Multi-walled carbon nano-tubes for enhancing the performance of cementitious composites

Mohd Moonis Zaheer, Mohd Shamsuddin Jafri and Varisha

Department of Civil Engineering, Zakir Hussain College of Engg. and Tech., AMU Aligarh-202002, India.

E-mail: mooniszaffeer@rediffmail.com

Abstract. Due to exceptional properties, multi-walled carbon nano-tubes (MWCNTs) are designated as a promising reinforcing material for the nano-modified cementitious composites. The performance of cementitious composites with MWCNTs on the mechanical, durability, and microstructure properties was investigated in this study. The MWCNTs were effectively dispersed by the sonication method using high-frequency ultrasonic waves. The flexural strength, compressive strength, density, porosity, and stress-strain curves of cementitious composites reinforced with different concentrations (0.1, 0.2, 0.3, 0.4, and 0.5 wt%) of MWCNTs were studied. The enhanced flexural and compressive strength demonstrates the exceptional reinforcing behaviour of the MWCNTs. Additionally, density outcome indicates that as the percentage of MWCNTs in the matrix increases, density increases, and the optimum content was obtained as 0.3 wt%. The pores of cementitious composites can be reduced by adding carbon nano-tubes, which was perceived through a microstructural study using SEM micrographs. Study outcomes establish that in addition to the advantages provided by the nano-tube reinforcement in augmenting strength, nano-tubes can also help in reducing the porosity of the composites. The effectiveness of this promising nanomaterial related to its field application is also highlighted.

Keywords: Cementitious composites, Compressive strength, Flexural strength, Microstructure, Porosity, Multi-walled carbon nano-tubes, Treatment of nano-tubes.

1. Introduction

The mechanical strengths (flexural, compressive, and split tensile strength) are comparatively small in cementitious composites, and hence nano-cracks are formed under small tensile loads. In the recent past, various approaches to mitigate this drawback have been well documented in the published literature [1,2]. Among these approaches, the addition of different nanoparticles as reinforcements has been successful in improving the strength of mortar or concrete [3–5]. The uniform distribution of nanoparticles in the cement matrix creates abundant nucleation sites which are responsible for homogeneous and denser microstructure by filling pore spaces.

Past investigations on mechanical properties of cementitious composites reinforced with MWCNTs showed improved properties compared to control composites [6–8]. Owing to lesser production cost, most of the researchers preferred multi-walled carbon nano-tubes (MWCNTs) as compared to single-walled carbon nano-tubes (SWCNTs). Khashaba [7] reported a 7% enhancement in the flexural strength of cement paste at 0.2% MWCNTs. In one of the studies, a tensile test was performed by adding 0.5% multi-walled carbon nano-tubes and reported a 19% enhancement in the tensile strength [9]. Effect of adding
untreated MWCNTs and CNFs in mortar mechanical properties, like elastic modulus, flexural strength, ductility, and Toughness at 7, 14, and 28 days was studied by [10]. In a recent study, the effect of the diameter of untreated MWCNTs on the mechanical properties of cement mortar was studied by [11].

Compared to other nanomaterials, carbon nano-tubes has a distinct advantage in the pozzolanic reaction with hydration products. Due to nano dimensions, MWCNTs possess a distinct pozzolanic reaction at the early ages of hydration, making the cementitious composites more compact and durable. Effect of nano- and microparticle additives on the mechanical and durability properties of mortar exposed to sulphate attacks was investigated by [12] and showed that the nano-silica and micro-silica particles were more effective against sulfate attacks. The durability of concrete containing different types of carbon nano-tubes was investigated by [13] and found that concrete with a high percentage of nano-tubes of lower aspect ratio performed better. A critical review of the mechanical strength, durability, and microstructure of cementitious composites can be found in the review paper by Carrico et al. [14]. A literature survey shows that an organized study that presents both the mechanical and durability properties of treated MWCNTs reinforced cement composites at different curing ages is relatively unknown. Hence, in this paper, the influence of varying content of treated MWCNTs on mechanical, durability, and microstructure characteristics of cementitious composites have been investigated. The effectiveness of this promising nanomaterial related to field application and its economic feasibility in construction is also highlighted.

2. Experimental programme

2.1 Materials

The ordinary Portland cement (43 grade), Ultra-Tech, as per specifications of IS: 8112-2013 and the Standard Sand, which meets the requirements of IS: 383-1970 (2002) provided by Tamil Nadu Minerals Ltd., Chennai were used. Various properties of Standard Sand (S-sand) are given in Table 1. The treated MWCNTs supplied by United Nanotech Innovations Pvt. Ltd, Bangalore were used in all the mixes. The specifications of MWCNTs are presented in Table 2. A polycarboxylate based high range water reducing admixture (HRWRA), was used to assist in uniform mixing of MWCNTs in water.

| Property | Specific Gravity | Fineness Modulus | Zone | Bulk density (kg/m³) |
|----------|-----------------|------------------|------|----------------------|
|          |                  |                  |      | Loose state | Compact state |
| Obtained values | 2.58           | 2.69             | III  | 1660              | 1820          |

| Specifications | Colour | Surface Treatment | Purity (%) | Average Diameter | Average Length | Amorphous carbon (%) | Surface area |
|----------------|--------|------------------|------------|------------------|-----------------|----------------------|-------------|
| Description    | Black  | Treated          | >99        | 10 -20 nm        | 1-5 μm         | <1                   | 370 m²/g    |

2.2 Specimen preparation

Several investigators reported different methods for the dispersion of MWCNTs; nevertheless, the most widely used being the ultra-sonication method. Discrete batches for MWCNTs were prepared at different contents (0.1, 0.2, 0.3, 0.4, and 0.5wt%). A mixture of water and superplasticizer (0.4% by weight of cement) was added by the calculated amount of MWCNTs. The solution was then sonicated in a bath sonicator for 20 minutes.
The w/c ratio used in the present investigation was 0.5, and the cement to sand ratio in the mortar was 1:3. The various mortar mixes are presented in Table 3.

The sonicated solution was poured into the dry mixture of cement and sand and mixed thoroughly manually. The moulds conforming to IS: 10078-1982 was lightly oiled before casting the specimens. After manual mixing, the blended mix was poured into the moulds of size 160 × 40 × 40 mm³. The samples were kept in moulds at 100% relative humidity for 24 hours and then cured in water until testing at the age of 7, 14, and 28 days. These specimens were designated as flexural specimens. Control specimens (without MWCNTs) were also cast using the same procedure. Different stages of sample preparation and testing are shown in Figure 1(a-f). Flexural and compression tests were performed on the three specimens of each type, and the average of these was taken as representative for that mixture.

![Figure 1](image-url)

**Figure 1.** Various stages of the experimental programme.

**Table 3.** Mixes of cement sand mortar (1:3) with different contents of MWCNTs.

| Mixes     | Cement (g) | S-sand (g) | MWCNTs (%)/(g) |
|-----------|------------|------------|-----------------|
| Control   | 140        | 420        | 0.0/0.0         |
| 0.1% MWCNT| 140        | 420        | 0.1/0.14        |
| 0.2% MWCNT| 140        | 420        | 0.2/0.28        |
| 0.3% MWCNT| 140        | 420        | 0.3/0.42        |
| 0.4% MWCNT| 140        | 420        | 0.4/0.56        |
| 0.5% MWCNT| 140        | 420        | 0.5/0.70        |
2.3 Flexural and compression tests
As per Indian standard IS: 4031 (Part 8) – 1988, 54 specimens of 160 × 40 × 40 mm³ were cast and tested for flexural strength under centre point loading. For calculating flexural strength, deflections corresponding to each load were measured and recorded. Euler–Bernoulli elastic beam theory given by Eq. 1 was applied to evaluate corresponding stresses and strains.

\[ \sigma = \frac{dP}{4l} \quad \text{and} \quad \varepsilon = \frac{12d}{L^2}y \]  

(1)

where \( \sigma \) and \( \varepsilon \) denote, respectively, the flexural tensile stress and the strain at the bottom-most layer of the flexural specimen at each load increment, \( L \) denotes the simply supported span of the specimen (100 mm), \( d \) is the half-depth of the specimen cross-section (20 mm), \( I \) is the moment of inertia of the beam cross-section, \( P \) is the applied load, and \( y \) is the deflection at mid-span. Flexural strength is obtained by Eq. 2 and is given as:

\[ R = \frac{6M}{B^3} \]  

(2)

where, \( R = \) Flexural strength; \( M = \) Maximum bending moment under central point loading; \( B = \) Side of the prism cross-section.

After the flexural strength tests, cubes were cut from the uncracked portion of flexural specimens to the size of 40 × 40 × 40 mm³ (see Figure 1d) as per IS: 4031 (Part 8) – 1988 using a saw cutter. From one flexural specimen, two prisms were made, making the total prisms count as 108. Half of these prisms were used for compression testing, and remaining were employed for density and porosity measurements. The compression test was performed using the AIMIL compression testing machine; the load was applied at the rate of 200kg/cm²/min. After destructive testing, mortar fragments of each mix were picked and stored in acetone for SEM analysis.

2.4 Durability tests
Density and porosity tests were performed on 40 × 40 × 40 mm³ size cubes. Density and porosity were determined as per IS: 1528 (Part 15) – 2007. Porosity is an essential parameter in determining the quality of the cementitious composites. The procedure for determining these parameters was explained in [15].

2.5 Scanning Electron Microscope
Small crushed concrete fragments collected from select mortar mixtures were prepared for Scanning Electron Microscope (SEM) analysis by first drying them at 80°C for 24 hours. It was then allowed to cool for 24 hours before the fragments were gold-coated by a layer of approximately 20 \( \mu \)m using an automated sequence sputter coating machine. The SEM from JOEL, Japan, was used to study the mortar samples was a model JSM-5610 microscope equipped with an oxford ISIS EDS system.
3. Discussion of results

3.1 Flexural and compressive strength

The effects of different contents of MWCNTs on the mechanical strength (flexural and compressive) of mortar at 7, 14, and 28 days of curing were investigated. These results are shown in Figure 2 and Figure 3, respectively, which presented the average strength of three specimens at different curing ages. Compared to control specimens, the flexural strength of 0.3 wt% composites was increased by 31%, 25%, and 29% at respective curing periods. It can be due to the interaction of MWCNTs and calcium Silicate Hydrate (CSH), which leads to an efficient bond between the nano-tube and cement matrix, bridging micro-cracks, and enhancing load transfer ability. Additionally, the flexural strength was reduced at 0.4 wt% of MWCNTs, though strength is still higher than its control specimen counterpart. The reduction in strength at higher MWCNT content is due to two reasons. Firstly, due to less water availability for hydration reaction as more water adheres to nano-tube surfaces. Secondly, MWCNTs get agglomerated and entrapped water within their lumped mass, causing insufficient hydration of composite. Compare to the control, an identical trend is also observed for compressive strength. From the above discussion and variation of strength outcomes, it can be established that optimal MWCNT concentration for obtaining good strength mortar is 0.3 wt%.

Figure 2. Flexural strength of mortar specimens with various wt% of MWCNTs.

Figure 3. Compressive strength of mortar prisms with various wt% of MWCNTs.
Figure 4 shows the ratio of average compressive strength of prisms with different MWCNT content to that of control ones at 28 days. Prisms up to 0.3% of MWCNTs show an increase in strength. The reverse trend is obtained for prisms with more than 0.3% addition of MWCNTs. This may be due to reduced workability of the mixture and increased voids in the cement mortar.

![Figure 4](image.png)

**Figure 4.** Ratio of compressive strength with various wt% of MWCNTs to control prisms.

### 3.2 Stress-strain behaviour

Figure 5 and Figure 6 show the stress-strain curve of control specimen and specimen with 0.3% MWCNT at 28 days, showing an increase in both ultimate stress and strain at failure. Fig 6 shows multi peaks behavior, which can be correlated to pull out mechanism of MWCNTs from fine cracks in the composite matrix. This phenomenon is of vital importance for the strain to failure (ductility) of the nano-composites. Therefore, it can be established that the mechanical strengths of the cementitious composites are enhanced substantially with the incorporation of 0.3% MWCNTs.

![Figure 5](image.png)

**Figure 5.** Stress-strain diagram of control flexural specimen.
3.3 SEM micrographs

For justification of the mechanical test results, an investigation of the SEM micrographs for the microstructural study was conducted. Figure 7 (a) shows the SEM micrograph of a clump of MWCNT at 30,000 × magnification. The image clearly shows the string of MWCNTs clumping together, strong clumping between each individual MWCNTs caused by strong Vander Walls forces, responsible for nano-tubes agglomeration.

For investigating nano-tubes effectiveness in strength improvement, it is essential first to examine it without MWCNTs. As shown in Figure 7 (b), a wide crack could be observed in the control mortar specimen. As reported by [16], a high aspect ratio and large specific surface area are unique properties of MWCNTs, thereby developing an efficient bond with hydration products, leading to improved mechanical properties. Ideally, the strong packing effect of uniformly dispersed nano-tubes in the cement matrix will substantially enhance the density and lowers the porosity of cement composites. Micrograph (Figure 7c) clearly shows the crack bridging mechanism of carbon nano-tubes across micro-cracks. These micrographs showed pull out and breakage of MWCNTs, which results in improved load distribution characteristics from the cementitious matrix to CNTs in case of flexure. As the percentage of nano-tubes increased beyond 0.3 wt% (Figure 7d), clear agglomeration is observed, which could be the reason for the decrease in mechanical strength.
3.4 Durability Properties

The influence of durability properties like density and porosity on the quality and performance of mortar is quite important, noting that increased porosity has a negative effect on the mechanical properties of mortar. In this study, the durability properties with different amount of MWCNTs at various ages were tested using the procedure outlined in IS: 1528 (Part 15)-2007.

The influence of MWCNTs on the durability of mortar at 7, 14, and 28 days is shown in Figure 8 and Figure 9, respectively. Compared to the control prisms, the porosity of MWCNTs added cement mortar was decreased gradually. The porosity of prisms having 0.3 wt% of MWCNTs was reduced by nearly one-fourth (25%) at 28 days. It is confirmed that the microstructure of mortar was more dense and compact, the incorporation of nano-tubes filled pores. Consequently, the mechanical properties of composites added with MWCNTs were substantially enhanced due to the refinement of unfilled voids and pores.

Figure 7. SEM images of (a) Dry MWCNTs (b) Control (c) 0.3% (d) 0.4% MWCNT composites at 28 days.
Therefore, from the presented results for the MWCNT prisms, it is clearly established that the porosity is decreasing from 7 to 28 days (see Figure 9). The reverse trend is found for the density (see Figure 8). In broad terms, prisms with 0.3% MWCNT concentration showed optimum results. Beyond this ratio, an increase in MWCNT content showed a negative impact on respective properties. Although this finding is important from an economic point of view, the smaller the content of MWCNTs in the cementitious composites, the lower the cost of mortar or concrete; for desired properties, one may ensure uniform dispersion of nano-tubes in the cementitious matrix [15].

3.5 Economic feasibility and field application of nano-composites
Table 4 represents the cost comparison of the specimen having 0.3% MWCNT content with a control specimen. The increase in the cost of a sample was found to be 43.68 Indian Rupees (INR). The present use of nanomaterials in the construction world may be costly because of price issues. However, a bright future is anticipated concerning commercial applications due to technological advancement for its production. Actually, with the increased utilization of nanomaterials in various fields, including the construction sector, bulk production of nanomaterials will become a reality. This will help in reducing the cost of nanomaterials and results in lowering the cost of composites with benefits such as enhanced mechanical and durability properties.
Due to its superior properties and dimensions, MWCNTs have diverse applications in various fields such as nanoelectronics, solar cells, environment, and petroleum engineering from drilling and cementing oil wells, process, and refining in each stage, concrete and cementitious composites formation, etc. Sizeable researches are being conducted related to the suitability of nanotechnology in the petroleum industry [17]. All of this is due to its large specific surface area and reactive particle surface, which creates a strong interfacial bond between these nano-tubes and cementitious matrix, resulting in strengthening of the structure on the part of mechanical and durability aspects. Many cementing problems are encountered during the production of petroleum, like shrinkage of cement, borehole damage, well integrity, cement failure because of mechanical stress, corrosion of casing, etc. To counter these issues, proper selection of nano-tube and its application plays a vital role in the oil and gas industry.

Table 4. Cost comparison of one control sample with 0.3% MWCNTs.

| Material | Unit cost (INR) | Quantity needed | Cost (INR) |
|----------|----------------|-----------------|------------|
|          |                | Control sample  | With        |
|          |                |                 | MWCNTs     |
|          |                | Control sample  | With        |
|          |                |                 | MWCNTs     |
| Cement  | 7.8/kg         | 140 g           | 140 g      | 1.092 | 1.092 |
| S-sand  | 10/kg          | 420 g           | 420 g      | 4.2   | 4.2   |
| MWCNT   | 104/g          | -               | 0.42 g     | -     | 43.68 |
| Water   | 0.5/litres     | 77 ml           | 77 ml      | 0.0385 | 0.0385 |
| Total Cost (INR) | 5.33 | 49.01 |

4. Conclusions and recommendations

The present investigation intended to investigate the influence of MWCNTs on the mechanical and durability properties of mortar. Results of mechanical tests showed that early age strength of mortar was promoted with the incorporation of nano-tubes, indicating quick hydration of cement in the presence of nano-tubes. This outcome is possibly due to the increased formation of Ca (OH) \(_2\). The porosity results showed that the porosity of mortar was decreasing with the addition of nano-tubes and made the microstructure denser. Moreover, microstructural analysis using SEM verified that MWCNTs could act as a bridge and inhibit crack arrestor leading to improved load distribution capacity across the matrix. The outcome of the study showed that the optimal content of MWCNTs for maximum strength and durability properties is 0.3 wt%. Cost analysis showed that there is not much increment for MWCNT admixed mortar samples than the plain counterpart. But in the current scenario, the use of such material is not practical from an economic point of view because of less utilization. With the increasing trend of using MWCNTs in making cement composites will automatically enhance its production, making it economically feasible.

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