Mechanical and durability characteristics of multiwalled carbon nano tube in concrete

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Abstract: Concrete is the widely used reliable constructions material worldwide in the field of Civil Engineering with various reforms using advanced Technology. One of the encroachments is the Nano science and it has also played a remarkable role in the field of material science. Eventually Nano materials were used in the concrete to intervene new material at Nano scale and thereby increasing the Mechanical, Chemical and durability property. Various Nano materials are being used in civil Engineering, off all those Nano materials used in the concrete are Nano silica, Multi walled Carbon Nano tubes, and Nano Titanium oxide. These Nano materials are used in producing High performance concrete which exhibits tremendous strength and durability of concrete. The material that is used in this research paper is Carbon Nano tubes. The multiwalled carbon Nano tubes exhibits exceptionally high Mechanical Property and also act as a reinforcing material for the high performance concrete. These multiwall carbon Nano tubes are effectively incorporated in concrete by ultrasonic method and using surfactant. There are interfacial interactions between carbon nanotubes and the hydrations of cement, which enhances a high bonding strength between the reinforcement and cement matrix. Mutiwalled carbon nanotubes are various ratio is incorporated with the concrete of mix proportion M40 grade of concrete. Their mechanical property is thereby compared with the nominal concrete mix. In this research the fine aggregate is also partially to fully replace by manufactured sand as the demand for the river sand is high, an alternate is sought. Besides the mechanical property and the complex reinforcement of cement matrix, the Nano concrete exhibits early strain capacity which shows a considerable improvement in the long term durability of the concrete.

Keywords: Multiwall carbon Nano tubes, Compressive strength, Flexural Strength, Durability, Scanning electron microscope.

1. INTRODUCTION

Portland cement is the most common type of cement used worldwide and it’s the basic ingredient for the concrete. The cement is prepared through the calcination and burning at a temperature of about 1450 °C. [4]The raw material being used are the calcium, silicon, aluminium, iron and other ingredients. On burning the materials in the kiln, the elements unite to form a clinker which looks like a grey ball about the size of a marble. The clinker is mixed with a small amount of calcium sulphate and then finely ground to make the cement. These raw materials are readily available throughout the world at low cost. Consequently, the property of the cement varies from one cement plant to another.

Evolution of concrete has started from normal grade concrete from grade 5–45 [2, 3].But this grade of concrete used to provide adequate strength which is the nominal concrete. Eventually in 1960’s a unique design of structure was created which can withstand load carrying capacity from 50 Mpa to 90Mpa which is called as the high strength concrete. [6,7].Several Mineral admixture like Silica fume,
Metakaolin, fly ash and other pozzolans were added along with super plasticizers to increase the strength of concrete. Of all these materials, Silica fume was the most commonly used material to attain higher strength with an adequate replacement of cement content.

On the contrary with the advancement in science new materials were developed by nano technology. These nano materials has been used in concrete in recent decades with the demand for producing an ultimate High performance concrete (UHPC). These are new class of concrete with exception properties of strength and durability. Nano silica is one of the newest technologies in nano process which has been used as an alternative to silica fume [32]. Since the breakthrough of nano silica, many nano based particles has been developed to be used in concrete [31].

Nano alumina [33], titanium oxide [34], carbon nano tube and polycarboxylates are examples of nano materials used in nano concrete.

1.1. Introduction to Carbon Nanotubes.
Carbon nanotubes (CNT) has been extensively used as a reinforcing material in cement composite. CNT have ultra high strength and stiffness, with young's modulus upto 1 TPa and exceptional tensile strength in the range of 20 to 100 GPa [1]. On the other hand, they possess extremely high aspect ratios (1:1000) and surface area (200–300 m2/g), as well as very low density (1500 kg/m3) [5]. Henceforth CNTs are used as cement reinforcement, potentially it was able to stop the propagation of small nano-cracks and also it was able to improve the cement material property [28], like the low tensile behaviour and lower strain capacity. Literally CNTs have effectively used to enhance the fracture mechanism and early age strain capacity of cement pastes and mortars, reducing or preventing crack initiation [8,9]. The reinforcing efficiency of CNTs depends on various factors, such as CNT type, and the quality of their dispersion, interaction and bond strength with the cement matrix [10]. CNTs tend to agglomerate due to their hydrophobic properties, high surface area and strong van der Waals forces between adjacent tubes. [11,18] These intrinsic characteristics make their separation and dispersion a challenge. [12,13]. In this case, the dispersion is often achieved through a combination of ultrasonic energy and a compatible surfactant [14–16].

Research has proven the mechanical characterization of CNT-reinforced cement pastes or mortars, but the outcome of the durability is comparatively less. Han et al. [23] did a comprehensive study on the transport properties of CNT-reinforced mortars. Water sorptivity, water permeability, and gas permeability were thoroughly improved with the incorporation of 0.2 wt% of CNTs. From rapid chloride migration tests Wang et al. [24] reported that pastes with different amounts of CNTs exhibited lower migration coefficients than non-reinforced pastes, confirming that CNTs are able to improve the microstructure of cement-based materials. Li et al. [25] analysed the compressive strength degradation after subjecting both reference and CNT reinforced mortar samples to 90 freezing and thawing cycles. Reinforced mortars exhibited better performance.

Also a minimum work has been done on concrete reinforced with CNTs. Noteworthy are the works of Kerienè et al. [26] and Wille and Loh [27], which essentially focus on the mechanical behaviour of CNT-reinforced concretes. Kerienè et al. [26] studied the influence of CNTs on nonautoclaved and autoclaved aerated concretes. CNTs were added in amounts ranging from 0.0008% to 0.06%wtc, which resulted in a maximum enhancement of 11% of both 28-day compressive and flexural strength. Wille and Loh [27,30] added 0.022% of multiwalled CNTs to ultra-high-performance concrete and concluded that their addition did not influence the 28 days compressive strength. All the research were mainly focussed on the mechanical behaviour and some on the durability aspect. This study aims to investigate the mechanical and durability of concrete with CNTs and the natural sand is partially to fully being replaced by Manufactured Sand.
2. EXPERIMENTAL PROGRAM

2.1 Raw Materials
The raw materials used to fabricate the high performance Nano concrete specimens include ordinary Portland cement of grade 53, Fine aggregate (River sand) and Manufactured sand, (M sand), Coarse aggregate, Multi walled carbon nano tubes water, High range water reducing agent polycarboxylate for dispersing the carbon Nano tubes. Two types of nano tubes were used, MWCNT’s were purchased from Institute of Environmental Nano Technology (IENT), Carboxylic Functionalised Graphene[COOH] purchased from Adnano Technologies is produced by chemical exfoliation method and further it is treated to add-COOH group at the edges of the surface. The SEM, TEM analysis figure 1 shows that the length of the CNT IS 5 micron and the outer diameter being 60-80nm. The properties of the MWCNT’s is listed in table 1. Poly carboxylic acid was purchased from AASTRA chemicals that assist in dispersing of MWCNT’s. To enhance the workability of the concrete and also to reduce the water cement ratio, High range water reducing agent with the commercial name CONPLAST 420 SP was used.

Table 1. Properties of MWCNT

| MWCNT | Purity | Outer Diameter | Inner Diameter | Length | Surface area | Carbon Content | Bulk Density | Colour |
|-------|--------|----------------|----------------|--------|-------------|---------------|--------------|--------|
| Properties | 99 | 10-30nm | 5 | >10µm | 110-350m²/g | >90% | 0.14 g/cm³ | Black |
| | | 10nm | — | 5 | | | | |

2.2. Dispersion of multi-walled CNTs
Multi walled carbon nano tubes that was purchased was in black powdered form were dispersed by sonification to deagglomerate the MWCNT’s figure 2. The carbon nano tubes has a complex matrix due to van der waals forces which tends to form the agglomerate. These bundled CNT’s are incorporated into the concrete with surfactant to maintain the stability of dispersion. The method adopted to disperse each type of CNT’s differs, i.e. the amount of surfactant and the duration of the sonification are done according to the previous research[17]. The optimum ratio of MWCNTs to dispersant was 1:1 for CNTPL and 1:0.5 for CNTCOOH. Sonication time of 30 minutes were maintained for both types of CNT’s. These MWCNTs and surfactant were stirred initially by magnetic stirring with 40% of water being added and these suspension was further subjected to sonification for 15 minutes at 2 to 3 intervals in both cases of the MWCNT’s. The dispersed carbon nano tubes has a direct significant effect on the hydration of the cement, increasing the hydration rate considerably higher than ordinary super plasticizers used in the controlled concrete.

2.3. Mixture compositions, concrete mixing and tests
To analyse the strength and durability of the different types of CNTs in concrete, the concretes M40 with w/c of 0.40 were produced with similar composition, differing only in the type and amount of
CNTs. Controlled concrete were mixed for the three mix design so that the results are compared with the Nano concrete. Mix ratio compositions are listed in Table 2. The proper dispersion in concrete mixes was only achieved at low CNT contents which was researched earlier [19]. The optimum amount of CNTs by weigh of cement was determined considering between 0.015 – 0.1% weight of cement. The results of mechanical characterization of cement pastes with 0.015–0.1%wtc of the same type of CNTs used in this study; 0.05%wtc was determined to be used in case of both MWCNT and COOH CNT. According to researchers, [20,21], high concentrations of low aspect ratio CNTs are needed to attain the same reinforcement level of longer CNTs, but short CNTs with lower aspect ratios are easier to disperse, being possible to effectively incorporate higher amounts without excessive agglomeration. Whereas, low aspect ratio results in larger spacing between the nano tubes and few fibres are available at the cracking surface, producing a lower CNT-matrix bonding strength.

![Figure 2. Undispersed CNT and Dispersed CNT](image)

**Table 2: Mix proportion**

| Material     | M40  | M50  | M60  |
|--------------|------|------|------|
| Cement       | 400  | 422  | 504  |
| FA           | 660  | 621  | 683  |
| CA           | 1168 | 1284 | 1108 |
| Water        | 160  | 147  | 142  |
| Super plasticizer | 2.4  | 5.06 | 4.7  |

**2.4 Experimental Methods**

The study is to analyse the influence of the cement with CNT’s composition, the structural behaviour. The mix proportion of M40, M50 and M60 with water cement ratio of 0.4 and 0.35 were used for analysis. The results were compared with the controlled concrete. The concrete mixture is produced in an electrical concrete mixer with the coarse aggregate and the fine aggregate are mixed with 60 % of the total concrete mix water. The Fine aggregate that is used in this research is manufactured sand. The fine aggregate are replaced partially to fully (25%, 50%, 75% and 100%). It is mixed in the mixer for about 3 minutes. Then the cement and the remaining water and the dispersed CNT’s are added. Gradually the super plasticizers are added into the mixer after about 1 minute of mixing. The concrete is totally mixed approximately for about 8 minutes. The mixed concrete workability is checked by slump cone and flow table. The results are given in table 3.

**Table 3: Mix proportion for M40 grade concrete**

| Mixes | Cement | Sand | CA   | W/C  | CNT |
|-------|--------|------|------|------|-----|
| C1    | 400    | 660  | 1168 | 0.4  | 0   |
| M2    | 400    | 660  | 1168 | 0.4  | 0.05|
| M3    | 400    | 660  | 1168 | 0.4  | 0.07|
| M4    | 400    | 660  | 1168 | 0.4  | 0.08|
| M5    | 400    | 660  | 1168 | 0.4  | 0.1 |
| M6    | 400    | 660  | 1168 | 0.4  | 0.15|
| C2    |        |      |      |      |     |
To determine the compressive strength (3 days, 7 days, 28 days) cube of size 150mmx150mm x 150 mm are casted. The split tensile strength is done in accordance with IS 5816:1970; cylinders are casted with 150 mm diameter and 300 mm long. Sulphate resistance, Alkalinity was tested in accordance with IS 516:1959, cube of size 100mm x 100 mm were used. Also to ensure the chloride attack, Rapid chloride penetration test was conducted with cylinder specimen of diameter 150 mm and 50mm thick.

3. RESULTS AND DISCUSSION

3.1 Workability and Compressive strength

Slump cone test is the common method to determine the workability of concrete. This method is done in accordance with IS 1199:1959. The test results indicate that workability or the consistency is appropriate for the Carbon nano tubes induced concrete.

The 3 days, 7 days, 28 days compressive strength of various mix are plotted in the bar chart. Concrete cubes of size 150 x 150 x 150 mm where casted as per In S 516:1959 were casted. Test specimens shall be stored in a place, free from vibration, in moist air of at least 90 percent relative humidity and at a temperature of 27° ± 2°C for 24 hours ± ½ hour from the time of addition of water to the dry ingredients as per Indian Standards. The test results are given in figure 3 represent the comparative result with the controlled concrete. There is a drastic improvement in the compressive strength of concrete regardless of the type of MWCNT’s used as mentioned in figure 4, figure 5, figure 6 and figure 7. This could be because of the filler effect and the bridging effect of the nano tubes. Regardless of the water cement ratio, both the types of CNT’s exhibit higher strength. It is found that MWCNT’s of 0.1% with low aspect ratio has shown 22% increase. However COOH CNT’s showed a good result on 0.05% the weight of cement. It has been discussed by the researchers that high aspect ratio CNTs are expected to provide higher pull-out strength and better reinforcement due to their more effective bridging effect [22,29],

As it agglomerate more. Consequently, deagglomerateion can be achieved by lower amount of CNT’s as mention by researchers[29]. Hence the optimal amount of CNT that can be mixed was found to be 0.1% the weight of cement with 75% replacement of fine aggregate with Manufacture sand. The effect of super plasticizers helped in the dispersion of CNT’s with water cement ratio of 0.4. However the sonification had an adverse effect on the CNT’s which reduced the fiber matrix adhesion.
Figure 5: Compressive strength of M40 Grade Concrete with different Variation of CNT’S

Figure 6: Compressive strength of M40 Grade concrete with different Variation of CNT’S

Figure 7: Variation in 28 days compressive strength on Functionalized CNT

3.2 Reinforcing Effect due to MWCNT’s

The flexural strength increase of nano concrete when compared with the results of conventional concrete, depends on the relative concentration of MWCNT’S used. It was observed that it has 35% higher flexural strength using the nano composite concrete with an addition of (0.1% wt of the cement) as described in figure 9, figure 10, figure 11, when compared with the controlled concrete as in figure 8. To study the reinforcing effect of the concrete, beams of size 500mm x 100mm x 100mm were casted as per IS 516:1959. The test specimen is water cured for 28 days and the flexural strength of the beam is found to be 43% higher than the concrete without nano tubes. Cement. The considerable increment in the Flexural strength of the nano concrete is due to the dispersion of the Nano fiber dispersion of MWCNT’s in the cement matrix resulting in the decrement of fiber free area and hence enhancing the flexural behavior of the nano concrete when compared with the concrete without nanotubes. Conclusively, the cement matrix fiber is increased by the effective dispersion of CNT’s of small quantity to increase the mechanical property of concrete. The results and the comparative analysis of the flexural property are mention in figure 12. The young’s modulus of nano indented concrete shows 48% increase in contrary with conventional concrete.
Figure 8: Flexural strength of M40 Grade Concrete with different Variation of CNT’S

Figure 9: Flexural strength of M40 Grade concrete with different Variation of CNT’S

Figure 10: Flexural strength of M40 Grade Concrete with different Variation of CNT’S

Figure 11: Flexural strength of M40 Grade Concrete with different Variation of CNT’S

Figure 12: Variation in Flexural strength of different grades of concrete with functionalized CNT
4. CONCLUSION

- The high performance concrete which is reinforced with multiwalled carbon nano tube was studied. Various methods of dispersing of carbon nanotubes are also significant process in achieving the high performance in concrete. Following are the conclusion.
- Two types of multi wall carbon nanotubes were studied (Type I Pristine Carbon Nano tubes and Type II Carboxyl functionalized carbon nano tubes CNTCOOH). The Dispersion technique, mechanical characteristics were analysed experimentally.
- The maximum strength was found to be with addition of 0.1% weight of cement. However the functionalized CNT showed a lower strength when compared with pristine CNT though the aspect ratio remains the same.
- By proper dispersion of MWCNT by sonification and treating with polycarboxylate ether based super plasticizer induces a well stabilized MWCNT suspension which when incorporated with the concrete without affecting the workability and also to obtain a good interface in the concrete mix.
- Compared with the controlled concrete, the nano concrete has high amount of C-S-H gel, also acts as a filler with large surface area and hence a lesser porosity. Since these MWCNT has a diameter of (10-30nm),it reduces the size of the pores and hence to attain a higher strength.
- The compressive strength of the MWCNT concrete has shown 22% higher than the conventional concrete. The flexural property was found to be 35% higher on using pristine carbon nano tubes.

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