"EFFECT OF CARBON NANOTUBE AS CEMENT REPLACEMENT IN MORTAR ON MECHANICAL PROPERTIES"

A thesis submitted in partial fulfilment

Of the requirement for the award of degree of

MASTER OF ENGINEERING

IN

STRUCTURES

Submitted by:

ChandraShekhar Kumar

Roll no. : 821022005

Under the supervision of

Dr. Shruti Sharma

Assistant Professor, CED

Thapar University

DEPARTMENT OF CIVIL ENGINEERING
THAPAR UNIVERSITY
(Established under the section 3 of UGC Act, 1956)
PATIALA-147004 (PUNJAB)
INDIA

JULY – 2014

DECLARATION

The author hereby declares that this thesis entitled **"Effect Of Carbon Nanotube As Cement Replacement In Mortar On Mechanical Properties"**, in whole or part, has not been used to obtain any degree in this, or any other, institute. Except where references have been given in text, it is entirely the authors own work. The author confirms that the library may lend or copy this thesis upon request for academic purposes.

C. S Kumar

(CHANDRASHEKHAR KUMAR)
Roll No.: 821022005

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This is to certify that the thesis entitled **"Effect Of Carbon Nanotube As Cement Replacement In Mortar On Mechanical Properties"** being submitted by **Mr. ChandraShekhar kumar, Roll No 821022005** in partial fulfilment for the award of degree of **Masters of Engineering in Structural Engineering** at **Thapar University, Patiala** is a bonafide work carried out by him under our guidance and supervision and that no part of this thesis has been submitted for the award of any other degree

Dr.Shruti Sharma
Assistant Professor
Civil Engineering
Thapar University, Patiala

COUNTERSIGNED

NAVEEN KWATRA
Chairman, Board of studies
Department of Civil Engineering
Thapar University, Patiala

S. K. MOHAPATRA
Dean, Academic Affairs
Thapar University, Patiala

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ABSTRACT

Cement mortar is a building compound which is the most commonly used material on this plane which is prepared by mixing sand and cement with a specified amount of water. The cement mortar can be used for a number of applications, such as plastering over bricks or other types of masonry. This is referred as sand cement-mortar blends today often incorporate different types of materials to create various types of cement mortars.

The ingredients in cement mortar vary, which depends on the manufacturer specifications. A normal cement mortar will include both sand and cement, with lime added to the mix. Other types of aggregates may be added which depends on the texture that is preferred for the mortar. In recent years, the addition of nano- materials such as clay have helped to create cement mortar products that provide additional strength without negatively impacting the binding powers of the cement mortar.

Within the last decade the performance of cement mortar has been significantly improved by applying different kinds of micro and nano-particles from fundamental research disciplines that has not been used for construction materials before. Nanotechnology seems to hold the key that allows construction and building material to replicate the features of natural systems improved until perfection during millions of years. Until today concrete has been seen as a structural material but nanotechnology can help to make it a multi-purpose smart material.

Processes occurring at the nano-scale ultimately affect the engineering properties and the performance of the bulk material. By the use of nanotechnology the structure of the fundamental calcium-silicate-hydrate(C-S-H) gel which is responsible for the mechanical and the physical properties of the cement pastes, including shrinkage, creep, porosity, permeability and elasticity can be modified to obtain better durability.

This thesis investigates the efficacy of Carbon Nanotube in enhancing the behaviour of cement mortar and improving its mechanical properties.

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CHAPTER 1
INTRODUCTION

1.1 GENERAL

Concrete, the most common material in the world is a nanostructured, multiphase composite material that ages over time (Sanchez and Sobolev, 2010). It is composed of on amorphous phase, nanometer to micrometer size crystals and bound water. The properties of concrete exist in and the degradation mechanism occur across, multiple length scales (nano to micro to macro), when the properties of each scale derive from those of the next smaller scale (Figure 1.1).

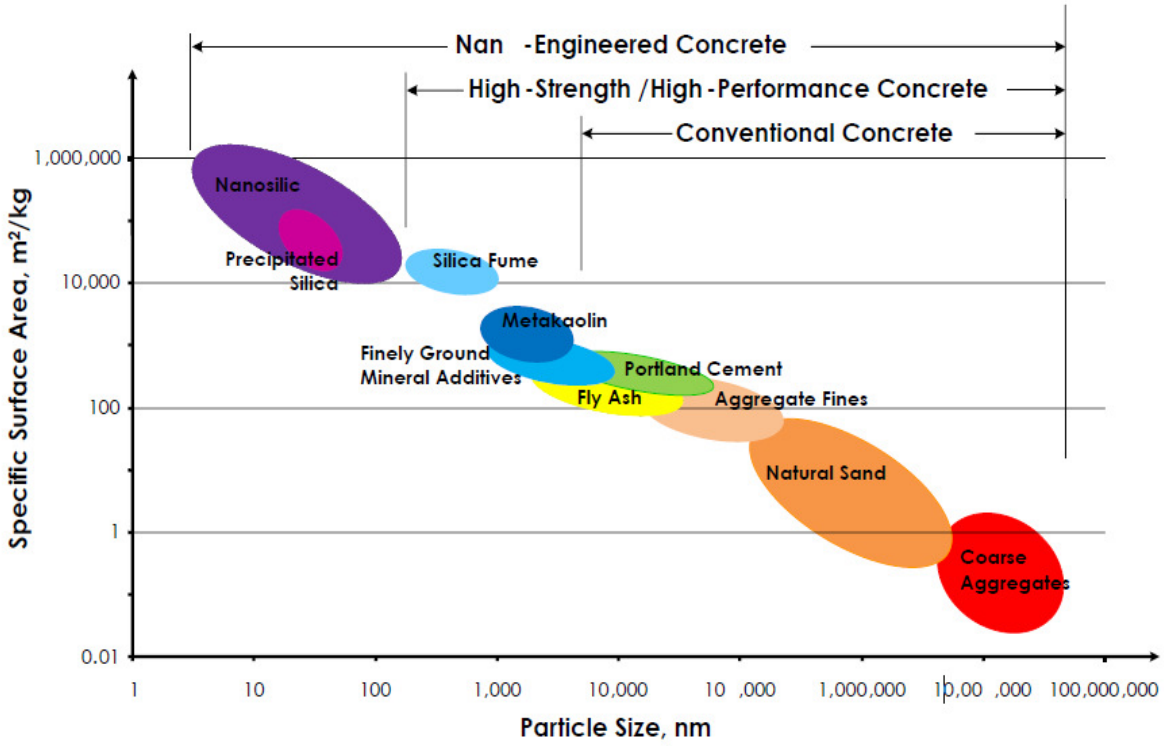


Figure 1.1: Particle size and specific surface area related to concrete materials (adapted from Sobolev, 2005).

Nano engineering of concrete can take place in one or more of the three location such as (a) in the solid phases (b) in the liquid phase (c) at the interfaces between liquid – solid and solid – solid (Garhoczi, 2009).

The mechanical behavior of the concrete material depends to a great extent on structural elements that are effective on a micro and nanoscale. The size of the calcium silicate hydrate (C-S-H) phase, the primary component responsible for strength and other properties in cementations system, falls in the few nanometers range (Taylor, 1997). The structure of C-S-H is much like clay, with thin layers of solids separated by gel pores filled with interlayer and absorbed water (Mehta, 1986).

This has significant impact on the performance of concrete, because the structure is sensitive to moisture movement, at times resulting in shrinkage and consequent cracking if accommodations in element sizes are not made (Jennings et. al. 2007). Hence nanotechnology may have the potential to engineer concrete with superior properties through the optimization of material behavior and required performance to significantly improve mechanical performance, durability & sustainibility.

The development of nanotechnology based concrete material requires a multidiscipline approach. Consisting of team of concrete material experts; Civil Engineers, chemists, physicists and material scientists. Porro et. al. (2010) presented an overview of have nanotechnology could be applied to concrete technology, emphasizing the multidiscipline approach required for successful breakthrough leading to ultra high performance materials and new multiscale models that enable the prediction of balk materials properties from compassion parameters.

Grove et. al. (2010) identified opportunities for nanotechnology leading to a new concrete products and materials and also for improving the sustainable and reducing the environmental footprint of concrete based material in the future. Finally Brigisson et. al. (2010) identified the following key breakthroughs in concrete technology that are most likely to result from the use of nanotechnology.

- Development of high performance cement and concrete materials as measured by their mechanical and durable properties.
- Development of sustainable concrete material and structure through engineering for different adverse environment, reducing energy consumption during cement production and enhancing safety.
- Development of intelligent concrete material through the integration of nanotechnology based self-sensing and self-powdered materials and cyber infrastructure technologies.
- Development of novel concrete materials through nanotechnology based innovative processing of cement and cement paste.
- Development of fundamental multiscale model (s) for concrete through advanced characterization and modeling of concrete at the nano -micro, and micro scales.

Carbon nanotubes (CNT) are relatively young nanostructures. Despite the big research effort worldwide from its discovery in 1991, many of its properties are still under investigation. CNTs are composed of carbon atoms arranged forming a cylindrical structure, similar to a rolled graphene sheet. This structure gives them unique properties which make this material attractive for a variety of applications. For example, CNTs have exceptional mechanical properties such as high stiffness and high strength.

These properties allow various applications of CNT in a wide variety of fields where the performance of the material or the device can be considerably improved by the introduction of carbon nanotubes. One of the main applications in the field of polymer composite materials is their reinforcement through the use of CNTs. The extraordinary mechanical properties of CNTs make them very suitable for design of materials with a high strength and a low weight. A material of these characteristics is necessary in the aerospace sector, where the compromise between strength and weight has always been a concern. Also,

applications in the field of electronics are very promising as CNTs can act as a conductor or a semiconductor depending on its atomic configurations. Other aerospace applications include the fabrication of nano and micro electromechanical systems, sensors and thermal insulation.

1.2 STRUCTURE OF CNT'S

The basic crystalline forms of elemental carbon have been a well-known material for a long time. They have been used extensively across history in the forms of diamond, graphite and amorphous carbon. Over the last twenty years, some new carbon atom arrangements have been discovered. In 1986, Kroto and Smalley discovered the C60 molecule, also known as buckyball. This new form paved the way for a completely new class of carbon molecules: the fullerenes.

A wide variety of atom arrangements is made possible by the range of configurations of the electronic states of carbon atoms. The most common of these structures are shown in Fig. 1.1. The newest of them is the carbon nanotube (CNT), which was discovered by Iijima in 1991. However, this structure had already been observed by himself in 1979, when the first clear transmission electron microscopy (TEM) clear images were obtained.

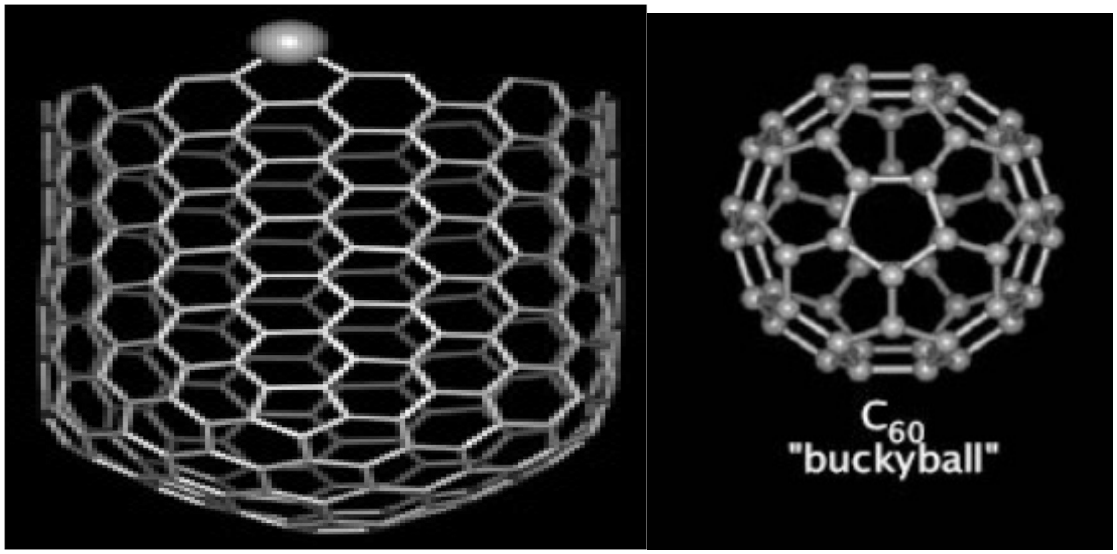
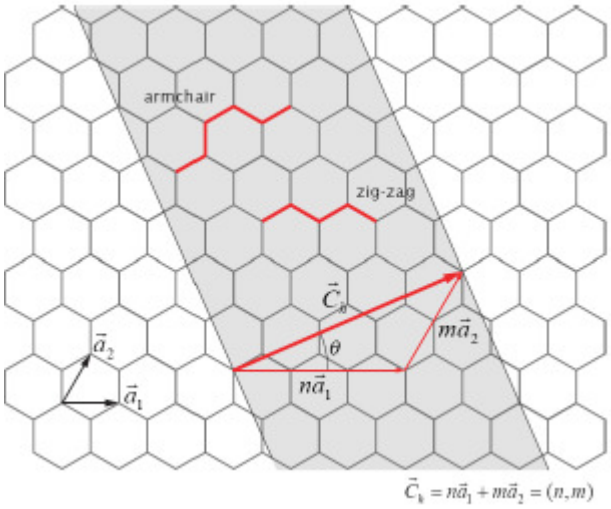


Fig. 1.1A Schematic representation of different types of fullerenes

A single-wall carbon nanotube (SWCNT) can be defined by a hollow rolled cylindrical graphene sheet with a diameter of about 0.7-10 nm. However, most observed SWCNTs have diameters under 2 nm. There are also nanotubes with multi-walled structures, which will be discussed later. Nanotubes with lengths of several millimeters have already been obtained. The aspect ratio (length/diameter) of this cylindrical structure can be as large as 104-105. Taking this into account and neglecting the two ends of the nanotube, we can consider it as a one-dimensional nanostructure .

Nanotubes have an exceptional combination of properties: small size, low density (similar to graphite), high stiffness, high strength and a variety of electronic properties. Such outstanding properties allow the application of CNTs in a wide range fields as reinforcing elements in high strength composites, electron sources in field emission displays and small X-ray sources, ultra-sharp and resistant atomic force microscopy (AFM) tips with high aspect ratios, gas sensors and components of future nanoscale electronics.

A nanotube is composed by carbon atoms forming six-membered carbon rings with the shape of a hexagon. The angle of this hexagon with the axis of the cylinder will determine the structure of the nanotube. Many possible structures exist as there are infinite angles in which a graphene sheet can be rolled into a SWCNT



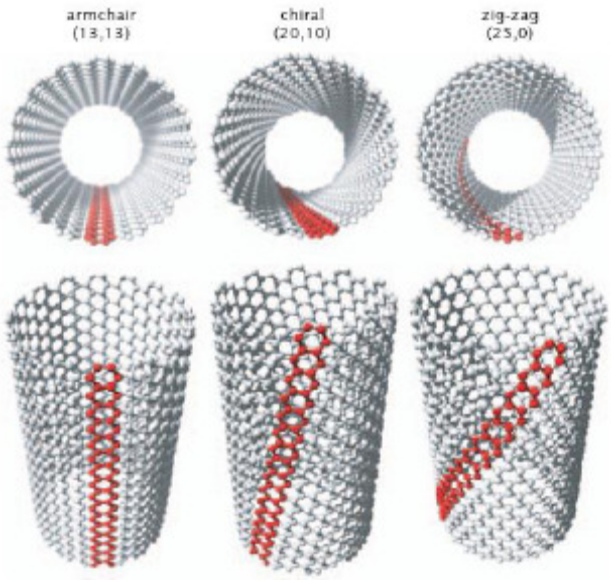


Fig. 1.2 Schematic illustrations of the structure of an armchair, chiral and zig-zag carbon nanotubes (top) and schematic diagram of nanotube formation by "rolling-up" a graphene sheet (top)[Kroto Et.al (1985)]

Carbon nanotubes can be classified as achiral or chiral. The first type can be defined as a nanotube whose mirror image has the same structure as the original. There are two cases of achiral nanotubes: armchair and zigzag, which correspond to the first and third nanotube. Their names come from the shape of their cross-sectional ring, as shown in the scheme at the right of the same figure. Nanotubes whose mirror image is different to the original are called chiral .

These structure variations can be cataloged according to the chiral vector or chiral angle θ. Fig. 1.2 shows a graphene sheet and the unit vectors that will determine the chirality. According to that, the chiral vector is:

$$C_h = n\bar{a}_1 + m\bar{a}_2 = (n, m)$$

The twist that the angle θ determines is clearly shown in Fig. 1.2. The extreme cases are θ=0° for the armchair configuration and θ=30° for a zigzag carbon nanotube. The angles in between correspond to chiral CNTs.

The importance of this issue is due to the fact that it determines some properties of the carbon nanotube, especially the conductivity . Graphite is considered to be

a semi-metal, but it has been shown that, depending on tube chirality, nanotubes can be either metallic or semiconducting .

Carbon nanotubes can be single-walled or multi-walled (SWCNT and MWCNT respectively). SWCNT have already been defined. A MWCNT consists of multiple rolled layers of graphite which can be seen as concentric single-walled tubes. The distance between layers in MWCNTs is similar to the distance between graphene layers in graphite, approximately 3.3 Å.

There is an intermediate case, which is called double-walled carbon nanotubes (DWCNT). The mechanical and chemical properties of each type of CNT are slightly different. Moreover, the nanotube surface can be chemically modified to, for instance, improve the adhesion to a polymer matrix .It can be seen that strengthening of a polymer due to CNT increases as diameter decreases but single-walled CNT are inefficient as there are prone to bundle formation

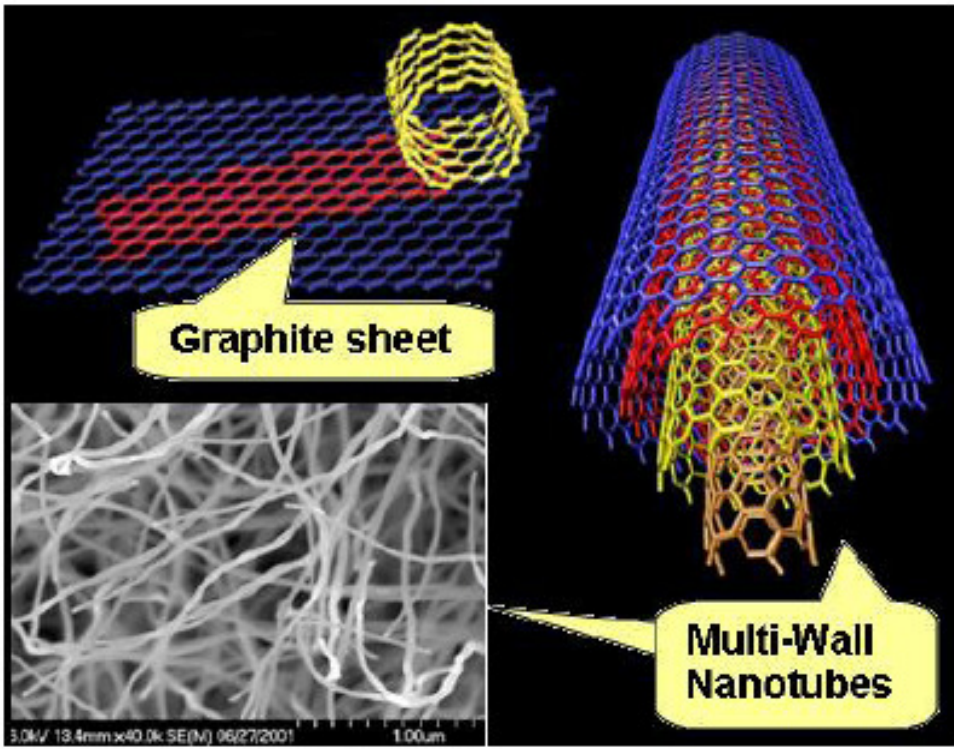


Fig 1.3 Graphite sheet of nanotubes (Nanopedia, 2008)

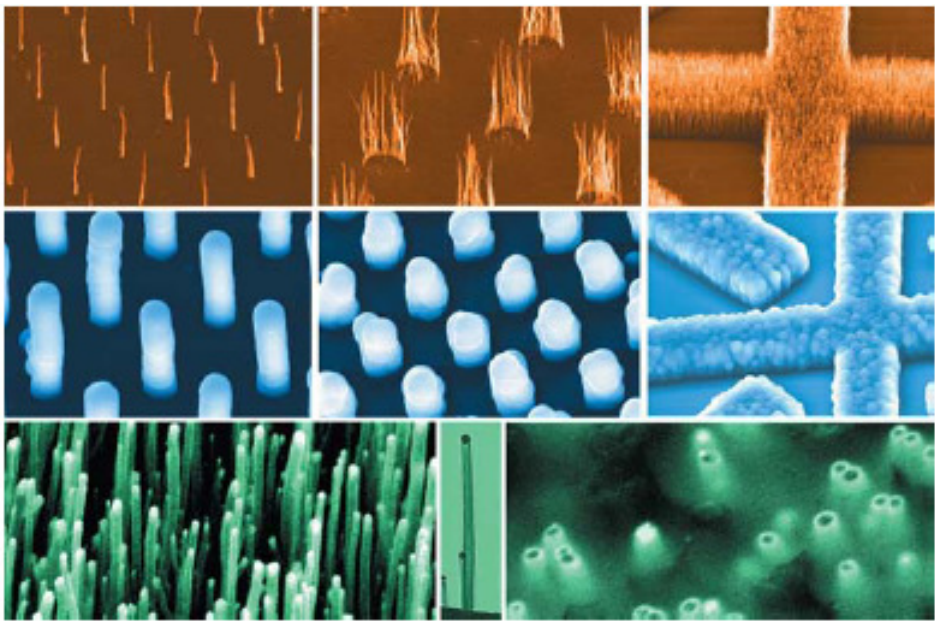


Fig 1.4 Nanotubes (NASA, 2008)

SEM IMAGE CNT

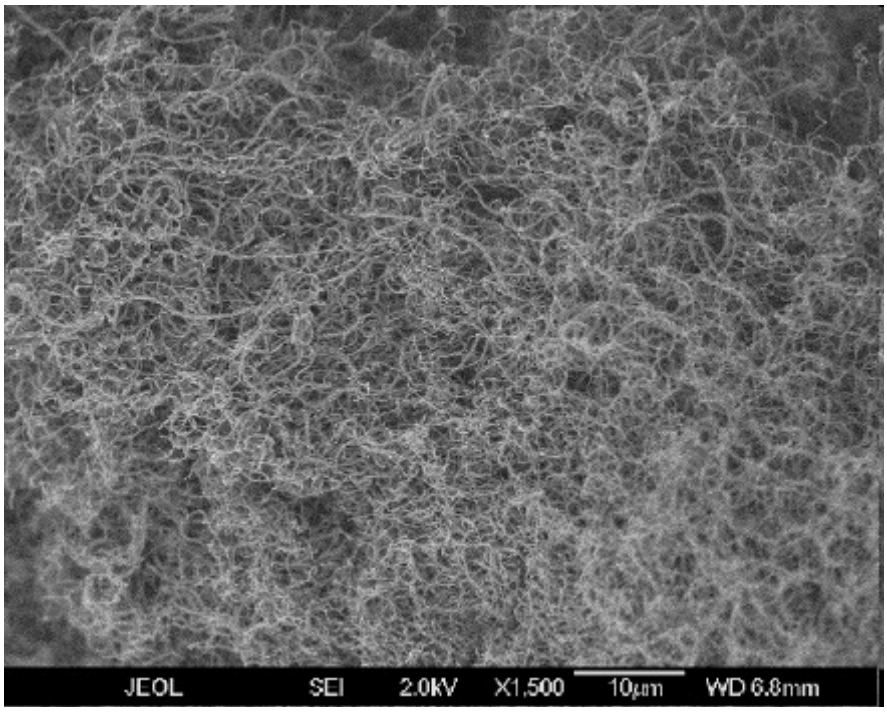


Fig 1.5 Carbon Nanotube as Concrete filler (micro scale)[Rossi Et.al (2006)]

1.3 NANOTECHNOLOGY IN CONCRETE

1.3.1. Concrete: a complex, nano-structured material

Concrete, the most ubiquitous material in the world, is a nanostructured, multi-phase, composite material that ages over time. It is composed of an amorphous phase, nanometer to micrometer size crystals, and bound water. The properties of concrete exist in, and the degradation mechanisms occur across, multiple length scales (nano to micro to macro) where the properties of each scale derive from those of the next smaller scale . The amorphous phase, calcium-silicate-hydrate (C-S-H) is the ‘ ‘glue” that holds concrete together and is itself a nanomaterial.

Viewed from the bottom-up, concrete at the nanoscale is a composite of molecular assemblages, surfaces (aggregates, fibers), and chemical bonds that interact through local chemical reactions, intermolecular forces, and intraphase diffusion. Properties characterizing this scale are molecular structure; surface functional groups; and bond length, strength (energy), and density. The structure of the amorphous and crystalline phases and of the interphase boundaries originates from this scale.

The properties and processes at the nanoscale define the interactions that occur between particles and phases at the microscale and the effects of working loads and the surrounding environment at the macroscale. Processes occurring at the nanoscale ultimately affect the engineering properties and performance of the bulk material.

1.3.2. Definition of nanotechnology in concrete

The nanoscience and nano-engineering, sometimes called nanomodification, of concrete are terms that have come into common usage and describe two main avenues of application of nanotechnology in concrete research .Nanoscience deals with the measurement and characterization of the nano and microscale structure of cement-based materials to better understand how this

structure affects macroscale properties and performance through the use of advanced characterization techniques and atomistic or molecular level modeling.

Nano-engineering encompasses the techniques of manipulation of the structure at the nanometer scale to develop a new generation of tailored, multifunctional, cementitious composites with superior mechanical performance and durability potentially having a range of novel properties such as: low electrical resistivity, self-sensing capabilities, self-cleaning, selfhealing, high ductility, and self-control of cracks.

Concrete can be nano-engineered by the incorporation of nanosized building blocks or objects (e.g., nanoparticles and nanotubes) to control material behavior and add novel properties, or by the grafting of molecules onto cement particles, cement phases, aggregates, and additives(including nanosized additives) to provide surface functionality, which can be adjusted to promote specific interfacial interactions.

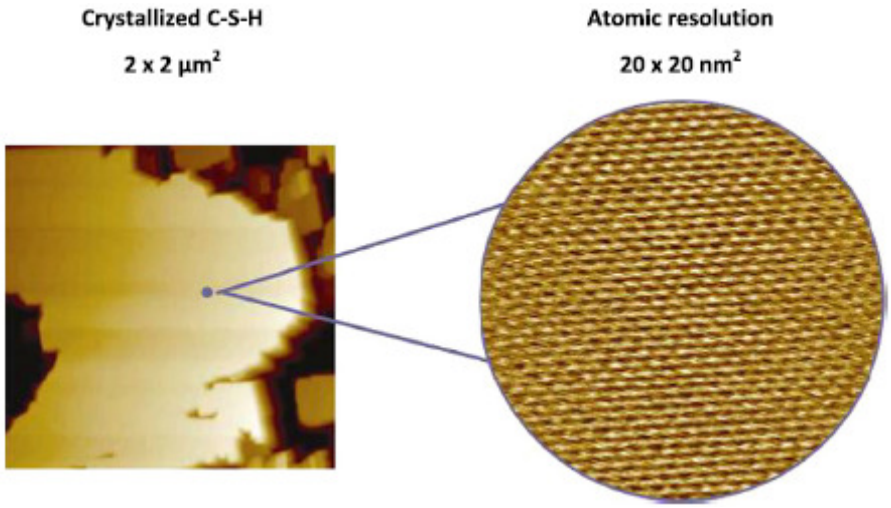


Fig. 1.6. Nanoscale structure of C‑S‑H crystallized on calcite substrate and revealed by AFM (Ca/Si = 0.9). Reprinted with permission from the American Ceramic Society Bulletin, 2005, Vol. 84, N 11 [7].

1.4 Nanomaterials Used for Cement mortar or concrete

1.4.1 Titanium Dioxide Nanoparticles (TiO2)

The titanium dioxide nano-particles are added to concrete to improve its properties. This white pigment is used as an excellent reflective coating, or added to paints, cements and windows for its sterilizing properties. The titaniumdioxide breaks down organic pollutants, volatile organic compounds and bacterial membranes through powerful photo catalytic reactions, reducing air pollutants when it's applied to outdoor surfaces. Being hydrophilic gives self cleaning properties to surfaces to which it is applied, because the rain water is attracted to the surface and forms sheets which collect the pollutants and dirt particles previously broken down and washes them off.

1.4.2 Silicon Dioxide Nanoparticles (SiO2)

Nano-SiO2 could significantly increase the compressive strength ofconcretes containing large fly ash volume at early age, by filling the poresbetween large fly ash and cement particles. Nano-silica decreases the setting time of mortar when compared with silica fume (microsilica) and reduces bleeding water and segregation by the improvement of the cohesiveness.

1.4.3 Zinc Oxide Nanoparticles (ZnO)

Zinc oxide is a unique material that exhibits semiconducting and piezoelectric dual properties. It is added into various materials and products, including plastics, ceramics, glass, cement, rubber, paints, adhesive, sealants, pigments, fire retardants. Used for concrete manufacturing, ZnO improves the processing time and the resistance of concrete against water.

1.4.4 Silver Nanoparticles

Silver is an especially attractive metal due to its remarkable size and shape dependent optical properties, highest efficiency of Plasmon excitation, and

highest electrical and thermal conductivity in the bulk among all metals. These special properties have led to promising applications of silver nanoparticles catalysis for the selective oxidation of styrene, environmentally friendly antimicrobial coatings, real-time optical sensors, printed electronics and photonics. Silver nanoparticles are nanoparticles of silver i.e. silver particles of between 1 nm and 100 nm in size. While frequently described as being silver some are composed of a large percentage of silver oxide due to their large ratio of surface to bulk silver atoms.

Over the last decade silver nanoparticles have found applications in catalysis, optics, electronics and other areas due to unique size-dependent optical, electrical and magnetic properties. Currently most of the applications of silver nanoparticles are in antibacterial/antifungal agents in biotechnology and bioengineering, textile engineering, water treatment, and silver-based consumer products.

1.5 Nanotechnology in Construction Industry

Nanotechnology makes construction faster, cheaper, safer, and more varied. The automation of nanotechnology construction can allow for the creation of structures from advanced homes to massive skyscrapers much more quickly at much lower cost. In the coming future, Nanotechnology can be used to sense cracks in foundations of architecture and can send nanobots to repair them.

Nanotechnology is the most prominent research area that encompasses a number of disciplines such as electronics, bio-mechanics and coatings. These disciplines guide in the areas of civil engineering and construction materials. When nanotechnology is implemented in the construction of homes and infrastructure, such structures will be stronger. If buildings are stronger, then less of them will require reconstruction and less waste will be produced.

Nanotechnology in construction involves the use of nano-particles such as alumina and silica. The manufacturers are also investigating the methods of producing nano-cement. If cement with nano-size particles can be manufactured and processed, it will open up a large number of opportunities in the fields of ceramics, high strength composites and electronic applications.

Nanomaterials have a high cost as compared with conventional materials, which means that they are not likely to feature in high-volume building materials.

1.6 Objective of Work

Cement mortar is the most commonly used construction material on planet.It presents a higher permeability that allows water and other aggressive elements to enter which leads to carbonation and chloride ion attack, resulting in corrosion problems. Use of Carbon nanotube in this field proves to be a great enrichment to the cement mortar to improve its properties. Following are some of the advantages of the using nanotechnology in cement mortar:

- Carbon Nanotube helps to make mortar a multipurpose smart functional material.
- The use of nanotube is used to increase the strength and durability of cementitious composites as well as for pollution reduction.
- Production of thermal insulation materials with a performance ten times commercial current options.
- Production of coats and thin films self-cleansing ability and self colour change to minimize energy consumption.
- Production of cheap corrosion free steel.
- Production of nanosensors and materials with sensing ability and self-repairing ability.

To date Carbon nanotube applications and advances in the construction and building materials fields have been uneven. Exploitation of Carbon nanotube in

cement mortar on a commercial scale remains limited with few results successfully converted into marketable products. Although nanotube has potential to be the key to a brand new world in the field of construction but scientists are still trying to grasp their astonishing complexities.

1.7 Closing Remarks

This chapter deals with various types of material in civil engineering applications with main focus on Carbon nanotube. Undoubtedly, nanotube has the potential to be a key to the brand new world in the field of construction and building materials. Until today cement mortar has primarily been seen as a structural material but Carbon nanotube helps to make it as a multi-purpose "smart material". Since the present study deals with the effect of Carbon nanotube addition to cement mortar paste, the next chapter presents a review of the work done so far in the use of Carbon nanotube in the cementitious material.

CHAPTER 2
REVIEW OF LITERATURE

2.1 General

This chapter presents an exhaustive review of the latest works done using carbon nanotube as filler in cement mortar. The important contributions of the researchers are discussed and how carbon nanotube has affected the cementitious material properties. Main focus is to discuss the effect of carbon nanotube on mechanical, thermal, chemical and micro-structure properties in cementitious materials.

2.2 Yakovlev Et.al (2006)

The main task of the presented research was to investigate the carbon nanotubes, synthesized from aromatic hydrocarbons and as well as to investigate the possibilities of production and main technological properties of Portland cement based foam concrete reinforced by dispersed carbon nanotubes. The method of stimulation of dehydropolycon-densation and carbonization of aromatic hydrocarbons in chemical active environment (melts of aluminium, copper, nickel, iron salts) was used for carbon nanotubes synthesis.

The results of investigation of the synthesized carbon nanotubes by X-ray photoelectron spectroscopy showed that they contain (80 – 90) % of carbon. The examination of the carbon nanotubes microstructure by electron microscope have shown that the nanotubes have a cylindric form, with diameter ranging up to 100 nm and length up to 20 μm. The nanotubes are agglomerated to fiber shaped agglomerates with a diameter up to 30 μm and a length up to 10 mm. The carbon nanotubes were used as a high strength dispersed reinforcement for production of foam non-autoclave concrete produced on the base of Portland cement.

The results of the investigation of the reinforced non-autoclave cemente foam concrete showed that the use of carbon nanotubes (0.05 % by mass) in production of these concretes allows to decrease its heat conductivity up to (12 – 20) % and increase its compressive strength up to 70 %.

An improvement in physico-mechanical proper-ties of non-autoclave foam concrete after hardening is possible only when the wall pores are reinforced. Taking into account the wall thickness, effective reinforcement can be achieved only by nanotube foam materials, the so called carbon nanotubes, the dimensions of which are of a power less that the wall pore diameter.

Two materials exsist in nature which comply to these requirements and can be used as dispersing reinforcements, i.e.: halloysite Al4[Si4O10](OH)8·4H2O and chrysotile Mg6[Si4O10](OH)8·4H2O. Both have a tubular structure and nanoscale diameters (Fig.2.2.1).

The structure of these two materials is made up of a two layer packet of the kaolinite type, where between the two layers, a hexagonal layer of water molecules is situated.

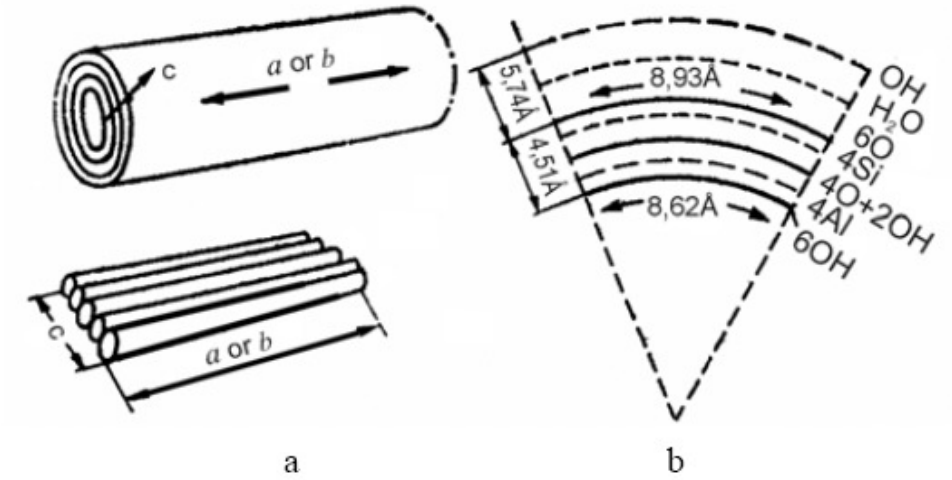


Fig.2.2.1. A scheme illustrating the tubular form of halloysite : a – tubular form; b – tube cutting

One of the possible forms of metastable carbon nano-forms could be the quasitubular structure, i.e.: a long cylinder form package of atomic “ribbons” cut from a graphitic network (Fig. 2.2.2).

One of the main elements of such a structure is the graphite layer – the surface layed out between two proper hexagonals of carbon atoms situated at the top. The graphite layer can form an extension in the form of a full cylinder.

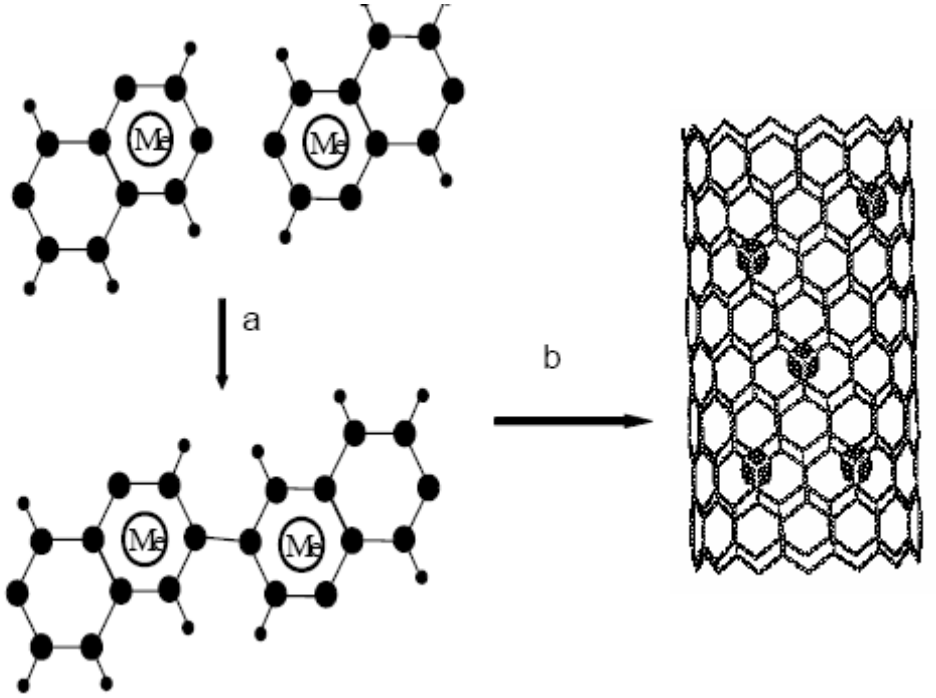


Fig.2.2.2 A possible synthesis scheme for carbon nanotubes from eutectic melts of aromatic hydrocarbons undergoing dehydropolycondensation and carbonization reactions

The length of the nanotubes can reach tens of microns and up to several times surpass its diameter, which generally is only a few nanometers. Inverstigations have shown , that most of the nanotubes are made up of several graphite layers situated one above the other and wounded about one common axis. The distance between the layers practically is about 0.34 nm, which corresponds to the distance between the layers in crystalline graphite.

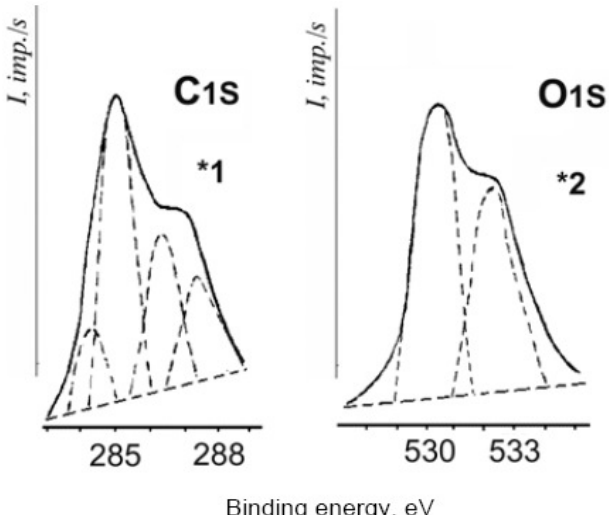


Fig. 2.2.3. XPS spectra (C1s, O1s) of carbon – metal containing specimens obtained from mixture of anthracene, phenylanthracene and copper monochloride with microdispersed copper

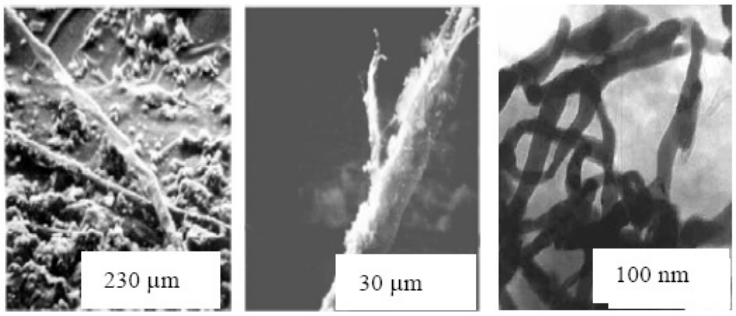


Fig. 2.2.4. Microstructure of carbon – metal containing new – growths obtained from aromatic hydrocarbons by the stimulated dehydropolycondensation and carbonization method: a – general view; b – a fragment of cleaved fibre shaped formation ; c – carbon nanotubes

Table 2.1. Physico-mechanical characteristics of cement foam concrete

№	Amount of nanotubes, % based on the composition mass	Average density, kg/m^3	Compressive strength, MPa	Heat conductivity coefficient, λ, W/mK	Pore diameter, μm	Condition of wall pores
1	0	330	0.18	0.07	40 – 600	perforated
2	0.05	309	0.306	0.056	60 – 150	homogeneous

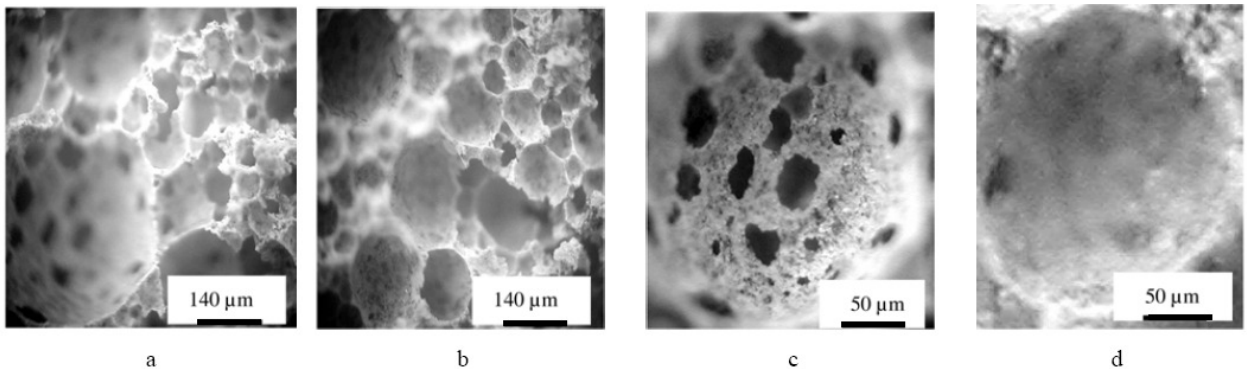


Fig. 2.2.5. Cement foam concrete structure: a – without nanotubes, b – with 0.05 % nanotubes; pore walls; c – without nanotubes (perforated), d – stabilised with addition of 0.05 % of nanotubes

As we can see from Table 2.1, the modification of cement foam concretes by the addition of carbon nanotubes allowed us to decrease in average density from 330 kg/m3 to 309 kg/m3 and at the same time to increase the compressive strength by 70 % (from 0.18 MPa to 0.306 MPa). The modification allowed to lower the heat conductivity by 20 % (from 0.07 W/m K to 0.056 W/m K).

The comperative analysis of the compressive strength values of cement foam concretes with densities up to 350 kg/m3 and the compressive strength values of 500 kg/m3 density cement foam concrete, not reinforced and reinforced by carbon nanotubes, showed that the modification by carbon nanotubes allows to increase the compressive strength of cement foam concrete approxi-mately by the same percent, inspite of its density value. The compressive strength value of 500 kg/m3 density not reinforced cement foam concrete by carbon nanotubes is 0.87 MPa, compressive strength value of the same density cement foam concrete reinforced by carbon nanotubes is 1.45 MPa (increased by 65 %)

2.3 Musso Et.al (2009)

Here we can see that Cement matrix composites have been prepared by adding 0.5% in weight of multi wall carbon nanotubes (MWCNTs) to plain cement paste. In order to study how the chemical–physical properties of the nanotubes can affect the mechanical behavior of the composite, we compared the specimen obtained by mixing the same cement paste with three different kinds of MWCNTs. In particular, as-grown, annealed and carboxyl functionalized MWCNTs have been used.

The phase composition of the composites was characterized by means of thermo gravimetric analysis coupled with mass spectroscopy, while the mineralogy and microstructure were analyzed by means of an X-ray diffractometer and scanning electron microscope. The results are interpreted and discussed taking into account the chemical and physical properties of the MWCNTs by means of EDX, TGA, SEM and Raman analysis. Proper dispersion and adequate load transfer are the main challenges in the search for efficient carbon nanotube reinforced cement composites.

The present work compares the results obtained with flexural and compressive measurements performed on unreinforced cement and three different cement-based composites containing as-grown, annealed and functionalized MWCNTs, respectively. Furthermore, the phase composition of the composites is characterized by means of thermo gravimetric analysis (TGA) coupled with mass spectroscopy (MS), while the mineralogy and microstructure are analyzed by means of an X-ray diffractometer(XRD) and scanning electron microscope (SEM).The results are discussed with regard MWCNTs properties,

Table 2.3.1
Features of the three different MWCNTs dispersed in the cement

Property	p-CNT	a-CNT	f-CNT
Depostion TECHNIQUE	CVD	CVD	CVD
Avg dia(nm)	40-80	40-80	20-Oct
Avg length(um)	400-1000	200-400	0.1-10
Carbon purity(wt%)	>92	>99	>95
Metal oxide impurty(wt%)	<6	<1	<5
COOH Functionalization(wt%)	0	0	<4

Pristine MWCNTs (labeled p-CNTs from now on for brevity purposes) have been synthesized in Physics Department at Politecnicodi Torino (Italy) , while annealed MWCNTs (labeled a-CNTs from now on) have been provided by Nano Carbon TechnologiesCo., Ltd., Akishima-shi, Tokyo (Japan) and carboxyl-group functionalized MWCNTs (Nanocyl 3101, labeled f-CNTs from now on) have been purchased to Nanocyl S.A.1 Nanotubes features are reported in Table

The cement composite samples were prepared in rotary mixer by adding cement, water, sand and 0.5 wt.% of CNTs powder with respect to cement. Moreover, superplasticizer (Mapei, Dynamon SP1,2 an admixture based on modified acrylic polymer for precast concrete) and viscosity modifying agent have been added to the mixture during the stirring stage, to help increasing cohesion and homogeneity of concrete mixture and also to avoid segregation and bleeding.

Table 2.3.2

Composition of the prepared samples. For each composition three samples have been cast in order to perform mechanical tests at 1, 7 and 28 days.

Components	Cement additive	Cement CNT Additive
Cement standard	450kg/cum	450kg/cum
water(w/c=0.4)	180kg/cum	180kg/cum
Sand standard	1720kg/cum	1720kg/cum
Superplastisizer(w%)	1.1	1.1
Viscosity modifier(w%)	0.5	0.5
MWCNTS(w%)	0	0.5

Three-points bend tests (span = 100 mm) were performed onto the 28 days cured prism shaped samples (40 x 40 x 160 mm3),according to UNI-EN standards. The modulus-of-rupture (MOR) is the surface stress at failure in bending and is equal to: $\sigma = 3F.L/2\ B\ t^2$

where b is the beam width, t the height, l the span and Fmax is the maximum force in a bent beam at the instant of failure. Then, onto the two fragments obtained by each prism, compressive tests were also performed on a 40 x 40 mm2 surface, by means of self-aligning squared seating platens. The compression resistance is the maximum force at the instant of rupture. The load was then applied vertically at a cross arm rate of 0.1 mm/min, for both tests.

After the mechanical tests, the samples were roughly crushed to separate the aggregates from the binder, which was then finely ground with a concrete and a pestle. The powder obtained by grinding the binder was finally sieved with a sieve having apertures of 40µm. These samples were characterized by means of TGA (Mettler Toledo, TGA/SDTA 851_)-MS (Balzer QuadstarTM 422 V60) from 20° C to 1000°C and an heating rate of 15 °C/min,
XRD (XRD, X'Pert Philips), SEM.

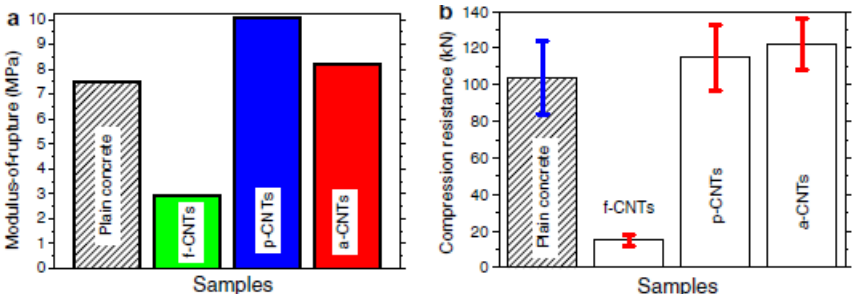


Fig. 2.3.1 Modulus-of-rupture (a) and compression resistance (b) of concrete. With and without MWCNTs.

2.4 Metaxa Et.al (2010)

This research investigates changes in the fracture mechanics characteristics and nanoscale properties of cement paste materials reinforced with nanofibers, such as multiwall carbon nanotubes (MWCNTs) and carbon nanofibers (CNFs). The effect of the nanofibers on the microstructure of cement paste was also investigated.

It was found that MWCNTs and CNFs reinforce cementitious materials by controlling cracks at the nanoscale level and improving the Young's modulus and the flexural strength of the matrix. The use of MWCNTs was also found to improve the nanomechanical properties of cement matrix. In particular, nanoindentation results have shown that the incorporation of MWCNTs led to the reduction of the nanoporosity of the matrix and significantly increased the amount of high stiffness C-S-H gel. Additionally, the nanocomposites reinforced with CNFs showed improved fracture behavior when compared to the samples with MWCNTs

Crack formation in cement based materials initiates from the nanoscale where microfibers can not be effective. With the introduction of nanofibers a new field for reinforcement within concrete was developed (Konsta-Gdoutos et al. 2008, Konsta-Gdoutos et al. 2009, Metaxa et al. 2009, Shah et al.2009). This research investigates the changes in the fracture properties, nanostructure and nanoscale mechanical properties of cement paste reinforced with highly dispersed multiwall carbon nanotubes(MWCNTs) and carbon nanofibers (CNFs).

The results suggest that nanofibers substantially improve the nanoscale properties and fracture characteristics of cementitious matrices, by controlling the matrix cracks at the nano level. Comparing the response of the nanocomposites reinforced with MWCNTs to the ones with CNFs it was found

that CNFs provide the nanocomposite with the capacity to carry higher loads at lower strains.

The nanocomposites were prepared using Type I ordinary Portland cement (OPC) and commercially available, as received, nanofibers, such as multiwall carbon nanotubes (MWCNTs) and carbon nanofibers(CNFs). The geometry of the nanofibers is shown in Table 2.2.1. It is observed that both nanofibers exhibit similar length range but different diameter, with MWCNTs to demonstrate almost 3 times higher aspect ratio

Table 2.4.1

	Diameter, nm	Length, μm	Aspect Ratio
MWCNTs	20-40	30-100	1600
CNFs	60-150	30-100	650

In general, MWCNTs and CNFs are described as ultra-high strength materials, characterized by a high tensile modulus, tensile strength, electrical and thermal conductivity and corrosion resistance.

The flexural strength rate of the nanocomposites incorporating either MWCNTs or CNFs up to the age of 28 days of hydration is shown in Figure 2.3.1. The samples reinforced with nanofibers at all ages exhibit higher flexural strength than plain cement paste.

In particular, an increase up to 25% is achieved when MWCNTs are utilized. The use of CNFs results in an increase of the flexural strength up to 45%. Comparing the two nanocomposites it is observed that despite the fact that MWCNTs exhibit a higher aspect ratio due to their smaller diameter and larger amounts of nanotubes is reinforcing the cement matrix since the concentration of the fibers is constant, CNFs provide the matrix with the ability to carry higher flexural loads at lower strains. A possible explanation could be that the bonding between the CNFs and the matrix is enhanced due to the unusual outer surface texture of the carbon nanofibers.

The CNFs used in this study exhibit graphite planes which extend beyond the diameter of the nanofiber and are present along the circumference of the fiber. These edges probably help anchor the fiber in the matrix, preventing interfacial slip and enable more sufficient load transfer across nanocracks and pores. The Young's modulus of the samples reinforced with either MWCNTs or CNFs at the age of 3, 7 and 28 days is illustrated in Figure 2.3.2. Similar to the flexural strength results, samples reinforced with nanofibers clearly exhibit improved Young's modulus over OPC specimens. Specifically, an increase of the Young's modulus of 44% to 50% over plain cement specimens is achieved with the use of MWCNTs. In the case of the samples with CNFs, an increase of at least 50% is observed

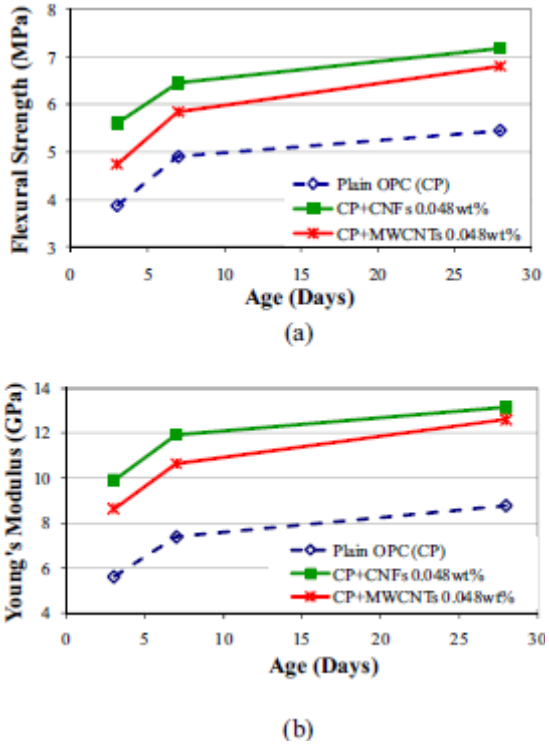


Figure 2.3.2. Flexural strength (a) and Young's modulus (b) of plain cement paste (w/c=0.5) and cement paste reinforced with either 0.048% by weight of cement MWCNTs or CNFs.

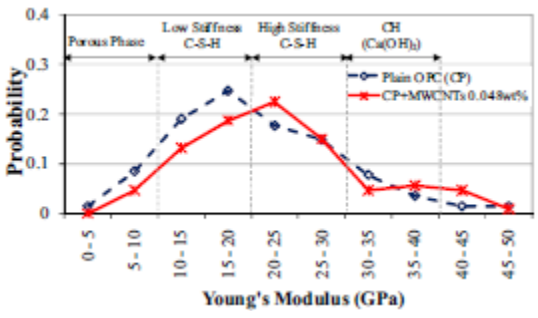


Figure 2.3.2. Probability plots of the Young modulas of plain cement paste(w/s 0.5)& cement paste R/F with 0.048%MWCT

2.5 Rashid K. Et.al (2012)

This research is done to study the effects of functionalized carbon nanotubes (CNTs) and carbon nanofibers (CNFs) on the mechanical properties of cement composites, both untreated and treated CNFs and CNTs were added to cement paste in concentrations of 0.1% and 0.2% by weight of cement. The surface-treated nanofilaments were functionalized in a solution of sulfuric acid (H2SO4) and nitric acid (HNO3). The nanofilaments were dispersed by using an ultrasonic mixer and were then cast into molds.

Each specimen was tested in a custom-made three-point flexural test fixture to record the mechanical properties (i.e., the Young's modulus, flexural strength, ductility, and modulus of toughness) atthe age of 7, 14, and 28 days. The microstructure was analyzed by using a scanning electron microscope. Untreated CNTs and CNFs were found to enhance the mechanical properties of cementitious materials, whereas the acid-treated CNTs and CNFs degraded the mechanical properties.

Untreated carbon nanofilaments are known to be very hydrophobic, and their high van der Waals force causes them to rapidly agglomerate (i.e., form bundles) when dispersed in water without any surfactant.

Two methods are commonly used to enhance the long-term dispersion of nanofilaments within aqueous solutions: application of chemical surfactants and acid functionalization (Vaisman et al. 2006).Typical acid functionalization uses two highly concentrated acids. The first is nitric acid (HNO3), which oxidizes the surface, and the second is sulfuric acid (H2SO4), which "roughens" the surface. When the surface of a nanofilament is roughened, the carboncarbon bonds are broken, creating defect sites. This allows the nitric acid to create functional groups on the surfaces of the nanofilaments.

Varying the ratio of nitric to sulfuric acid will either increase or decrease the amount of functionalization (Ago et al. 1999;Bahr and Tour 2002; Datsyuk et al. 2008; Lakshminarayanan et al.2004; Zhang et al. 2008). However,

increasing the degree of functionalization by changing the ratio of nitric to sulfuric acid will hinder the performance of the nanofilaments. When the amount of sulfuric acid is increased, the surface becomes rougher. This roughness is what allows the functional groups to bond; however, the rougher the surface, the weaker the nanofilaments. Another negative side effect of sulfuric acid is its ability to dissolve through sections of the nanofilaments. This cuts the nanofilaments into smaller lengths, reducing their aspect ratios. In this research, cement paste was reinforced with both untreatedand a cid-treated CNTs and CNFs at concentrations of 0.1% and 0.2% by weight of cement. The flexural strength of the batches was compared by using a custom-built three-point bending frame. A scanning electron microscope (SEM) was used to analyze the microstructure of the fractured surfaces.

The cement used for the tests was a commercially available Type I/II portland cement. The CNTs were NC7000 MWCNTs supplied by Nanocyl, which are produced by a catalytic carbon vapor deposition (CCVD) process. They had a well-controlled diameter of 9.5 nm and an average length of 1.5 μm, with an average aspect ratio of 150. The CNFs were Pyrograf III nanofibers from Applied Sciences, Inc., with a diameter ranging from 60 to 150 nm and a length of 30–100 μm. The CNFs had an average aspect ratio (length to diameter) greater than 1000.

Table 2.5.1. Physical Properties of Carbon Nanotubes and Carbon Nanofibers

	CNFs	CNTs
Diameter	60–150 nm	9.5 nm
Length	30–100 μm	1.5 μm
Specific surface area	50–60 m^2/g	250–300 m^2/g
Purity	≥ 90%	≥ 90%

Functionalization of the nanofilaments was carried out using the following method: First, 0.9 g of either CNTs or CNFs was added to 300 mL of a solution with a sulfuric to nitric acid ratio of 2:1. The solution was refluxed for 1 h at 85°C and continuously stirred with a magnetic stirrer. After refluxing, the

solution was diluted in 4 L of distilled water. The temperature was checked to ensure that the solution was less than 35°C before filtering.

Once cool enough, the solution was filtered through a polytetrafluorethylene membrane with a 0.45-μm pore size. The remaining solution was then washed with water and filtered again until it reached a neutral pH. After all the acid was washed from the surface of the nanofilaments, the remaining solution was dried in an oven at 60°C and at a relative humidity of less than 5% for at least 24 hours, or until all the water had evaporated.

Table 2.5.2 Mix Design of the Test Specimens

Test specimens	Water/ cement ratio	Untreated CNFs: % by weight of cement	Treated CNFs: % by weight of cement	Untreated CNTs: % by weight of cement	Treated CNTs: % by weight of cement
Reference	0.4	0	0	0	0
UF1	0.4	0.1	0	0	0
TF1	0.4	0	0.1	0	0
UF2	0.4	0.2	0	0	0
TF2	0.4	0	0.2	0	0
UT1	0.4	0	0	0.1	0
TT1	0.4	0	0	0	0.1
UT2	0.4	0	0	0.2	0
TT2	0.4	0	0	0	0.2

The force and displacement from the three-point flexural tests were converted to stress and strain by using simple strength of materials relations for a three-point bending beam

After the mechanical tests, random samples were taken to observe the microstructure under the SEM.

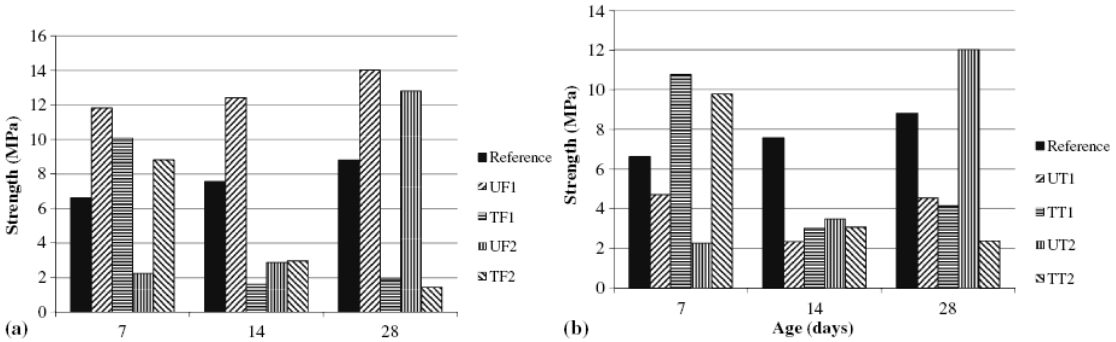


Fig. 2.5.1 Max strength for both untreated and treated nanofilaments: (a) carbon nanofibers; (b) carbon nanotubes

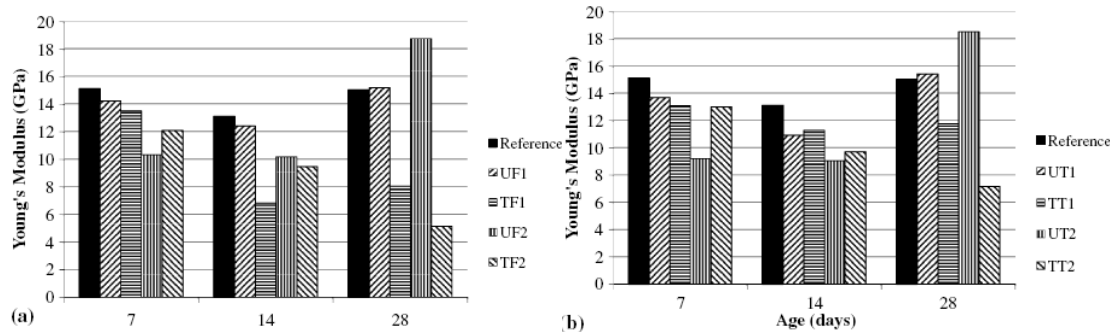


Fig. 2.5.2. Young's modulus for both untreated and treated nanofilament

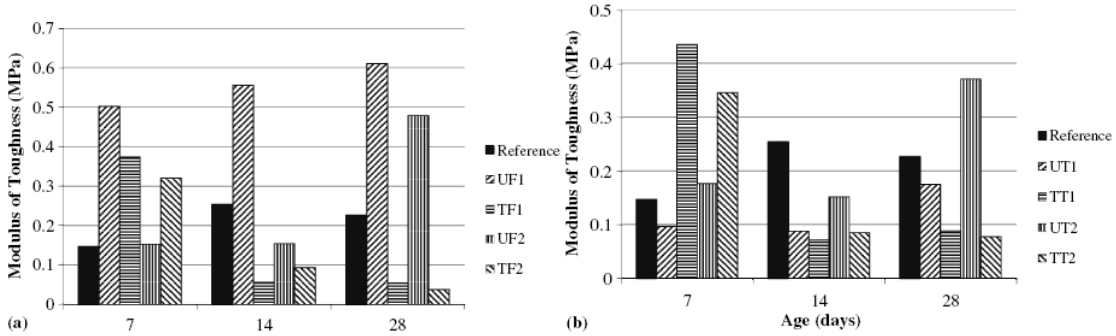


Fig. 2.5.3. Modulus of toughness for both untreated and treated nanofilaments: (a) carbon nanofibers; (b) carbon nanotubes

2.6 Schmidt Et.al (2012)

This is part of current research projects aiming at designing concretes improved by applying different kinds of micro- and nanoparticles and by applying analytical methods from fundamental research disciplines that had not been used for construction materials before, e.g. atomic force microscopy. One prominent result is Ultra-High Performance Concrete (UHPC) with its steel-like compressive strength which allows for slender but nevertheless very long lasting and thus sustainable concrete structures.

On top of that several research projects performed at the University of Kassel, which this contribution likes to review, aim at making concrete an impervious, ceramic-like, acid resistant multifunctional ‘ ‘smart’ ’ material with added values by further changing its nano- and microstructure and/or applying reactive coatings e.g. with the ability to degenerate air pollutants.

The outstanding strength and durability of UHPC is based on the very special microstructure of the cement matrix. Depending on the maximum grain size of the aggregates, UHPC contains between 550 and 800 kg cement per m3, up to about 250 kg/m3 of microsilica (pyrogenous SiO2) and a significant amount of other mineral fillers to improve the packing density of the matrix, and to increase the amount of nanoscaled C‑S‑H cement phases densifying the microstructure. A secondary effect results from a very low effective w/c-ratio of about 0.20 only (c = cement + microsilica).

While ordinary concrete is a porous medium with a high content of capillary pores, UHPC is characterized by a very dense and homogenous structure similar to the microstructure of the aggregates used.

The performance of today’ s UHPC can be further improved by nanotechnological approaches. In a deeper insight into the challenges and promises that nanotechnology provides for the development of high-performance concretes is given, and it also highlights the unusual characteristics and

difficulties that arise and have to be overcome in the nanocosm. As an example, a further increase in both strength and resistance to corrosive media can be expected by incorporating synthetic nanosilica particles with a carefully controlled particle size distribution extending the packing optimization to the nanoscale.

Furthermore, so called ‘‘alternative binders’’ which are largely free of Portland cement clinker – they are based e.g. on puzzolanic fly ashes from combustion of hard coal, ground granulated slag, or mixtures of both, activated by sulfuric or alkaline accelerators – yield a structure that proves stable against most acidic attacks.

This is part of current research projects aiming at designing concretes that are produced under with mineral binders and behave like ceramics. Activating agents can be alkali salts (carbonates, sulfates), alkali hydroxides or alkali silicates, also known as waterglass. These binder systems form calcium free reaction products with high chemical resistance especially to acids – even against biogenic sulfuric acid – and sulfates. They are particularly suitable for highly stressed building elements, found in the field of industrial sewer systems, and e.g. biogas production

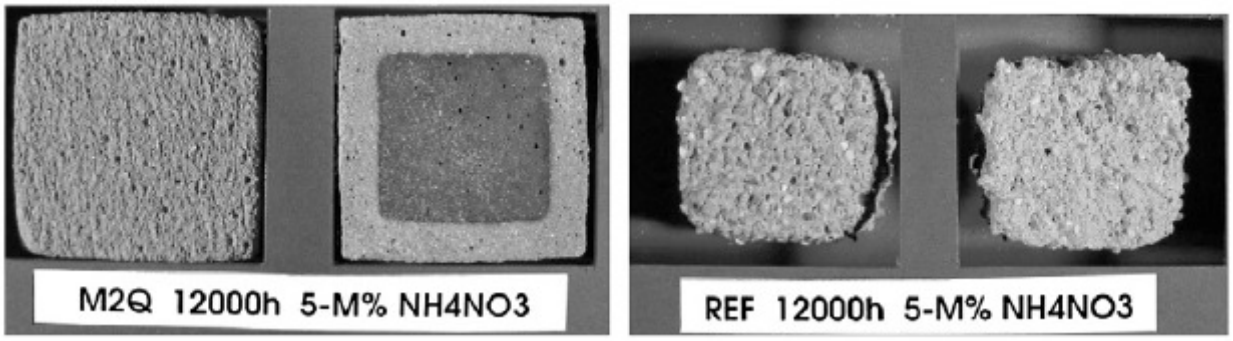


Fig. 2.6.1. Ordinary concrete (REF) and UHPC (M2Q) after being submerged in 5 mass% ammonium nitrate solution at 20 ºC for 12,000 h

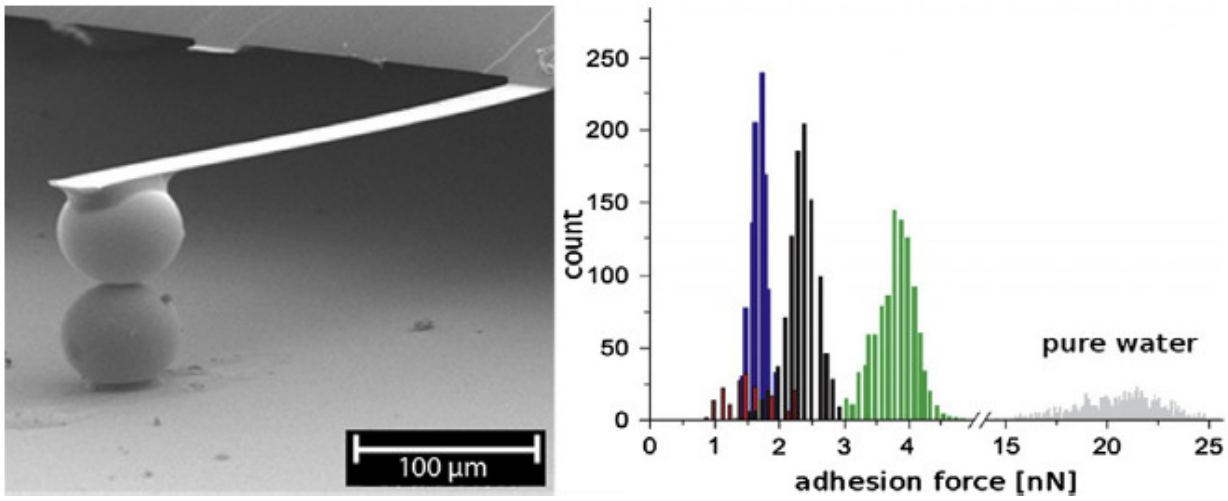


Fig 2.6.2. SEM micrograph of the measurement setup and interpartikel forces determined in an AFM cell without and with different superplasticizer

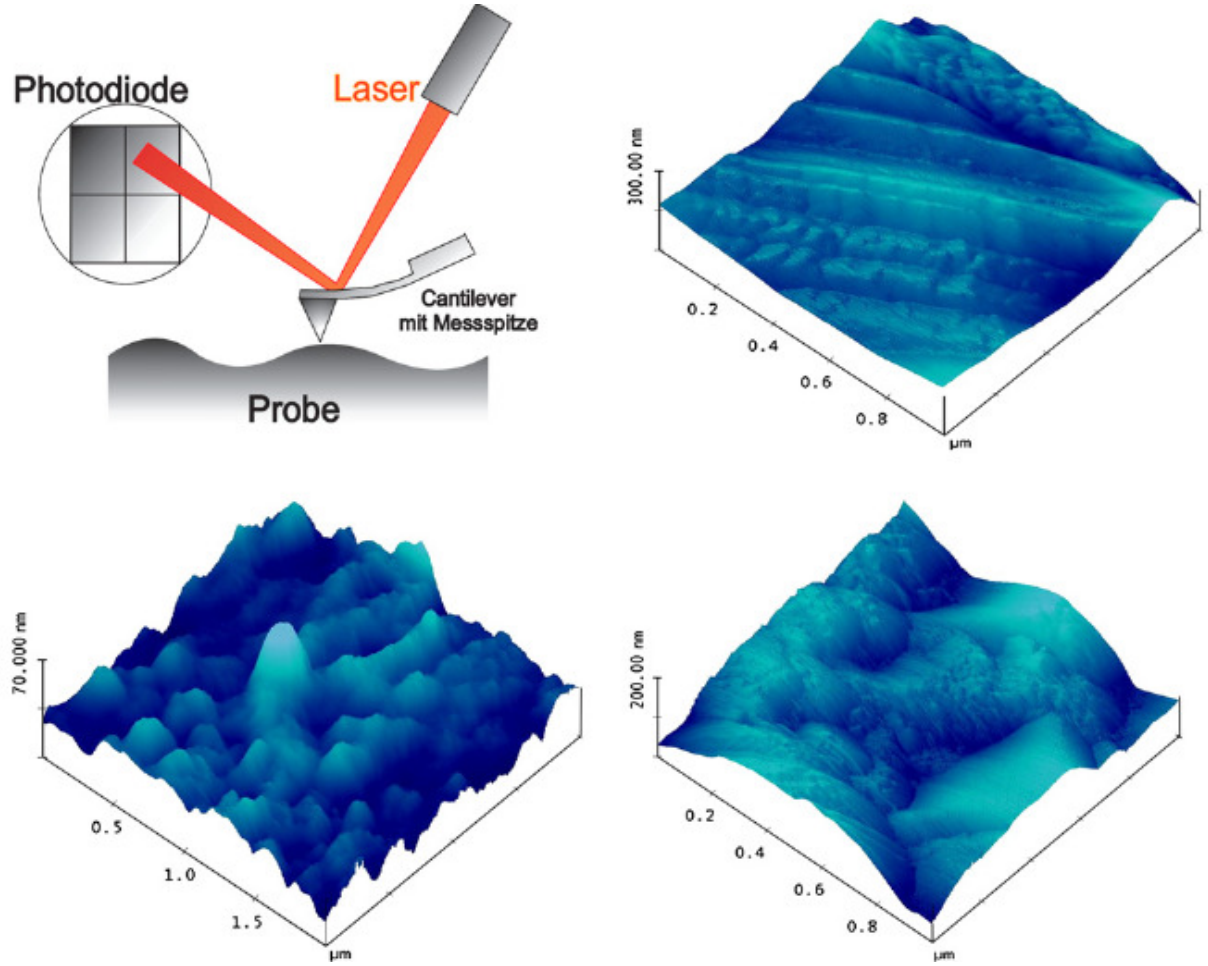


Fig. 2.6.3. AFM pictures showing the early hydration reactions on the surface of a cement grain when coming in contact with water. Base length 1x 1 um.

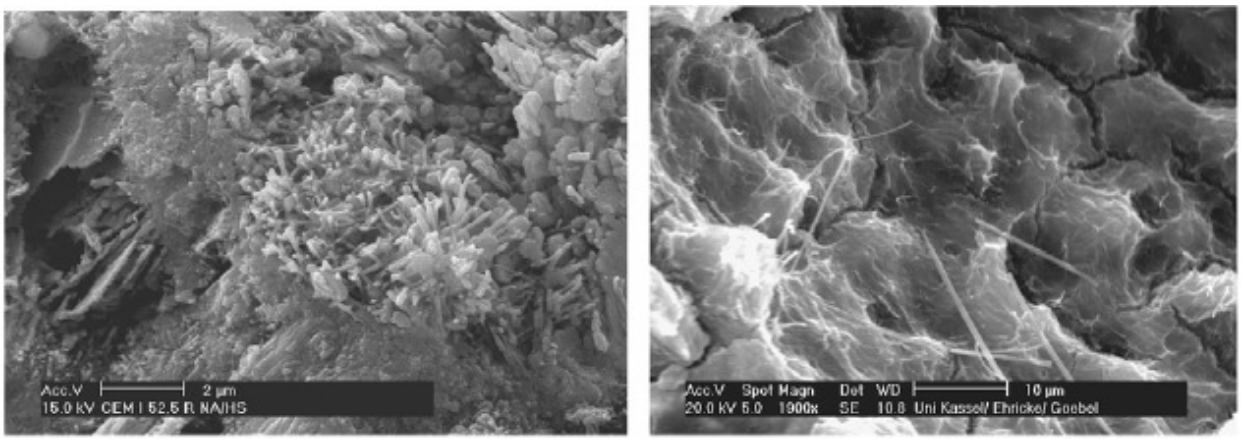


Fig. 2.6.4 Left: hydrated Portland-cement: C-S-H-phases and acid solubel portlandit. Right: GGBF-Slag + nanosilica + alcaline accelerator: stable cement-like phases

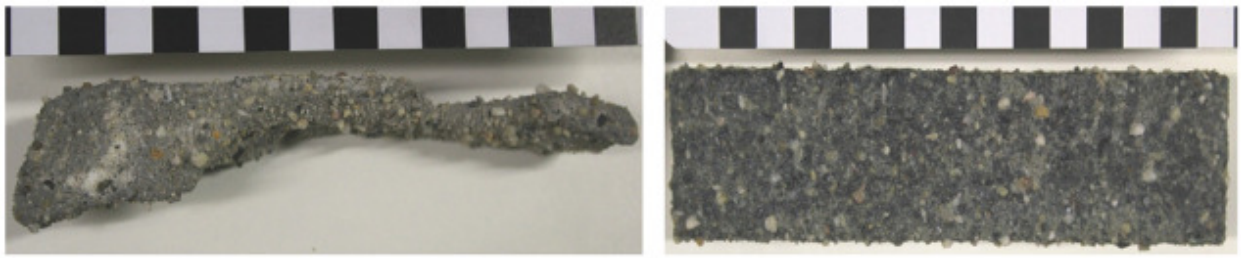


Fig. 2.6.5. Left: cementitious mortar with OPC CEM I. Right: alkaline-activated mortar of GGBS with potassium waterglass, both after 14 days storage in lactic acid (pH = 2)

The presently achievable compressive strength of about 200 MPa for UHPC can be increased even further by using of nanoscale silica and adapted production processes. It was found that the UHPC mixture that was used for the Gaertnerplatzbridge in Kassel (max. grain size 0.5 mm, 733 kg OPC, 230 kg SF, 183 kg quartz -powder/m3; effective w/c 0.20) could be further increased up to 500 MPa when the fresh concrete had been consolidated under a constant uniaxial pressure of 50 MPa for the first 4 h after moulding, and subsequently stored at 250 ºC for 7 days.

Along the way,due to the evaporation of free water the w/c-value sank to only 0.14. Extrapolating from recent experiences it may be possible to produce precast concrete elements for special applications (e.g. prestressed girders, highly-loaded columns, truss joints) that can bear much higher loads than recent UHPC. It might even replace high-strength steel or cast steel in many applications.

2.6 Bharj Et.al (2014)

In this paper the role of carbon nanotubes (CNTs) on the compressive strength characteristics of hydrated Portland IS 1489 cement paste has been studied. Standard specimens (40 mm × 40 mm × 160 mm) as per IS: 516-2004 were prepared by mixing 0.1% CNTs by weight to cement for determining the compressive strength of composites. The specimens were tested after 7, 14, 28 and 35 days of curing. Results show an increase in compressive strengths in Cement–CNTs composites having CNT content of 0.1% by weight of cement. The increase in compressive strengths with both techniques; mixture of CNTs with cement in powder form and mixture of CNTs with cement in hydrated form were 8.5% and 22%, respectively by holding the specimen for 28 days of curing. Increase in curing time by 7 days from 28 to 35 days did not bring any appreciable increase in compressive strength because of the complete absorption of all the ingredients into the mixture due to saturation.

Studies are still on exploring efficiency of the CNTs in the matrix of cement Portland cement (PC) has been used as a major binder material.

The performance of concrete can be significantly increased by addition of nanoparticles hydration of cement forming complex chemical can be improved by adding nanoparticles. The compressive strength can be significantly enhanced.

Nano compounds binds the aggregates together and strength of the cement paste is increased with the addition of nano particles.These provides

strength to cement concrete. Water-cement ratio, porosity, bonding between cement and mesopores as reported in earlier studies. Different in size of aggregates are some of the major factors that govern strength of concrete.Researchers have attempted to improve the the strength of cement concrete.chemical dispersion and bonding strength by various composition of cement remains the most important treatments. Saez de Ibarra et al. used gum Arabic as a factor that affects its strength. CNTs are considered dispersing agent to find slight gain in compressive one of the most beneficial materials for nano- strength and Young's modulus. reinforcement.

The unique mechanical,electrical and chemical properties of CNTs make them an attractive nanocomposites. Wansom et al.investigated the electrical properties of CNT-cement using a polycarboxylate based candidate for reinforcement of composite materials. It superplasticizer and methylcellulose. More recently, is due to the presence of carbon atoms with their in order to obtain homogenous dispersions of CNTs in tendency to make strong covalent bonds with other water, Cwirzen et al. used polyacrylic acid polymers elements due to their electronegative character which and sonication.

The results showed a slight increase in compressive strength produce stronger materials in form of composites.. Thus, it becomes the strongest as well as flexible It has been demonstrated that interfacial adhesion can be attributed to the interfacial known material so far. So with the development of chemical bonds and interaction between polar groups new nanosized materials in the form of tubes, fibers as hydroxyl or carboxyl on the surface of the and particles have opened a new field for nano sized reinforcing fiber and the active groups present in the reinforcement within concrete.Two major matrix resin. These chemical groups can originate challenges for using carbon nano structures (fibres, strong chemical bonds between CNT and particles, tubes) to form cement concrete are the cementitious matrix, thus enhancing the uniform

dispersion and inefficient bonding in cement reinforcement efficiency. In the present study, the matrix, as reported by Makar et al . and Groert. Poor effect of compressive strength of cement paste as well dispersion of CNTs leads to the formation of many as CNT-cement composite has been experimentally defect sites in the nanocomposite and limits the investigated for both CNT-cement composite in powder form and CNT-cement composite in hydrated state.

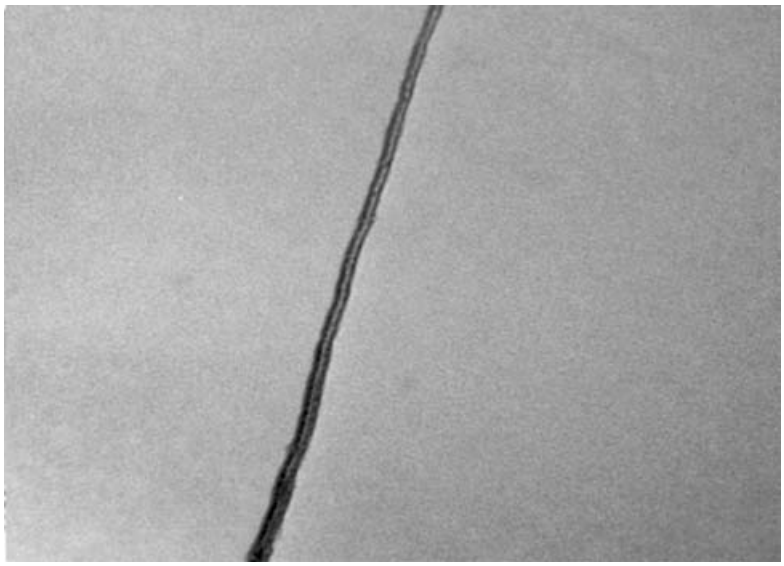


Fig2.6. 1 — TEM micrograph of synthesized MWCNTs

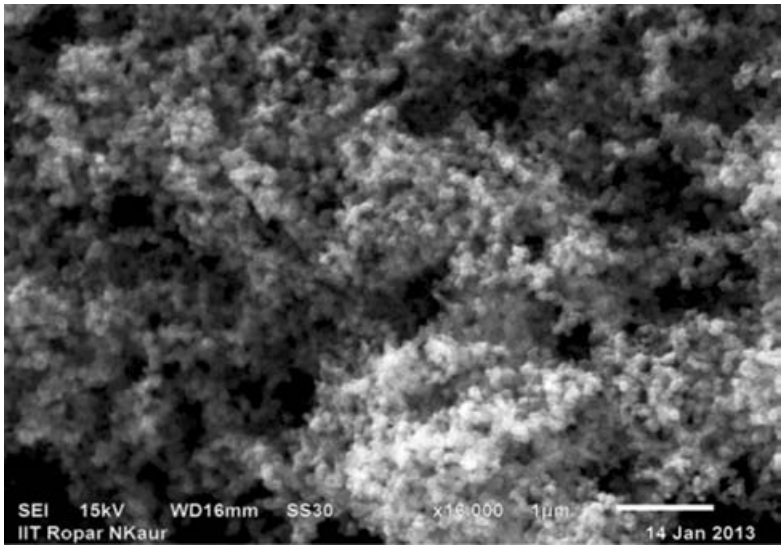


Fig. 2.6.2 — SEM image of purified MWCNTs

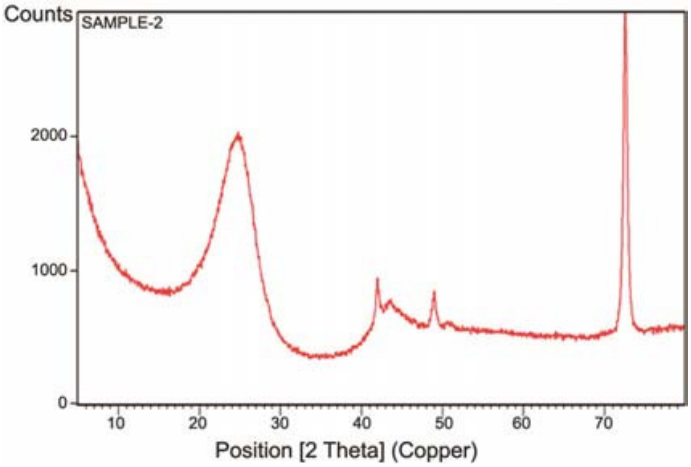


Fig. 2.6.3 — XRD spectra showing peaks of ordered MWCNTs

attributed to amorphous carbon present in the sample. form so as to determine the influence of dispersion In Fig. 2.6.3, the XRPD pattern of synthesized MWCNTs and functionalization on as-grown CNT with open at LPG flow rate of 05.1 pm and O2 flow rate of flame synthesis using domestic LPG as the carbon 41 pm is shown. The diffraction peaks were observed feedstock obtained under controlled parameters of at 23.13°, 41.98° and 49°. The strong reflection peak

flow rate, substrate temperature, and exposure time. at 23.13° confirmed that the MWCNTs were crystalline in nature as this peak arises due to interlayer stacking of graphene sheets.

The approximate diameter of MWCNTs calculated as 12.13 nm Cement was Commercial grade Portland cement PC (IS: 1489) . As grown CNTs were used as the source material for all specimens. characterized by Reneshaw Invia Raman Microscope

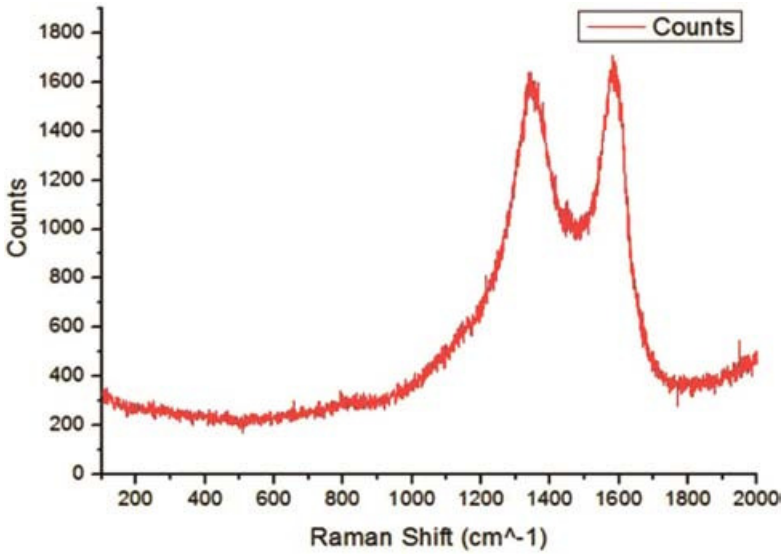


Fig. 2.6.4 — Raman spectra showing D band and G band peaks of MMWCNT

CNTs were prepared by an open Flame Synthesis with He-Ar laser (514 nm) with 50% laser strength. method using domestic LPG as fuel and oxygen as an **Figure 2.6.4** shows the results of Raman analysis showing oxidizer.The carboneous soot (20 g) was collected G band at 1586.2 cm-1 and D band at 1351.4 cm−1.from the substrate mounted on the test rig in small part.

The ratio between the D band and G band is an batches (0.5 to 1 g/min) during 5 h of continuous indicator of the quality of CNTs in a sample. (I D/ I G)

operation. Cross flow micro filtration technique was was calculated as 0.94 which indicated that highly used to remove amorphous carbon and other ordered MWCNTs were present in this sample. unwanted species. The collected soot was heated from about 15 min to remove traces of amorphous carbon.

As per IS: 516-1959 (Reaffirmed 2004 Indian Finally, the samples were dried and characterizations Methods of tests for strength of concrete),three

of the as grown CNT samples were done. specimens each of pure cement, Aqueous mixing Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Raman spectroscopy and X ray diffraction (XRD) techniques were used to obtain information about CNT structures of the

specimen synthesized. Figure 1 shows the TEM micrograph of the CNTs obtained from LPG. It is observed that CNTs were of multiwall in nature with

diameter in the range 8-25 nm and lengths approximately in the range of 120 nm. SEM image of the purified sample is shown in Fig. 2.6.2. The surface morphology of the synthesized MWCNTs seems to be uniform. The SEM micrograph shows clear evidence of the formation of carbon nanotubes. Additionally, there are some small agglomerates which can be used.

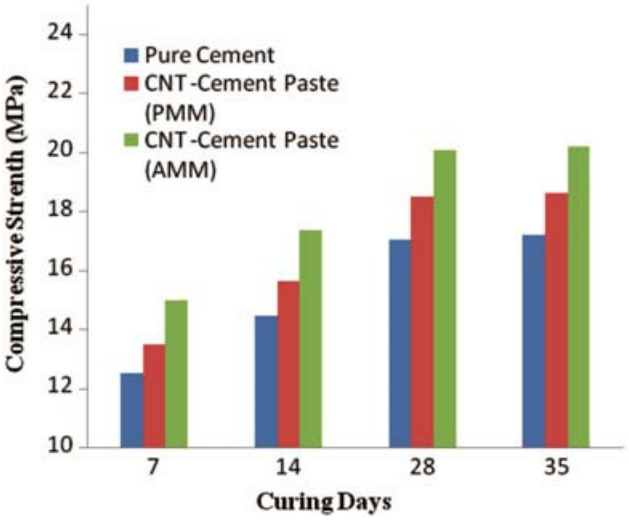


Fig. 2.6.5 — Comparison of the compressive strength of pure cement paste, CNT –cement paste (PMM) and CNT-cement paste (AMM)

The specimens were tested after aqeous method and Powder mixing method of size curing for 7, 14, 28 and 35 days and Fig. 2.6.5 shows the 40mm×40mm×160 mm each for 7, 14, 28 and 35 bar chart of the average readings taken. curing days were prepared.

The compressive strength of the specimens was tested with Hydraulic Mechanical Testing System .In Aqueous mixing method (AMM), weight of PC was taken as 400 g to which 0.4 g of CNTs (0.1%) (MTS) by placing the specimen in the MTS dispersed in 170 ml of deionized water (DI) was compressive testing machine and applying axial load added to form the paste. The water/cement ratio taken 0.425 was at a uniform rate till failure occurred. Mechanical stirring was simultaneously done for 15 min. For uniformity. dispersion, the mixture was then placed in a sonicator.

The homogenous dispersion of CNT is of high for about 90 min. water/CNTs mixture was importance to achieve the desired level of strength (DI)was gradually added to the cement and hand mixing was done using a stirrer for 3 min. For a homogeneous reinforcement within the composite. However, due to Van der Waals forces resulting from large surface mixing,mechanical mixer at 1400 rpm was also used. area of CNT tend to adhere together and it becomes difficult to separate them. No surfactant was used in the present work. Manual and for powder mixing of CNTs and cement water was found to be less effective for uniform dispersion of nanotubes. Specimens of size 40 mm × 40 mm × 160 mm were prepared using wooden moulds at room temperature.

The moulds were left to solidify for 24 h, and then This process was not capable of producing required specimens were taken out of the moulds and placed in energy to break the agglomeration of CNTs. water for curing. The specimens were tested after Therefore, the compressive strength of CNT-curing for 7, 14, 28 and 35 days. cement composite formed with powder mixing method was found to be less as compared to aqueous 2.2.2 Powder mixing method mixing method as shown in Fig. 5. Aqueous mixing In Powder mixing method (PMM), a powder of CNTs and DI water was done using sonicator.

mixture of 400 g of cement and 0.4 g (0.1%) CNT Ultrasonic waves were transmitted into water and was prepared.

Then 170 ml of DI water was added to CNTs causing alternate expansion and compression of this mixture. Water/cement ratio of 0.425 was taken in the mixture. Microscopic bubbles were same as in the case of AMM. The mixture was kep created by this pressure fluctuation. These bubbles for ultra-sonication to get uniform dispersion of CNTs increased in volume during negative pressure in cement.

The whole mixture was then further mixed excursions and imploded viciously during the positive by using a mechanical mixer for better mixing of excursion. The collapin of bubbles give rise to huge CNTs and cement. Mixture was put in the wooden number of shock waves, acoustic streaming, high mould for 24 h. It was then taken out and put in water pressure and extreme temperature. The total energy produced by the cumulative effect of this process is extremely high and capable of breaking.

2.7 Closing Remarks

In this chapter, the research done so far on nanotube in cementitious material. It is very clear from the review of literature that addition of nanotube in vary proportions, with their high surface, have improved the compressive, flexural and split tensile strength and other properties such as SEM, XRD of the cement mortar. In the following chapter, the experimental study carried out in this research using nanotube as addition to cement mortar has been elaborated and detailed.

CHAPTER 3

EXPERIMENTAL PROGRAM AND METHODOLOGY

3.1 General

The basic aim of the research is to investigate the effect of replacement of carbon nanotube in varying proportions to cement mortar as filler to the cement mortar paste. The effect on the mechanical, and the micro-structure property by the addition of carbon nanotube was studied. Cement mortar samples with cement: sand ratio as 1:3 was prepared and carbon nanotube was added as filler in varying proportion. Water/cement ratio was kept constant at 0.38.

3.2 Properties of Constituent Materials

3.2.1 Cement

Cement is a fine powder which is grey in color. Cement and water forms a paste that binds the other materials.The cement used in the study was Ordinary Portland Cement (OPC) and the properties if the cement used are presented below in

Table 3.1: Properties of cement used

Properties	**Observed Values**		
Initial Setting Time (minutes)	110		
Final Setting Time (minutes)	235		
Specific Gravity	3.01		
Normal Consistency	29%		
Compressive Strength(N/mm^2)	3 days	7 days	28 days
	24.8	36.08	45.65

3.2.2 Sand

Standard sand was used throughout the research work obtained from Tamil Nadu Ennore. The specifications provided by the supplier are shown in Table 3.2 and match with the requirements of the specification given by **IS: 650-1991.**

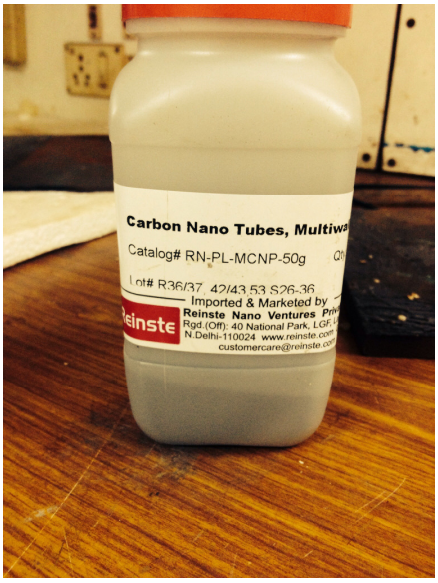
Table 3.2: Particle size distribution

Type of Grade	Particle size
Grade1	Particle size smaller 2mm and greater than 1mm.
Grade2	Particle size smaller 1mm and greater than 500microns.
Grade3	Particle size smaller 500 microns and greater than 90 microns.

3.2.3 Water

Portable water was used for preparing cement mortar samples. The water/cement ratio for making samples was 0.38.

3.2.4 Carbon Nanotube used Carbon Nanotube used in this work was obtained from NanoVenture Noida,it was black in color.

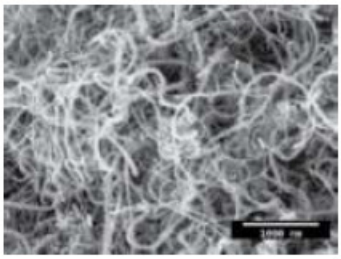
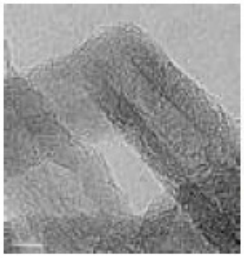
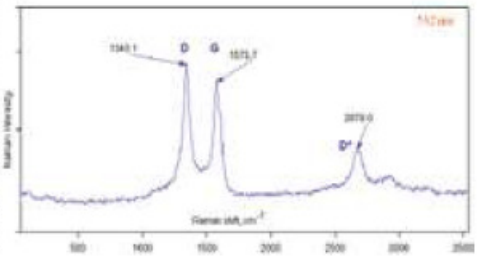


It's specification as supplied by vendor was as follows:-

Carbon NanoTubes and Fullerenes

Carbon Nanotubes, multiwalled

Carbon purity: min. 95 %
Number of walls: 3-15
Outer diameter: 5-20 nm; Inner diameter: 2-6 nm; Length: 1-10 µm
Apparent density: 0.15-0.35 g/cm^3
Loose agglomerate size: 0.1-3 mm

RN-MCNP-1g	1 g
RN-MCNP-10g	10g
RN-MCNP-50g	50g
RN-MCNP-100g	100g

Carbon Nanotubes, multiwalled, charged, water soluble

Carbon nanotubes (CNTs) type RN-MCNP, additionally modified by -COOH or -SO_3H groups. Soluble in water forming dark, transparent suspensions stable for many months. *Images: Top: aq. suspensions of unstable unmodified (left) and stable modified CNTs.*

COOH- modified:

RN-MCNP-COOH-100mg	100 mg
RN-MCNP-COOH-500mg	500 mg
RN-MCNP-COOH-1g	1 g

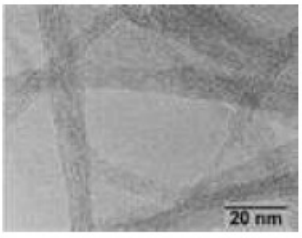
SO_3H- modified:

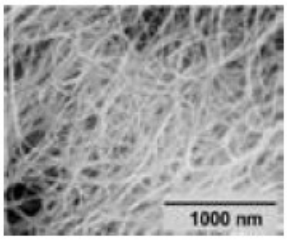
RN-MCNP-SO3H-100mg	100 mg
RN-MCNP-SO3H-500mg	500 mg
RN-MCNP-SO3H-1g	1 g

Carbon Nanotubes, single-walled

Produced by arc discharge method. SWCNTs assembled in bundles
Carbon purity: > 90 %; Diameter: ca. 1.4 nm; Length: > 10 µm

RN-SCNP-100mg	100 mg
RN-SCNP-500mg	500 mg





3.3 Sample Preparation

3.3.1 Cement mortar samples with carbon nanotube

Mortar prepared according to ASTM provisions with cement to sand ratio of 1:3. The carbon nanotube was properly dispersed in the cement matrix. The Multivalved carbon nanotube dispersion can be done by two methods i.e. aqueous mixing (AM) and Surfactant mixing (SM).

(a) Aqueous mixing: In aqueous mixing the dispersion of Multivalved carbon nanotube was done by using ultra-sonicator in calculated quantity of water.

(b) Surfactant mixing: In case of powder mixing Multivalved carbon nanotube was mixed vigorously with surfactant as supplied by vendor for 4-5 hours for the proper dispersion of carbon nanotube in the cement mortar.

3.3.2 Samples for mechanical properties

Table 3.3 Specimen details for mechanical test

Specimen	Specifications(mm)	Test Conducted
Mortar Cubes	70.6×70.6×70.6	Compressive Strength Split tensile
Mortar Beams	40×40×160	Flexural Beams

3.3.3 Samples for chemical and micro-structure properties

Table 3.4 Specimen details for microstructure test

Specimen	Test Conducted
Powder retained at respective days of curing	XRD SEM

3.5 Mix proportion for cube and beam

Specimen	Specifications(mm)	Ingredient per mould
Mortar Cubes	70.6×70.6×70.6	cement 200 gm Sand type-I 200gm
		Sand type-II 200gm
		Sand type-III 200gm
	W/c 0.38	water 76 gm
Mortar Beams	40×40×160	cement 160 gm
		Sand type-I 160gm
		Sand type-II 160gm
		Sand type-III 160gm
	W/c 0.38	water 60.8 gm

3.4 Experimental Program& Methodology

3.4.1 Mechanical properties

Mechanical properties test was performed to investigate the effect of incorporation of Multivalved carbon nanotube in various proportions of 0.025%, 0.05%, 0.075%, and 0.1%. In mechanical properties; compressive strength, flexural strength and split tensile strength was investigated at the ages of 3, 7 and 28 days. In case of compressive strength and split tensile strength the loading rate was taken as 70 kN/min and incase of flexural strength the loading rate was taken as 2.65kN/min.

Table 3.6 Details & nomenclature of cement mortar samples

Details of addition of CNT in CM by weight of cement	Nomenclature
0% Nanotube/Plain CM sample	CM (Control)
0.025%Nanotube	CNT 0.025
0.05%Nanotube	CNT 0.05
0.075%Nanotube	CNT 0.075
0.1%Nanotube	CNT 0.01

3.4.2 Chemical composition and micro-structure of mortars

The chemical composition of the samples are investigated using X-ray diffractometer analysis (XRD) with Cu radiation and also graphite 30 kV and voltage of 40 mV was used with diffraction intensity in the range of 10-80o.

The micro-structure of the mortar samples are examined by using scanning electron microscopy (SEM) analysis which is used to identify the changes which occurs in the micro-structure and also the formation and deformation of phases in the mortar sample.

The experimental program of the research work thesis work is shown in **Fig. 3.2**

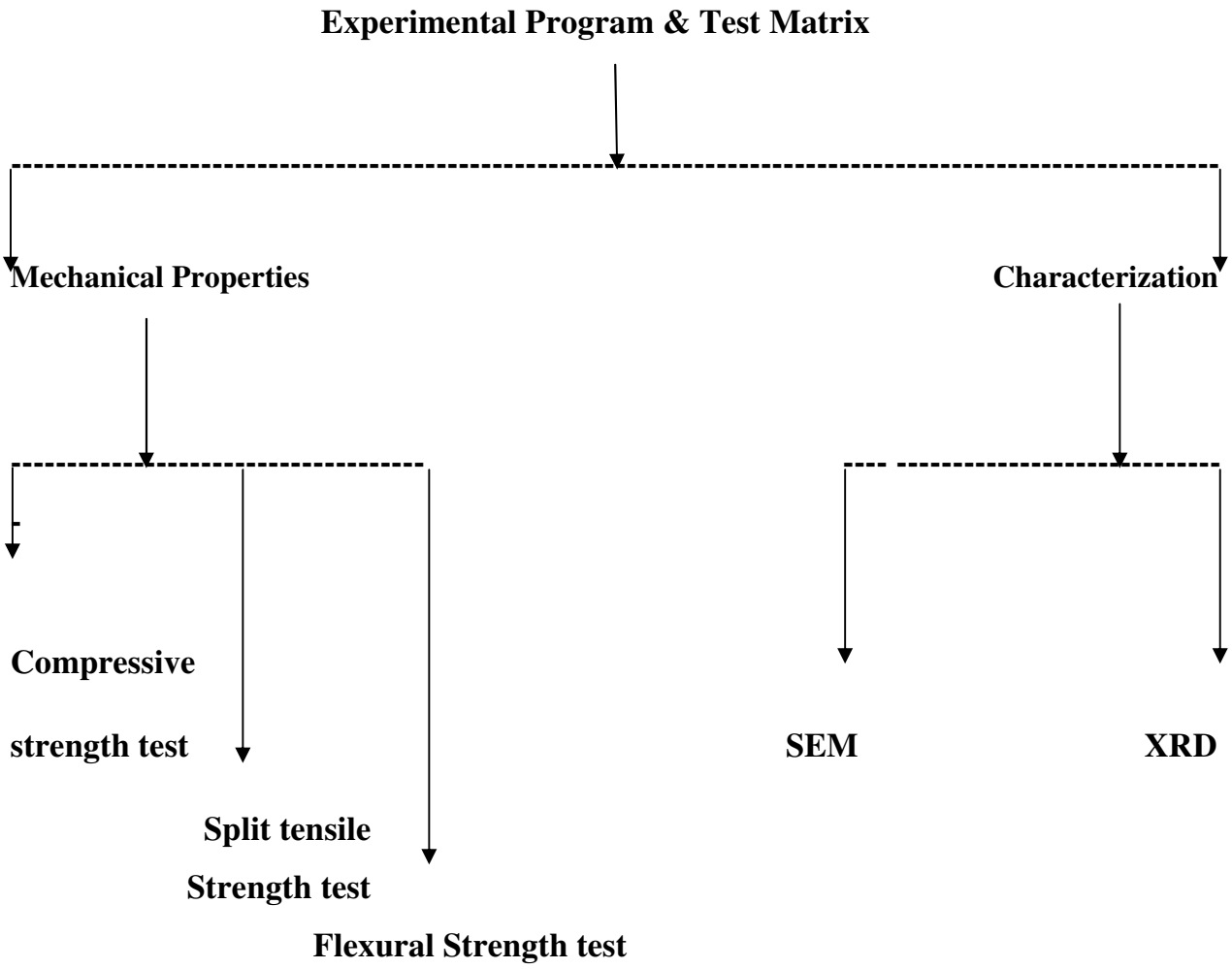


Fig. 3.2: Experimental Program and test matrix

3.5 Casting

Before casting the moulds should be properly cleaned and oiled. The screws should be tightened properly in the perfect dimension before casting. Care should be taken that no gap should be left in mould so that mortar starts coming out. The three grades of standard sand should be weighed with perfect accuracy. The mortar was prepared by hand mixing on the non absorbing platform. Then cement was added to this mixture. Then water was added to the mixture. For each mix 18 cubes (70.6×70.6×70.6mm), 9 for compressive strength for 3,7 and 28 days and 9 for split tensile test for 7, 14 and 28 days was casted. For the same mix 9 beams (40×40×160mm) for flexural strength test for 7, 14 and 28 days were casted.

3.6 Test Conducted

3.6.1. Compressive strength Test (IS: 516-1959)

The compressive strength test is performed on cubes to determine compressive strength at various ages.

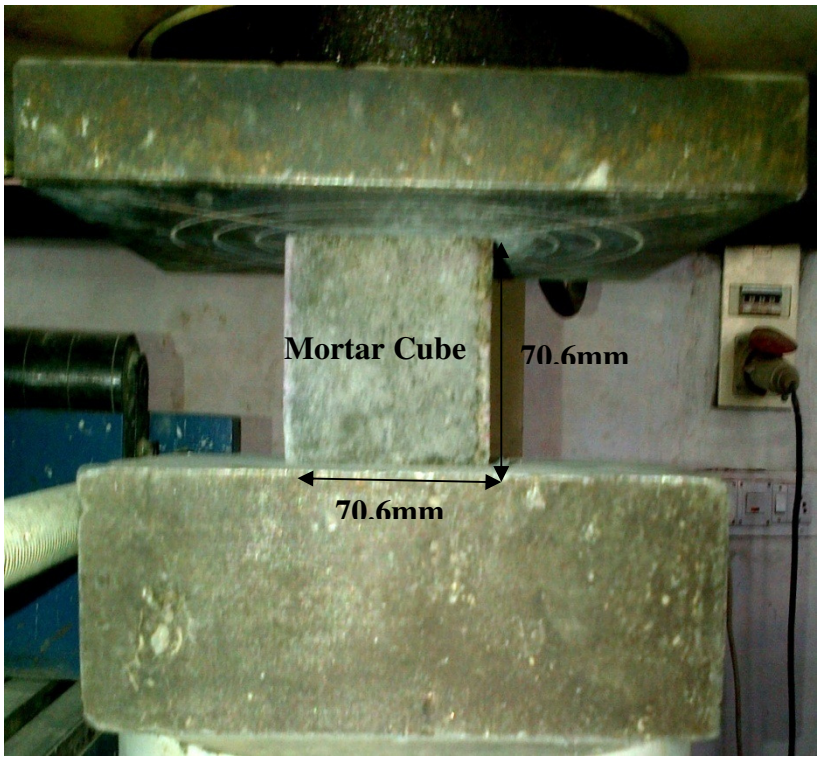


Fig. 3.3 Compressive strength test on cube.

Testing Machine: The testing machine used was "Hung-Ta", of capacity 20 ton for the tests and capable of applying the load at the rate specified which is 70kN/min for 70.6×70.6×70.6mm size of mould. The testing machine was equipped with two steel bearing platens with hardened faces. One of the platens (preferably the one that normally will bear on the upper surface of the specimen) was fitted with a ball seating in the form of a portion of a sphere, the centre of which coincides with the central point of the face of the platen. The other compression platen was plain rigid bearing block. The bearing faces of both platens was preferably larger than the nominal size of the specimen to which the load is applied.

Age at test

Tests shall be made at 3, 7 and 28 days. Where it may be necessary to obtain the early strengths, tests may be made at the ages of 24 hours ± ½ hour and 72 hours ± 2 hours. The ages calculated from the time of the addition of water to the dry ingredients.

Number of specimens

At least three specimens, preferably from different composition, shall be made for testing at each selected ages of 3, 7 and 28 days.

Formula used

Compressive Strength = $\frac{P \times 1000}{70.6 \times 70.6}$ ..... (3.1)

Where P = Load at fracture (kN)

3.6.2 Flexural strength test

The flexural strength test is performed on mortar beams to determine the flexural strength at various ages.

Testing Machine: The testing machine used was "Hung-Ta", of capacity 20 ton for the tests and capable of applying the load at the rate specifiedwhich is 2.65 KN/min for 40×40×160 mm size of mould. The testing machine was equipped with two steel bearing platens with hardened faces. One of the platens (preferably the one that normally will bear on the upper surface of the specimen) was fitted with a ball seating in the form of a portion of a sphere, the centre of which coincides with the central point of the face of the platen. The other compression platen was plain rigid bearing block. The bearing faces of both platens was at least as large as, and preferably larger than the nominal size of the specimen to which the load is applied.

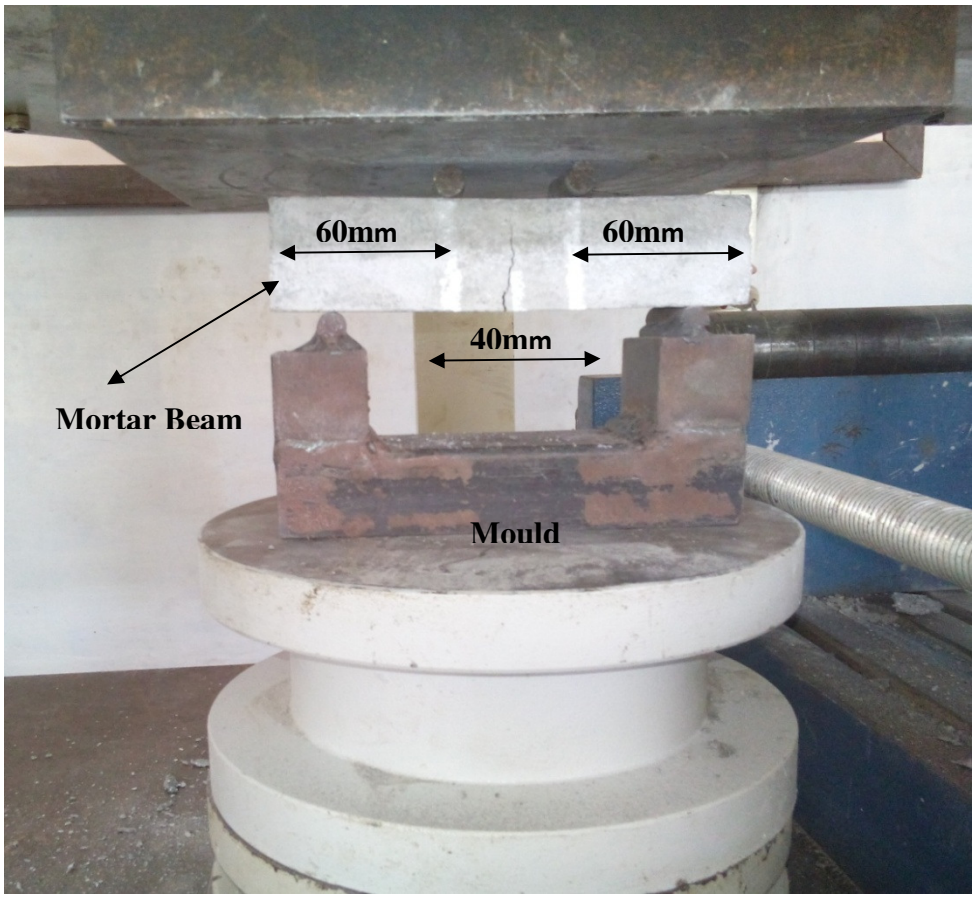


Fig. 3.4 Beam under two point loading.

Age at test

Tests , done at 7, 14 and 28 days. Where it may be necessary to obtain the early strengths, tests may be made at the ages of 24 hours ± ½ hour and 72 hours ± 2 hours. The ages calculated from the time of the addition of water to the dry ingredients.

Number of specimens

Three specimens, preferably from different composition, made for testing at each selected ages of 7, 14 and 28 days.

Formula used

f_t (Flexural strength/ Modulus of rupture) = $\frac{M}{Z}$

$= \frac{(P \times x) \times 6}{bd^2}$

$f_t = \frac{(P \times x) \times 6 \times 1000}{bd^2}$ N/mm^2……**(3.2)**

Where P = Load at which beam fails (kN)

3.6.3 Split tensile strength test

Apparatus

Testing Machine: The testing machine was "Hung Ta". The machine have capacity of 20 ton to perform the tests and capable of applying the load at the rate of 70 kN/min on 70.6×70.6×70.6 mm size of the mould. It comply with the requirements given in IS 516 and the bearing faces of both platens provide a minimum loading area of 12 mm x the length of the cube, as the case may be so that the load should be applied over the entire length of the specimen.

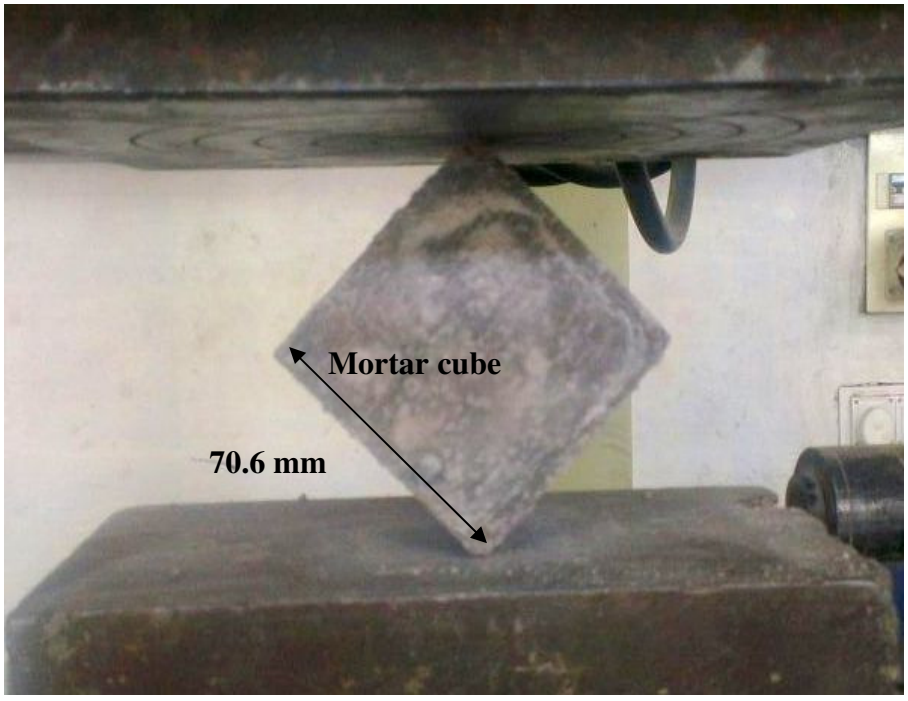


Fig. 3.5 Cube under split tensile test.

Age at test

Tests made at 7, 14 and 28 days. Test at age of 56 days can also be performed. Where it may be necessary to obtain the early strengths, tests can made at the ages of 24 hours ± ½ hour and 72 hours ± 2 hours. The ages was calculated from the time of the addition of water to the dry ingredients.

Number of specimens

Three specimens, preferably from different composition, made for testing at each selected ages of 7, 14 and 28 days.

Formula used

Split tensile strength= $\frac{0.5187P}{S^2}$…… (3.3)

Where P= Load at fracture(N)

S= Side of cube(mm)

3.7 Characterization Techniques

3.7.1 X-ray diffraction (XRD)

X-ray investigation on the samples were characterized by X-ray diffractometer with CuKα radiation for the identification of existing phases, crystal structure, lattice parameter of the crystalline solids. The sample is irradiated with monochromatic X-rays and the counters record the reflected radiation. The X-ray diffraction pattern were recorded using Bruker's diffractogram with CuKα (λ=1.54Å) obtained from Cu target using an inbuilt Ni filter. The 2Θ values for XRD patterns, in the range of 10^{o}-90^{o}. The X-ray diffraction peaks were identified using Powder Diffraction Files (PDF).

3.7.2 Scanning electron microscopy (SEM)

SEM is conducted to study the micro-structure properties of the samples. The samples which are already casted and cured for 28 days are used for the test. This test is used to identify the changes which had occurred inside the micro-structure and also the formation and deformation of the phases.

3.8 Closing Remarks

In this chapter, the experimental details of various tests and the methodology for investigating effect of NC on mechanical, thermal, chemical composition and micro-structure properties have been discussed. In the following chapter the experimental results obtained is presented.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 General

In this chapter the results of the cement samples and the mortar samples made with the addition of Multiwall nanotube in the varying proportions by weight of cement are presented and discussed. The properties such as Compressive Strength, Splitting Tensile Strength, Flexural Strength and thermal behaviour of final product are discussed and the comparisons between different mixes are represented.

4.2 Compressive Strength

To study the effect of addition of Multiwall nanotube in different proportions with cement on compressive strength. The addition level of Multiwall CNT is 0.025%, 0.05%, 0.075%, and 0.1% by weight of cement. Specimens are cured in water and tested at ages of 3, 7 and 28 days.

4.2.1 Results by aqueous mixing

The test results of aqueous mixing are shown in Fig. 4.1 and Table 4.1. In this case the dispersion of Multiwall CNT was done by using ultra-sonicator in aqueous medum for 5 hours bfore castng and without usng any dispersing agent or surfactant to see the effect of this on strength.

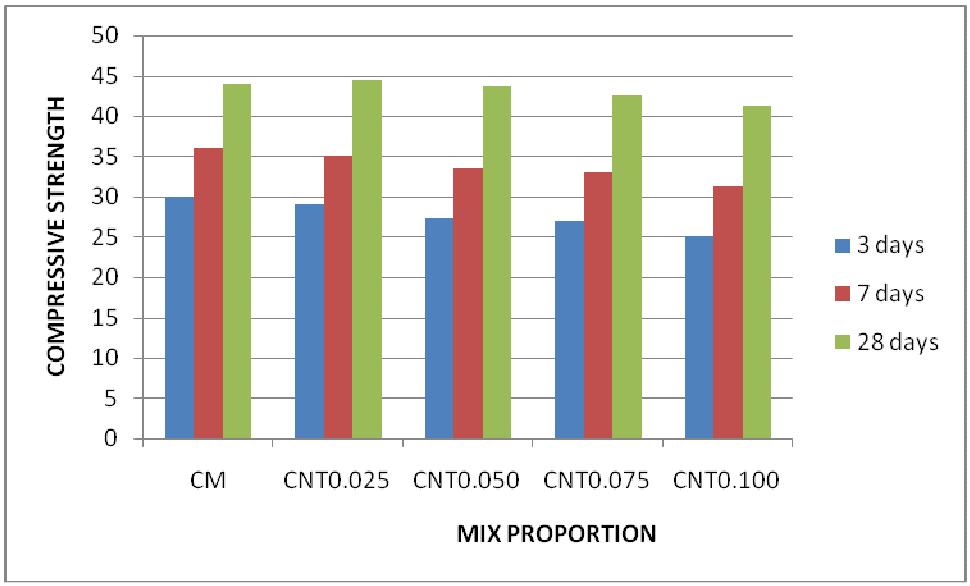


Fig. 4.1: Compressive strength of cement mortar with Multiwall CNT by aqueous mixing

Table 4.1: Compressive strength of cement mortar with Multiwall CNT by aqueous mixing

MIX	Compressive Strength (N/mm^2)			Average Compressive Strength (N/mm^2)		
	3 days	**7 days**	**28days**	**3 days**	**7 days**	**28days**
CM	30.2	35.81	43	30.4	36	40
	30.5	35.58	38			
	30.5	36.56	39			
0.025% CNT	29	34.5	44.9	29	35	44.5
	28.5	35	44.11			
	29.5	35.5	44.52			
0.05% CNT	27.3	33.5	43.7	27.3	33.5	43.7
	27.5	33	43.7			
	27.1	34	43.7			
0.075% CNT	27	32.5	41.2	27	33	42.5
	26.5	33.5	42.5			
	27.5	33	42.8			
0.10% CNT	24.5	30.5	40.9	25	31.2	41.3
	25.5	31.4	41.2			
	25	31.7	41.8			

The water cement ratio in all cases discussed above remains same i.e. 0.38. The test results indicated that, for 3 days compressive strength decreases progressively by 10%, for 7 days the compressive strength decreases by 9% and for 28 days the compressive strength increases by 10% as shown in Fig.4.1.The decrease in strength occurs mainly due to improper dispersion of CNT(Aqueous medum) in the cement and also coagulation occurs in the mortar mix.The results in the case aqueous mixing was not appropriate so other method for dispersion of nanotube was adopted i.e. dispersion of Carbon Nanotube by Surfactant.

4.2.2 Results by mixing in Surfactant

In this case the dispersion of Carbon Nanotube was done by dispersing CNT n water using surfactant supplied by vendor by means of ultrasoncator for 5 hours before casting. The prepared CNT aqueous mix s then used for casting of cube and beam specimens. The Compressve strength test results for 3,7 and 28days are shown in Fig. 4.2 and Table 4.2.

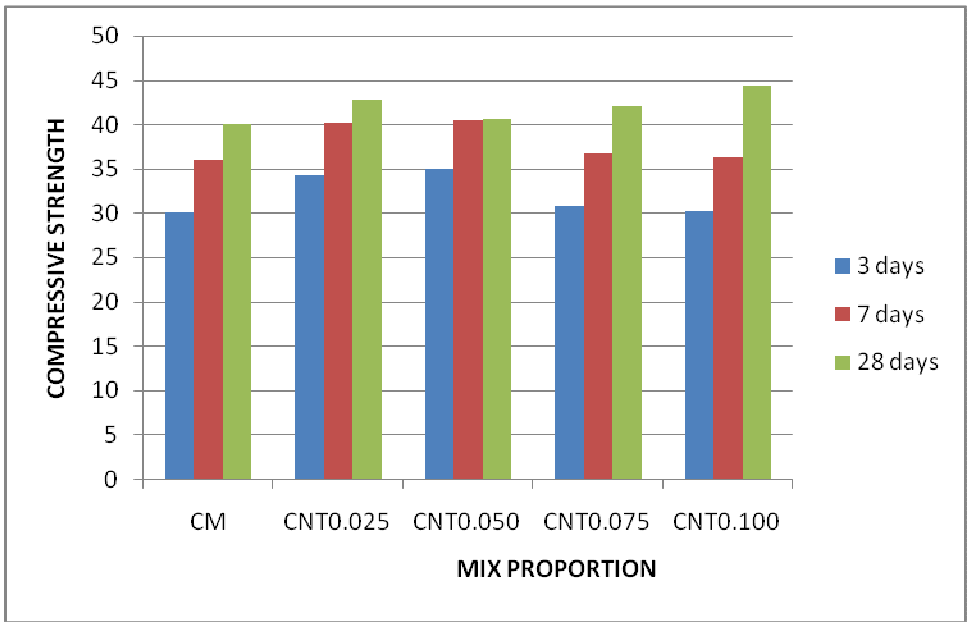


Fig. 4.2: Compressive strength of cement mortar with carbon nanotube with surfactant

Table 4.2: Compressive strength of cement mortar with CNT in surfactant

MIX	Compressive Strength (N/mm^2)			Average Compressive Strength (N/mm^2)		
	3 days	**7 days**	**28days**	**3 days**	**7 days**	**28days**
CM	30.2	35.81	43	30.4	36	40
	30.5	35.58	38			
	30.5	36.56	39			
0.025% CNT	31.32	37.52	40.9	34.25	40.12	42.75
	36.42	42.23	44.8			
	35	40.61	42.54			
0.05% CNT	35.1	40.68	38.75	34.94	40.4	40.64
	32.4	38	40.614			
	37.31	42.49	42.54			
0.075% CNT	32.41	38.24	37.86	30.79	36.66	42.05
	27.5	33.39	45.39			
	32.44	38.34	42.8			
0.10% CNT	32.5	38.29	36.72	30.16	36.22	44.36
	28.12	33.93	50.67			
	29.85	36.43	45.7			

*Increase in strength is reported using CNT dispersed by using surfactant in aqueous medium by ultrasonification for 5 hours.

*From **Fig. 4.2** it is clear that with the addition of Multiwalld CNT in Cement mortar compressive strength goes on increasing upto particular limit.

* In case of 3 days the strength increases up to 14% for 0.025%CNT &0.05% CNT and remain same as CM for 0.075%CNT &0.1%CNT which itself is higher dosage .

* For 7days in case of 0.025%CNT & 0.05%CNT the strength increases by 11% whereas in case of 0.075%CNT & 0.1%CNT the strength remain same as compared to control samples.

* For 28 days in case of 0.025%CNT & 0.075%CNT strength increase by 5% for 0.05%CNT strength remain same as compared to CM and for 0.01%CNT strength increased by 10% as compared to control samples.

*Hence it can be concluded that addition of CNT increase compressive strength 15-19%

*Strength ncrease observed upto 0.05% CNT dosage,hence optmum CNT dosage shall be 0.05%.

4.3 Split Tensile Strength

Split tensile strength studies were carried out at the age of 7, 14 and 28 days. Test specimen are 0.025%CNT,0.05%CNT,0.075%CNT,0.1%CNT.

4.3.1 Result by aqueous mixing

The test results of aqueous mixing are shown in Fig. 4.3 and Table 4.3. In this case the dispersion of Multiwall CNT was done by using ultra-sonicator in aqueous medum for 5 hours bfore castng and without usng any dispersing agent or surfactant to see the effect of this on strength.

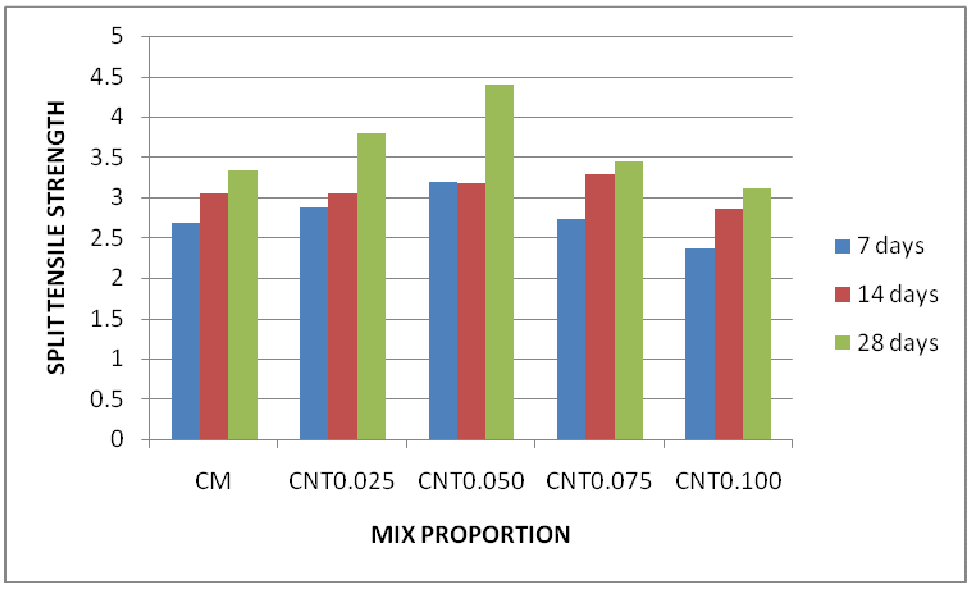


Fig. 4.3: Split tensile strength of cement mortar with Multiwall CNT by aqueous mixing

Table 4.3: Split tensile strength of cement mortar with Multiwall CNT by aqueous mixing

MIX	Split tensile Strength (N/mm^2)			Average split tensile Strength (N/mm^2)		
	7 days	14 days	28days	7 days	14 days	28days
CM	2.56	3.93	3.66	2.68	3.04	3.33
	2.88	2.62	3.03			
	2.59	2.57	3.31			
0.025% CNT	2.75	3.3061	4.02	2.88	3.055	3.79
	3.11	2.8023	3.8			
	2.78	3.0595	3.56			
0.05% CNT	3.24	3.3586	4.6	3.19	3.18	4.4
	3.11	3.0122	4.28			
	3.21	3.1697	4.34			
0.075% CNT	2.61	2.8233	3.06	2.73	3.285	3.44
	2.64	3.6399	3.81			
	2.95	3.3922	3.44			
0.10% CNT	2.57	2.7666	3.15	2.36	2.85	3.11
	2.16	2.8915	2.74			
	2.35	2.8726	3.44			

As seen in table, test results indicated the addition Multiwalld CNT at different percentages. The CNT was added with respect to the weight of the cement. It is observed that 7 days strength with addition of CNT upto 0.05% goes on increasing by 10-12% than start decreasing by 10-12%. There is increase of upto10% splitting tensile strength of 0.05% and 0.75%CNT in cement mortar respectively, when compared to control mix at age of 28 days.

4.3.2 Results by mixing in Surfactant

The test results of surfactant mixing are shown in Fig. 4.4 and Table 4.4. In this case the dispersion of Carbon Nanotube was done by dispersing CNT n water using surfactant supplied by vendor by means of ultrasoncator for 5 hours before casting. The prepared CNT aqueous mix s then used for casting of cube and beam specimens

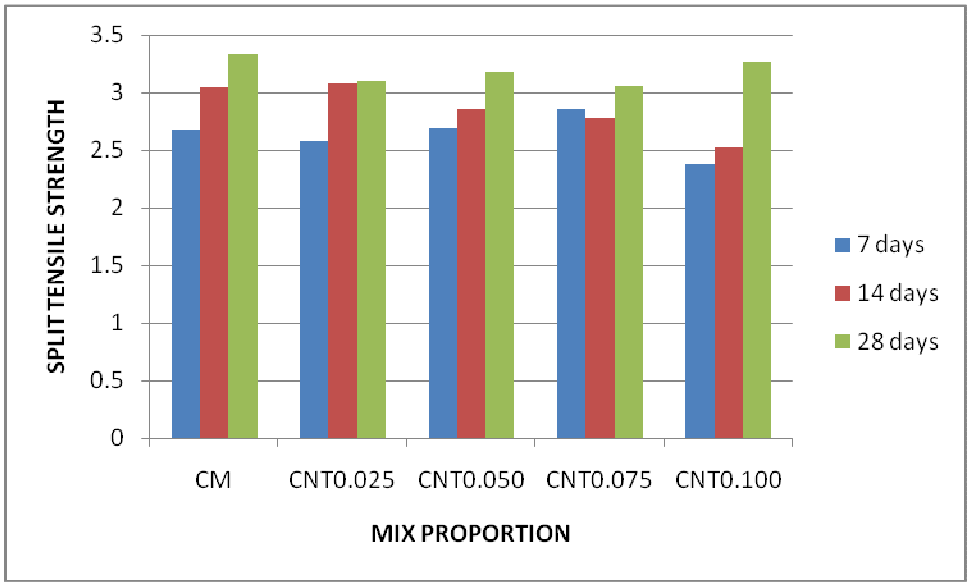


Fig. 4.4: Split tensile strength of cement mortar with Multiwall CNT by Surfactant mixing

Table 4.4: Split tensile strength of cement mortar with Multiwall CNT by Surfactant mixing

MIX	Split tensile Strength (N/mm^2)			Average split tensile Strength (N/mm^2)		
	7 days	14 days	28days	7 days	14 days	28days
CM	2.56	3.93	3.66	2.68	3.04	3.33
	2.88	2.62	3.03			
	2.59	2.57	3.31			
0.025% CNT	2.50	2.76	2.54	2.58	3.08	3.1
	2.63	3.48	3.56			
	2.59	2.98	3.17			
0.05% CNT	2.71	3.40	3.25	2.69	2.85	3.18
	2.56	2.97	3.10			
	2.80	2.14	3.17			
0.075% CNT	2.81	2.78	2.68	2.86	2.78	3.06
	2.91	2.75	3.26			
	2.85	2.81	3.21			
0.10% CNT	2.36	2.26	3.20	2.38	2.52	3.27
	2.38	2.66	3.34			
	2.37	2.61	3.27			

As seen in table, test results indicated the addition Multiwalld CNT at different percentages. The CNT was added with respect to the weight of the cement. It is observed that 7 days strength with addition of CNT upto 0.075% goes on increasing by 5% than start decreasing by 5%. There is decrease of upto10% splitting tensile strength of 0.05% 0.075% and 0.1%CNT in cement mortar respectively, when compared to control mix at age of 28 days.

4.4 Flexural Strength

Flexural strength was carried out at the age of 7, 14 and 28 days. Test specimen are 0.025%CNT,0.05%CNT,0.075%CNT,0.1%CNT.

Test results are shown below in **Table 4.5** and **4.6**.

4.4.1 Result by aqueous mixing

The test results of aqueous mixing are shown in Fig. 4.5 and Table 4.5. In this case the dispersion of Carbon Nanotube was done by dispersing CNT n water using surfactant supplied by vendor by means of ultrasoncator for 5 hours before casting. The prepared CNT aqueous mix s then used for casting of cube and beam specimens.

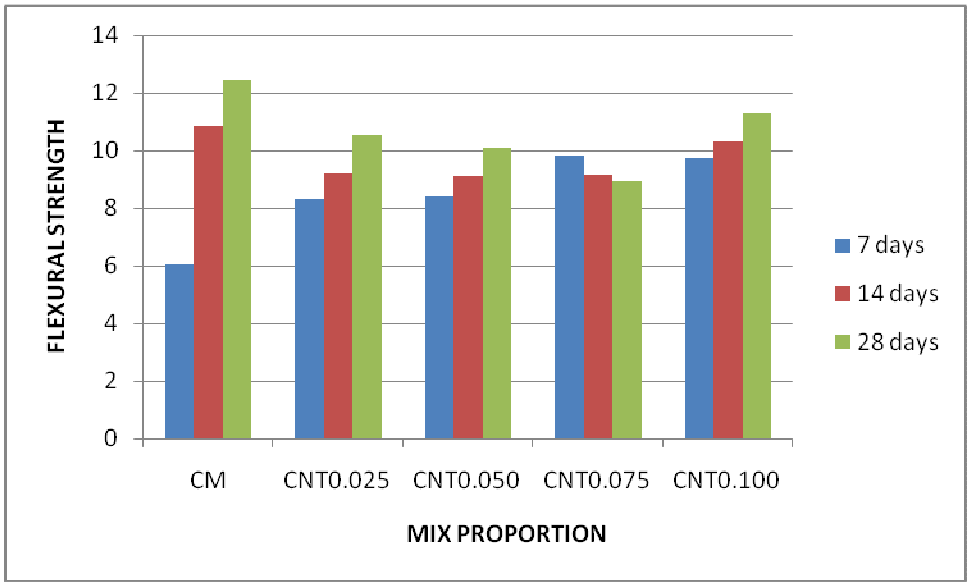


Fig. 4.5: Flexural strength of cement mortar with Multiwall CNT by aqueous mixing

Table 4.5: Flexural strength of cement mortar with Multiwall CNT by aqueous mixing

MIX	Flexural Strength (N/mm^2)			Average Flexural Strength (N/mm^2)		
	7 days	14 days	28days	7 days	14 days	28days
CM	6.22	10.65	12.88	6.04	10.85	12.44
	5.88	11.24	11.98			
	6.01	10.66	12.46			
0.025% CNT	8.1375	9.4	12	8.33	9.2	10.55
	7.7625	8.85	9.75			
	9.0806	9.35	9.9			
0.05% CNT	7.6313	8.89	10.875	8.38	9.12	10.11
	8.625	9.16	10.088			
	8.8875	9.31	9.375			
0.075% CNT	10.575	9.3	9.3375	9.82	9.15	8.94
	9.45	8.86	8.775			
	9.4313	9.28	8.7			
0.10% CNT	8.8125	9.94	11.438	9.75	10.29	11.3
	10.125	10.55	11.869			
	10.313	10.38	10.613			

As seen in table, test results indicated the addition of Multiwall CNT at different percentages. The CNT was added with respect to the weight of the cement. There is increase of 48% to 53% strength with 0.025% to 0.75%addition of CNT in the cement mortar respectively, when compared to control mix at age of 7 days. It shows upto 10% strength reduction with 0.025% to 0.75%addition of CNT in the cement mortar respectively, when compared to control mix at age of 14 days. It shows upto 12% strength reduction with 0.025% to 0.75%addition of CNT in the cement mortar respectively, when compared to control mix at age of 28 days.

4.4.2 Results by mixing in Surfactant

The test results of surfactant mixing are shown in Fig. 4.6 and Table 4.6. In this case the dispersion of Carbon Nanotube was done by dispersing CNT n water using surfactant supplied by vendor by means of ultrasoncator for 5 hours before casting. The prepared CNT aqueous mix s then used for casting of cube and beam specimens

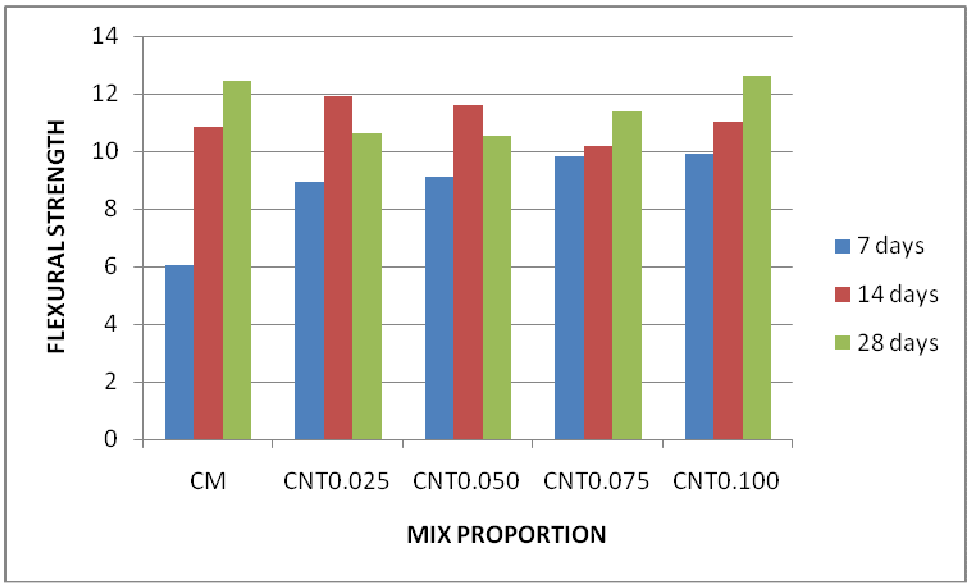


Fig. 4.6: Flexural strength of cement mortar with Multiwall CNT by Surfactant mixing

Table 4.6: Flexural strength of cement mortar with Multiwall CNT by Surfactant mixing

MIX	Flexural Strength (N/mm^2)			Average Flexural Strength (N/mm^2)		
	7 days	14 days	28days	7 days	14 days	28days
CM	6.22	10.65	12.88	6.04	10.85	12.44
	5.88	11.24	11.98			
	6.01	10.66	12.46			
0.025% CNT	9.03	12.131	7.5	8.95	11.92	10.62
	9.02	12.375	12.938			
	8.8	11.25	11.4			
0.05% CNT	9.2	11.438	7.35	9.09	11.62	10.53
	9.03	12.525	12.6			
	9.05	10.875	11.625			
0.075% CNT	10.075	7.5	12.675	9.8	10.2	11.38
	9.25	11.475	10.875			
	10.1	11.625	10.575			
0.10% CNT	9.78	11.475	14.063	9.89	11	12.63
	9.86	10.688	11.869			
	10.02	10.838	11.936			

From Fig. 4.6 it is clear that with the addition of Multiwall CNT flexural strength goes on increasing. From Table 4.6 it is clear that for 0.025% to 0.1% CNT dosage for 7 days the strength increases by 53.17% as compared to control samples. For 14days in case for 0.025% to 0.1% CNT dosage the strength increases by 10.06% as compared to control mix. For 28 days in case for 0.025% to 0.1% CNT dosage there was decrease in strength i.e. strength decreases by 19.89% as compared to control samples.

4.5 X-Ray Diffraction (XRD)

Fig. 4.7shows the variations of X Ray Diffraction (XRD) graphs of plain and Multiwall CNT modified cement paste in which CNT added in the proportion of 0.025%, 0.05%, 0.075%, and 0.1% which are hydrated for 28 days.

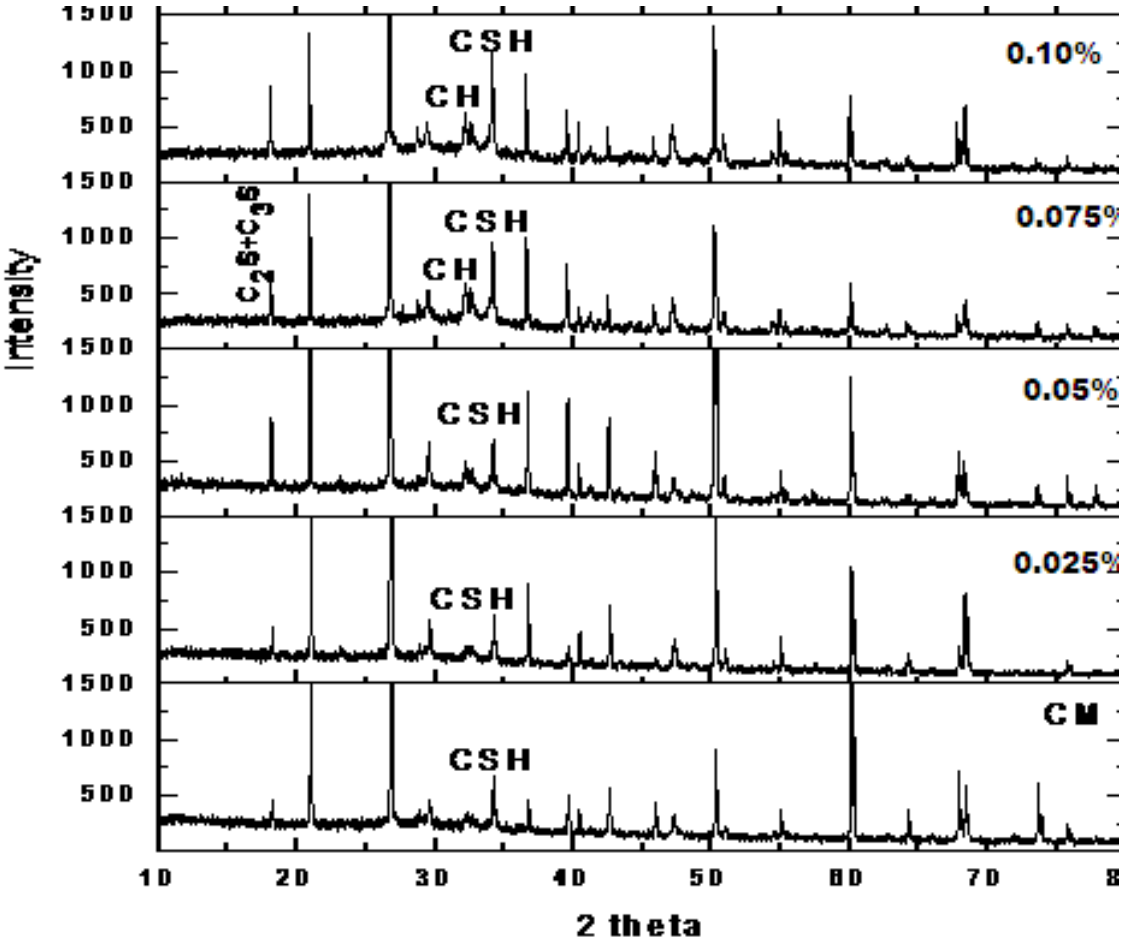


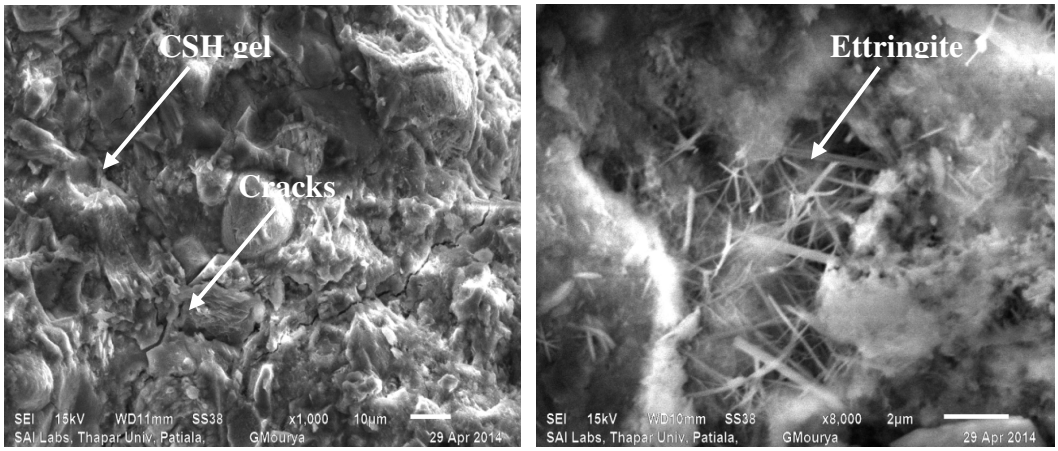
Fig. 4.7: XRD pattern for plain and Multiwall CNT modified cement pastes hydrated for 28days (at all additions)

The main compounds detected are calcium silicate hydrate (CSH) and calcium hydroxide (CH). It is clear from the **Fig. 4.7** that CH peaks decreases with increase in the quantity of Multiwall CNT whereas, CSH peaks goes on increasing with increase in the quantity of Multiwall CNT.

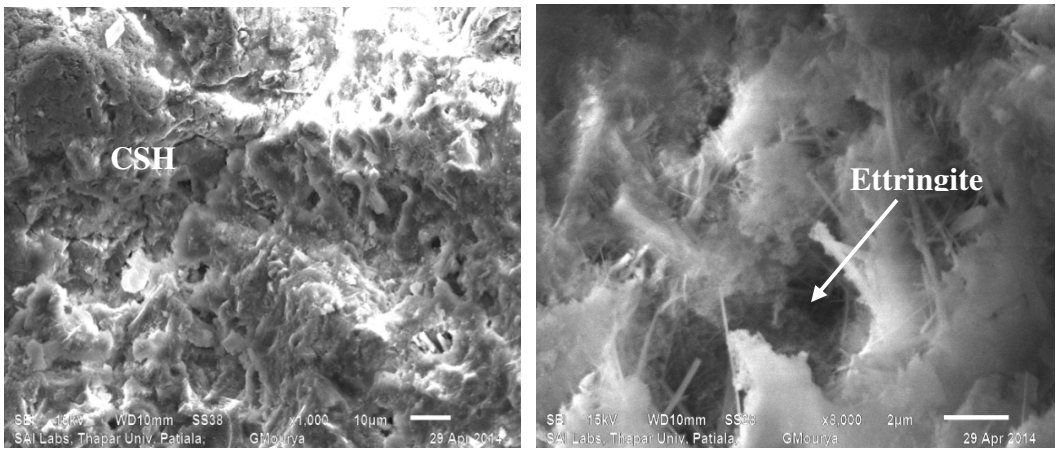
The increase and decrease of CSH and CH intensity phases in Multiwall CNT cement paste hydrated for 28 days is mainly due to the pozzolanic reaction of Multiwall CNT with the free lime liberated during the process of hydration.

4.6 Scanning Electron Microscopy

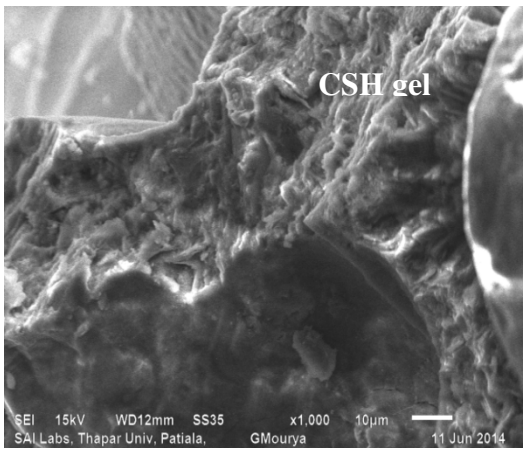
SEM was carried out at the age of 28 days for variable proportions of CNT. Test results are shown below in **Fig. 4.8**. Test results indicated the addition of Carbon Nanotube at different percentages. The CNT was added with respect to the weight of the cement. With the increase the addition of CNT at 0.075% strength goes on decreasing. The micro-structure shows the formation of CSH gel, cracks, needle hydrates and voids.

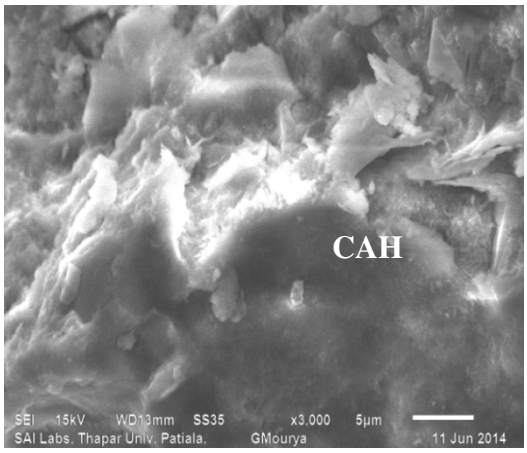


(a) CM hydrated for 28 days.

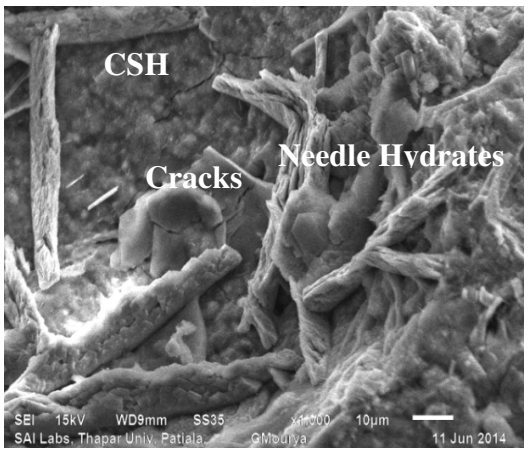


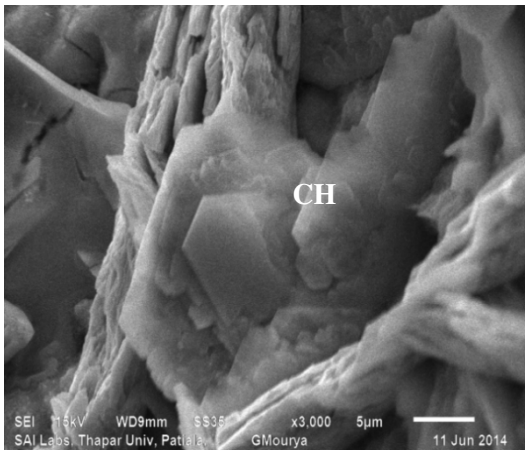
(b) CNC0.025 addition in cement mortar hydrated for 28 days.



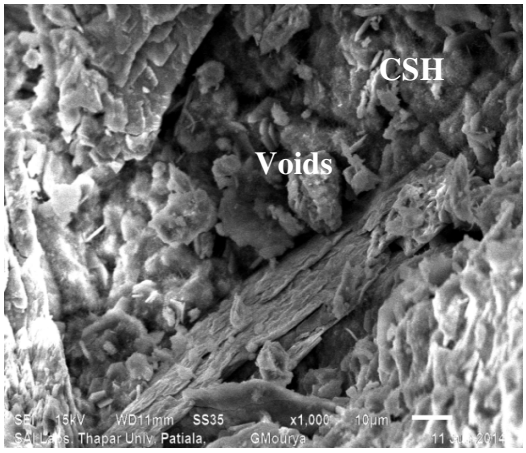


(c) CNT0.05 addition in cement mortar hydrated for 28 days.





(d)CNT0.075 addition in cement mortar hydrated for 28 days.



(e)CNT0.1 addition in cement mortar hydrated for 28 days.

Fig. 4.8: SEM micrographs of Multiwall CNT cement pastes hydrated for (28 days)

Fig. 4.8 shows the SEM micrographs of Multiwall CNT cement pastes hydrated for 28 days. The test samples of the micro-structure were obtained from the central part of the specimens.

The SEM micrographs show all hydrated products such as CSH, CH etc. **Fig. 4.8 (a)** shows the microstructure of the cement paste without CNT. From Fig. 4.8it is concluded that CSH existed in the form of gel and SEM image also shows needle like crystals.

Fig. 4.8(b, c, d) represents the micro-structures of the mixture which containing 0.025%, 0.05% and 0.075% Multiwall CNT as compared to control mix the micro-structure is denser and compact. The improvement of micro-structure improves the mechanical properties of the CNT modified cement mortar.

The Multiwall CNT improves the micro-structure and strength of the cement paste by a mechanism as follows; when the nano-particles are uniformly dispersed in the cement paste the hydrated products of cement will deposit on nano-particles due to their more surface area during hydration. Multiwall CNT will participate in the hydration process to generate the CSH through reacting with CH therefore the strength increases with the addition of CNT.

Fig. 4.8 (e) represents the micro-structure containing 0.1% Multiwall CNT which causes decrease in the strength. The micro-structure represents the poor hydration and unhydrated cement grains. This results in decrease in mechanical properties of the sample.

4.7 Closing Remarks

In this chapter, the testing results were discussed. It is very clear from the results that nano-particles act as filler in the mortar mix to increase the strength. In the next chapter, conclusion were discussed which are drawn out from the results of the previous chapter.

CHAPTER 5

CONCLUSIONS & FUTURE SCOPE

5.1 General

The mechanical, thermal, micro-structure properties and chemical composition have been computed in the present work with the addition of 0.025%, 0.05%, 0.075% and 0.1% CNT in the cement mortar. On the basis of present work the following conclusions are drawn.

5.2 Effect of Dispersion

- Dispersion of Multivalve CNT by surfactant mixing shows better results as compared to aqueous, as the coagulation is less and shows more appropriate results.Technology as well as technique development for proper dispersion of CNT specifically for concrete application is required.

5.3 Effect of CNT on Compressive Strength

- Compressive strength of CNT of cement mortar for aqueous mixing shows progressive decrease in strength for 3, 7 days i.e. 10%, 9% with the addition of CNT as compared with control mix sample. The results are not appropriate in this case so surfactant mixing was adopted.
- Surfactant mixing shows progressive increase in strength with the addition of CNT for 3, 7 and 28 days. The strength in case of 3 days increases by 14.04% in case of CNT. In case of 7 days strength increases by 11.45% for CNT samples as compared with control mix sample and for 28 days strength increases by 5.78% for CNT samples.

5.4 Effect of CNT on Split Tensile Strength

- Split tensile strength shows progressive increase in strength with the addition of CNT for 7, 14 and 28 days. The strength in case of 7 days increases by 12.70% in case of CNT. In case of 14 days strength increases by 4.83% for CNT samples as compared with control mix sample and for 28 days strength increases by 8% for CNCT samples.

5.5 Effect of CNT on Flexural Strength

- Flexural strength shows progressive increase in strength with the addition of CNT for 7, 14 and 28 days. The strength in case of 7 days increases by 53.66% in case of CNT. In case of 14 days strength decreases by 10.73% for CNT samples as compared with control mix sample and for 28 days strength decreases by 11.30% for CNT samples.

5.6 Effect of CNT on Microstructure Properties

- The results from XRD, represent the higher formation of CSH and more consumption of CH and SEM micrographs show that the microstructure is appeared quite dense, compact which can be explained by greater surface area and also due to swelling quality of the CNT which act as a filler in the pores.

5.7 Future Scope

- Considering all aspects it is suggested that optimized condition to obtain more strengthened cement mortar has to be established.
- We get better Flexural strength at optimum dosage of 0.05%,So CNT potential in term of flexural strength shall be furthermore explored.
- CNT provide at denser concrete matrix which is durable in term of corrosive saline atmosphere. So its potential shall be further explored in corrosive environment.

- Overall economy in term of flexural strength is obtained,Which shall be further explored in term of post tensioning beam system.
- Further work would be carried out with other percentages of nano-materials such as nanofibers, nanosilica etc. to get better yield of cement mortar.
- Dispersion of CNT is very much essential to explore its potential. Dispersion of CNT through aqueous mixing can be investigated by using various dispersing or stabilizing agents. Techniques shall be developed for proper dispersion of CNT for concrete applicatons.

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