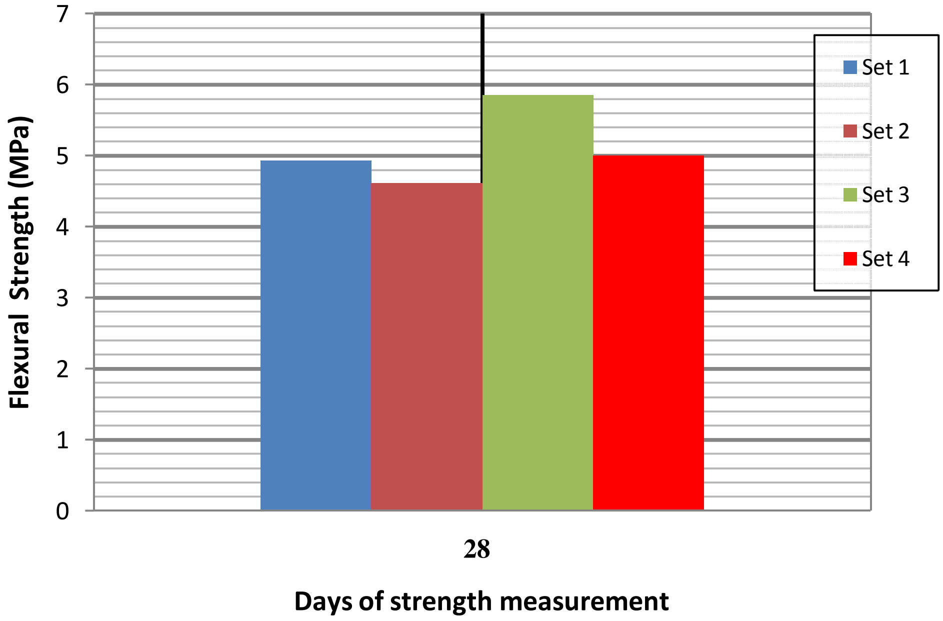


Figure 4.41: Flexural strengths of composite samples with w/c ratio of 0.60 at 28 day

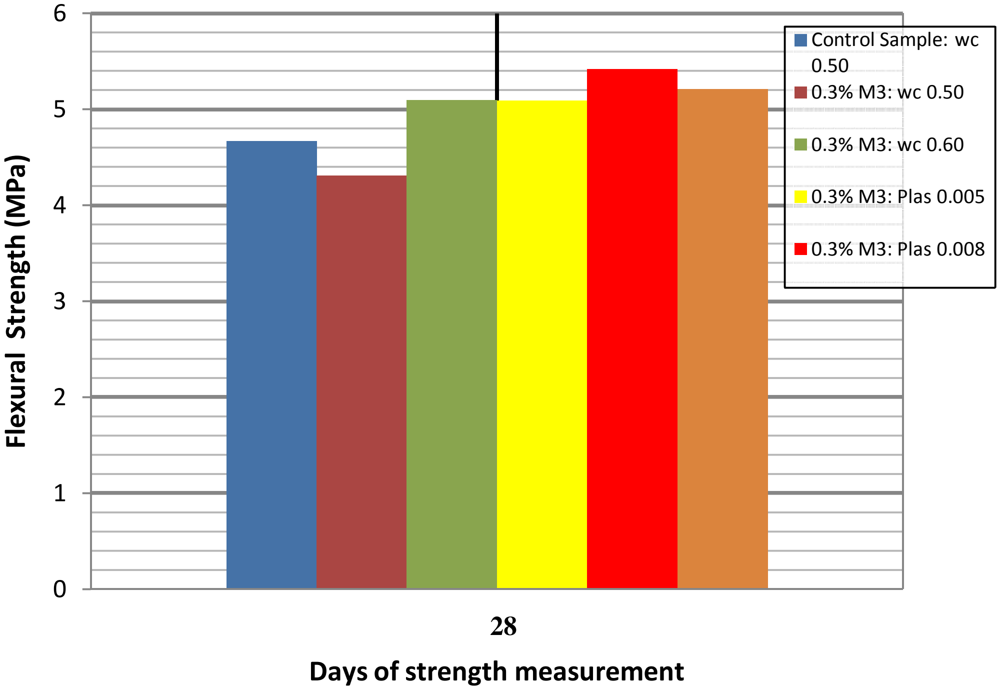


Figure 4.42: Flexural strengths of control and composite samples with different mix proportions at 28 day

4.4.1 Parametric Study

A parametric study was performed with different dosage rates of M3 addition and using plasticizer proportion of 0.008 as surfactant. The dosage rates of M3 ranged from 0.05 to 0.3%. The flexural strengths were measured at 3, 7 and 28 day. Figures 4.43 and 4.44 show the 28 day flexural strengths of 0.1 and 0.2% dosage rate of M3 reinforced composites. A total of 24 samples in 4 sets were made for each composite. The mean flexural strengths of 5.58 and 5.45 MPa were obtained by 0.1 and 0.2% M3 reinforced composites, respectively. Composites with 0.05% M3 had mean flexural strength of 4.93 MPa at 28 day (Figure 4.45). The 28 day flexural strengths of control samples and composites having different dosage rate of M3 are shown in Figure 4.46. For all composites, plasticizer proportion of 0.008 was used as surfactant. The maximum flexural strength, at 28 day, was obtained by 0.1% dosage rate of M3. The flexural strength of this dosage rate was 19.5% higher than that of control samples. Composites with 0.2 and 0.3% dosage rate of M3 had similar 28 day flexural strength. The flexural strengths of 0.2 and 0.3% M3 reinforced composite were 16.7 and 16% greater as compared to control samples, respectively. The dosage rate of 0.05% produced the lowest flexural strength among composites. However, these composites had 5.5% higher 28 day flexural strength than control samples.

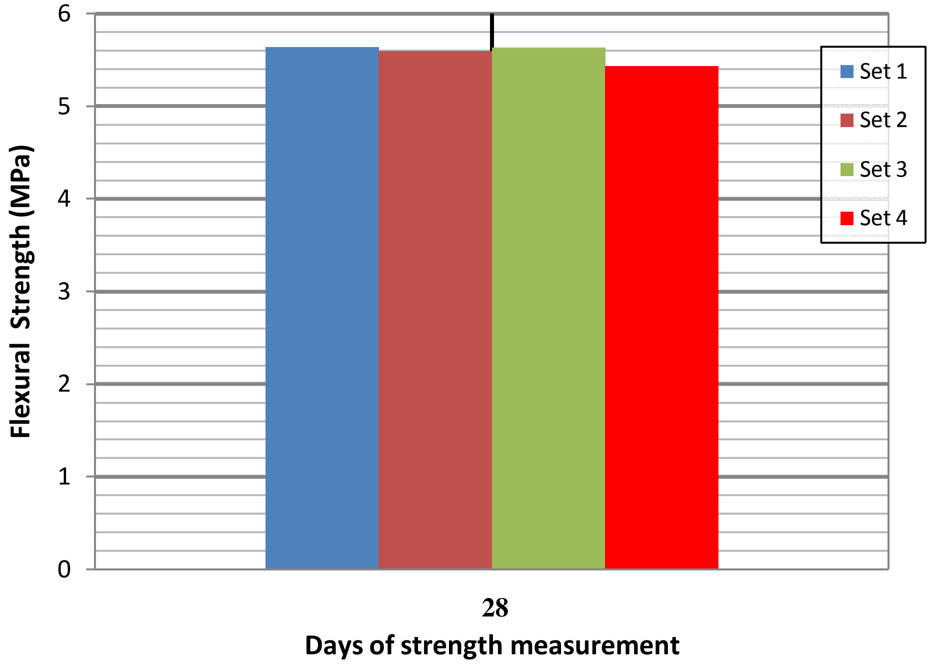


Figure 4.43: Flexural strengths of composite samples with 0.1% of M3 and plasticizer proportion of 0.008 at 28 day

Figure 4.47 shows the flexural strength of control and composite samples with different dosage rates of M3 at 7 day. The dosage rates were ranged from 0.05 to 0.3%. The 7 day flexural strengths of all composites were found to be higher than that of control samples. The 0.1% dosage rate of M3 produced the highest 7 day flexural strength among the composites. The flexural strengths of 0.1, 0.2, and 0.3% M3 reinforced composites were 24.5, 18 and 19.7% higher, respectively, as compared to control samples at the age of 7 day. Composites with 0.05% M3 had 7.5% higher 7 day flexural strength relating to control samples.

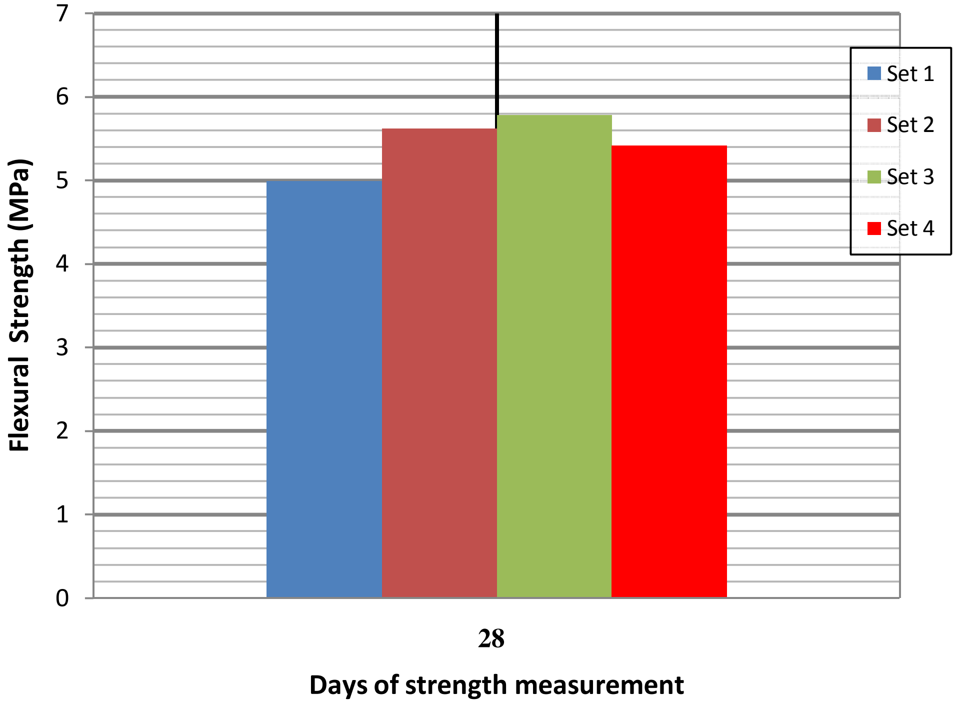


Figure 4.44: Flexural strengths of composite samples with 0.2% of M3 and plasticizer proportion of 0.008 at 28 day

The flexural strengths of control and composite samples at the age of 3 day are presented in Figure 4.48. Composites with 0.1% M3 had 24% higher flexural strength than that of control samples at 3 day. The dosage rate of 0.2% achieved the maximum flexural strength in this case. These composites produced 25.5% higher 3 day flexural strength as compared to control samples. The flexural strength of 0.3% M3 reinforced composites was 21% greater than control samples. Composite samples with 0.05% dosage rate obtained the lowest 3 day flexural strength among the composites and had about 8% higher flexural strength in comparison with control samples.

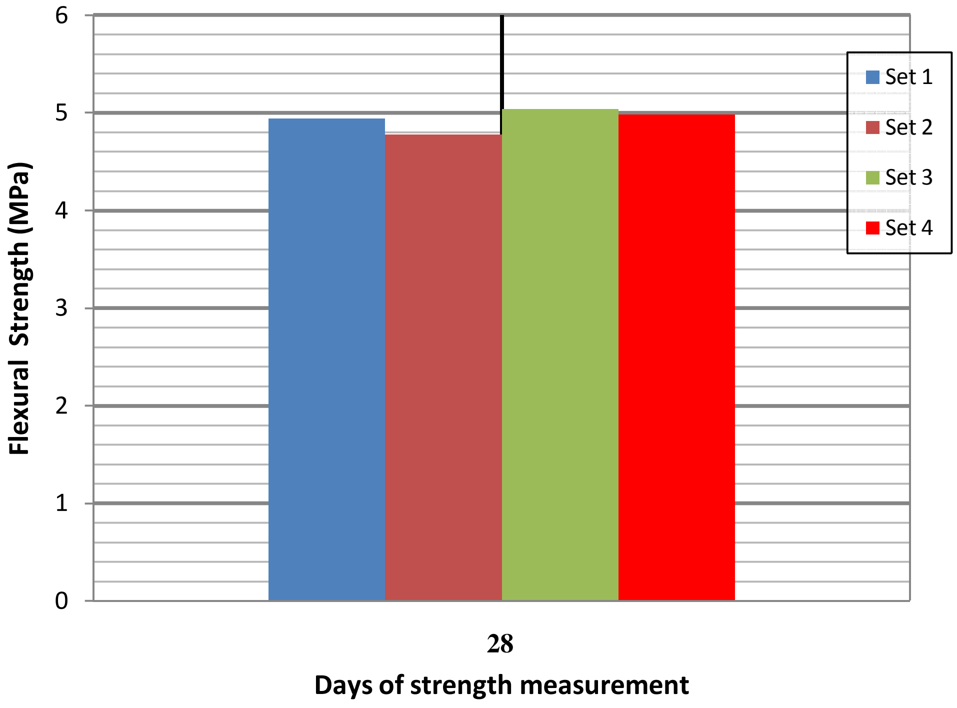


Figure 4.45: Flexural strengths of composite samples with 0.05% of M3 and plasticizer proportion of 0.008 at 28 day

Flexural strengths of composite samples at the age of 3, 7 and 28 day are shown together in Figure 4.49 to have a clear idea on the affect of nanotubes addition on flexural strength of cement mortar. The flexural strengths of control samples at those ages are also presented in Figure 4.49 for comparison. It is evident that addition of MWNT resulted in higher flexural strengths at all ages as compared to control samples. The dosage rate of 0.1% M3 produced the maximum flexural strength in majority of cases. However, addition of 0.2 and 0.3% M3 also resulted in relatively higher flexural strengths at all ages. The flexural strength of composite with 0.3% dosage rate was about 3% lower than that of composites with 0.1% M3 at 28 day. The 3 and 7 day flexural strengths of 0.3% dosage rate were 2.25% and 4% lower than the flexural strengths of 0.1% M3 added composites. Similar trend was also observed in case of 0.2% dosage rate. The dosage rate of 0.05% obtained the lowest composite flexural strengths at all ages.

It is obvious from Figure 4.46 that samples reinforced with MWNT clearly exhibit improved flexural performance over control samples. The dosage rate of 0.1% M3 performed relatively better than the dosage rate of 0.2 and 0.3%. Flexural behavior of cement mortar reinforced by nanotubes largely depends on crack bridging and fiber pull out actions of nanotubes. The higher concentration of MWNT has higher probability of clumping of nanotubes. Also the tendency of agglomeration increases with greater amount of nanotubes. The eventual result of these tendencies is relatively less uniform distribution of nanotubes along fracture surfaces. Therefore, the lower dosage rate of 0.1% produced somewhat higher flexural strength than that of dosage rate of 0.2 and 0.3%. However, the performance of these two dosage rates of 0.2 and 0.3% in flexure were significant as composites with 0.2 and 0.3% M3 obtained quite higher flexural strengths at all ages of 3, 7 and 28 day. Though the lower concentration of 0.05% M3 ensures more uniform dispersion of nanotubes across the cement matrix, they produced the lowest flexural strength among all composites at all ages. The 3, 7 and 28 day flexural strengths of 0.05% M3 reinforced composites were 12.5, 13.6 and 11.6% lower than that of composites with 0.1% M3, respectively. The reason behind this is the amount of MWNT was too small to arrest sufficient amount of nano cracks. This behavior also proves the existence of an optimum concentration of MWNT which produces the composites with desired mechanical performances.

Table 4.12: Test Information of Control and Composite Samples in Flexure at 28 day

Type of Sample	Amount of M3 (%)	w/c ratio	Amount of plasticizer (as part of cement by wt.)	No. of Samples	28 day mean flexural strength (MPa)
Control	NA	0.50	NA	30	4.67±0.44
Composite	0.3%	0.50	0.005	30	5.09±0.35
Composite	0.3%	0.50	0.008	36	5.42±0.41
Composite	0.3%	0.50	0.010	24	5.21±0.38
Composite	0.3%	0.50	NA	12	4.31±0.33
Composite	0.3%	0.60	NA	24	5.10±0.67
Composite	0.2%	0.50	0.008	24	5.45±0.40
Composite	0.1%	0.50	0.008	24	5.58±0.24
Composite	0.05%	0.50	0.008	12	4.93±0.36

Table 4.13: Test Information of Control and Composite Samples with different dosage rate in Flexure at 7 day

Type of Sample	Amount of M3 (%)	w/c ratio	Amount of plasticizer (as part of cement by wt.)	No. of Samples	28 day mean flexural strength (MPa)
Control	NA	0.50	NA	12	3.30±0.33
Composite	0.3%	0.50	0.008	12	3.95±0.29
Composite	0.2%	0.50	0.008	12	3.89±0.24
Composite	0.1%	0.50	0.008	12	4.11±0.44
Composite	0.05%	0.50	0.008	12	3.55±0.31

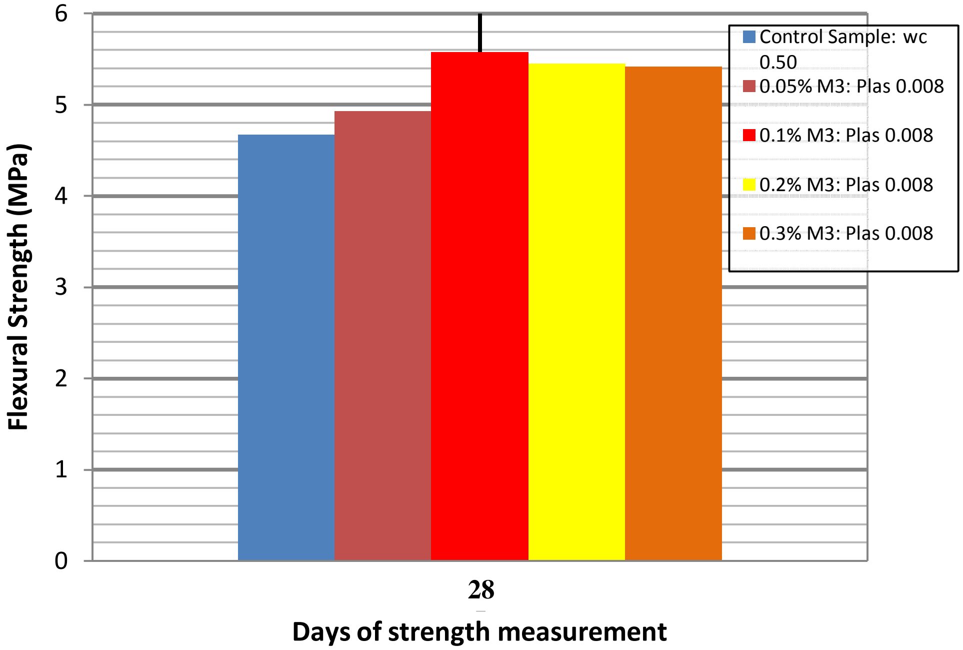


Figure 4.46: Flexural strengths of control and composite samples with different dosage rate of M3 at 28 day

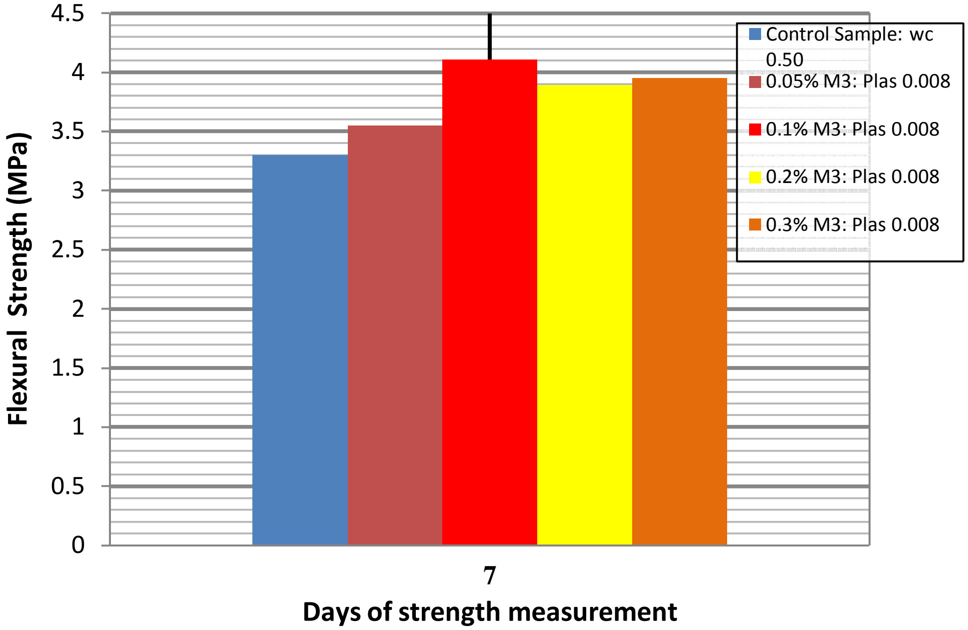


Figure 4.47: Flexural strengths of control and composite samples with different dosage rate of M3 at 7 day

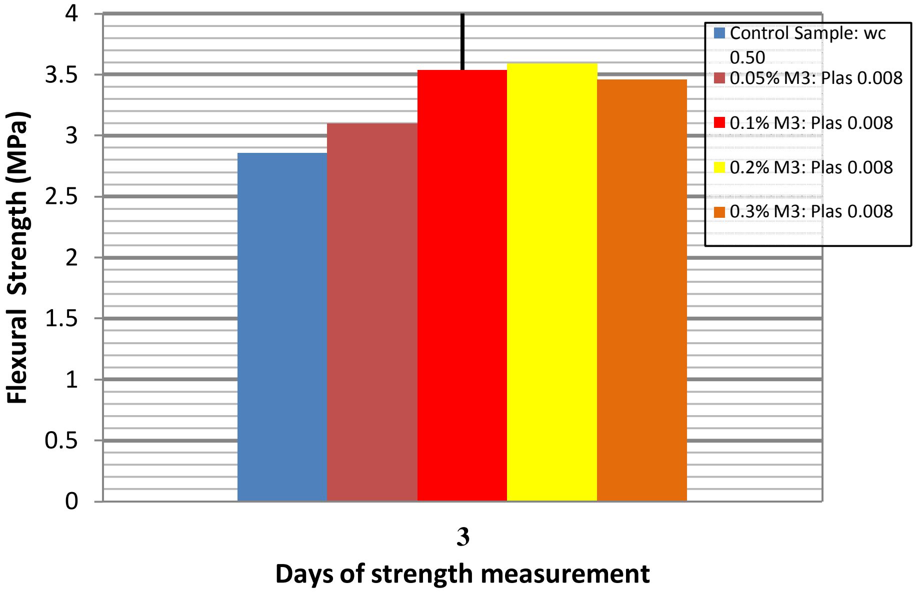


Figure 4.48: Flexural strengths of control and composite samples with different dosage rate of M3 at 3 day

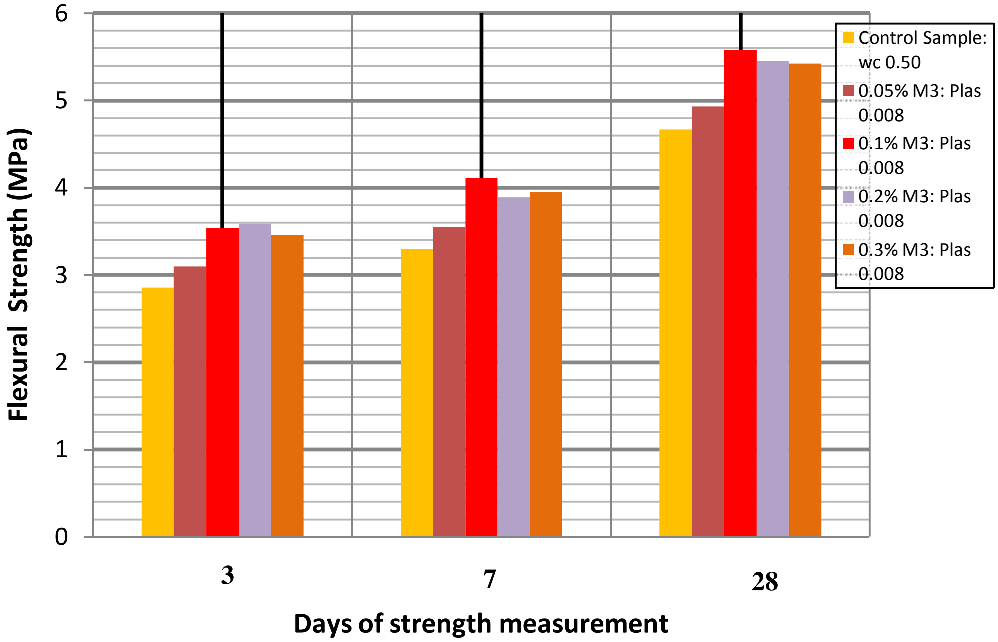


Figure 4.49: Flexural strengths of control samples and composite samples with different dosage rate of M3 at different ages

Table 4.14: Test Information of Control and Composite Samples with different dosage rate in Flexure at 3 day

Type of Sample	Amount of M3 (%)	w/c ratio	Amount of plasticizer (as part of cement by wt.)	No. of Samples	28 day mean flexural strength (MPa)
Control	NA	0.50	NA	12	2.86±0.39
Composite	0.3%	0.50	0.008	12	3.46±0.25
Composite	0.2%	0.50	0.008	12	3.59±0.33
Composite	0.1%	0.50	0.008	12	3.54±0.31
Composite	0.05%	0.50	0.008	12	3.10±0.31

4.4.2 Hypothesis Testing

Hypothesis testing was also carried out for flexural strengths of control and composite samples. The ‘t’ distribution was used for hypothesis testing. Test statistics of ‘t’ distributions were provided in section 4.3.4. The P-value approach was utilized for hypothesis testing. The test statistics of hypothesis testing on flexural strengths are provided in Tables 4.15 through 4.17. The null hypothesis was rejected when the P-value was less than 0.05. The commonly used chart (available in any statistic book) of percentage points $t_{\alpha,v}$ of 't' distribution was used to calculate the P-value.

Table 4.15: Information of Hypothesis testing of Flexural Strengths at 28 day

Sample1	**Sample 2**	**X_1**	**X_2**	**n_1**	**n_2**	**S_1**	**S_2**	**T_0***	**v**	**P-value**	**Comment**
0.3% M3 composite w/ w/c ratio of 0.60	Control Sample	5.10	4.67	24	30	0.67	0.44	2.71	38	<0.01	Null hypothesis can be rejected
0.3% M3 composite with plas 0.005 as surfactant	Control Sample	5.09	4.67	30	30	0.35	0.44	4.10	55	<0.005	Null hypothesis can be rejected
0.3% M3 composite with plas 0.008 as surfactant	Control Sample	5.42	4.67	36	30	0.41	0.44	7.10	60	<0.005	Null hypothesis can be rejected
0.3% M3 composite with plas 0.010 as surfactant	Composite w/ w/c ratio of 0.60	5.21	4.67	24	30	0.38	0.44	4.84	51	<0.005	Null hypothesis can be rejected
0.3% M3 composite with plas 0.008 as surfactant	0.3% M3 composite w/ w/c ratio of 0.60	5.42	5.10	36	24	0.41	0.67	2.10	34	<0.025	Null hypothesis can be rejected
0.3% M3 composite with plas 0.008 as surfactant	0.3% M3 composite with plas 0.010 as surfactant	5.42	5.21	36	24	0.41	0.44	1.86	47	<0.05	Null hypothesis can be rejected

Table 4.15 – *Continued*

0.2% M3 composite with plas 0.008 as surfactant	Control Sample	5.45	4.67	24	30	0.40	0.44	6.81	51	<0.005	Null hypothesis can be rejected
0.1% M3 composite with plas 0.008 as surfactant	Control Sample	5.58	4.67	24	30	0.24	0.44	9.67	46	<0.005	Null hypothesis can be rejected
0.1% M3 composite with plas 0.008 as surfactant	0.3% M3 composite with plas 0.008 as surfactant	5.58	5.42	24	36	0.24	0.41	1.90	57	<0.05	Null hypothesis can be rejected
0.1% M3 composite with plas 0.008 as surfactant	0.2% M3 composite with plas 0.008 as surfactant	5.58	5.45	24	24	0.24	0.40	1.37	37	<0.10	Null hypothesis cannot be rejected
0.05% M3 composite with plas 0.005 as surfactant	Control Sample	4.93	4.67	24	30	0.36	0.44	2.39	52	<0.025	Null hypothesis can be rejected

Table 4.16: Information of Hypothesis testing of Flexural Strengths at 7 day

Sample 1	**Sample 2**	**X_1**	**X_2**	**n_1**	**n_2**	**S_1**	**S_2**	**T_0***	**v**	**P-value**	**Comment**
0.3% M3 reinforced composite w/ w/c ratio of 0.60	Control Sample	3.95	3.30	12	12	0.29	0.33	5.12	21	<0.005	Null hypothesis can be rejected
0.2% M3 composite with plas 0.005 as surfactant	Control Sample	3.89	3.30	12	12	0.24	0.33	5.00	20	<0.005	Null hypothesis can be rejected
0.1% M3 composite with plas 0.008 as surfactant	Control Sample	4.11	3.30	12	12	0.44	0.33	5.10	20	<0.005	Null hypothesis can be rejected
0.1% M3 composite with plas 0.008 as surfactant	0.2% M3 composite with plas 0.008 as surfactant	4.11	3.89	12	12	0.44	0.24	1.50	17	<0.10	Null hypothesis cannot be rejected
0.1% M3 composite with plas 0.008 as surfactant	0.3% M3 composite with plas 0.008 as surfactant	4.11	3.95	12	12	0.44	0.29	1.05	19	<0.25	Null hypothesis cannot be rejected

Table 4.17: Information of Hypothesis testing of Flexural Strengths at 3 day

Sample 1	**Sample 2**	**X_1**	**X_2**	**n_1**	**n_2**	**S_1**	**S_2**	**T_0***	**v**	**P-value**	**Comment**
0.3% M3 reinforced composite w/ w/c ratio of 0.60	Control Sample	3.46	2.86	12	12	0.25	0.39	4.50	18	<0.005	Null hypothesis can be rejected
0.2% M3 composite with plas 0.005 as surfactant	Control Sample	3.59	2.86	12	12	0.29	0.33	4.95	21	<0.005	Null hypothesis can be rejected
0.1% M3 composite with plas 0.008 as surfactant	Control Sample	3.54	2.86	12	12	0.31	0.39	4.73	20	<0.005	Null hypothesis can be rejected
0.1% M3 composite with plas 0.008 as surfactant	0.2% M3 composite with plas 0.008 as surfactant	3.54	3.59	12	12	0.31	0.33	-0.38	21	<0.40	Null hypothesis cannot be rejected
00.1% M3 composite with plas 0.008 as surfactant	0.3% M3 composite with plas 0.008 as surfactant	3.54	3.46	12	12	0.31	0.39	0.56	20	<0.40	Null hypothesis cannot be rejected

The results of hypothesis testing prove that nanotubes reinforced composites perform better in flexure than control samples. Composites with different dosage rate of M3 ranged from 0.05% to 0.3% obtained higher flexural strength as compared to control samples. The addition of plasticizer as surfactant was again proved to be an effective mixing technique to disperse nanotubes uniformly within the cement paste. The flexural strengths of composites with plasticizer proportion of 0.008 were also compared with composites having w/c of 0.60 with no plasticizer, plasticizer proportion of 0.005 and plasticizer proportion of 0.010, respectively. The corresponding P-values of all these three case were lower than 0.05. Therefore, the plasticizer proportion of 0.008 was found to be the most effective proportion in case of flexure. Similar phenomenon was also found in case of compressive strengths of composites. Hypothesis testing between 0.1% and 0.3% dosage rate had P-value less than 0.05. This means that composites with 0.1% M3 obtained higher flexural strength than that of composites with 0.3% dosage rate at 28 day, statistically. The P-value obtained from the hypothesis testing between 0.2 and 0.1% dosage rate of M3 was greater than 0.05. So null hypothesis cannot be rejected and statistically these two dosage rate produced similar flexural strengths at 28 day.

The P-value of the hypothesis testing between flexural strengths of 0.1 and 0.3% dosage rate was greater than 0.05 but less than 0.25 at 7 day. Therefore, null hypothesis cannot be rejected. Similar result was also obtained for 0.2% dosage rate of M3. The P-value in this case was greater than 0.05 but less than 0.10. Therefore, at 7 day there were no statistically significant differences between flexural strengths of 0.1, 0.2 and 0.3% dosage rate of M3 for P-value of 0.05.

The hypothesis testings were also carried out between flexural strengths of control and composite samples at 3 day. It was statistically proved that all composites obtained higher flexural strength than that of control samples. Alike 7 day flexural strengths, no significant differences were found between the dosage rates of 0.1, 0.2 and 0.3%. However the P-values were higher in this case that means at 3 day, the differences in flexural strengths were less than that of at 7 day.

It is evident from hypothesis testing that no significant differences in flexural strengths were observed between the dosage rates of 0.1, 0.2 and 0.3% at 3 and 7 day. This type of behavior is predictable since addition of nanotubes accelerate the hydration process at early age. The eventual outcome is the less fluctuation of strength attainment at early ages of nanotubes reinforced composites. Similar behavior was also observed in some cases of compressive strengths test particularly in plasticizer addition not as surfactant. The dosage rate of 0.1% statistically performed better in flexure than most of the composites at 28 day. However, composites with 0.2% dosage rate had statistically similar flexural strength at 28 day as obtained by 0.1% dosage rate. It was also found from hypothesis testing that null hypothesis cannot be rejected between the 28 day flexural strength of 0.2 and 0.3% M3 reinforced composites. Therefore, it can be concluded that concerning flexural strength, the tentative optimum dosage rate of MWNT ranges from 0.1% to 0.3% with 0.1% dosage rate giving the better performance.

4.5 Discussion

The behavior of MWNT reinforced composites in compression and flexure was evaluated and statistical analysis was carried out. It was found that MWNT reinforced composites performed better both in compression and flexure. It was also observed that flow values can be utilized to assess the quality of MWNT dispersion within the cement matrix. Utilization of plasticizer as surfactant makes the dispersion of MWNT into aqueous solution more stable and eventually produced stronger composites. It has also become obvious that properties of MWNT reinforced composites primarily depend on proper distribution of nanotubes. The tentative optimum proportion of plasticizer to be used as surfactant was found as 0.008 in terms of weight of cement. This proportion of plasticizer produced the maximum strength both in compression and flexure. It was found that the tentative optimum dosage rate of MWNT ranged from 0.1% to 0.3% with lower concentration of MWNT performed better in flexure.

CHAPTER 5

PHASE III STUDY: APPLICABILITY OF MWNT REINFORCED CEMENT COMPOSITE AS REPAIR MATERIAL

5.1 Introduction

The third phase of the study is presented in this chapter. The applicability of MWNT reinforced cement composites as concrete repair material was evaluated through setting time, bleeding and slant shear tests. These parameters are important to assess the quality of a cementitious mortar to be used as repair material. MWNT dosage rates of 0.1 and 0.3% were utilized to reinforce composites. These two dosage rates were selected based on previous two phases of study. It was found that nanotubes reinforced composites set quickly than the control samples. Bleeding was not observed in composite samples. Results of slant shear tests were also encouraging and indicated the potential of application of nanotubes reinforced composites as repair material.

5.2 Setting Time of Composites

The time of setting represents the onset of the solidification phase at which fresh mortar can no longer be properly handled or injected. This test is significant for evaluating the effect of MWNT addition on setting time of cementitious mortar. The setting time is particularly important for repair purposes concerning practical use of repair mortar in field. The setting times were determined using the Vicat apparatus described in ASTM C807 (ASTM C807, 2008). The ASTM C807 test procedure is for determination of the time of setting of hydraulic cement mortar. The modified setting time test utilizes thicker steel needle of 2.0 mm instead of 1.0 mm needle. The 1.0 mm needle is used for determination of setting time of cement paste.

5.2.1 Sample Preparation and Testing

Mortar samples were prepared using the rotary mixture with flat beater. After preparation, the samples were kept in moisture room for 30 minutes without being disturbed. For testing, samples were then placed on Vicat apparatus and the needle was set in contact with the surface of mortar samples. The needle was then released to penetrate and allowed to set for 30 seconds. The reading of penetration was measured and recorded. The penetration readings were then determined at every 30 minutes till the needle failed to touch the bottom of the mold. After that the reading was taken at 10 minutes interval until a reading of 10 mm or less was obtained. From all recorded penetration reading, the time when penetration was 10 mm, was determined through interpolation. Each penetration of needle was done at a distance of 10 mm from any previous penetration and from the inside edge of the mold. The difference in time between the mixing of mortar and a penetration of 10 mm was the setting time of cementitious mortar. Figures 5.1 through 5.4 show some testing images of setting time of mortar using modified needle.

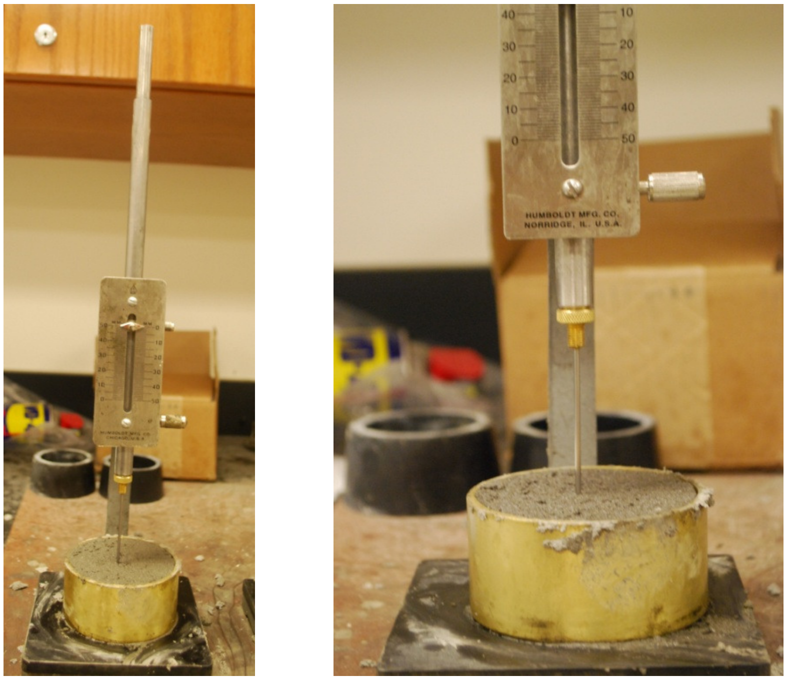


Figure 5.1: Needle in contact with mortar surface just before release

Figure 5.2: Needle penetration touching the bottom of mold

Figure 5.3: Needle penetration of less than 10 mm

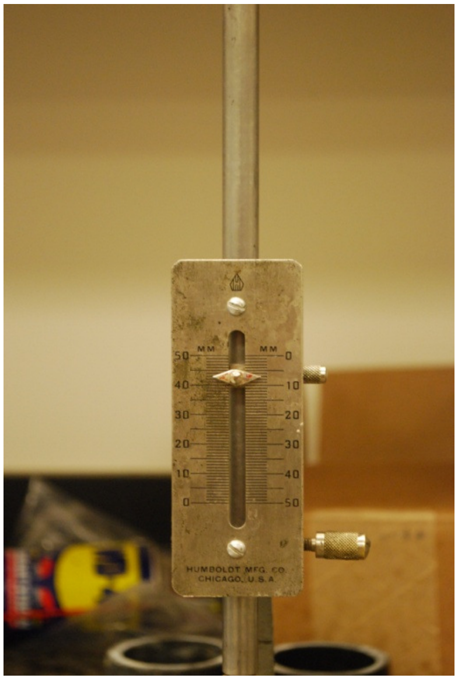


Figure 5.4: Scale reading mounted on Vicat apparatus

5.2.2 Determination of Time of Setting

Control and composite samples reinforced with 0.1 and 0.3% M3 were prepared and tested for time of setting. Control samples were produced with w/c ratio of 0.50 and 0.60. Control samples with plasticizer addition were also made for comparison. Different amounts of plasticizer ranging from 0.005 and 0.008 as surfactant were added to make composites. Table 5.2 provides the setting time of both control and composite samples. The time of setting of cement mortar was calculated using the following expression,

$$T = \left(\left(\frac{H - E}{C - D} \right) \times (C - 10) \right) + E$$

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

The time of setting was reported to the nearest 1 minute. According to ASTM C807, when multiple sets are made the difference between any two sets should not be more than 43 minutes. This check was performed in every case when required. A sample calculation is provided in the following section. Table 5.1 shows the recorded reading for time of setting tests of 2 sets of control samples. The w/c ratio was 0.5 for both the sets. The corresponding time in minutes of each recorded penetration reading are also provided in Table 5.1.

Table 5.1: Test information of Setting Time of 2 Sets of Control Samples

Set 1		Set 2	
Time (minutes)	Reading (mm)	Time (minutes)	Reading (mm)
30	40	30	40
60	40	60	40
90	40	90	40
120	36	120	37
130	34	130	36
140	34	140	35
150	28	150	34
160	20	160	23
170	11	170	11
180	4	180	5

$Sample\,1:$

$E = 170$

$H = 180$

$C = 11$

$D = 4$

$$Time\ of\ Setting = \left(\left(\frac{H-E}{C-D}\right)\times(C-10)\right)+E$$

$$=\left(\left(\frac{180-170}{11-4}\right)\times(11-10)\right)+170$$

$$=171.43$$

$$\therefore Time\ of\ Setting, t = 171\,\text{min}$$

$Sample\,2:$

$E = 170$

$H = 180$

$C = 11$

$D = 5$

$$Time\ of\ \ Setting = \left(\left(\frac{H-E}{C-D}\right)\times(C-10)\right)+E$$

$$= \left(\left(\frac{180-170}{11-5}\right)\times(11-10)\right)+170$$

$$= 171.67$$

$$\therefore Time\ of\ \ Setting, t = 172\ \text{min}$$

Table 5.2: Setting Time of Control and Composite Samples

Type of Sample	Amount of M3 (%)	w/c ratio	Amount of plasticizer (as part of cement by wt.)	No. of Sets *	Time of Setting (mins)
Control	NA	0.50	NA	S1*	171
				S2	172
				S3	179
				S4	177
Control	NA	0.60	NA	S1*	209
				S2	208
				S3	221
Control	NA	0.50	0.005	S1*	290
				S2	302
				S3	306
Control	NA	0.50	0.008	S1*	343
				S2	340
				S3	331
Control	NA	0.55	0.005	S1*	317
				S2	324
Composite	0.3%	0.50	NA	S1*	133
				S2	128
				S3	125
Composite	0.2%	0.50	NA	S1*	124
				S2	127

Table 5.2 – *Continued*

Composite	0.2%	0.50	NA	S3	131
Composite	0.1%	0.50	NA	S1*	128
				S2	138
				S3	135
Composite	0.3%	0.60	NA	S1*	180
				S2	188
				S3	175
Composite	0.1%	0.60	NA	S1*	191
				S2	185
				S3	188
Composite	0.3%	0.50	0.008	S1*	248
				S2	250
				S3	242
Composite	0.3%	0.50	0.005	S1*	238
				S2	235
				S3	240
Composite	0.1%	0.50	0.008	S1*	255
				S2	268
				S3	261
Composite	0.3%	0.55	0.005	S1*	293
				S2	300
Composite	0.3%	0.60	0.003	S1*	276
				S2	284

*S1: Set 1, S2: Set 2, S3: Set 3, S4: Set 4

It was observed that composite samples with nanotubes settled early as compared to control samples having the same mix proportions. Control samples with w/c ratio of 0.50 had time of setting of around 175 minutes. Composites reinforced with 0.1-0.3% M3 had setting time in between 125 and 135 minutes. Control samples with plasticizer proportion of 0.008 had setting time of about 340 minutes. Setting times for 0.3 and 0.1% M3 reinforced composites with plasticizer proportion of 0.008 as surfactant were observed as about 245 and 260 minutes, respectively. Similar pattern was also observed for other mix proportions of control and composite samples. It was also found that the variation in setting time with the change in concentration of M3 between 0.1 and

0.3% was little. Therefore, presence of nanotubes accelerates the initial setting of cement mortar. This behavior is predictable as the rate of hydration is higher in case of nanotubes reinforced composites. Figures 5.5 through 5.7 show the comparison between time of setting of control and composite samples having different mix proportions.

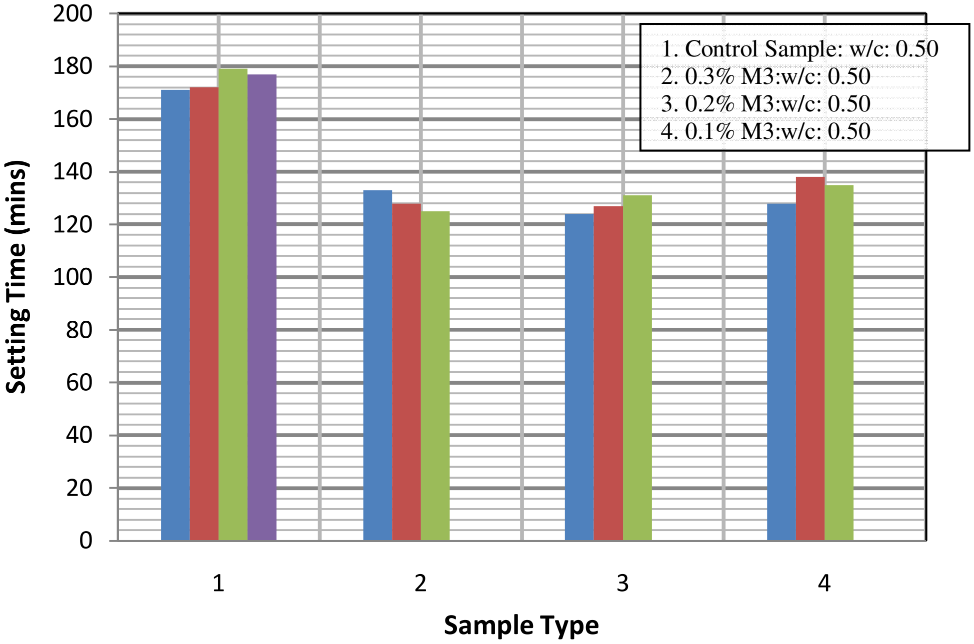


Figure 5.5: Time of setting of control samples and composites with different dosage rate of M3 having w/c ratio of 0.50

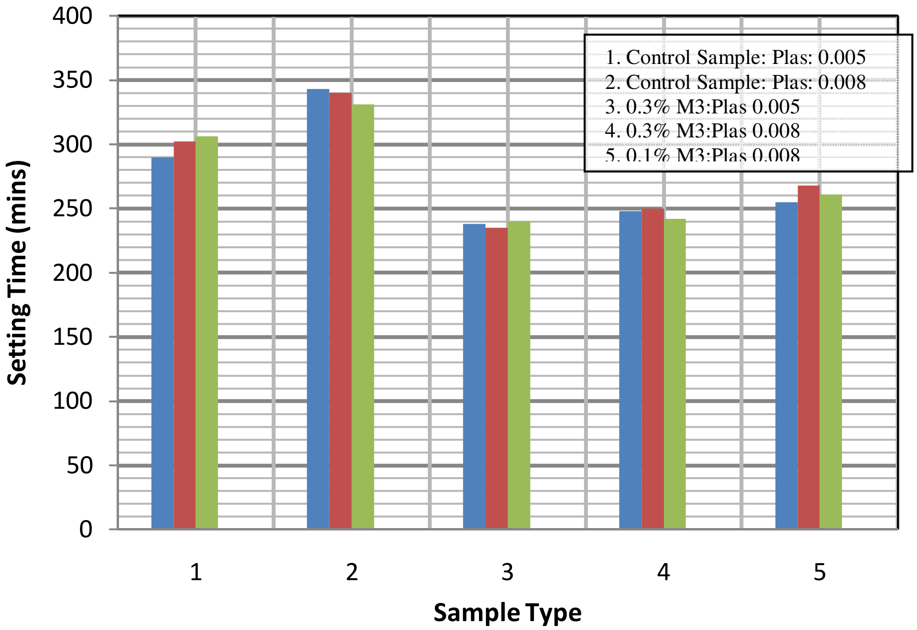


Figure 5.6: Time of setting of control samples and composites with plasticizer (w/c ratio: 0.50)

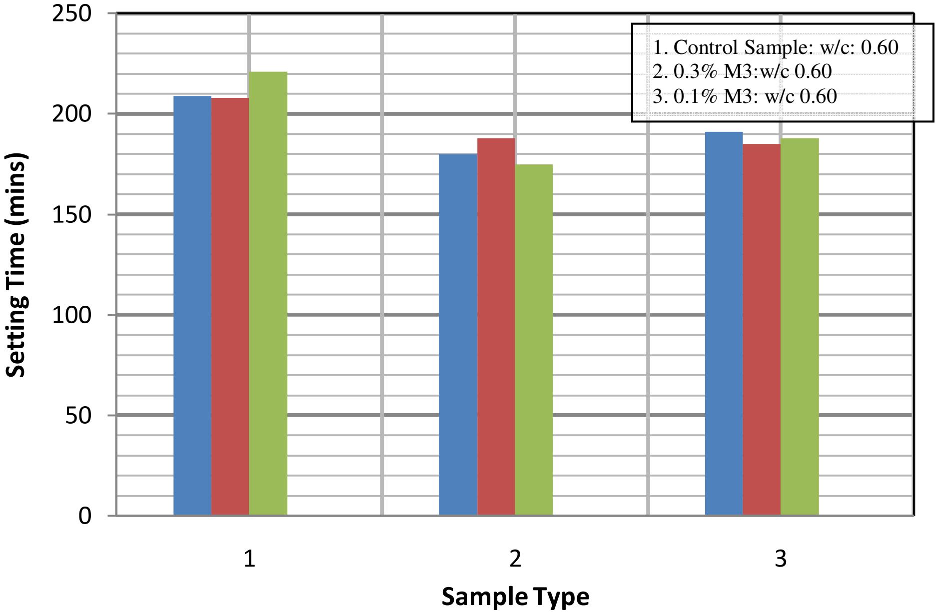


Figure 5.7: Time of setting of control samples and composites with different dosage rate of M3 having w/c ratio of 0.60

5.3 Bleeding of Composites

Bleeding is the appearance of free water on the surface of the unset mortar, as the relatively heavy solid particles settle because of gravity and represents the quality of the mortar mix. Bleeding of the freshly mixed mortar was measured following the procedure given in ASTM C940 (ASTM C940, 2008). Excessive bleed may leave several uncontrolled open channels within the mortar mass and eventually results in porous and weak samples. It also adversely affects the durability of the sample. Therefore, composite samples should be free from bleeding to be used as an effective repair material.

5.3.1 Sample Preparation and Testing

An 800 ml quantity of freshly mixed cement mortar was produced for each testing of bleeding. Both control and composite samples were made and tested for bleeding. Composite samples were prepared with 0.1 and 0.3% dosage rate of M3 having different mix proportions for comparison. After completion of mixing, the temperature of the mix was measured and recorded. The mix was then poured into a 1000 ml glass graduated cylinder and covered. The difference between the upper surface of mortar and bleed water was then recorded if any difference was observed. The process was continued at 15 minutes interval for the first 60 minutes and then at 1 hour interval. The height of bleed water was then expressed as a percent of the original height of the mortar. This height was referred to as the percent final breed.

Table 5.3 provides the bleeding result and corresponding temperature of both control and composites samples. It was observed that none of the samples, either control or composite, exhibited bleeding. Figures 5.8 through 5.10 show images of bleeding test carried out during the study.

Table 5.3: Bleeding Test result of Control and Composite Samples

Type of Sample	Sample Size	Amount of M3 (%)	w/c ratio	Amount of plasticizer (as part of cement by wt.)	Bleeding (%)	Temp (^{0}F)
Control	3	NA	0.50	NA	None	67
Composite	3	0.3	0.50	NA	None	82
Composite	3	0.3	0.60	NA	None	88
Composite	3	0.3	0.50	0.008	None	82
Composite	3	0.1	0.50	NA	None	80
Composite	3	0.1	0.50	0.008	None	81

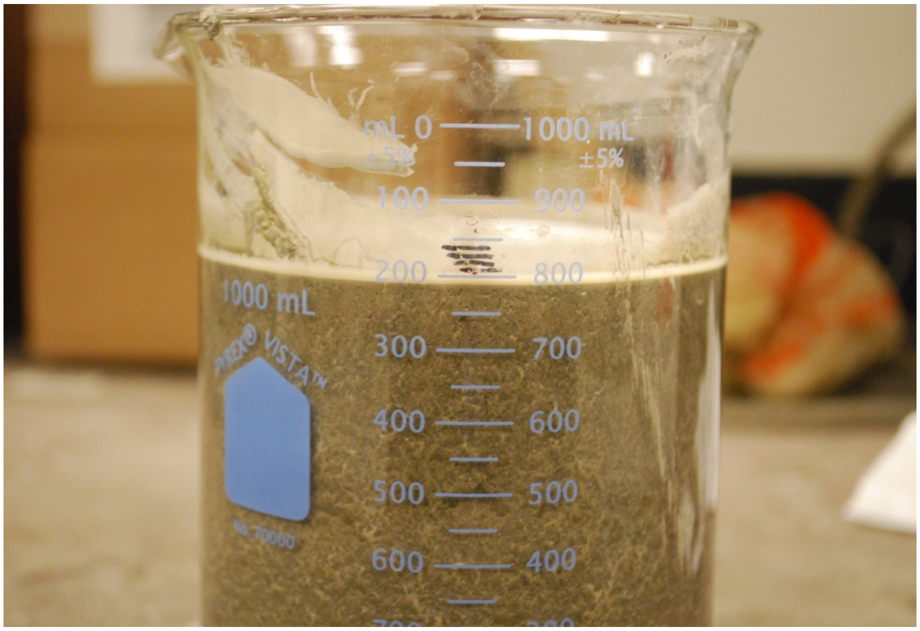


Figure 5.8: The level of upper surface of mortar and water at the beginning of the test of 0.1% M3 reinforced composite samples with plasticizer: 0.008

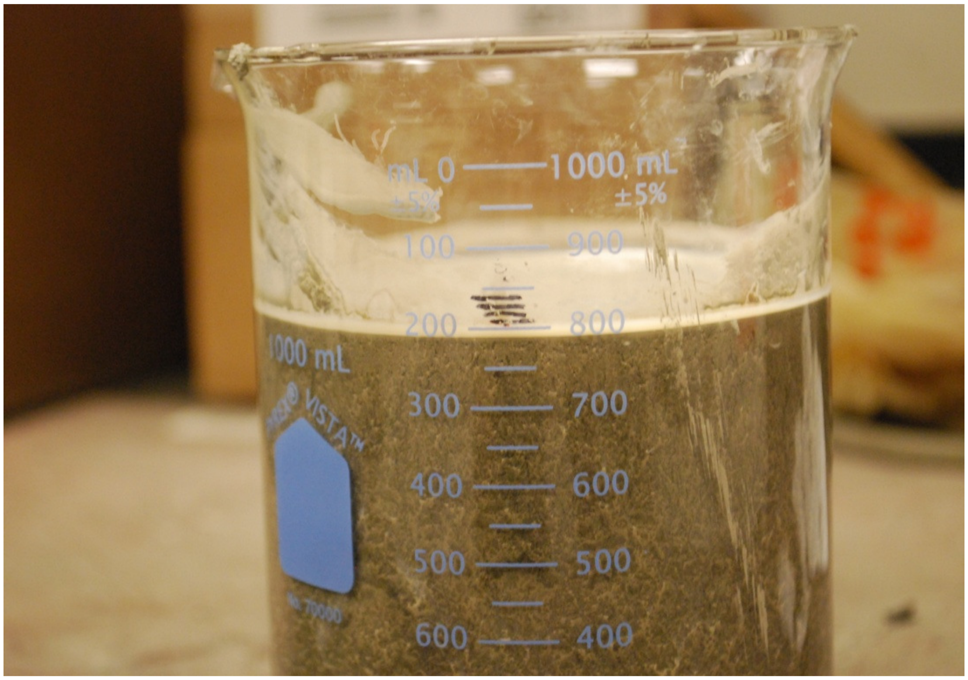


Figure 5.9: The level of upper surface of mortar and water after 3 hours of the start of test of 0.1% M3 reinforced composite samples with plasticizer: 0.008

Figure 5.10: Temperature measurement during bleeding test

5.4 Slant Shear Test

The bond strength between the repair material and concrete substrate plays an important role in the efficiency of repair material used in concrete structures. Slant shear tests are typically employed to measure this bond strength. The bond between the repair material and the old concrete usually presents a weak link in the repaired structure. The MWNT reinforced composites should exhibit good bonding strength with existing concrete substrate to be utilized as repair material. Slant shear test was conducted to evaluate the bonding strength. Slant shear strengths of control and composite mortar were measured following the procedure given in ASTM C882/C882M-05 (ASTM C882, 2010) and DMS 4655 (DMS 4655, 2009). Epoxy resins are widely used to repair cracks in concrete structures. TXDOT utilizes Pro-Poxy 300 for quick repair of cracks in bridges. Slant shear test of specimens jointed by Pro-Poxy 300 Fast were also carried out for comparison.

5.4.1 Sample Preparation and Testing

The cylinders with 75 mm by 150 mm dimensions were produced according to ASTM C882/C 882M and DMS 4655 procedures. The compressive strength of cylinders should be higher than the slant shear strength of the repair material in order to suppress the failure of pre-cast cylinders. After suitable curing, the slant test cylindrical specimens were saw cut into halves with a diagonal bonding area at an angle of 30^0 from the vertical, as illustrated in Figure 5.11. Fresh normal cement and CNT-cement mortar layers with a thickness of 3 mm were then placed on the diagonal bonding area between the two saw cut halves. Also epoxy resin was used on the bonding area of other specimens for comparison purpose. The thickness of epoxy resin was used as 0.5 mm according to ASTM standard. The slant shear strengths of specimens repaired by CNT-cement mortar and epoxy resin were obtained by conducting a series of compression tests.

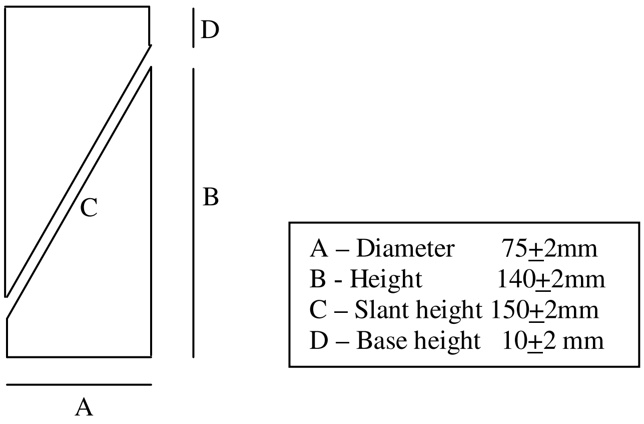


Figure 5.11: Dimensions of cylindrical specimens used for the standard slant shear test of ASTM C 882/ C 882M

Slant shear tests were carried out at 3, 7 and 28 days. Composites samples were made with 0.1 and 0.3% dosage rate of M3 with plasticizer proportion of 0.008 as surfactant. Dispersion of nanotubes was accomplished by sonication process as described before. The w/c ratio was kept at 0.50. Control samples were made with w/c ratio of 0.50. In each case, a total of 3 cylindrical specimens were jointed together and tested at designated days.

5.4.2 Concrete Cylinder Preparation

According to DMS 4655 the concrete cylindrical specimen to be used for slant shear testing should have compressive strength between 34.5 and 41.4 MPa at 28 day. Concrete cylinders were made following the ACI mix design procedures. The w/c ratio of 0.44 was used for the concrete mix. Coarse and fine aggregates were collected from Hanson Pipe & Precast. The properties of coarse aggregates are provided in Table 5.4 and Figure 5.12 shows the gradation of coarse aggregates. Table 5.5 provides the fineness modulus calculation of fine aggregate.

Table 5.4: Properties of Coarse Aggregates

Maximum Size	3/4 in
Relative Density	2.64
Absorption	1%

Table 5.5: Fineness Modulus (FM) of Sand

Sieve Size	retained (gm)	% Retained	Cumulative % retained	% Passing	Cumulative % passing
4.75	11.1	1	1	99	99
2.36	210	14	15	86	85
1.18	245	16	31	84	69
600	224	15	46	85	54
300	461.6	31	77	69	23
150	316.6	21	98	79	2
	1505		268		

$$\therefore \text{ Fineness Modulas}, FM = \frac{268}{100} = 2.68$$

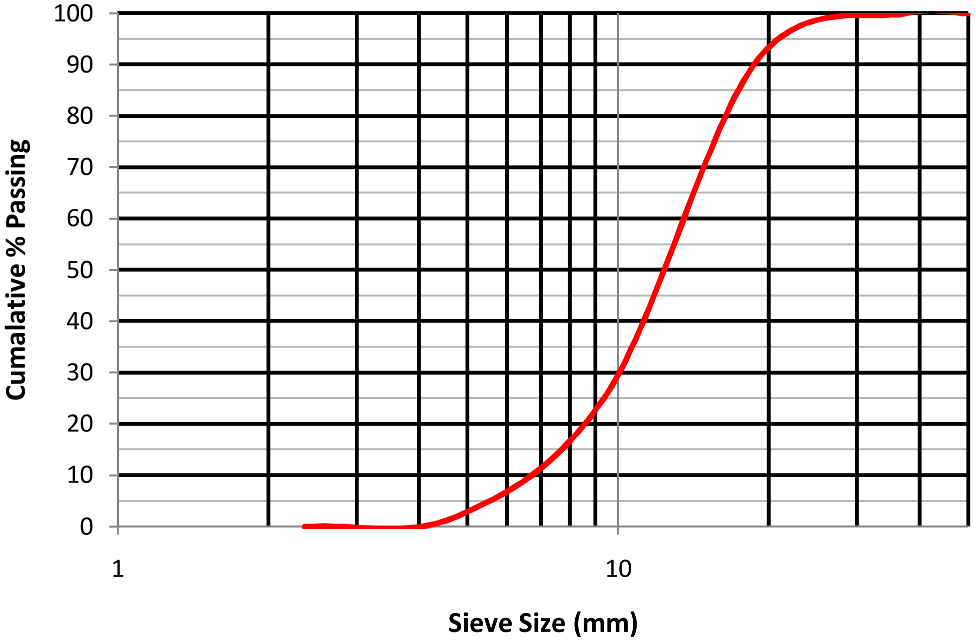


Figure 5.12: Gradation of Coarse Aggregates

Two sets of cylindrical specimens were tested for compressive strength at 28 day. Each set contained 3 samples. Table 5.6 shows the compressive strength test data of concrete cylinders. Both sets had compressive strengths within the limit given by DMS 4655.

Table 5.6: Compressive Strength of Concrete at 28 Day

Set No.	Cylinder No.	Dia (in)	Area (in^2)	Load (kips)	Strength (ksi)	Mean Strength (Mpa)
1	1	2.975	6.95	42.1	6.06	41.3
	2	2.975	6.95	41.3	5.94	
	3	2.97	6.92	41.2	5.95	
2	1	2.99	7.02	39.3	5.6	39.7
	2	2.985	6.99	39.6	5.67	
	3	2.98	6.97	41.8	6	

5.4.3 Slant Shear Testing

Cylinders were cut into two halves according to ASTM 882 using a saw cutter. All loose surface material was removed from the bonded surface and cylinders were then kept under water for 24 hours. After 24 hours of water soaking, cylinders were cleaned with a water absorbent cloth and allowed to air dry for 15 minutes. Then epoxy resins and fresh cementitious mortar (both control and reinforced with M3) were applied on the prepared surfaces and jointed together. The thickness of epoxy resin was 0.5 mm and cementitious mortar was 3 mm. The slant shear test results are given in Table 5.7. Figures 5.13 through 5.21 show images of slant shear testing conducted in the Civil Engineering Laboratory Building (CELB) at UT Arlington. In Figure 5.22 a comparison between slant shear strengths at different ages is presented.

Table 5.7: Slant Shear Test Results

Sample Type	Slant Shear Strength at 3 day (MPa)	Slant Shear Strength at 7 day (MPa)	Slant Shear Strength at 28 day (MPa)
Plain Cement Mortar	6.5	7.4	10.1
0.1% M3	7.8	9.1	12.3
0.3% M3	8.0	8.7	11.7
Epoxy resin	13.8	14.9	15.9

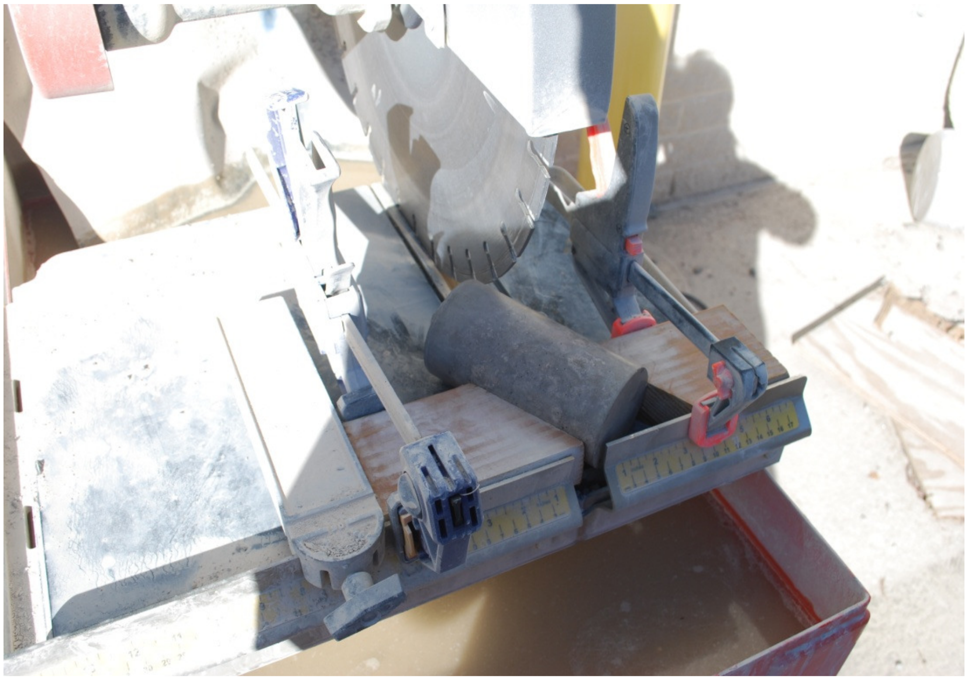


Figure 5.13: Cutting cylindrical specimens into two halves at 30^0 with vertical

Figure 5.14: Cylindrical specimens cut into two halves at 30^0 with vertical for slant shear test

Figure 5.15: Cylindrical specimens bonded together by M3 reinforced composite

Figure 5.16: Cylindrical specimens bonded together by epoxy

Figure 5.17: Film wrapped bonded cylindrical specimen

Figure 5.18: Load applied on epoxy bonded cylindrical specimen

Figure 5.19: Epoxy bonded cylindrical specimen after testing

Figure 5.20: M3 reinforced mortar bonded cylindrical specimen after testing

Figure 5.21: Normal cement mortar bonded cylindrical specimen after testing

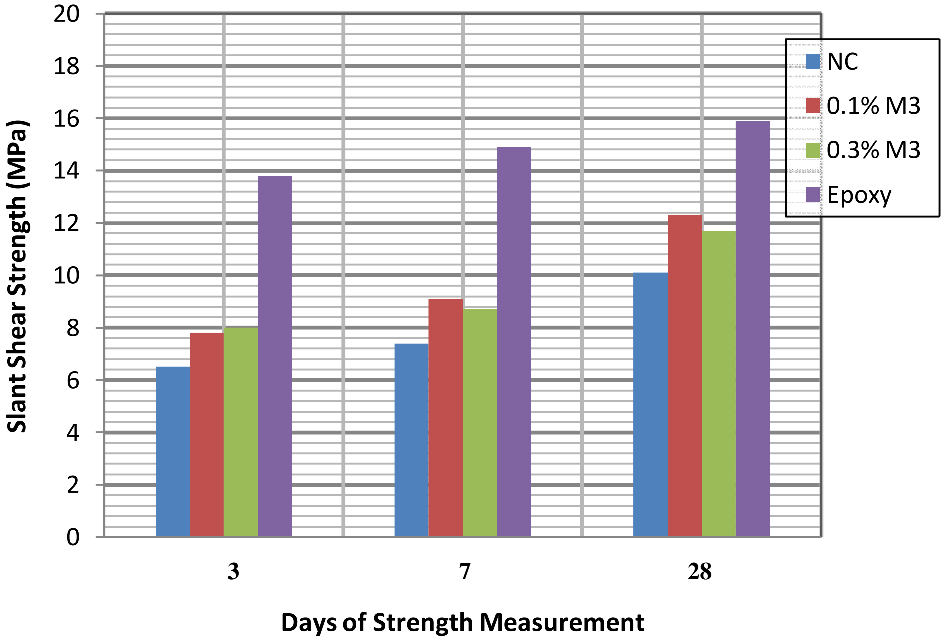


Figure 5.22: Slant shear strength of epoxy resin and normal & composite cement mortar at different ages

It was found that slant shear strength of epoxy at 3 and 7 days were much greater (almost double) than that of both control and composite mortar. This type of behavior was expected as Pro Poxy 300 Fast is quick hardening epoxy resin and gains strength very quickly. The slant shear strengths of composites were about 22% and 20% higher as compared to normal cement mortar at 3 and 7 days, respectively. At 28 day, the composites had about 17.5% higher slant shear strength than that of control mortar. The 28-day slant shear strengths of cylindrical specimens repaired using M3 reinforced mortar were relatively close to that repaired using epoxy. Therefore, it can be said that cementitious mortar reinforced with surface treated MWNT provides relatively comparable slant shear strength at the age of 28 day as compared to epoxy resin.

5.5 Discussion

The suitability of MWNT reinforced composites as concrete repair material was carried out through setting time, bleeding and slant shear tests. The setting time results show that nanotubes reinforced cement mortar hardened quite rapidly than that of normal cement mortar. Rapid setting is very important for a material to be used as repair material. It was also observed that composites showed no sign of bleeding. Bleeding can adversely affect the overall strength and durability of a repair material. Slant shear strengths of nanotubes reinforced composites were higher than that of control samples at all ages of 3, 7 and 28 day. The 0.1% dosage rate performed a little better as compared to 0.3% dosage rate in slant shear tests. As compared to epoxy, composites exhibited lower slant shear strengths particularly at early age of 3 and 7 day. The 28 day' slant shear strengths of composites achieved relatively higher value of 12.1 MPa. Initial test results on applicability of MWNT reinforced cement composites as repair material demonstrates good potential to carry out further investigation.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Introduction

In this chapter, the summary of the research findings of the current study is presented followed by major research contributions and future research recommendations. The study was based on testing of various important properties of a typical cement mortar mix reinforced with MWNT. The basic key issues, such as mixing method, workability, water cement ratio, mix proportions, etc were addressed comprehensively. Effects of various types and dosage rates of MWNT were explored in terms of strength properties. The actual testing included compressive strength, flexural strength, flowability, setting time, slant shear, and bleeding of MWNT reinforced mortar. For each test, control samples without nanotubes were prepared and tested along with the MWNT reinforced samples for comparison purposes.

6.2 Research Findings

Mixing of nanotubes within cement matrix is the key to develop composites having desirable properties. MWNT attract each other strongly due to Van der Waal's forces and in turn agglomerate in the form of knotted ropes and clumps. Agglomerated nanotubes are extremely difficult to disentangle. Therefore, ultrasonication is required to disperse MWNT within the cement matrix. Ultrasonication creates pressure waves in liquid through probe and it produces millions of shock waves by forming and violent collapsing of microscopic bubbles. The collective effect of energy released by each bubble is extremely high and results in breaking clumps and agglomeration of MWNT and disperses them relatively uniformly. The compressive strengths of composites with different mixing techniques proves the importance of proper sonication as 70% and 30% variation was found in compressive strengths at the age of 7 and 28 day, respectively. Also from SEM images, it is observed that MWNT can be fairly evenly distributed throughout the cement paste by sonication.

It is evident from the study that there exists an optimum concentration of MWNT and mix proportion to produce strong composite with desirable mechanical properties. In the first phase of the study, in most cases composites with w/c ratio of 0.60 produced the highest compressive strength. The dosage rate of 0.3% performed better in majority of instances. Composites having lower water content like 0.485 had extremely low workability and resulted in very low compressive strength. MWNT has large surface area and due to strong capillary forces water is drawn into them. Consequently water is detached from the rest of the mixture causing workability to decrease. Workability was also increased through plasticizer addition keeping w/c ratio at 0.485 but failed to achieve higher compressive strength at the age of 28 day. This means that workability is not the single issue causing the lower strength of composites. A possible explanation is that less water remains available for proper hydration as more water adheres to nanotube surfaces. Water also gets entrapped within agglomerated clumped MWNT if not properly dispersed and hinder the hydration reactions to form hydrated products which is essential to develop hardened cement paste. Also more aqueous solution provides more spaces for MWNT to disperse through sonication that eventually result in uniform dispersion. Though w/c ratios of more than 0.60 provide more solution for dispersion, have negative effect on composite strength as too much water lessens strength of cementitious composites. Therefore, for untreated MWNT with no use of surfactants or plasticizer, a tentative optimum w/c ratio would be around 0.60. Between 0.1 and 0.3% dosage rates of MWNT with w/c ratio of 0.60, increase in compressive strengths were observed for all seven types of multiwalled nanotubes. Composites with MWNT concentration greater than or equal to 0.5% resulted in very low compressive strengths, particularly at 28 day. More MWNT addition caused insufficient dispersion and produced weaker composites. Again if MWNT are not uniformly distributed they agglomerate to each other and creates weaker zone within the cement matrix. These entangled and clumped MWNT make the cement paste very viscous and greatly reduce the workability. These phenomena occur whenever higher dosage rates of MWNT were used.

It has been found that size of nanotubes notably influence the strength of composites. MWNT with OD 30 nm or less, obtained almost equal compressive and flexural strengths, with the highest compressive and flexural strength was achieved by the smallest size of MWNT having OD smaller than 8 nm. Smaller MWNT are distributed at much finer scale and consequently filling the nano pore space within the cement matrix more efficiently. Therefore, it can be concluded that smaller MWNT has beneficial effect on the strength properties of cementitious mortar. MWNT with smaller diameter fill the nano-sized pores more effectively and in turn resulting in more compact composites. Also, more interfacial bonding can be achieved between nanotubes and cement matrix.

Behavior of surface treated MWNT reinforced composites was also investigated. In all cases, composites with treated MWNT yielded higher compressive strengths than that of untreated ones. Acid treatment makes the MWNT more soluble to the solution by hindering their agglomeration. As a result, MWNT can be uniformly dispersed and eventually produced strong composites. Therefore, it became obvious that dispersion of nanotubes was the key to develop nanotubes reinforced cement composites. Flexural samples were made with the treated MWNT with the w/c ratio of 0.60. Two dosage rates of 0.2 and 0.3% were used. It was also observed that MWNT reinforced composites performed better in flexure than compression in terms of percentage increase in strength as compared to control samples. This is due to crack bridging and fiber pull out behavior of nanotubes are more pronounced in tension than compression.

From the 2nd phase of the study, it was observed that quality of MWNT dispersion within the cement matrix can be evaluated through the flow value of mix. Higher flow values represent better dispersion of nanotubes and inadequate distribution of nanotubes make the mix viscous resulting in low flow values. For the same mix proportion, higher flow values represent more uniform dispersion of nanotubes resulting in more stable mix. Mix proportions having w/c ratio between 0.60 and 0.62 produced the highest compressive strengths both at 7 and 28 days.

It was also observed that sonication of nanotubes into water alone was not capable of producing stable mixes in all instances. Utilization of polycarboxylate based super plasticizer as surfactant to distribute MWNT within cement matrix ensured both adequate dispersion of nanotubes and workability of cement paste that is necessary to produce strong composites. Application of polycarboxylate based plasticizer as surfactant deters nanotubes to agglomerate and make nanotubes more soluble. Appropriate dispersion of nanotubes also reduces the water demand as no water gets entrapped within the clumped nanotubes that eventually results in proper hydration of cement paste. In addition, adequate dispersion guarantees effective filling of nano space by nanotubes and ensures better reinforcement behavior. A tentative optimum proportion of plasticizer of 0.008 in terms of weight of cement was obtained. MWNT reinforced composites with plasticizer addition as surfactant yielded higher 7 and 28 day compressive and flexural strengths than that of composites sonicated with water only. The tentative optimum dosage rate of MWNT was ranged from 0.1-0.3%. The compressive strengths of MWNT-composites were about 30% and 16% higher as compared to control samples at 7 and 28 days, respectively. The maximum 7 and 28 day flexural strengths of composites were 24.5% and 19.5% greater than that of control samples. Statistical analysis was carried out in the form of hypothesis testing. The result of hypothesis statistically proved that cementitious composites reinforced with nanotubes performed better both in compression and flexure than normal cement mortar containing no nanotubes.

It was found from the third phase of the study that nanotubes reinforced cementitious composites hardened relatively rapidly as compared to normal cement mortar. Rapid setting is one of the important properties for a material to be used as concrete repair since in many instances quick restoration of structure is needed. Excessive bleeding of a repair mortar can lead to weakness, porosity and lack of durability caused by numerous uncontrolled open channels within the mortar mix. It was found that composites with multi walled nanotubes showed no sign of bleeding at all. Slant shear test results reflected the potential of MWNT reinforced cement composites to be applied as concrete repair material. Slant strengths of nanotubes reinforced composites were higher than that of control samples at all ages of 3, 7 and 28 day. In comparison with epoxy resin, the slant shear strengths of nanotubes reinforced composites were much lower at early age of 3 and 7 day but the 28 day slant shear strength was relatively close to that of specimens repaired by epoxy resins. To make concluding comment on applicability of nanotubes reinforced composites in concrete repair requires further research. From initial results, it can be said that these composites can be considered to repair concrete spalling. Nanotubes reinforced composites also have high potential to repair concrete cracks as they possess good flexural strength. Therefore, further investigation on the applicability of nanotubes reinforced cementitious composites in concrete repair is of great importance.

6.3 Research Contribution

The major research contributions of the study are summarized below:

(i) A mixing technique has been developed to address the issues related to dispersion of nanotubes within cement matrix. Polycarboxylate based super plasticizer has been adopted to use as surfactant. The proposed mixing method consists of adding nanotubes in sequences with varying amplitudes. The dispersion of nanotubes has been found to be stable. Closely spaced flow values and higher compressive and flexural strengths have been achieved through the novel mixing method.

(ii) An extensive parametric study has been conducted using different types of multiwalled nanotubes and various mix proportions. Seven different sizes of treated and untreated MWNT have been utilized. Statistical analysis in the form of hypothesis testing has been conducted. Based on the parametric study and statistical analysis, a tentative optimum mix proportion has been proposed. The mix proportion consists of plasticizer proportion of 0.008 in terms of the weight of the cementitious material. Tentative optimum dosage rates of treated MWNT, ranging from 0.1-0.3% of the weight of cementitious material, have been proposed to be used as reinforcement. MWNT with OD smaller than 30 nm has been suggested as the effective size to produce cementitious composites.

(iii) It has been suggested that application of MWNT reinforced cement mortar as concrete repair material has excellent potential. Nanotubes reinforced composites exhibited desirable behavior in setting time, bleeding and slant shear tests. This type of investigation is the first of its kind. The initial outcome was extremely encouraging and need further investigations which have been proposed in the recommendation part of the study.

6.4 Future Research

The study has dealt with multi walled nanotubes, collected from a single source. The study was based on compressive and flexural strengths of composites. The applicability of composites as concrete repair material was evaluated through setting time, bleeding and slant shear strength tests. Therefore, following recommendations can be taken into consideration to increase the understanding on behavior of cementitious composites reinforced with nanotubes.

In this study, MWNT were collected from a single source. Using MWNT from other sources is recommended for further research. Ordinary Type II Portland cement has been used as cementitious material in the study. The effect of addition of MWNT in other types of Portland cement could be an interesting investigation for future study. The starting point could be the tentative optimum mix proportion and dosage rates of MWNT recommended by the current investigation. In this research, the parametric study has been based on strength properties of composites. Some other mechanical properties like toughness of material, both in compression and flexure, can be estimated in future research. Due to crack bridging and fiber pullout mechanisms of nanotubes, it is expected that application of CNTs can enhance the overall toughness of the composites.

Application of SWNT as composite reinforcement can be evaluated. SWNT are of much smaller size ranging from 1-3 nm in OD. It has already been found that composites performed better with the decrease in size of nanotubes. Therefore, application of SWNT as reinforcement within cement matrix has good potential for future investigation.

In the present study, the applicability of repair material has been evaluated through setting time, bleeding and slant shear tests. To increase the fluidity of the grout, different combinations of plasticizer and water content can be investigated. Durability of composites can be accessed through sulfate attack resistance, deicing material resistance, permeability, drying shrinkage tests. The bond strength between rebar and repair material is another important factor in accessing the efficiency of a repair material. The rebar pull-out test can be conducted in future to determine bond strength between rebar and composites. Full size beam repair test can be carried out to examine the real time behavior of nanotubes reinforced composites as concrete repair material.

REFERENCES

Agull, V. J., Ligero, V. C., Rico, D. P., Casas, M. J. G., Martinez. A. G., Royo, J. M. M., and Moreno, J. G. (2009). "Mortar and Concrete Reinforced with Nanomaterials." Nanotechnology in Construction 3, 383-388.

Ajayan, P. M., and Zhou, O. Z. (2001). Topics in Applied Physics, 80, 391.

Altoubat, S., Yazdanbaksh, A., and Rieder, K. -A. (2009). "Shear Behavior of Macro-Synthetic Fiber-Reinforced Concrete Beams without Stirrups." Materials Journal, 106(4), 381-389.

American Society for Standard Testing and Materials (ASTM), (2008). “Standard Test Method for Compressive Strength of Hydraulic-Cement Mortars.” ASTM C 109-07, West Conshohocken, PA.

American Society for Standard Testing and Materials (ASTM), (2008). “Standard Test Method for Flexural Strength of Hydraulic-Cement Mortars.” ASTM C 348-02, West Conshohocken, PA.

American Society for Standard Testing and Materials (ASTM), (2008). “Standard Test Method for Flow of Hydraulic Cement Mortar.” ASTM C 1437-07, West Conshohocken, PA.

American Society for Standard Testing and Materials (ASTM), (2009). “Standard Test Method Time for of Setting of Hydraulic Cement Mortar by Modified Vicat Needle.” ASTM C 807-08, West Conshohocken, PA.

American Society for Standard Testing and Materials (ASTM), (2008). “Standard Test Method for Expansion and Bleeding of Freshly Mixed Grouts for Preplaced-Aggregate Concrete in the Laboratory.” ASTM C 940-98, West Conshohocken, PA.

American Society for Standard Testing and Materials (ASTM), (2008). “Standard Test Method for Bond Strength of Epoxy-Resin Systems Used with Concrete by Slant Shear.” ASTM C 882-05, West Conshohocken, PA.

American Society for Standard Testing and Materials (ASTM), (2008). “Standard Test Method for Density, Relative Density (Specific Gravity) and Absorption of Coarse Aggregate.” ASTM C 127-07, West Conshohocken, PA.

American Society for Standard Testing and Materials (ASTM), (2008). “Standard Test Method for Density, Relative Density (Specific Gravity) and Absorption of Coarse Aggregate.” ASTM C 127-07, West Conshohocken, PA.

American Society for Standard Testing and Materials (ASTM), (2010). “Standard Specification for Chemical Admixtures for Concrete.” ASTM C494/C494M-10, West Conshohocken, PA.

American Society for Standard Testing and Materials (ASTM), (2010). “Standard Specification for Chemical Admixture for Use in Producing Flowing Concrete.” ASTM C1017/C1017M-07, West Conshohocken, PA.

Balázsi, Cs., Wéber, F., Kövér, Zs., Shen, Z., Kónya, Z., Kasztovszky, Zs., Vértesy, Z., Biró, L.P., Kiricsi, I., and Arató, P. (2006). “Application of Carbon Nanotubes to Silicon Nitride Matrix Reinforcements”, Cur. Appl. Phys., 6, 124-130.

Baughman, R. H., Zakhidov, A. A., and Heer, W. A. (2002). Science, 297, 787.

Campillo, I., Dolado, J.S., and Porro, A. (2004). "High-performance Nanostructured Materials for Construction." Proceeding of the 1st International Symposium on Nanotechnology in Construction, Paisley, Scotland, Royal Society of Chemistry, London.

Collins, P. G., Bradley, K., Ishigami, M., and Zettl, A. (2000). Science, 287, 1801.

Cwirzen, A., Habermehl-Cwirzen, K., and Penttala, V. (2008). "Surface Decoration of Carbon Nanotubes and Mechnical Properties of Cement/Carbon Nanotube Composites." Adv. Cem. Res., 20, 65-73.

Fischer, G., and Li, V. C. (2007). "Effect of Fiber Reinforcement on the Response of Structural Members." Engineering Fracture Mechanics, 74(1-2), 258-272.

Gay, C., and Sanchez, F. (2010). "Performance of Carbon Nanofiber-Cement Composites with a High-Range Water Reducer." Journal of the Transportation Research Board, No. 2142, 109-113.

Javey, A., Wang, Q., Ural, A., Li, Y., and Dai, H. (2002). Nano Letters, 2, 929.

Konsta-Gdoutos, M. S., Metaxa, Z. S., and Shah, S. P. (2010). "Highly Dispersed Carbon Nanotube Reinforced Cement Based Materials." Cement and Concrete Research, 40, 1052-1059.

Kuzumaki, T., Ujiie, O., Ichinose, H., and Ito, K. (2002). Journal of Materials Research, 13, 2445.

Li, G.Y., Wang, P.M. and Zhao, X. (2007). “Pressure-Sensitive Properties and Microstructure of Carbon Nanotube Reinforced Cement Composites.” Journal of Cement & Concrete Composites, Elsevier Ltd.

Li, G.Y., Wang, P.M. and Zhao, X. (2004). “Mechanical Behavior and Microstructure of Cement Composites Incorporating Surface-Treated Multi-walled Carbon Nanotubes.” Journal of Cement & Concrete Composites, Elsevier Ltd.

Li, H., Xiao, H., Yuan, J. and Ou, J. (2004). "Microstructure of Cement Mortar with Nano-particles." Composites: Part B; 35:185-189.

Li, V. C., and Maalej, M. (1996). "Toughening in Cement Based Composites. Part II: Fiber Reinforced Cementitious Composites." Cement and Concrete Composites, 18(4), 239-249.

Louie, S. G. (2001). "Topics in Applied Physics." 80, 113.

Lourie, O., and Wagner, H.D. (1998). "Evaluation of Young's Modulus of Carbon Nanotubes by Micro-Raman Spectroscopy." J. Mater. Res. 13 (9), 2418-2422.

Lourie, O., Cox, D.M., and Wagner, H.D. (1998). "Buckling and Collapse of Embedded Carbon Nanotubes." Phys. Ref. Lett. 81 (8), 1638-1641.

Lupo, F., Kamalakaran, R., Scheu, C., Grobert, N., and Rühle, M. (2004). “Microstructural Investigations on Zirconium Oxide-Carbon Nanotube Composites Synthesized by Hydrothermal Crystallization”, Carbon, 42, 1995-1999.

Ma, R. Z., Wu, J., Wei, B. Q., Liang, J., and Wu, D. H. (1998). Journal of Materials Science, 33, 5243.

Maile, A. and Huang, C.P. (2006). "The Chemistry and Physics of Nano-cement." NSF-REU, University of Delaware.

Makar, J.M.; Chan, G.W. (2009). " Growth of Cement Hydration Products on Single Walled Carbon Nanotubes." Institute for Research in Construction, NRC-CNRC.

Makar, J., Margeson, J. and Luh, J. (2005). “Carbon nanotube/cement composites-early results and potential application”, 3rd International Conference on Construction Materials: Performance, Innovations and Structural Implications, Vancouver, B.C., Aug. 22-24, pp. 1-10.

Makar, J.M. and Beaudoin, J.J. (2003). “Carbon Nanotubes and Their Application in the Construction Industry.” 1st International Symposium on Nanotechnology in Construction, Paisley, Scotland, pp. 331-341.

Mangat, P. S., Motamedi-Azari, M., and Shakor Ramat, B. B. (1984). "Steel Fibre-Cement Matrix Interfacial Bond Characteristics Under Flexure." International Journal of Cement Composites and Lightweight Concrete, 6(1), 29-37.

Pablo, P. J., Goméz-Navarro, C., Martinez, M. T., Benito, A. M., Maser, W. K., Colchero, J., Goméz-Herrero, J., and Basó, A. M. (2002). Applied Physics Letters, 80.

Salvetat, J.-P., Bonard, J.-M., Thomson, N. H., Kulik, A. J., Forró, L., Benoit, W., and Zuppiroli, L. (1999). Applied. Physics A, 69, 255.

Savastano, J. H., Warden, P. G., and Coutts, R. S. P. (2005). "Microstructure and Mechanical Properties of Waste Fibre-Cement Composites." Cement and Concrete Composites, 27(5), 583-592.

Scrivener, K.L. and Kirkpatrick, R.J. (2007). “Innovation in Use and Research on Cementitious Material.” Journal of Cement and Concrete Research, Elsevier Ltd.

Tasis, D., Pispas, S., Galiotis, C., and Bourpoulos, N. (2007). “Growth of Calcium Carbonate on Non-covalently Modified Carbon Nanotubes”, Matr. Lett., 61, 5044-5046.

Terranova, M.L., Orlanducci, S., Fiori, A., Tamburri, E., Sessa, V., Rossi, M., and Barnard, A.S. (2005). “Controlled Evolution of Carbon Nanotubes Coated by Nanodiamond: the Realization of a New Class of Hybrid Nanomaterials”, Chem. Mater., 17, 3214-3220.

Texas Department of Transportation (TXDOT), (2009). "Concrete Repair Materials, Departmental Material Specification." DMS-4655, August 2009-February 2011.

Thostenson, E.T. and Chou, T.-W. (2002). "Aligned Multi-walled Carbon Nanotube-Reinforced Composites: Processing and Mechanical Characterization." Journal of Physics D: Applied Physics, 35: L77-L80.

Walters, D. A., Ericson, L. M., Casavant, M. J., Liu, J., Colbert, D. T., Smith, K. A., and Smalley, R. E. (1999). "Elastic strain of freely suspended single-wall carbon nanotube ropes." App. Phys. Let., 74, 3803-3805.

Wang, C., Li, K.-Z., Li, H.-J., Jiao, G.-S., Lu, J., and Hou, D.-S. (2008). "Effect of Carbon Fiber Dispersion on the Mechanical Properties of Carbon-Fiber Cement-Based Composites." Materials Science and Engineering: A, 487(1-2), 52-57.

Yazdanbakhsh, A., Grasley, Z., Tyson, B., and Abu Al-Rub, R. K. (2010). "Distribution of Carbon Nanofibers and Nanotubes in Cementitious Composites." Journal of the Transportation Research Board, No. 2142, 89-95.

Yu, M.F., Files, B.S., Arepaali, S., and Ruoff, R.S. (2000). "Tensile Loading of Ropes of Single Wall Carbon Nanotubes and Their Mechanical Properties." Phys. Ref. Lett. 84 (24), 5552-5555.

Yu, M.F., Lourie, O., Dyer, M. J., Moloni, K., Kelly, T. F., and Ruoff, R.S. (2000). "Strength and Breaking Mechanism of Multiwalled Carbon Nanotubes under Tensile Load." Science, 287 (5453), 637-640.

Zhan, G.-D., Kuntz, J. D., Wan, J. and Mukherjee, A. K. (2003). "Single-wall Carbon Nanotubes as Attractive Toughening Agents in Alumina-based Nanocomposites." Nature Materials, 2(1): 38-42

Zheng, L. X., O'Connell, M. J., Doorn, S. K., Liao, X. Z., Zhao, Y. H., Akhadov, E. A., Hoffbauer, M. A., Roop, B. J., Jia, Q. X., Dye, R. C., Peterson, D. E., Huang, S. M., Liu, J. and Zhu, Y. T. (2004) "Ultralong single-wall carbon nanotubes." Nature Materials, 3: 673-676.

BIOGRAPHICAL INFORMATION

Tanvir Manzur received his B.Sc. degree with Honors in Civil Engineering from Bangladesh University of Engineering and Technology (BUET) in 2003. He received his M.Sc. degree in Civil and Structural Engineering in 2006 from the same university. He was the recipient of the Deans Award for every session for obtaining CGPA higher than 3.75 and received Merit Scholarship in every academic year for securing top 5% position. After graduation he started his career as a lecturer in the Department of Civil Engineering, BUET. He has more than four years of teaching experience in Bangladesh at university level. He also served as a member of the Bureau of Research, Testing and Consultation (BRTC), BUET. He was routinely involved in providing laboratory and field testing services through BRTC. He started his doctoral studies in the Civil Engineering Department of UT Arlington in Summer, 2007. During his graduate studies at UTA, he had an opportunity to work as a graduate teaching assistant and graduate research assistant under Dr. Nur Yazdani. His major research interests include application of nanotechnology in construction industry, cement and concrete properties, behavior of cementitious composites reinforced with nano fibers, hazard mitigation, engineering education etc. His future plan is to continue his career as a faculty mentor and researcher in the field of civil and structural engineering.