NANO MODIFIED MULTI-FUNCTIONAL CEMENTITITIONS MORTAR WITH HYBRID INTRUSIONS OF CNTS/GNPS

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Fall 2015-MS Structural Engineering

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This is to certify that the

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A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Structural Engineering

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Declaration

I certify that this research work titled "*NANO MODIFIED CEMENTITIONS MORTAR WITH HYBRID INTRUSIONS OF CNTS/GNPS"* is my own work. The work has not presented elsewhere for assessment. The material that was used from other sources has been properly acknowledged/referred.

Signature of Student

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ABSTRACT

With the advancement in technology, construction industry also evolved new methods to counter the problems related to fresh as well as hardened properties of cement composites. This experimental study explores the feasibility of development of hybrid nano intruded cement mortar system. The idea was to substitute high-cost Carbon nanotubes (CNTs) with low cost milled graphite powder without compromising its mechanical and electrical properties. CNTs and graphite nano platelets (GNPs) in different ratios were dispersed by ultra-sonication into aqueous solution and the effect of CNT/GNP ratios on the fresh and hardened properties of cement mortar were investigated. Combination of CNTs and GNPs in a ratio of 8:1 (C1G0.125) was observed to synergistically enhance the compressive strength and flexural strength by 46.5% and 124.7% compared to control formulation with acacia gum (CS-AG).Similarly 74.8% of early age shrinkage arrest and 11% better resistance against external sulphate attack was observed. Furthermore decrease in 48.3% of electrical resistivity was also recorded in case of C1G0.125. Study of external morphology of hydrated products and their interaction with nanoparticles using Field emission scanning electron microscopy confirmed crack bridging, crack divergence and pull-out behaviour by nano particles.

Key Words: Hybrid Nano Intrusions, Carbon Nanotubes, Graphite Nano Platelets, Cement Mortar, Mechanical Properties, Sulphate Attack, Electrical Resistivity

Dedication

I dedicate this work to all

Researchers

And

To my parents.

Acknowledgments

I am grateful to Almighty Allah whose countless blessings gave me the strength to complete this research work.

I bestow my sincere thanks to my mentor and advisor Asst. Prof. Dr. Rao Arsalan Khushnood, department of structural engineering, NUST Institute of civil engineering (NICE) for his advice, untiring guidance, incredible patience, and supervision. He inspired me through his punctuality, professionalism, diligence, and sincerity. I am grateful to him for his encouragement and motivation. He always urged me to achieve the best. All credit goes to him for making me a hard worker, focused and ambitious.

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I am very grateful to all the respondents for their valuable contribution to this research and in the end I would like to pay my earnest and honest gratitude to my family especially my parents for their unconditional support, encouragement, prayers and patience.

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CHAPTER 1

INTRODUCTION

1.1 General

Cement is most widely used material in construction industry due to its exceptional binding properties. Although ordinary Portland cement possess excellent compressive strength but due to its brittle nature it shows very less resistance against tensile stresses and fails at very low strain level which make it vulnerable to cracks. Many researchers used traditional fibers i.e. steel/carbon fibers to overcome this problem but these fibers failed to stop crack initiation at micro and nano scale [1]–[3]. With the advancement in technology these macro size fibers are replaced by nano sized materials i.e. Carbon nano-tubes and Graphite nano-platelets. As cement composites show tremendously low tensile strength, brittle failure, and are also vulnerable to micro cracking as a result of internal stresses induced due to shrinkage at early ages. To address these limitations, reinforcement of cement matrix is typically provided at micro and nano scale using micro fibers and nanofibers, respectively. These nano materials showed excellent resistance against crack initiation and its propagation.

The primary focus of this research is the increase in the reinforcement efficiency of mortar samples by the hybrid intrusions of Carbon Nano Tubes and Graphite Nano/Micro Platelet suspensions. Mortar has been used in this research because many researches on reinforcement efficiency of cement using CNTs and GNPs have already been conducted. Also cement particles due to their smaller size make cement paste homogeneous. As a result reinforcement efficiency of nano particles in mortar samples is not fully utilized. This work could have been done on concrete samples but large amount of CNTs and GNMPs were required so making concrete samples was neither economical nor feasible for this research. The choice of mortar was also influenced by the fact that concrete is best represented by mortar as (i) concrete only contains course aggregate which is not present in mortar (ii) Course aggregate is the only inert material in the whole concrete mix (iii) All other components of concrete that actively take part in chemical reaction are present in mortar.

With the development of nanomaterials, such as carbon nanotubes (CNTs) and graphite nanoplatelet dispersions, has provided opportunities to improve the performance of cement pastes. Recently it is revealed that by the addition of nano particles, properties of concrete can be improved by modifying the structure of hydration products [4]. Now with the advancement in technology, cement composites can be developed at nanoscale.

Nano Materials are present in three basic shapes i.e. 0-D nano particles, 1-D nano fibers and 2-D nano sheets [5], [6]. Carbon nanotubes (CNTs) provide remarkable tensile strength as well as multifunctional characteristics i.e. electrical conduction and piezoresistive properties. Carbon nanotubes are 1-D form of carbon in the form of fiber which possess an average aspect ratio even greater than 1000 [7]. CNTs when added to a cement or a concrete matrix refines its microstructure, enhances the strength, not only in compression but in flexural as well. Elastic modulus of such matrices carrying CNTs is also improved, porosity and void ratio reduces with inculcation of carbon nanotubes [8].

Modulus of Elasticity and strength of Graphite nanoplatelets are as good as to those of Carbon Nanotubes, showing its excellent mechanical properties [9]. Moreover, High aspect ratio along with high surface area of GNPs indicates its feasibility to be used as nano reinforcement in cement composites for strength enhancement. Graphite nanoplatelet (GNP) is the arrangement of carbon atoms in the form of 2-dimentional sheets, generated by graphite [10].

1.2 Problem Statement

Cement is the most popular construction material due to its exceptional binder properties. Ordinary Portland cement possess excellent compressive strength but due to its brittle nature it shows very less resistance against tensile stresses and fails at very low strain level which make it vulnerable to cracks. Almost, all the mechanical properties of cementitious composites are controlled by CSH which is a nano porous. So intrusion of CNTs possessing high tensile strength along with GNPs, which provide filler effect, will enhance the tensile characteristics of cement mortar and will provide dense micro structure of CSH gel.

1.3 Research Objectives

This experimental study will explore the feasibility of development of hybrid nano intruded cement mortar system. CNTs will be added in the cement matrix in order to enhance mechanical properties as well as to increase the electrical conductivity for different applications e.g. crack memorizing and strain sensing. Than CNTs will be replaced by low cost graphite nano-micro platelets (GNMPs) in order to achieve low - cost multifunctional cement composite while achieving the same/ superior properties as in case of CNTs. Following are the main objectives of this study.

1. To study feasibility of already developed dispersion scheme for CNTs in the preparation of homogeneously dispersed hybrid nano-modified matrix.
2. To investigate the synergistic effect of Carbon Nanotubes and Graphite Nanoplatelets injection on the mechanical properties, resistance against Sulphate attack and microstructure of cementitious matrix.
3. To explore electrical conductance ability and electromagnetic Shielding of the hybrid nano intruded cement matrix.

1.4 Research Approach

To achieve the above mentioned objectives Multi walled Carbon Nanotubes were imported form USA and GNMPs were imported from Korea for sampling. Locally available acacia Modesta was used as surfactant and for Sonication bath sonicator was used. For comparing the results of conventional mortar and modified nano intruded cement mortar, mix ratio was kept same throughout this research. To investigate mechanical properties and fracture mechanics cement mortar samples of dimension 160x40x40 mm were prepared as per DIN EN 196-1. While to investigate electrical properties 160x40x40 mm mortar specimens were prepared and copper meshes were introduced in specimens during casting in order to have close circuit to pass the electric current from specimens. For measuring electrical conductivity of mortar specimens 4 probe method was adopted. In which inner two terminals were used to measure voltage drop while outer two terminals were used to measure electrical current flowing through the circuit. While for mechanical properties, flexural strength and fracture mechanics cement mortar specimen were tested under compression and three point bend test respectively as per ASTM standards. SEM was performed to investigate the interaction of nano materials with the surrounding cementitious matrix. Test results were compared with the available literature.

1.5 Research Significance

Till now, lot of research has been carried out on mechanical properties and electrical characteristics of cementitious composites by the addition of CNTs and GNPs. To the best of author's knowledge, no previous research has investigated the hybrid effect of these two materials in cement composites. This research intended to explore the performance of hybrid CNTs/GNPs cement mortar in terms of microstructure, physical, mechanical, electrical properties and electromagnetic shielding properties.

The research undertaken to address the aforementioned objectives is presented in five chapters.

Chapter 1 is a preliminary chapter about the evolution and need of nano intruded cement composites, research objectives and research significance has been discussed. **Chapter 2** describes literature review in detail. A brief literature review about properties of CNTs and GNPs in general and when used in cementitious matrices has been provided. Different properties of these nano materials which is responsible for the strength enhancement and other improved properties.

Chapter 3 deals with the test setup. It explains which types of equipment are used to evaluate mechanical properties. Furthermore it presents an overview of the test procedure which describes the ways and methods to determine mechanical properties, electrical resistivity and electromagnetic shielding of nano intruded cement mortar. **Chapter 4** provides evaluation, analysis and discussion for results of material property tests. Results of fresh properties of nano intruded cement mortar and shrinkage investigations alongside resistance against Sulphate attack, electrical resistivity, electromagnetic shielding and microstructural study has also been presented. Further cost comparison has been discussed at the end.

Chapter 5 provides detailed conclusions and remarks.

CHAPTER 2

LITERATURE REVIEW

2.1 General

A brief introduction about Carbon Nano Tubes (CNTs) and Graphite Nano Platelets (GNPs), their production and usage in cementitious matrix has been discussed. Literature review about nano intruded cement composites, their mechanical properties, electrical characteristics, durability aspect and electromagnetic shielding properties are also presented in this chapter.

2.2 Graphite Nano Materials

Carbon-based particles are the widely used as an admixture these days for producing multifunctional cementitious composites. They are used due to their high aspect ratio, large surface area, high elastic modulus, high strength and high conductivity. Carbon fibers (CFs), carbon nano tubes (CNTs) and Graphite nano platelets (GNPs) were used while conducting previous researches and their results showed the increase in flexural as well as compressive strengths and also self-sensing properties were induced in cementitious composites.

2.3 Carbon Nanotubes

The word "nano" came from a Greek origin, meaning dwarf. Carbon atoms can arrange themselves in different geometric shapes to make allotropes of entirely different properties [11]. Carbon nanotubes (CNTs) consists of graphitic shells seamlessly wrapped into a cylindrical tube; thus, it can be further divided into two sub groups: First single-walled carbon nanotubes and Second Multi-walled carbon nanotubes.

Forces responsible to hold sheets of hexagonal networks are Van der Waals forces, with a spacing of 0.34 nm, and the diameters of CNTs are between 2 and 100 nanometers. CNTs are member of fullerenes family. There are two types of fullerenes i.e. spherical fullerenes or Bucky balls, and cylindrical fullerenes or Carbon nanotubes (CNTs). These are called nanotubes because of their extremely small diameters that range in the order nanometers. Despite of their extremely small size they possess high strength and extraordinary high elastic modulus [12], which has expanded the horizon of their applications to various fields of applications. **Figure 2-1** shows SEM micrographs of carbon nanotubes.

2.4 Application of Carbon Nanotubes

In 1991, CNTs were first discovered by Iijima [13] and the applications of CNTs are still growing. This discovery opened a new gateway towards the application of CNTs in various fields of engineering Carbon Nanotubes are being used in engineering, also in the field of environmental sciences, medicines and even in production electronic sensors [14]. Efforts are being put to increase the innovative applications of this novel material in different fields. The main application of nanotechnology these days is in the field of electronics, materials science, medicine and energy but in recent times nano-materials have found their way to the field of construction materials as well. By modifying the cementitious nano composites, CNTs can play a significant role in construction industry. Its high elasticity and strength can make the composites superior over classic, also the role of CNTs is quite obvious in composite polymer production Exceptional mechanical properties of CNTs i.e. High tensile strength and extraordinary modulus of elasticity can impart better properties to nano modified cement composites.

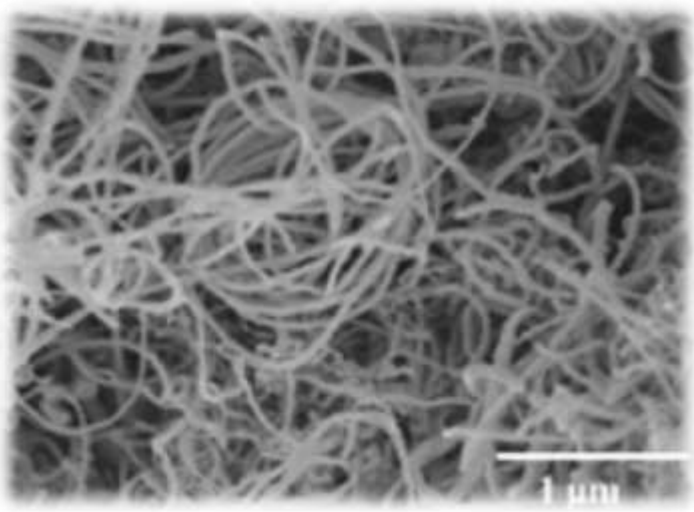


Figure 2-1 Scanning Electron Microscopic Image of Carbon Nanotubes [15]

Different application fields in which CNTs are successfully being used:

- Building materials
- Membranes
- Transistors
- Fillers
- Capacitors
- Medicines
- Sensors

The main problem related to Carbon Nanotubes (CNTs) is their high cost. Despite of rapidly growing production industry and fast growing application fields, commercialization of CNTs is still a big deal. To reduce the production cost, new methods are being introduced to eventually produce extremely pure form of CNTs with least cost. Application of CNTs in construction industry is directly related to their cost. Other issue related to application of CNTs is the strong attractive forces between individual CNTs which tend to make agglomerations. So to get required results CNTs must be evenly dispersed in cementitious matrix. Once the cost effective production and effective dispersion methods are revealed, CNTs applications in construction materials will expand more. Different Types of Carbon Nanotubes (CNTs)

CNTs are divided into three main types i.e. single, double and multi-walled. These types are nominated on the basis of Number of carbon atom sheets rolled into tubes.

2.4.1.1 Single Walled Carbon Nanotubes (SWCNTs)

A single sheet of carbon atoms rolled to form a tube named as single-walled Carbon Nanotube (CNT). The physical characteristics of SWCNTs depends on the diameter of individual tube. The diameter of a SWCNT ranges from 1-2 nanometers and the length depends on the process of production. Each nano tube is flexible in nature so can be bent to curve arcs. **Figure 2-2** [16] shows transmission electron microscopy (TEM) images of Single Walled Carbon Nanotubes.

2.4.1.2 Double Walled Carbon Nanotubes

Double layer of graphene rolled concentrically termed as double-walled CNT. Outer tube covers the inner tube as shown in **Figure 2-3 (b)** [13]**.**

2.4.1.3 Multi-walled Carbon Nanotubes (MWCNTs)

Multi-Walled CNTs are formed by multiple layers of carbon atoms (graphene sheets) rolled upon one another. The outer dia ranges from 2-100 nm. Removal of agglomerations and the dispersion of MWCNTs are the major problems in their application in construction materials. A Transmission Electron image of double and multi-walled CNT is shown in **Figure 2-3** [13].

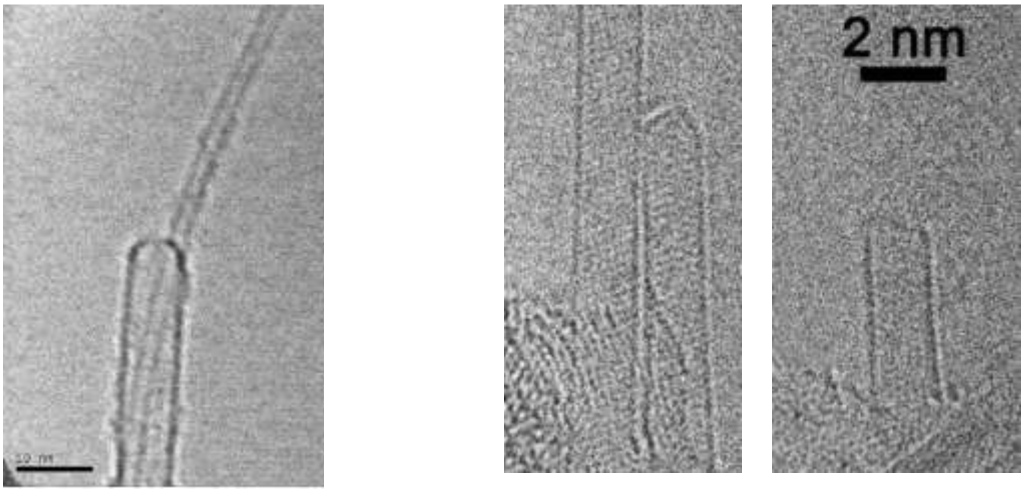


Figure 2-2 Transmission Electron Image (TEM) of Single Walled Carbon Nanotubes (SWCNTs) [16]

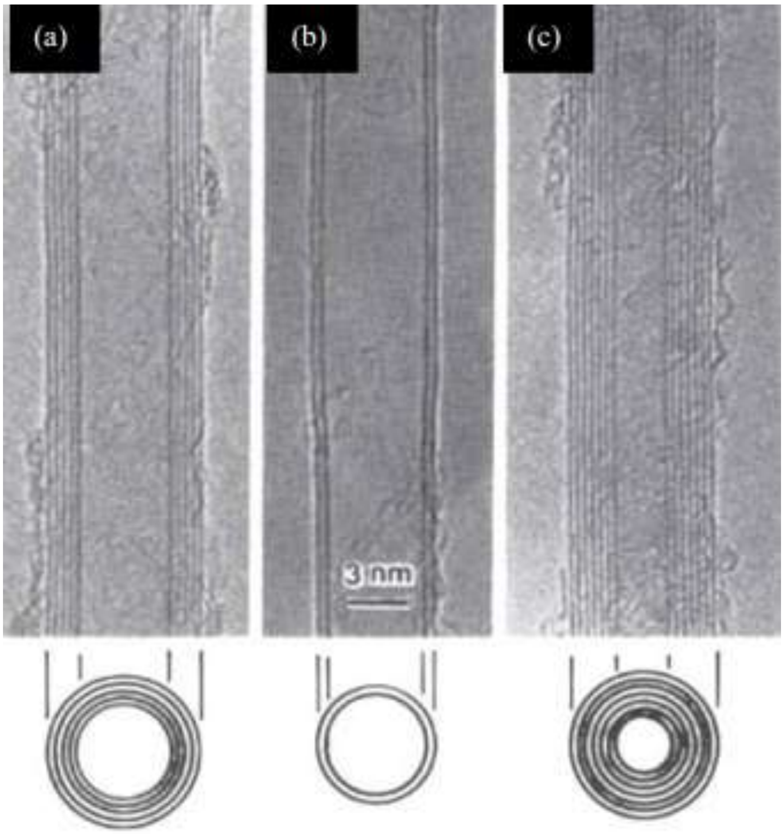


Figure 2-3 Transmission Electron Images of CNTs (a). MWCNT (b) Double Walled CNT (c) 7 Walled CNT [13]

2.4.2 Chirality Based CNT Types

Carbon atoms can be arranged in various geometrical shapes, termed as Chirality, to produce distinctive properties. Carbon is found in different geometrical configurations in practice. On chirality bases CNTs are categories in three different types e.g. Zigzag, Armchair, and chiral. The arrangement carbon atoms is represented with the help of a single-walled CNT in **Figure 2-4** [17].

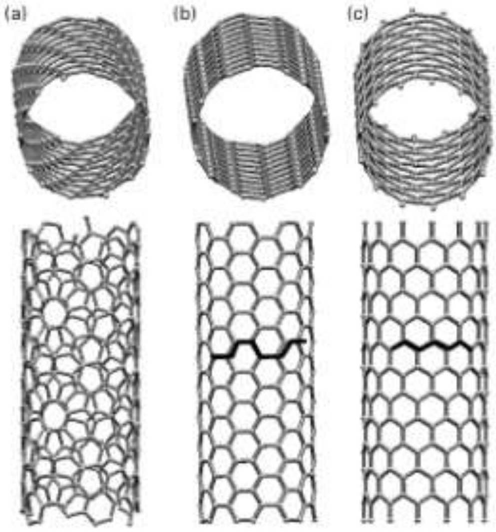


Figure 2-4 Types of SWCNTs Based on Chirality (a) Chiral SWCNT (b) Armchair SWCNT (c) Zigzag SWCNT [17]

2.4.3 Synthesis Process of Carbon Nanotubes (CNTs)

Carbon Nanotubes (CNTs) can be produced using different methods. Some of the techniques are listed below.

- Laser Ablation Method
- Electric Arc Discharge Method
- Chemical Vapor Deposition (CVD) Method

2.4.3.1 Laser Ablation Method

In this technique high intensity laser beam hits the carbon reserve and ablate it. In the presence of inert gases this technique produces carbon nanotubes (CNTs) in the form of threads. The temperature in this can rise up to 10000 ºC. In this method carbon source is vaporized twice by using laser pulses. In this method length of CNTs and diameter can be controlled and CNTs produced by this method possess diameter of 5-20nm and length can vary in microns. Experimental Setup is shown in Figure 2-5 [18].

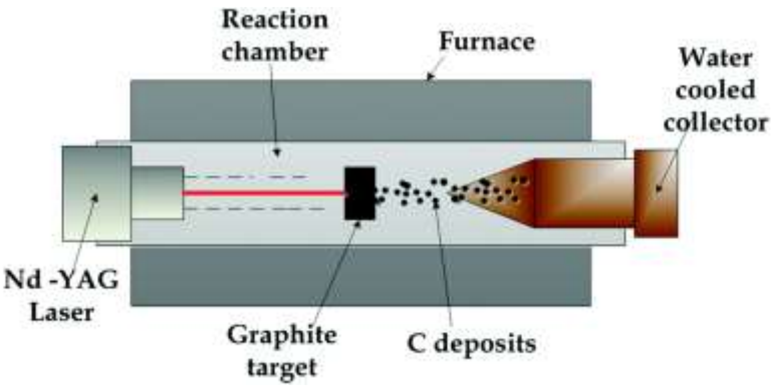


Figure 2-5 Experimental Setup of Laser Ablation Method for CNTs [18]

2.4.3.2 Electric Arc Discharge Method

In this method, a direct current of 50A is applied between two electrodes resulting in evaporation of carbon source surface and vapors later on condenses and deposits on the walls of the setup and electrodes. In order to synthesis SWCNTs Ni and CO are used as electrodes. By this technique best quality Carbon Nanotubes (CNTs) can be produced. Setup for electric arc discharge is represented in **Figure 2-6** [19].

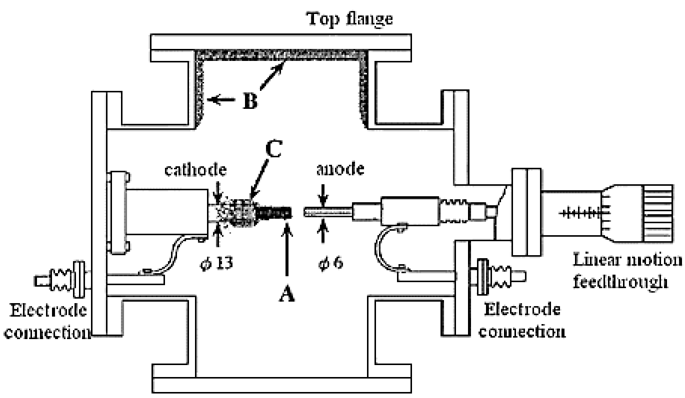


Figure 2-6 Schematic Diagram of Electric Arch Discharge Method for Production of SWCNTs. (A) Hard Deposits at End of Cathode (B) Deposits on the Walls of the Setup (C) Deposits on the surface of Electrode [19]

2.4.3.3 Chemical Vapor Deposition Method

CVD technique involves the reaction of catalyst and the gases with carbon at a temperature above 600 ºC. This is the most efficient and cost effective method for the production of CNTs. Schematic diagram for CVD technique is shown in **Figure 2-7** [20].

In this technique a mixture of hydrocarbon, inert gas along with a catalyst is introduced into the reaction compartment. Decomposition of hydrocarbons leads to production of

CNTs when the temperature rises up to 700-900ºC at atmospheric pressure. Diameter of CNTs produced by this method depends on the size of the metal particles. In this method CNTs with desired diameter and length can efficiently be produced.

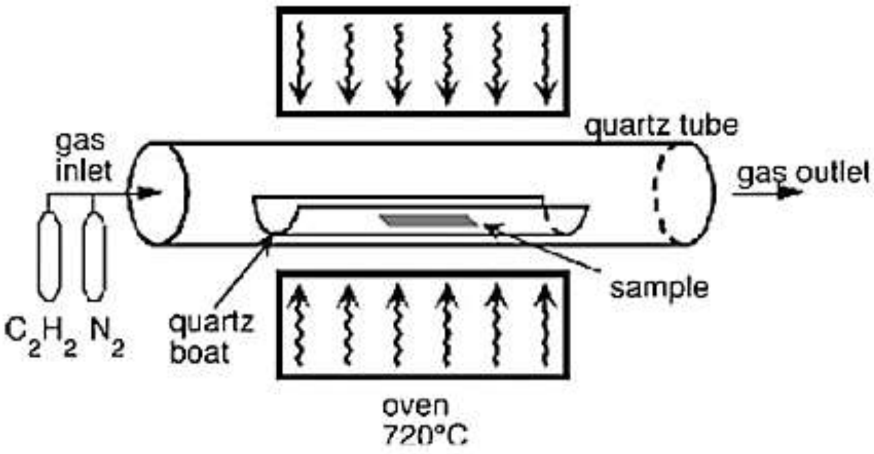


Figure 2-7 Schematic Diagram of Chemical Vapor Deposition Technique for Production of CNTs [20]

2.4.4 Properties of Carbon Nanotubes (CNTs)

Carbon nanotubes (CNTs) have exceptional mechanical strength, large aspect ratios and extraordinarily high surface areas. Carbon nanotubes (CNTs) have 100 times greater tensile strength as compared to steel and nearly similar electrical conductivity as that of copper. Due to strong sp2 bonding between carbon atoms, CNTs possesses exceptional mechanical, electrical and electromagnetic shielding properties.

2.4.4.1 Mechanical Properties

Due to strong sp2 bonding between carbon atoms, CNTs possess high stiffness and axial strength. No other material has exceptional mechanical properties like them. Nanotubes have Young's modulus of CNTs is about 1 Tera Pascal [8]. Tensile stress of CNTs is recorded as 63 Giga Pascal, 50 times higher than steel [21]. Carbon nanotubes are exceptionally stiff but also possess flexibility so can be bent without any structural fracture [22]. Transmission Electron Microscopic images revealed that Carbon Nanotubes are really flexible and do not break upon bending [20] [23].

2.4.4.2 Electrical Properties

CNT exhibit extra ordinary mechanical as well as electrical properties which makes it a remarkable material to be use in construction industry to make a way forward towards self-sensing cement composites. CNTs have remarkable properties in form of electrical conductivity to be used in conjunction with cement to construct self-sensing structures [24]–[27]. Strong sp2 covalent bonding between atoms with in CNT, make it possible to pass an electrical current of 4 × 109 A/cm2, greater than copper can pass without breakdown [28].

CNTs have unique electrical properties. CNTs possess tremendously low electrical resistance which makes them a good conductor of electricity as copper. CNTs can be semiconductors or conductors depending on the chirality, in either case their electrical conduction matches or exceeds that of copper [29]. Electronic characteristics of CNTs are mainly dependent on their diameters and chirality [30]. Carbon Nanotubes (CNTs) are being used in advanced electronics like transistors and switching applications [31]. Carbon nanotubes have recently been used in X-ray generation, emitters and sensors. Microscopy is another area of technology where CNTs have found their application e.g. scanning probe microscopy [32].

2.4.4.3 Electromagnetic Interference Shielding Properties

Materials with EMI shielding properties include conductive polymers, carbon fibers, metals, carbon nanotubes (CNTs), graphene Nano filler material, and conductive cement-based materials. Due to their nano/small size and high aspect ratio make nano materials as good conductor as well as provide good shielding against Electromagnetic waves (EMW).

As shielding effectiveness involves adsorption, reflection and multi reflection of radiation by a material which performances as a shielding against electromagnetic waves .As these radiation waves, having high frequencies tend to have effect on electronics .More over excess exposure to such waves frequency which are hazardous in nature may increase the likelihood of tumors growth in human body thus EMI shielding in modern era is desirable.

2.4.5 Dispersion of Carbon Nanotubes (CNTs)

To achieve improved mechanical properties of composites having carbon Nanotubes, it is mandatory to properly disperse it inside the matrix. The problem normally faced with improper dispersion of CNTs is the agglomeration and bundling of tubes inside the matrix for which different surfactants need to employ to make the CNTs homogenously disperse through cement matrix. Due to nano size and Van der Waals attractions between nano tubes, CNTs form agglomerates and it is difficult to separate them with ordinary procedures. Carbon nanotubes have a tendency to agglomerate, due to presence of strong intermolecular attraction forces called “Van der Waals”. This bundle formation or agglomeration makes it difficult to disperse them in nano-composites. This agglomeration is also seen as a source of potential defect in nano-composites that hinders the true potential of CNTs [33]. The process of de-bundling the CNTs and achieving their uniform distribution in nano-composites is called dispersion. De-agglomeration can be achieved in two possible ways.

a. Erosion (Use of low stress causes slow but continuous detachment of small fragments from agglomerated bundles)
b. Rupture (By use of high stress agglomerates are split into small fragments)

Effective dispersion can also be achieved using purification and functionalization of CNTs. During synthesis process some unwanted particles remain attached to CNTs bundles [14], these particles are removed from agglomeration by purification technique. Then the bundles or agglomerates can be broken using techniques like functionalization.

Functionalization is widely divided into two types.

a. Non-covalent functionalization
b. Covalent functionalization

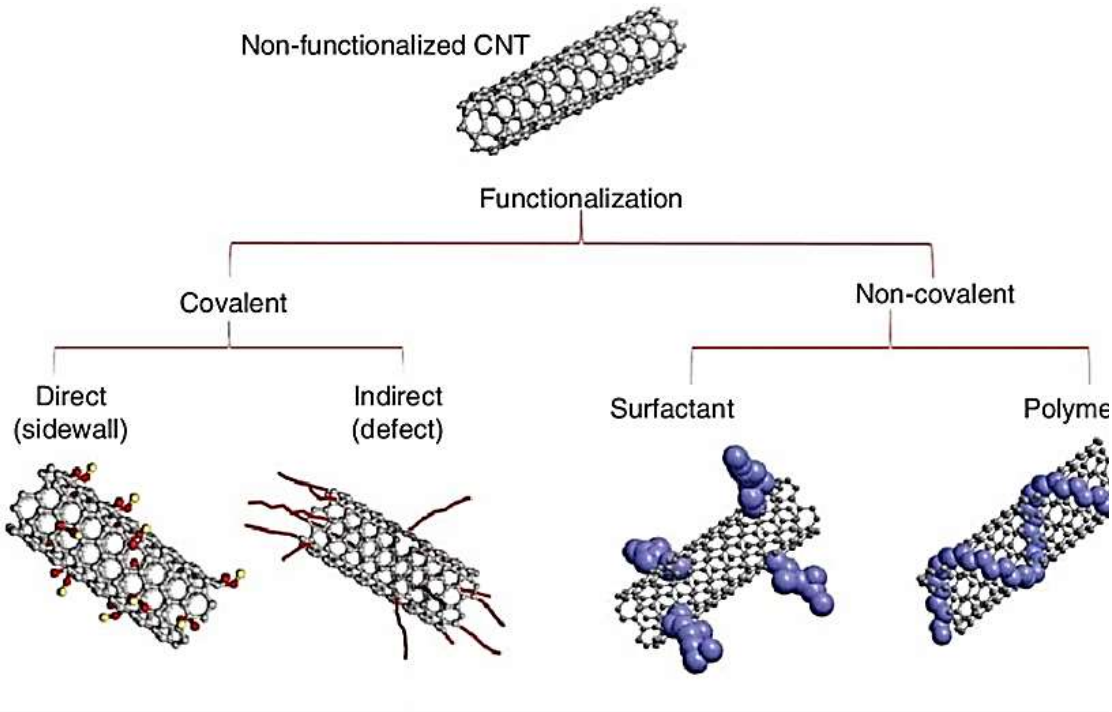


Figure 2-8 Different Techniques for Functionalization of Carbon Nanotubes (CNTs) [34]

Functionalization can be done using plasma, fluorine, acids, Amines, polymers and even bucky-balls. Most common functionalization types of CNTs are illustrated in **Figure 2-8** [34]. CNTs Dispersion or de-agglomeration in nano-composites can also be achieved by using surfactants. Surfactants like dodecyl-benzene, polyethylene glycol and sodium dodecyl sulfate have been successfully used disperse carbon nanotubes in water [14]. Physical dispersion is provided using ultrasonic energy, and this disruptive energy is provided in form of shock waves in conjuncture with aforementioned techniques.

2.5 Graphite Nanoplatelets (GNPs)

GNPs are produced by exfoliation of natural graphite. Their thickness varies from 1 to 25 nm (each layer having 0.5 nm thickness), and their diameter ranges from sub-micron level to tens of microns. This platelet shape of GNP has edges which can be chemically modified for better dispersion as compared to carbon nano tubes. It can be seen that GNP preserves excellent mechanical properties of Graphite. Due to sheet like structure of GNPs, these particles are free from agglomeration or bundles as in case of CNTs. So, their dispersion is easy as compared to CNTs. GNPs exhibit very similar properties to that of CNTs. Elastic modulus of GNPs has been reported to be 1TPa and its tensile strength ranges 10-20GPa.While surface area and aspect ratio have an average value of 2630m^2/g and 50-300 respectively. Structure of exfoliated graphite nanoplatelet is shown in **Figure 2-9**

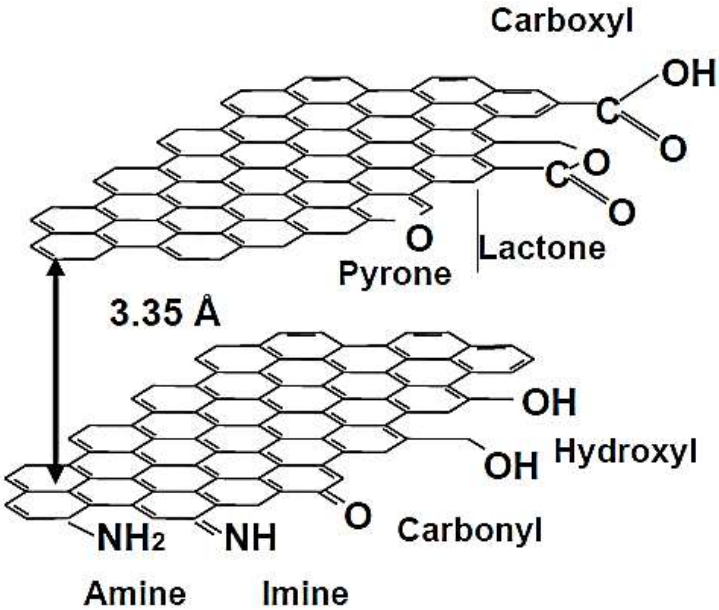


Figure 2-9 Structure of Exfoliated Graphite Nanoplatelets [35]

2.5.1 Advantages of Graphite Nano Platelets (GNPs)

The geometric properties of graphite nano materials provide them with the capabilities of controlling defect size and insemination in the composites. Graphite nano-platelets hinder the propagation of cracks by increasing the length of crack by diverting the crack from its primary path. The fracture toughness and diffusion resistance of composites in the presence of distinct reinforcement systems is increased. Close spacing of discrete reinforcement systems in composites due to the presence of graphite nano particles offers important advantages as compared to conventional (micro-scale) carbon fibers.

Graphite Nanoplatelets possesses high aspect ratio and large surface area, which are important for improving mechanical strength. Advantages of GNP over carbon nano tube are due to their platelet shape which helps these particles from entanglement problem which is very common in nano tube. At the last but not least, exorbitant price of carbon nano tube is biggest hurdle for extensive use of that material. Multiwall carbon nano tubes are priced at~$29/g, single wall carbon nano tubes cost $298/g [36] and GNPs costs $2/kg. All these conclusions revealed that potential of Graphite Nanoplatelets to be used as a substitute in preparing multifunctional nanocomposite of cement.

2.5.2 Strengthening Mechanism of Graphite Nanoplatelets (GNPs)

2.5.2.1 Toughening Effect

Intrusion of Graphite Nanoplatelets (GNPs) stops crack initiation and further propagation by crack bridging, this delays the crack opening hence causing increases its toughness [37]. This effect is called tortuosity factor which is referred as the ratio of actual depth of crack in nano intruded composite to the shortest crack depth in case of no intrusions of nano fillers.

2.5.2.2 Strengthening Effect

As modulus of elasticity of Graphite Nanoplatelet (GNP) is significantly greater than cementitious composites so under stress, load is transferred to the ITZ between GNP and the cementitious matrix. As compared with cement aggregate interface, GNP cement interface will carry a greater load thereby resulting in enhancement of the overall strength.

2.5.2.3 Small Size Effect

When the size of materials is reduced to Nano scale, qualitative changes are introduced in the material‘s properties. Although size of graphite nanoplatelets are in nano meter, they possess a very large surface area resulting in a larger interface. Along this interface the atoms are arranged in an irregular rather confusing pattern. When an external force is applied on a material, easy migration of atoms, causing resistance against deformations due to energy absorbance. Therefore intrusions of GNP particles in cementitious composites results in improved mechanical properties.

2.5.2.4 Surface Effect

When size of individual particle decreases, its surface atoms proportion increases and properties are changed as a result. If particle size is greater than atom‘s diameter, their effects are not significant as number of atoms on surface is lesser. But when the particle size is changed to the nano-scale, surface atoms ratio increases resulting in large surface area and greater surface energy. These properties helps in better interaction to achieve better absorption ability and improved chemical reactivity compared to materials with normal size. Hence, in nano intruded cement composites, at the interface, due to strong van der wall forces, greater interaction between cement matrix and GNPs are observed. They also serve as centralized reaction points around which hydration products of cement are formed making homogenous matrix. All these effects improve the microstructure of the nano intruded cementitious composites and increase their strength.

2.5.2.5 Filler Effect

Air entrained during the mixing process of cement composites cause significant reduction of density resulting in overall strength decrement. In concrete the pores size larger than 20nm are considered to be detrimental to its mechanical characteristics. Moreover, hydrated calcium silicate gel of hardened cement paste contains millions of gel pores [5]. These findings indicate that nano particles can be utilized for altering the structure of cementitious materials at Nano scale. GNP particles serve as efficient fillers due to the large surface area, small size and high surface energy.

2.5.3 Dispersion of Graphite Nanoplatelets (GNPs)

Reinforcement efficiency of GNPs can only be fully utilized if they are thoroughly dispersed. Thorough dispersion of Graphite Nano-platelets in mortar paste encounters some hindrances because of the hydrophobic nature of Graphite Nano-Platelets and strong attractive forces in-between the individual nano platelets of graphite. Different techniques used for the dispersion are the use of admixture, sonication, surfactants and functionalization.

During functionalization of graphite nanoplatelets carboxyl groups are attached to surface which change the behavior of GNPs from hydrophobic to hydrophilic, and thus facilitates their dispersion in the aqueous medium of fresh cementitious paste

Sonication technique can be used for the dispersion of the nano platelets in aqueous media. Sonication involves the use of high power, high frequency sound waves using a tip or horn, which agitate the molecules resulting in breakage of intermolecular bonds. Surfactants are amphiphilic composites which contains hydrophobic as well as hydrophilic compounds. The interaction of nano platelets with hydrophilic groups of surfactants is the essential mechanism helping the dispersion of nanoplatelets in aqueous media with the help of surfactants. Carbon nano platelets when coated by adsorbed surfactants, causes the dispersion of the nano platelets in the aqueous media.

2.6 Literature on Nano Intruded Cement Composites

2.6.1 Effect of Nano Intrusions on Mechanical Properties

- Due to their unique mechanical properties CNTs are used in cementitious systems to enhance its mechanical properties in the form of compressive and flexural strength along with improvement in fracture mechanics [38]–[41].
- Research conducted by Geng Ying Li et al. revealed that addition of CNTs in cement composites increases the compressive strength up to 19% while flexural strength enhanced up to 25% [42].
- Rashid K. Abu Al-Rub et al. stated the effect of aspect ratio on mechanical characteristics of cementitious composites. They used long and short MWCNTs, results revealed that 0.1wt% of long MWCNTs improves the flexural strength up to 65% as compared to cement matrix without CNTs. While flexural strength was increased by 269% when 0.2 wt% short MWCNTs were used. [7]
- Functionalization of CNTs through chemical reactions increase the bond strength of CNTs with surrounding cement matrix but this could also lead to

surface damage and breakage of CNTs to shorter lengths. Furthermore, acid functionalization of carbon nano tubes may lead towards its toxity [43].

- Jia-Liang Le et al. reported that durability of cement based composites can be enhanced by the addition of very small amount of GNPs [10].
- Flexural strength of cement mortar can be enhanced by the addition of GNPs. Maximum flexural strength can be achieved by the addition of 1% of GNPs [9], [44].
- In addition to flexural strength it was found that chloride migration, water permeability and chloride diffusion in concrete can be abridged by the addition of GNPs [45], [46].
- Qiong Liu et al. studied the effect of GNPs intrusions in cement mortar with variation in w/c and results revealed that by the addition of 0.8% of GNPs compressive strength was increased by 15% and 36% at w/c of 0.5 and 0.6 respectively and at w/c of 0.7 compressive strength was increased by 14% by the addition of 3.2% of GNPs [47].
- Baoguo Han et al. concluded that GNP particle act as nuclei due to its small size effect resulting in compact dense microstructure of cement composites in hardened state. Due to Surface effect of GNPs Van der Waals forces results in enhanced bonding with the surrounding cement matrix which not only stops the crack initiation but also helps in delaying the crack propagation by diverting the crack path due to its 2-dimenstional plate like structure [48].

2.6.2 Effect of Nano Intrusions on Electrical Resistivity on Cement Composites

- Strong sp2 covalent bonding between atoms with in CNT, make it possible to pass a current density of 4 × 109 A/cm2, even greater than copper without breakdown [28].

- For every conductive filler there is an optimum concentration at which, if dispersed evenly in the cement composite, electrical conductivity of matrix increases by several times thus converting a nonconductive cement matrix to semi conductive and/or conductive composite. That optimum concentration is termed as percolation threshold [49]–[51].
- In 2002, Research revealed that electrical conductivity of CNTs reinforced cement matrix is dependent on variation of fiber length as well as on fiber volume fraction. It is evident that electrical conduction network of carbon reinforced cement matrix could not formed if volume concentration of fiber is below a certain value even long fibers are utilized. While length of fiber has an effect on the threshold percolation value with negative relationship. So it can be concluded that fiber volume concentration effects electrical conductivity of carbon reinforced cement based matrix more than fiber length [50].
- CNT intrusion to cement based composite increases the electrical conductivity up to 8 orders while decrease in electrical resistivity to almost 1 Ω·cm is reported [52].
- It is further investigated that 0.1% of CNT dispersed using LAS surfactant gives a remarkable decrease in electrical resistivity of cement based nano composite [53].
- The work prompting to this progress involved improvement of self-sensing cement based composites which includes CNTs in conjunction with silica fume [54], functionalizing by surface treatment [42], [55] and mixing along with dispersion of CNT [56], [57].
- Recently a study revealed that Electrical conductivity of CNT based cement

matrix increases with curing time regardless of mixing method along with improved mechanical properties i.e. compressive strength [56].

- Electrical resistivity of cement based matrixes mainly depends upon the capillary water, containing salts, which act as electrolyte and passes electric current. Electrical resistivity of dry hardened cement is about 10^{15} ohm.cm while wet hardened cement has resistivity in the range of semiconductor with a value of 10^{8} ohm.cm [58][9].
- Main source of electrical conductivity of GNP are its pi-electron which participate in pi-bonding between its layers [59].
- Study revealed that Percolation threshold for cement mortar containing GNPs as conducting material remains almost constant regardless of the initial curing time. Percolation threshold for mortar containing GNPs is around 2% [60].
- Recent Research has been conducted on electrical resistivity of cement mortars containing GNPs having different properties in order to compare electrical conductivity of composites. Study showed that same conductivity can be achieved with lower dose of GNPs which results in reduction in cost. Difference in electrical conductivity is reported on the basis of different physical properties of GNPs. Graphene nanoplatelets having smaller size, greater aspect ratio and larger surface area showed a remarkable conductivity as compared to GNPs having smaller surface area and lower aspect ratio. Results showed that size of specimen is also one of the major factors during the determination of electrical resistivity. As the path of the current is longer smaller will be the chances of having a uniformly distributed network of GNPs along the path which results in high resistivity. So Size of specimen is also one of the major factor which must be considered during the determination of cement based composites having

GNPs [9].

- As strength of specimen depends on its age, similarly electrical resistivity of GNPs based cement composites also depends on age. Electrical resistivity of specimen increases with time until specimen gain a stable structure which is mainly 28 days after that electrical resistivity attains a constant value keeping other factors constant. Increase in resistivity can be justified that during early ages water is being consumed during hydration process which ultimately results in increase in resistivity. Another factor which leads towards increase in electrical resistivity is hydration products. These products may damage the connective network of GNPs which leads towards increase in resistivity [56][9].
- Temperature of specimen is also a major contributing factor towards electrical conductivity of cement composites having GNPs. As temperature of specimen increases, an increase in electrical conductivity is reported. Increase in temperature results in an increase in number of free electron from pi bonds which contributes towards increase in electrical conductivity. Second reason for this increase in conductivity is due to increase in temperature diffusion rate of ions increases which ultimately results in this increased electrical conductivity [9].

Table 1 Literature on Electrical Resistivity of Nano Intrusions

Reference	Author	Year	CNT/GNP Content	Resistivity	Remarks
[61]	Anna Laura Pisello et al	2017	2 wt % of MWCNTs	9.091e6 ohm*	Volumetric Resistance
[61]	Anna Laura Pisello et al	2017	2 wt % of GNPs	1.881e5 ohm*	Volumetric Resistance
[60]	Ali Al-Dahawi et al	2016	0.55 wt % of CNT*	Changed from 90.65 to 33.93 Ω m	Percolation Threshold
[60]	Ali Al-Dahawi et al	2016	1 wt % of CNT	Changed from 90.65 to 22.25 Ω m	
[60]	Ali Al-Dahawi et al	2016	2 wt % of GNP*	Changed from 90.65 41.10 Ω m	Percolation Threshold
[60]	Ali Al-Dahawi et al	2016	5 wt % of GNP	Changed from 90.65 to 33.89 Ω m	
[40]	Ali Al-Dahawi et al	2016	0.25 wt.% of CNT	Changed from 1797.3 to 497.3 ohm.m*	180 Days Curing
[40]	Ali Al-Dahawi et al	2016	0.25wt % of GNP	Changed From 1797.3 to 519.4 ohm.m*	180 Days Curing
[25]	Maria S. Konsta-Gdoutos and Chrysoula A. Aza	2014	0.1 wt % of CNT*	4.2e6 ohm.cm	Sample dried at 95° C for 3 days
[25]	Maria S. Konsta-Gdoutos and Chrysoula A. Aza	2014	0.1 wt % of CNT*	0.26e6 ohm.cm	Sample dried at 60° C for 3 days
[10]	Jia Liang lee et al	2014	4.8 wt % of GNP	Changed from 34000 ohm.cm to 3000 ohm.cm	
[9]	HUANG SIXUAN	2012	5 wt% of Graphite nano platelets*	813 ohm.cm**	*Wt % of cement and sand ** Cube specimen

2.6.3 Effect of Nano Intrusions on Electromagnetic interference shielding

Electromagnetic interference shielding is promoting as one of the multifunction aspect of cementitious composite due to the abundance and sensitivity of electrical systems, electronics as well as medical devices which are most likely to be negatively affected by electromagnetic waves which are infecting our surrounding with electromagnetic waves (EMWs) .The interference of these radiation can block signals of sensitive equipment, burn out electric circuits or even results in explosion. Existence of EMWs in the atmosphere is such a frightening level which elevates the dangers of electromagnetic interference, which may interrupt the usual functionalization of many electronic devices. Too much contact to such emissions in atmosphere may cause negative effect to human health, as these harmful rays have negative effect to human body thus shielding is essential to keep these sensitive devices from interfering with other's radiations. Such issues have motivated different researcher to explore new ways by which we can increases shielding effect against (EMWs).

- Composite material containing filler having unit size smaller then filler having larger unit size is more effective in shielding against (EMW).Cement [62] as far now possess poor shielding effect against (EMI) but intrusion of filler material having particles size in Nano and have high aspect ratio e.g graphite [37] carbon nanotubes (CNTs) [63][62][64][65][63][66] carbon fibers[67] make them a better shielding against (EMW) as they have conductive properties. Efforts have been made to improve (SE) of cement/matrix composite by intrusion of Nano/conductive fillers.
- Study investigated that the shielding effectiveness of varying CNTs and attained maximum shielding effectiveness at 0.6 wt% of Carbon Nanotubes in cement composite having frequency range of 2-8 Giga Hz and 8-18 Giga Hz [68].

- Investigations revealed the effect of dispersion using 0.6 wt% Carbon Nanotubes and silica fume content as 20 wt% in cement composite and attained maximum shielding effectiveness at different frequencies which were 0.94 Giga Hz, 2.46 Giga Hz and 10 Giga Hz [64].
- Maximum (SE) attained in cement composite that is 40 dB at 1 GHz frequency using 1.5vol% discontinuous carbon filaments having 0.1 mm diameter .However cement is less costly than polymer and to make cement composite for shielding from electromagnetic waves are useful but using carbon fibers or Nano materials in cement composite are however expensive [69].
- Studies showed that using flexible graphite which is the pure form of graphite with varying thickness can enhance the shielding efficiency as high as 101.9 dB to 129.4 dB at range pf frequency as 1.0 to 2.0 Giga Hz due to their high aspect ratio , conductivity and larger specific surface area [70].
- The effect of MWNTs on shielding effectiveness performance and attained maximum shielding with the incorporation of 1.5% of MWNTs in cement matrix at frequency of 0.8 GHz [71].
- Proper amount of Graphite in cement composite improve or enhance the shielding effectiveness and attained the maximum shielding by using 20% graphite power at frequency range in between 2-18 GHz [72].
- Using 3D CNTs/graphene hybrids in cement matrix will meet dispersion criteria and provide enhance absorption in matrix against (EMW) [73].
- Use of graphene oxide (GO) 30wt% in conjunction with Ferro fluid in cement composite enhances the shielding effectiveness against (EMW) of 46 Db at frequency range of 8.2-12.4 GHz [74].
- It was concluded that using Graphite powder as filler in cement composite matrix as it have high conductivity enhance the shielding effectiveness of 10-40dB when increasing the content of graphite by 30 vol% at frequency range in between 200-1600 MHz [62].

CHAPTER 3

EXPERIMENTAL WORK

3.1 Materials

Ordinary Portland cement of grade 53 was purchased under a brand name of BESTWAY CEMENTS, meeting all the requirements of ASTM C150 and EN/196/1 standards. According to ASTM C188 specific gravity of cement was evaluated to be 3.06. Chemical composition of cement is given in **Table 2**. Locally available sand having specific gravity of 2.6 and fineness modulus of 2.9 was used as fine aggregate. Poly carboxylate based third generation super plasticizer named Master Glenium, conforming to EN 934-2 and ASTM C494 Type F was used to make workable mortar.

MWCNTs used in this research were supplied by US Research Nanomaterials, Inc. Multi-walled Carbon Nanotubes were synthesized by Chemical Vapor Deposition technique with outer diameter of 20-30nm and length ranges 20 to 30µm. Physical properties and chemical composition of MWCNTs are given in **Table 3** and **Table 4** respectively. Graphite Nano/Micro Platelets were obtained by milling process of ordinary graphite powder.

Table 2. Chemical Composition of Cement

`	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	SrO	K2O	Cr_2O_3
68.14	15.62	8.61	3.69	1.33	1.82	0.75	--	--

Table 3. Properties of MWCNTs

	Outside Diameter (nm)	Inner Diameter (nm)	Length (µm)	Purity (%)	Specific Area (m^2/g)	True Density (g/cm^3)	Ash Content (wt %)
MWCNTs	20-30	5-10	10-30	>97	110	2.1	<1.5

Table 4. Chemical Composition of MWCNTs

C	Ni	Cl	Fe
98.4	0.92	0.44	0.22

3.2 Preparation of Nano Particle Dispersion

CNTs and GNPs have almost similar mechanical properties which make them as an alternative of each other. Till now these two materials are separately being used in enhancing the properties of cement composites so all the studies are done to disperse these nanomaterials separately. In this study, authors have tried to develop a dispersion scheme to have a highly dispersed composite of both CNTs and GNPs. This study will leads to a new era of multifunctional cement composites containing both CNTs and GNPs at the same time to have economical multifunctional cement composites with enhanced properties due to well dispersed nanomaterials in cement matrix.

Aqueous solution was prepared with total of 0.08 wt% of nano Particles related to binder content. **Table 5** shows the variation of CNTs and GNMPs in aqueous solution in different ratios with commutative of 0.08 wt% of binder. For Sonication process Jac 1505 bath sonicator was used at amplitude of 40 KHz.

3.3 Selection of Dispersant

Due to hydrophobic nature of Nano materials i.e. CNTs and GNMPs, their dispersion in aqueous solution is difficult. In addition to this, due to strong van der wall forces between individual particles, CNTs tends to agglomerate which make lumps of nano particles so achievement of evenly dispersed nano intruded cement mortar is difficult.[75] Based on recommendations in recent studies[9], [76] Acacia Modesta was

Figure 3-1 Schematic Diagram for Dispersion of Nano Materials in Aqueous Solution

used as surfactant to achieve well dispersed aqueous solution of CNTs and GNMPs. A schematic diagram representation stages in dispersion of nano materials in aqueous solution is shown in **Figure 3-1 Schematic Diagram for Dispersion of Nano Materials in Aqueous** Solution.

3.4 Mix Proportions

A total of 11 formulations were prepared. The aim was to identify an optimum proportion of CNTs and GNPs in cement mortar in order to find best mix proportion which has superior results along with the least cost. As CNTs were much costly as compared to GNPs. Cement to sand ratio was kept as 1:2 and water to cement ratio was 0.45. A liquid based super plasticizer was also introduced in the mix in order to get a workable cement mortar. Super Plasticizer was added with respect to cement in a proportion of 0.75%. Water and super plasticizer were kept constant in each mix. Mix proportions are shown in **Table 5**.

Table 5. Sample Description

Mix Proportions of Hybrid nano Intruded Cement mortar							
Sr. No.	**Formulation ID**	**CNT/ GNP**	**CNT Amount (%)**	**GNP Amount (%)**	**Acacia Gum (%)**	**S.P (%)**	**W/C**
1	CS (Control Sample)	--	--	--	--	0.75	0.45
2	CS-AG	--	--	--	0.08	0.75	0.45
3	C1G0	1:0	0.08	0	0.08	0.75	0.45
4	C1G0.125	1:0.125	0.071	0.009	0.08	0.75	0.45
5	C1G0.250	1:0.250	0.064	0.016	0.08	0.75	0.45
6	C1G0.5	1:0.5	0.053	0.027	0.08	0.75	0.45
7	C1G1	1:1	0.040	0.040	0.08	0.75	0.45
8	C1G2	1:2	0.027	0.053	0.08	0.75	0.45
9	C1G4	1:4	0.016	0.064	0.08	0.75	0.45
10	C1G8	1:8	0.009	0.071	0.08	0.75	0.45
11	C0G1	0:1	0.000	0.080	0.08	0.75	0.45

3.4.1 Mixing Regime and Preparation of specimens

Mixing process of materials conforming to ASTM C109/C109M-01 was performed using standard Hobart Mixer capable of rotating from 140± 5rpm to 280±5 rpm. For mixing purpose well dispersed aqueous solution of Nano particles were prepared by Sonication for 30 mins using a Jac 1505 bath sonicator at amplitude of 40 KHz. Surfactant, w/c and super plasticizer content was kept constant in all the formulations. The detail quantities are given in the **Table 4**.

Cement mortar prismatic specimens of size 160x40x40mm were casted to study Flexure properties, fracture mechanics and electrical conductivity. To perform electrical conductivity tests copper mesh of 36x60mm in size with an average opening of 6x6mm were introduced in the fresh cement mortar confirming proper embedment and bond with the surrounded matrix.

3.5 Testing Procedure

3.5.1 Water Absorption:

Water absorption of hybrid nano intruded cement mortar was measured by following ASTM C642 standards. After proper mixing and casting hybrid nano intruded cement mortar specimens were demolded after 24 hrs. After proper nomenclature samples were weighted as W1 with highly accurate electronic weighing balance and placed in curing tanks under water. After 28 days of water curing specimens were removed from water and surface were dried with towels and surface saturated specimens were again weighted as W2. Water absorption of 28 days water cured hybrid nano intruded cement mortar specimens were calculated using following equation.

$$\text{Water Absorption (\%)} = ((W2-W1)/W2)*100$$

3.5.2 Shrinkage Investigation:

Linear shrinkage response of fresh hybrid nano intruded cement mortar were investigated by using a German modified Shrinkage apparatus having a capability to measure the linear change in length up to 0.31 μm. After proper mixing fresh cement mortar specimens were placed in the measurement chamber of the apparatus and 36 hours of data was recorded for each formulation.

3.5.3 Flexural Strength:

Three point bend test conforming to ASTM C348-14 was conducted to evaluate the flexural strength of hybrid nano intruded cement mortar specimens having dimensions of 160x40x40mm. Test was performed for 3 specimens for each formulation at an age 28 days. Load controlled UTM was used at a rate of 0.025 MPa/min with clear span of 120mm.

3.5.4 Compressive Strength:

Compressive strength test for hybrid nano intruded cement mortar was conducted according to ASTM C349-14. After flexural strength test two halves of the each specimen were examined against any visual crack other than the flexural break path and then tested under compression in order to have idea about compressive strength of cement mortar. The test was conducted using load controlled Compression machine at a rate of 0.25 MPa/min.

3.5.5 Fracture Mechanics:

To evaluate mechanical properties i.e. Peak flexural response, Elastic modulus and Fracture toughness of hybrid nano intruded cement mortar specimens of size 160 x 40 x 40 mm were tested under strained controlled 20KN Shimadzu machine at a rate of 0.003mm/min. Before performing the test, 12mm deep and 2mm wide notch was introduced in each specimen using S.M.T 8723 grinder.

3.5.6 Electrical Resistivity:

Four probe method was used to determine the electrical resistivity of hybrid Nano intruded cement mortar. To serve the purpose 4 cupper meshes of size 60 x 36mm were imbed in fresh specimens during casting at spacing of 40 and 80mm from both ends. Later on these meshes served as electrode for the measurement of resistivity by 4 probe method. Resistivity was measure over a range of 3-30 Volts. Inner electrodes served as point to measure the voltage drop while outer 2 electrodes were used to measure the electric current flowing through the specimens.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Dispersion of hybrid Aqueous Solution of CNTs and GNMPs

In order to achieve a well dispersed aqueous solution of hybrid CNTs/GNMPs, bath Sonication technique was adopted with Nano particles to surfactant (Acacia Gum) ratio of 1:1 and time of Sonication was 30 minutes. Surfactant type, ratio and time of Sonication was selected based on the previous studies.[9], [76], [77] In order to characterize the dispersion results UV spectrometry was done to have a better understanding in form of absorption by the dispersed solution which relates to the degree of dispersion and homogeneity of solution [75]. As reported in the previous studies absorbance value was recorded on a single wavelength i.e. 500 nm because this wavelength is virtually unaffected by ambient conditions of nanotubes as at this wavelength [78], [79].

Results of UV-spectroscopy illustrated that maximum absorbance was observed in case of C1G0 i.e. Formulation only having CNTs, because all the parameters were set for better dispersion of CNTs alone referred to previous studies [9], [76], [77]. Relatively less absorbance value in cases of formulations having GNPs can be justified as due to the presence of larger particles of GNMPs the collusion between CNTs and GNPs increases which not only absorb more energy needed to disperse the particles but also when a larger particle i.e. GNMPs collide with CNTs due to momentum CNTs tends to roll up on the surface of GNMPs which impacted negative effects on the dispersion of particles in aqueous solution. This decrease in absorbance value could be due to the barrier effect of 2 dimensional GNPs which obstructed the sonication energy to reach the desired site i.e. CNT agglomerations.

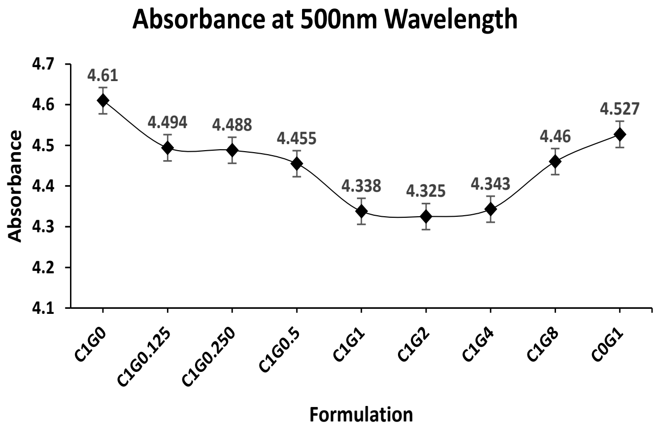


Figure 4-1 UV Spectroscopy Results

Figure 4-1 illustrates the absorbance value at 500 nm. When we move from C1G0 (CNTs alone) to C1G1 (equal quantity of CNTs and GNMPs) the overall dispersion of the solution decreases and can be demonstrated in the form of absorbance value. Similarly, when we move from C1G1 to C0G1 (GNMPs alone) again the absorbance value increases which shows increase in dispersion. This increase can be justified by the increase in homogeneity of solution having same size of particles and having the equal momentum in form of weight. As absorbance value of C0G1 is lesser than C1G0 which is due to the larger size and weight of GNMPs which needs more energy to disperse larger particles. Similarly, higher weight mean less number of individual particles in the solution which overall results in lesser amount of absorbance upon the dispersion [80].

4.2 Density and Air Content

Density of hybrid nano intruded cement mortar is given in the **Figure 4-2**. Density of control sample CS was found to be 2.2 g/cc which is the lowest in all the formulations. While the density of fresh cement mortar containing Acacia Gum i.e. CS-AG is 2.25 g/cc this slight increase in density is due to the presence of acacia gum. This is due to the hydrophilic nature of acacia gum [81], which absorbs water in its initial stage of mixing in cement mortar resulting in denser medium [82]. Intrusion of Carbon nano tubes also enhanced the density due to its filler effect which not only filled the small pores but also better surface interaction with surroundings hence resulting in dense micro structure [8]. This increase in density can also be justified by the dispersion results given in the **Figure 4-1**. So well dispersed CNTs and their filler effect resulted in dense microstructure. While lowest density is observed by C1G1 which could be due to poor dispersion as compared to other formulations. Similarly, density of C0G1 is found to be 2.29 g/cc. This can be justified by filler effect of GNMPs due to which overall porosity, pore size and pore connectivity is reduced resulting in increase in density [9].

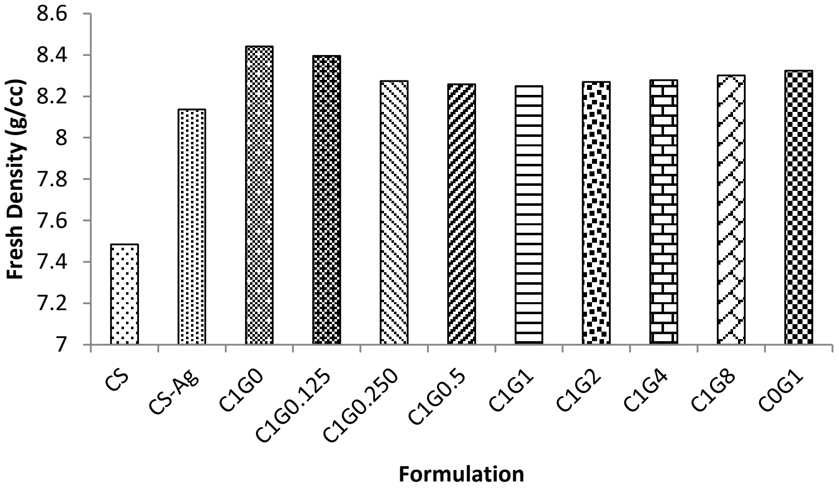


Figure 4-2 Density (g/cc) of Hybrid Nano Intruded Cement Mortar

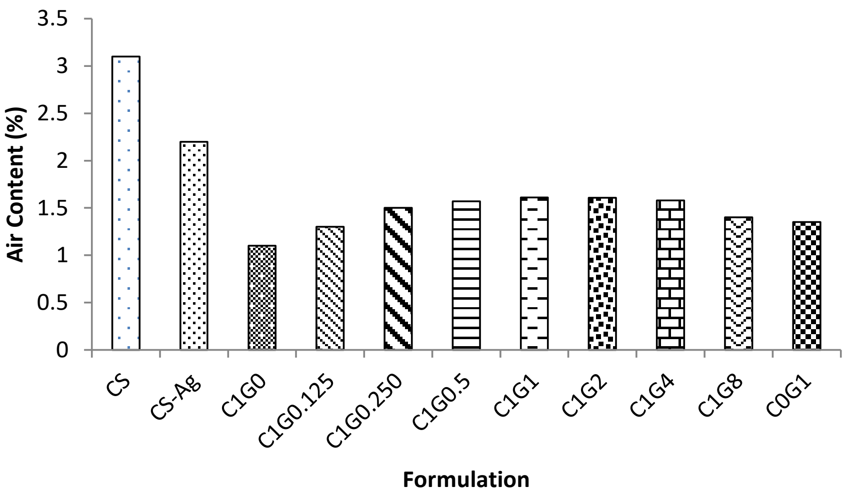


Figure 4-3 Air Content (%) of Hybrid Nano Intruded Cement Mortar

Luftgheltsprufer testing apparatus was used in determining the air content of cement mortar. Density is directly related to air content at initial stage. Higher the air content lower will be the density of cement mortar [83]. This relation can be justified as material containing more porosity and larger pore sizes will result in higher air content and lower will be the fresh density. C1G1 having lowest density among the formulations with hybrid intrusion of nano particles on the other hand air content of C1G1 in higher among the nano intruded cement mortar as illustrated in **Figure 4-3**. Homogenous and well dispersed nano particles not only cause reduction in air content but also density of hybrid intruded cement mortar is increased resulting dense microstructure due to filler effect on nano intrusions.

4.3 Water Absorbance:

Figure 4-4 shows the water absorption of conventional cement mortar and hybrid nano intruded cement mortar. Cement mortar with CNTs/GNPs have less water absorption as compared to cement mortar without nano graphitic intrusions. C0G1 having graphite nano platelets showed lowest water absorption of 0.57% after 28 days of curing and this is due to the 2 dimensional shape of the graphite nano platelets which act as a membrane to stop penetration and absorption of water into the pores in cement mortar hence causing overall reduction in water absorption [45].

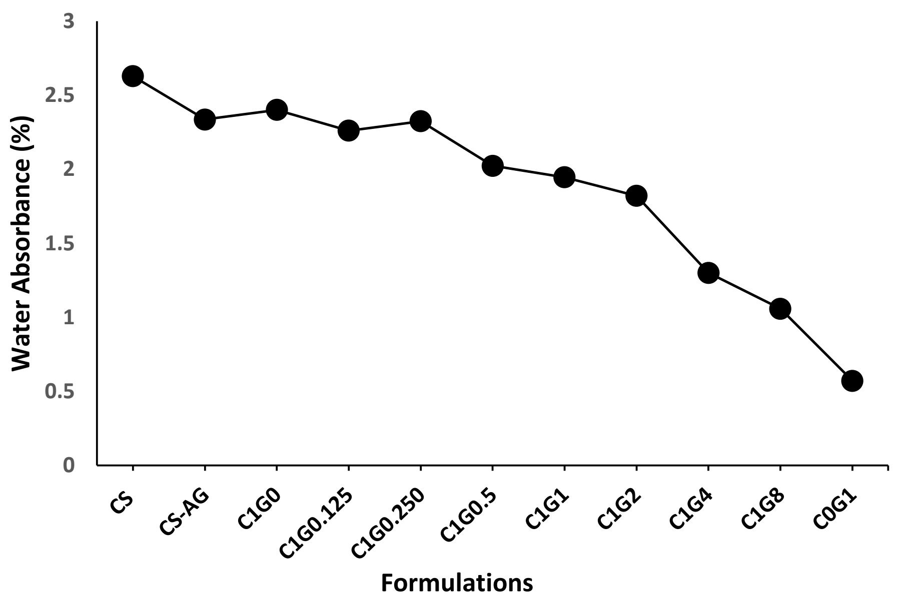


Figure 4-4 Water Absorption (%) of hybrid nano intruded cement mortar

While control sample CS without any nano intrusions showed the maximum water absorption with a value of 2.6% at 28 days of curing. C1G0 showed 2.4% of water absorption at 28 days of water curing and it can be concluded that CNTs are not so much effective as a barrier against water penetration due to their 1-dimensional shape. Percentage decrease in water absorption of nano intruded cement mortar compared to conventional one without any nano intrusions after 28 days of curing are 78%, 25.9% and 8.64% respectively for C0G1, C1G1 and C1G0.

4.4 Shrinkage Response:

Volumetric shrinkage has significant contribution in the initiation and propagation of nano cracks at early ages therefore Shrinkage response was studied. Early age shrinkage response of cement mortar with different ratios of dispersed CNTs and GNPs at controlled conditions of 95% humidity and 25°C temperature is shown in **Figure 4-5**. It was observed that intrusion of nano graphitic particles greatly enhanced the early age response of cementitious mortar against linear shrinkage.

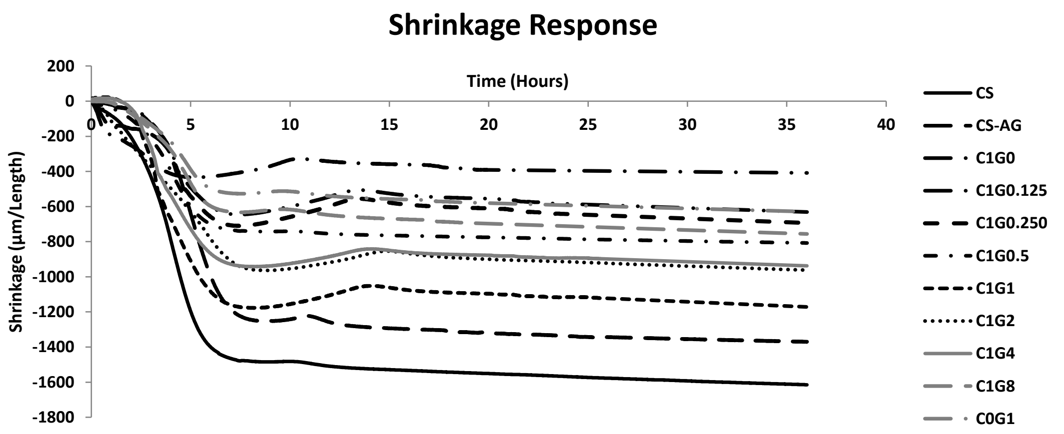


Figure 4-5 Total Linear Shrinkage with hybrid additions of CNTs and GNPs

Presence of small pores at early stages contributes towards the shrinkage. Reduction in pore size or number of pores can significantly reduce the overall shrinkage of cement mortar. So, Intrusions of well dispersed nano material i.e. CNTs and GNPs helped in the filling of the pores present at nano/micro scale resulting in significant improvement in the shrinkage response at early ages. Maximum shrinkage decreases by 74.8% was observed in C1G0 as expected due to better dispersion of CNTs and higher aspect ratio which have not only filled the pores but also retarded the crack propagation at early ages [84]. Shrinkage arrest in CS-AG was recorded as 19.3%. This is attributed towards the hydrophilic nature of Acacia gum which absorbs water during mixing and on later stages releases this water which contributes towards the temperature and shrinkage reduction [85]. Minimum shrinkage reduction observed in case of C1G1 was 31.7%. This less effective response can be justified by the non- dispersion of nano material in aqueous solution as shown in **Figure 4-1**.

4.5 Mechanical Properties:

4.5.1 Compressive Strength:

Compressive strength of hybrid nano intruded cement mortar at different ages is shown in Error! Reference source not found.. Intrusions of graphite nano materials into the ement mortar enhanced the overall mechanical properties. Compressive strength of cement mortar having graphite nano materials

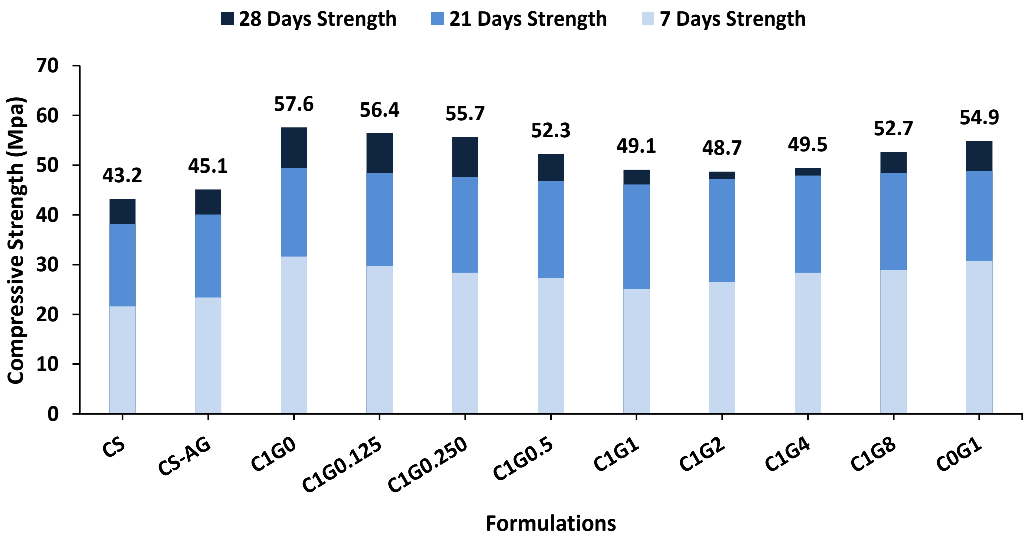


Figure 4-6 Compressive Strength of hybrid nano Intruded Cement Mortar at different ages

was found to increase with adding the nano material content and the highest strength obtained was found when we only added carbon nano tubes by 0.08% by weight of cement. Maximum strength at 28 days was found to be 57.6 MPa which is nearly 33% higher strength as compared to controlled sample. Similarly, Compressive strength observed by C0G1 i.e. formulation only having GNPs, is 54.9 MPa which illustrates the compatibility of GNPs with cement mortar and make it an excellent replacement to the high cost CNTs. C0G1 observed almost 27% increment in compressive strength.

Minimum strength was showed by C1G1 which is 48.7 MPa with 13.6% of strength enhancement as compared to control cement mortar. The overall behavior of Graphite nano Particles i.e. CNTs and GNPs towards the cement mortar was encouraging. Improved dry density, low air content and excellent dispersion lead to this improved compressive strength which evidences the filler effect of graphite nano particles and the bondage of these particles with the surrounding cement matrix [86].

4.5.2 Flexural Strength:

Flexural strength of cement mortar with varying concentration of CNTs and GNPs with cumulative content of 0.08% by weight of cement at 28 days of curing is shown in Error! Reference source not found.. Flexural strength of C1G0 was observed to be 10.17 Pa which is 124.4% higher than plain cement mortar. This extraordinary flexural strength increment can be illustrated by the higher expect ratio of CNTs, their crack bridging effect and pull out behavior which leads to enhanced flexural strength [87]. Flexure strength gradually decreases as we replacement CNTs with GNPs and minimum flexural strength was observed in C1G2 which is 7.18 MPa that was noticeably higher than the plain cement mortar by 58.5%. This reduction in strength can be justified by poor dispersion of CNTs **Figure 4-1** because addition of GNPs badly affected the dispersion of CNTs in aqueous solution. In case of GNPs alone i.e. C0G1 the response is still appreciable and there is increase in flexural strength to 8.68 MPa as compared to plain cement mortar which has overall

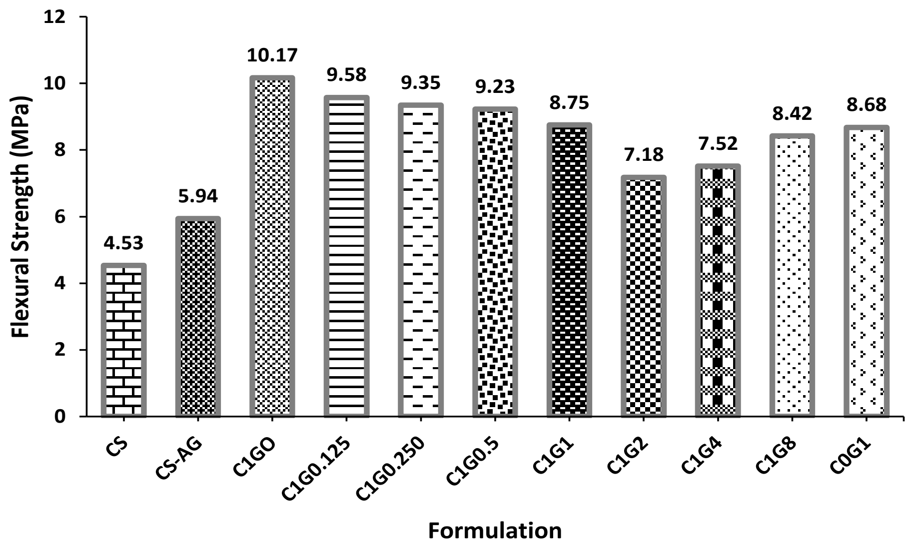


Figure 4-7 Flexural Strength of Hybrid nano Intruded Cement Mortar at 28 Days of Curing

Strength of 4.53 MPa. 66%, 85.96% and 91.61% strength interment was observed in C1G4, C1G8 and C0G1 respectively.

4.6 Fracture Properties of Cement Mortar:

4.6.1 Stress Strain Response in Flexure:

Stress strain response of plain cement mortar and with hybrid intrusions of CNTs and GNPs is presented in **Figure 4-8**. Stress strain response revealed an appreciable increase in the value of flexure strength as we added graphitic nano particles mortar. From **Figure 4-8** it is evident that well dispersed graphite nano particles not only increase the flexural strength but also the ductility which corresponds to higher strain value at ultimate failure [88]. In case of C1G0 maximum flexure strength (10.17 Mpa) was observed while its ultimate failure strain was higher than the control formulation. Ultimate failure strain in C1G0 was observed to be 0.88% as compared to 0.67% in case of control formulation resulting in overall 30.57% increase in ultimate failure strain. This increase in ductility could be justified by crack bridging, crack diversion and pull out behavior of CNTs [89]. As we increase the content of GNPs flexure strength of cement mortar increases as compared to control formulation but in this case filler effect of GNPs compact the micro structure resulting in dense matrix hence increasing the toughness of cement mortar which resulted in failure at low strain values as compared to C1G0 [9].

In Case of C0G1 maximum flexure strength was observed to be 8.68 MPa while corresponding strain value to be 0.74% resulting in overall 8.9% increase in strain as compared to control formulation. Similarly in case of C1G8 0.65% ultimate strain was observed which is 4.69% less than the control formulation. This decrease in ultimate strain can be justified by dense micro structure. Maximum Strain value (1.06 %) was observed by C1G2 corresponding to least flexural strength.in hybrid nano intruded formulations. Overall 57% increase in strain was observed as compared to control formulation which could be due to air voids which not only cause higher deflections at lower stress value but also decreases the ultimate failure stress.

4.6.2 Fracture Toughness:

Stress strain response of hybrid nano intruded cement mortar revealed as appreciable increase in first crack toughness with the corresponding increase in graphite nano particle content. While no improvement in post crack behavior is observed.

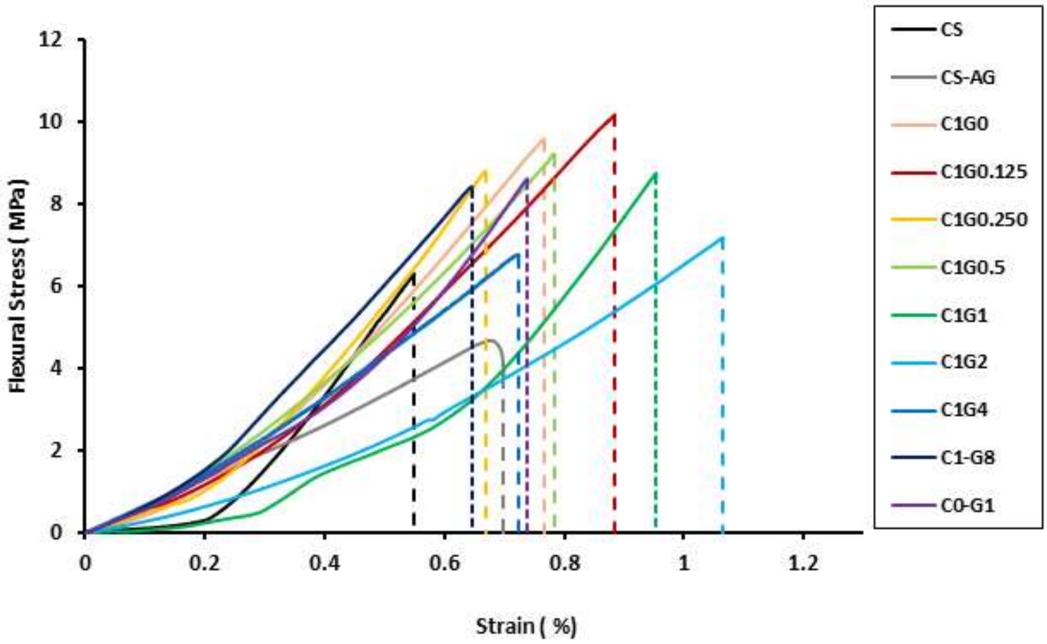


Figure 4-8 Stress Strain Response of Hybrid nano Intruded Cement Mortar

An overall toughness improvement of 60.2% was observed in case of C1G0 as compared to control formulation. This improved toughness could be the result of energy distribution along the nano particles and crack bridging effect of CNTs [88]. While maximum toughness improvement 86.8% was observed in case of C1G2 this could be due to the higher strain values resulting in overall toughness improvement. Almost 50% increment in value of first crack toughness was observed in case of C0G1. This improvement is due to plate like structure of graphite nano Platelets (GNPs) which not only provide better surface area to be in contact with surrounding matrix but also plays an important role in crack discontinuity[9], [48]. Low concentrations of nano material resulted in nearly no improvement in the post crack behavior of the hybrid nano intruded cement mortar as shown in **Figure 4-8**.

Table 6 Flexural Response of Hybrid nano Intruded cement Mortar at different concentrations of CNTs and GNPs at 28 days of curing

Denotation	Modulus of Elasticity (Mpa)	Flexural Strength (Mpa)	Toughness (KJm^{-3})	Ultimate Strain (%)
CS	6.689364	4.53	347.6	0.68
CS-AG	10.80751	5.94	281	0.55
C1GO	11.50154	10.17	557	0.88
C1G0.125	12.5118	9.58	533.17	0.77
C1G0.250	13.99917	9.35	573.67	0.67
C1G0.5	11.7938	9.23	625	0.78
C1G1	9.181666	8.75	600	0.95
C1G2	7.252525	7.18	649.38	0.99
C1G4	10.40931	7.52	475.8	0.72
C1G8	13.04513	8.42	492	0.65
C0G1	11.76561	8.68	520	0.74

4.7 Elastic Modulus:

Elastic modulus (Ec) is also one of the important parameter to relate material stiffness. Material stiffness is related to micro structure of the material. In case of hybrid nano intruded cement mortar, highest elastic modulus is observed in C1G0.250 due to its compact internal structure as compared to control formulation. Overall 109% increment was observed as shown in the **Figure 4-9**. Compact internal structure of cement mortar due to the presence of well dispersed CNTs and GNPs resulted in low porosity which resulted in the elastic modulus. While in case of C1G2 just 8.4% increment is observed this could be due to the poor dispersion of nano material that lead to high porosity which resulted in high deformations at lower load values hence decrement in the values of elastic modulus was observed. Though poorly dispersed graphite nano particles possess weaker interaction with surrounding matrix yet its presence in the matrix tends to create crack-discontinuity owing to the added heterogeneity in the form of internal voids and hence improved ultimate rupture strain.

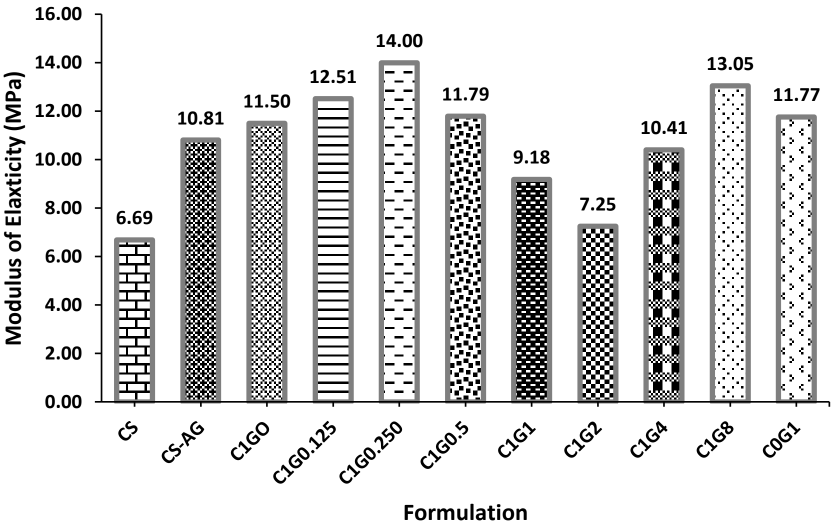


Figure 4-9 Elastic Modulus of Hybrid Nano intruded Cement mortar at 28 Days of curing

4.8 External Sulphate Attack

Resistance against external Sulphate attack on cement mortar mainly depends on permeability and water absorption capacity [90]. Effect of external Sulphate attack in terms of strength reduction of hybrid nano intruded cement mortar is shown in **Figure 4-10**. Maximum compressive strength reduction of 36.3% was observed in control formulation in which no nano intrusions were made. In control formulation 28 days compression strength was reduced from 43.2 Mpa to 27.5 Mpa after submersion of sample in Sodium Sulphate solution for 28 days. This reduction in strength is caused due to penetration and reaction of Sodium Sulphate solution with hydration products as initially porosity was maximum in this sample. Maximum resistance was shown by C0G1 and overall 12.2% of strength reduction was observed. Minimum water absorption contributed towards this resistance against strength reduction due to external Sulphate attack. In case of C1G0, structure of CNTs doesn't resist against penetration of Sulphate solution resulted in strength reduction. Overall 30.2% strength reduction was observed in C1G0. This strength reduction in all cement mortar specimens could be explained by the formation of delayed ettringite and gypsum formation which is expansive in nature resulted in internal cracks due to internal stresses [91].

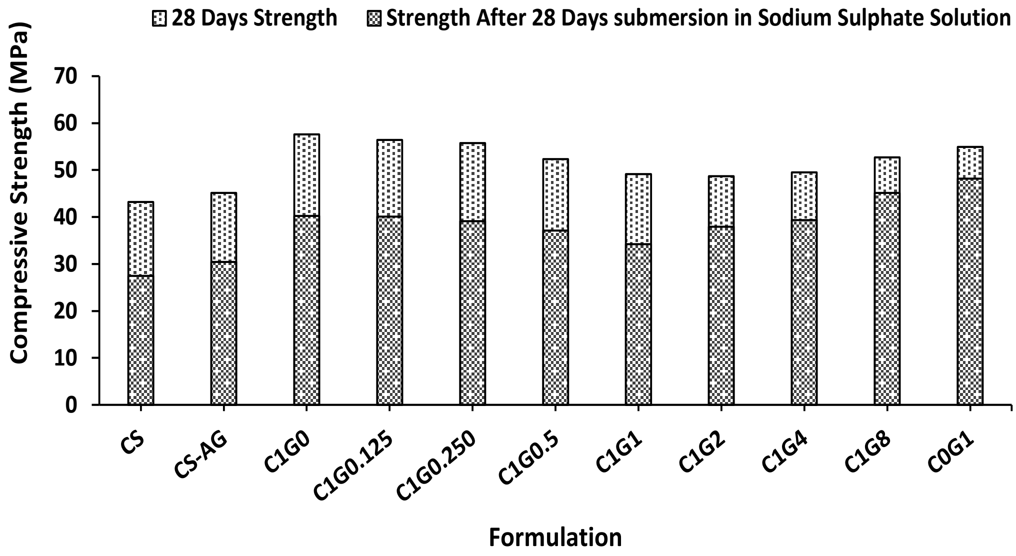
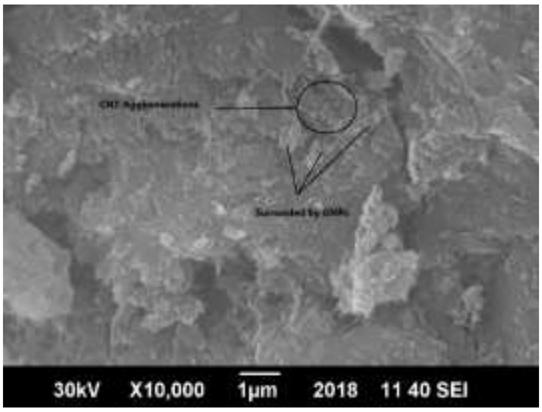
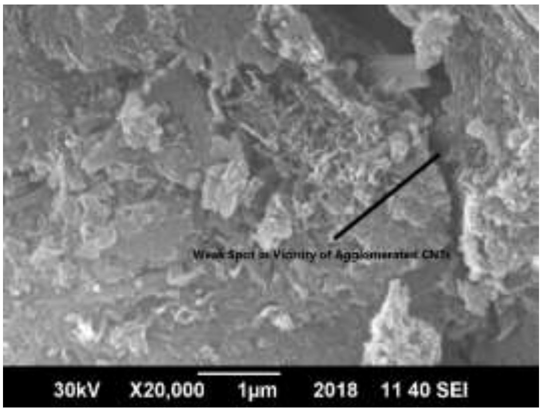


Figure 4-10 Compressive Strength after 28 days submersion in Sodium Sulphate Strength

4.9 Morphological studies using SEM Analysis:

Study of microstructure of hybrid nano intruded cement mortar and control formulations were conducted using field Emission scanning electron microscope by TESCAN. In **Figure 4-11** a typical formulation having both CNTs and GNPs is examined for physical morphology and to confirm dispersion of graphitic nano particles i.e. CNTs and GNPs in cement matrix. It can be seen that in the presence of GNPs the dispersion of carbon nano tubes is not much effective resulting in weak spots in the cement matrix which could be referred as the cause of decreasing strength. It can also be examined that CNTs surrounded by GNPs are in the form of agglomerations this might be due to the shielding effect of GNPs which lessened the intensity of sonication energy during the dispersion process.





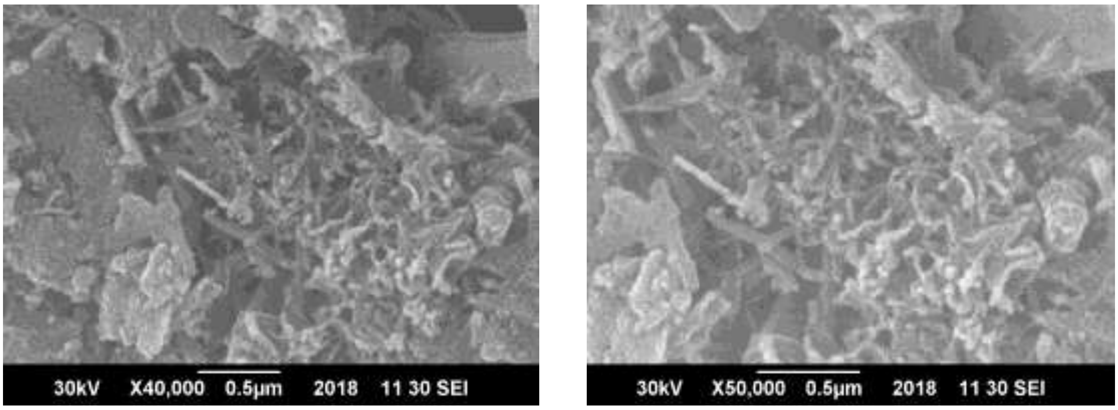


Figure 4-11. SEM Images at different Magnifications showing CNT agglomerations in presence of GNPs

Delayed ettringite formation can be visualized in **Figure 4-12 (b)** which is the major cause of strength reduction due to external Sulphate attack while no such formations were identified in the specimens without interaction with Sulphate solution.

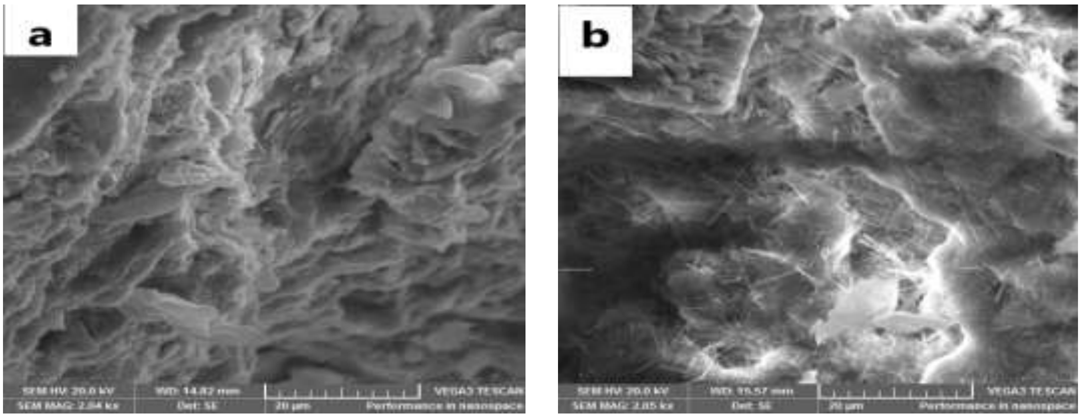


Figure 4-12. SEM images of C1G1 representing effect of external Sulphate attack (a) Without submersion in Sulphate solution (b) Delayed ettringite formation after 28 days submersion in Sulphate solution

In **Figure 4-15** gaps can easily identified in between CNTs which does not provide much effective barrier to water absorption. While formulations with more amount of GNPs i.e.C0G1 are denser as compared to CNTs alone which resulted in appreciable decrease in water absorption due to 2D shape of GNPs as given in **Figure 4-13**. In C1G0.125 relatively denser matrix can be seen due to presence of both CNTs and GNPs. Increased strength as compared to control formulation can be justified by pull out behavior of CNTs and proper bond with the surrounding matrix. While some of the CNTs entanglements can also be identified in **Figure 4-14** but due to low concentration of GNPs better dispersion of CNTs can be seen as compared to formulations with higher concentrations of GNPs as represented in **Figure 4-11**.

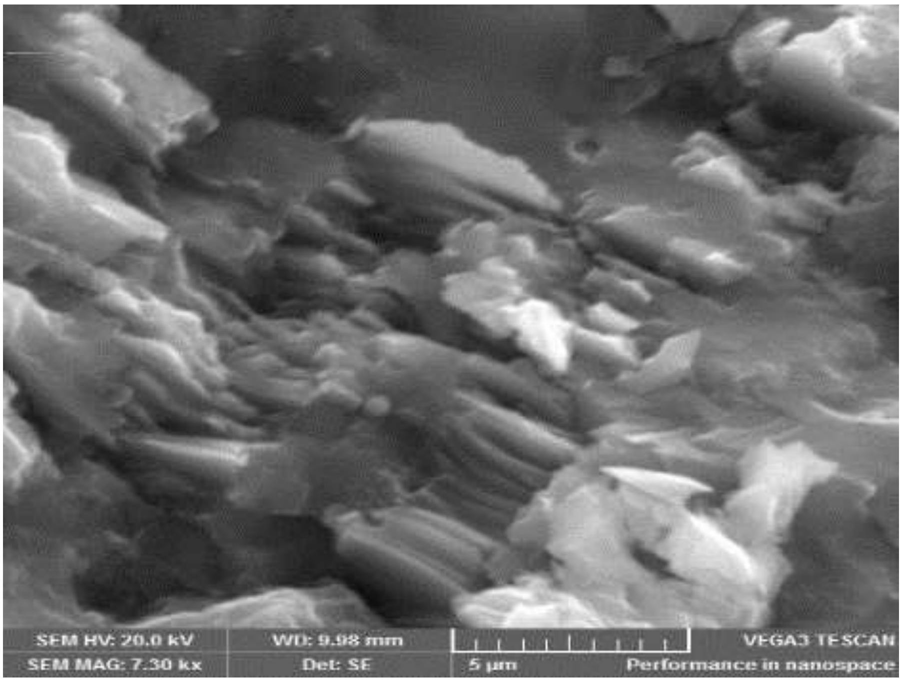


Figure 4-13. SEM Image of C0G1

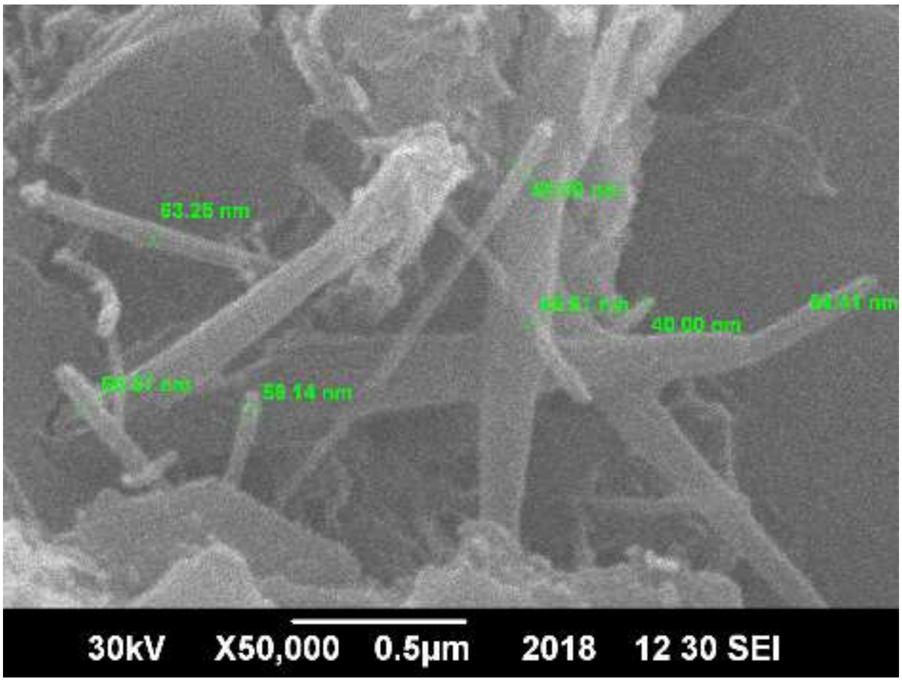


Figure 4-14. SEM Image of C1G0.125

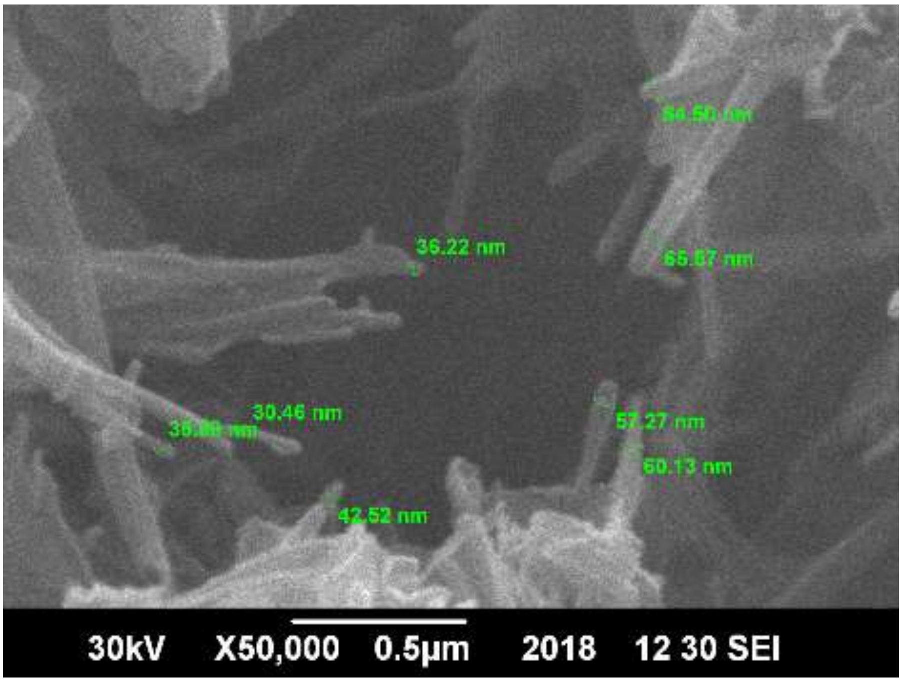


Figure 4-15. SEM Image of C1G0

4.10 Electrical Properties:

With the advancement towards multipurpose materials, it was a mere thought to have such a material which not only have better mechanical properties but also possess electrical conductivity so that material could be used in self-sensing. For that purpose different electrical conductive nano material i.e. CNTs, GNPs have been introduced into the cement matrix which not only serve as mechanical properties enhancer but also introduce electrical conductivity to the cement matrix. In this research combine effect of CNTs and GNMPs on electrical conductivity of cement mortar is studied.

4.10.1 Electrical Resistivity:

Electrical Resistance of hybrid nano intruded cement mortar in surface dry state having internal moisture is shown in **Figure 4-16**. Minimum electrical resistance is observed in C1G2 with a value of 6.4 kΩ-cm despite of poor dispersion of nano particles in this formulation as observed in **Figure 4-1**. It is observed that electrical resistivity of control formulation is lower than formulations with nano intrusions. Overall, 6.54, 7.78 and 8.1 kΩ-cm of electrical resistivity is observed in CS, G1G0 and C0G1. Electrical conductivity in control formulation and highest conductivity of C1G2 could might be due to combined effect of moisture absorbed by specimens during the period of curing and presence of conductive nano material. It is observed that in surface dry state electrical conductivity is mainly dependent on the internal moisture absorbed by the cement matrix [92], [93].

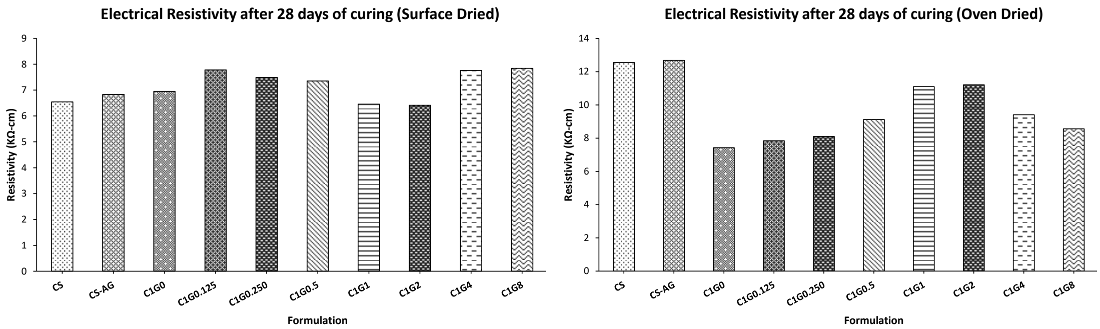


Figure 4-16 Electrical Resistivity of Nano Intruded cement mortar in Different dry states after 28 days of curing

To eliminate the effect of moisture on electrical conductivity of hybrid nano intruded cement mortar specimens were placed in oven at 100˚C for 24 hours. Electrical resistivity of oven dried hybrid nano intruded cement mortar is shown in **Figure 4-16**. After the removal of entrapped moisture with in the cement matrix electrical resistive is quite clear. Control formulation having maximum electrical resistivity with a value of 12.55 kΩ-cm. Minimum electrical resistivity was observed by C1G0. Overall 7.42 kΩ-cm of electrical resistivity was observed by C1G0. While after the removal of moisture, maximum resistance was observed by C1G2 in comparison to remaining hybrid nano intruded formulations. In case of C0G1 8.1 kΩ-cm resistance was observed. To compare the results of electrical resistivity of hybrid nano intruded cement mortar before and after the removal of moisture results are shown in **Figure 4-17**.

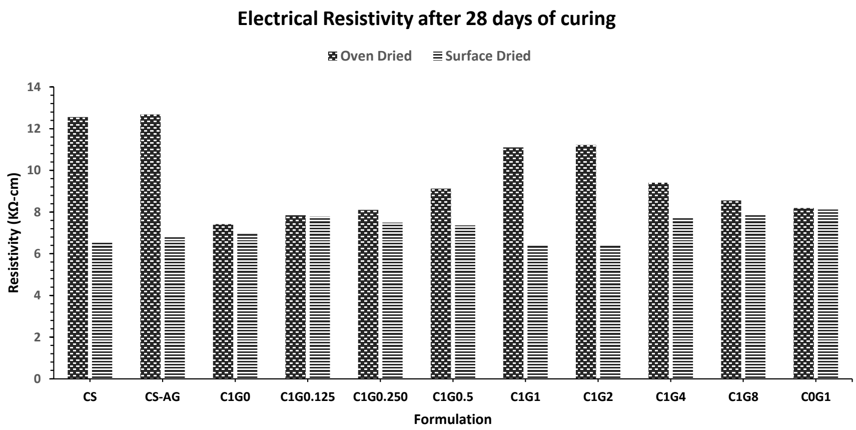


Figure 4-17 Electrical resistance of Hybrid Nano intruded Cement mortar before and after the removal of moisture

4.10.2 Effect of Voltage:

Electrical resistivity of hybrid nano intruded cement mortar in surface dried state at different values of DC voltage is shown in **Figure 4-18**. It can be seen that initially at low voltage i.e. 3 Volts electrical resistivity of all the formulations is higher while resistivity reduces as we increase the potential difference. Which is obvious as higher the potential difference higher will be the power of electrons to overcome the hindrance. Large variation of resistivity is observed in CS as resistivity changed from 7.52 to 6.29 kΩ-cm from 3 volts to 30 volts. While the formulations with nano intrusions are quite stable over the variation of voltage. It can be observed that voltage range of 10-30Volts is quite stable to measure the electrical resistivity of hybrid nano intruded cement mortar.

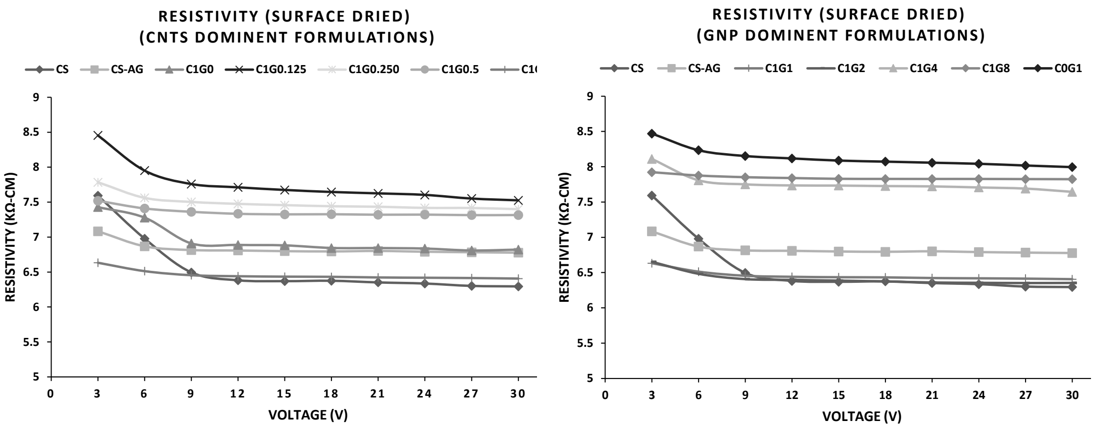


Figure 4-18 Electrical Resistivity of Hybrid Nano Intruded Cement Mortar in Surface Dried State at different Voltages

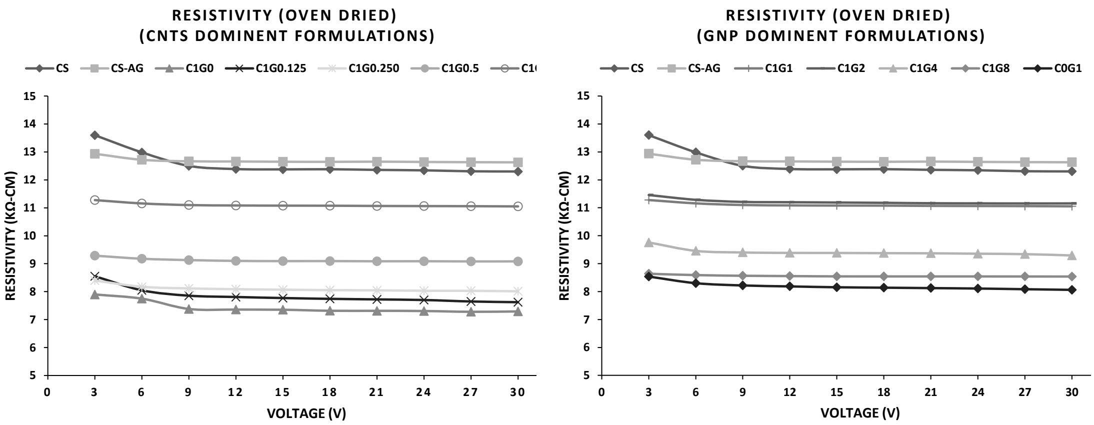


Figure 4-19 Electrical Resistivity of Hybrid Nano Intruded Cement Mortar in Oven Dried State at different Voltages

Similarly Electrical resistance of various formulations with hybrid nano intrusions over the variation of voltage from 3V to 30V in oven dried condition are shown in **Figure 4-19**. Oven dried specimens showed more stability towards variation in resistivity of the range of Voltage. In case of control formulation CS resistivity varied over a range of 12.98 to 12.3 kΩ-cm. While variation in resistivity in case of C1G0 was from 7.89 to 7.29 kΩ-cm. It can be observed that moisture present in specimens not only cause reduction in electrical resistivity but also cause variation in resistivity upon the variation in voltage.

CHAPTER 5

5.1 Conclusions

The dissertation has presented a series of experimental tests aimed at investigating shrinkage response, mechanical characteristics, electrical properties, resistance against Sulphate attack and physical morphology of cement mortar doped with hybrid nano intrusions of CNTs/GNPs. The following conclusions may be drawn based on results obtained in this experimental program.

- Mechanical and Electrical properties of hybrid nano intruded cement mortar were mainly dependent on the dispersion state of nano particles into the aqueous solution.
- 8:1 was found to be optimum ratio of CNTs and GNPs for hybrid dispersion in aqueous solution in the presence of acacia gum as surfactant.
- In C1G0.125 formulation shrinkage arrest, compressive strength and flexural strength were enhanced by 74.8%, 40.7% and 124.4% as compared to control formulation.
- Percolation threshold was shifted from 0.08wt% to 0.071wt% of CNT in the presence of 0.009wt% of GNPs and minimum electrical resistivity was measured in C1G0.125.
- Linear decreasing trend of water absorption was observed with the higher ratio of 2 dimensional Graphite nano particles, resulting better resistance against external Sulphate attack.

5.2 Recommendations

- It is recommended that better dispersion mechanism should be developed in order to have well dispersed aqueous solution of hybrid nano inclusions i.e. CNTs/GNPs
- Separate dispersed aqueous solutions should be made for CNTs and GNPs and then mix the both solutions to be used in cement composites so that agglomerations process during sonication process of hybrid CNTs/GNPs nano inclusions could be neutralized.

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