Refinement of Concrete Characteristic Properties with Multi Walled Carbon Nano Tubes

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ABSTRACT: Water-cement ratio governs durability of concrete. Appropriate water-cement ratio for addition of nano materials in concrete is under search. Also water quantity governs dispersion nano materials in cement paste. In this study effect of water-cement ratio (W/C) on the characteristic properties of multi walled carbon nano tube reinforced concrete is analyzed. Five concrete mixtures of different water-cement ratio (W/C) with and without carbon nano tubes (CNTs) were prepared. W/C of 0.40, 0.45, 0.48, 0.50 and 0.55 were used while quantity of carbon nano tube (CNT) was fixed at 1% by weight of cement (wbc). For fresh state compaction and slump test were performed while for sorptivity absorption by immersion test was conducted and strength was evaluated by compression, split tensile and flexure strength test. The workability of carbon nano tube reinforced concrete (CNTC) reduced by 60% and W/C=0.50 was found ideal for slump as well as strength. At this W/C compressive strength for CNTC increased by 7.20%, split tensile strength increased by 25.75% and flexural strength increased by 3.87%. Also relation coefficient between Water-Cement and Water absorption was as high as 0.9 in this study.

Keywords: Compressive strength, Concrete, Flexural strength, Multi walled Carbon Nano Tubes, Porosity, Split Tensile strength, Water-Cement ratio, Workability.

Abbreviations: wbc, weight by cement; REF, Reference Concrete; MWCNT, Multi Walled Carbon Nano Tubes; CNTC, Carbon Nano Tube reinforced Concrete; W/C, Water-Cement Ratio.

I. INTRODUCTION

Functionalities of concrete improved with addition of nano materials. Incorporation of nano materials in concrete with advancement in nano technology resulted in nano modified concrete. Nano material, such as Carbon Nano Tubes (CNTs) has potential to modify mechanical properties of concrete.

Carbon nanotubes are byproduct of the fullerene synthesis discovered in 1991 at the NEC Fundamental Research Laboratory in Japan [1]. Graphite sheets are made of tubes such as zigzag, chiral, and armchair that can form a single-walled or multi-walled nanotube, but remain as a hollow cylinder [2, 3]. Carbon nano tubes have excellent mechanical properties with Young’s modulus upto 1 TPa, tensile strength approximately 100 GPa and fracture at a strain up to 15%. CNT have a high specific surface area with a value of up to 1000 m²/g [4-6]. They also show very high thermal conductivity of 1700–3000 W/mk and very low electrical resistivity of 5 x 10⁶ – 2 x 10⁶ Ωm, similar to copper [7]. CNTs exhibit a low density even at high aspect ratio. They provide large interfacial contact area in matrix with out much weight penalty like conventional fibers, hence reinforce concrete more efficiently [8-10]. They potentially restrain the propagation of small nano cracks and prevent crack initiation [11, 12]. Basic properties CNTs have shown growing interest for the development of smart concrete. Due to high surface area and strong van der wall force between CNT bundles they tend to agglomerate [13, 14]. Therefore, the dispersion of CNTs play vital role for effective and innovative functionalities. For effective dispersion mechanical as well as chemical methods are employed. Mechanical methods involves ultra sonication magnetic stirring, and even hand mixing, while chemical methods involves use of surfactants and functionalization [15]. But no proper method to guarantee full dispersion is reported. At 0.4, 0.5 and 0.6 W/C Kim et al., (2014) [16] observed decrease in workability of mortar mixes when 0.1%, 0.3% and 0.5% MWCNTs, by weight of cement was incorporated to them. Similarly at 0.5 W/C Collins et al., (2012) [17] observed reduction of 14.5%, 32.8%, and 48.9% in slump diameter with 0.5%, 1%, and 2% addition of MWCNTs respectively. When Makar and Chan (2009) [18] added 1% of SWCNTs by weight to cement they observed acceleration of hydration reaction of the C₃S and change in morphology of C₃A. Hydration reaction rate increased as CNTs act as nucleation sites for hydration products. Not only SWCNTs increases hydration rate but MWCNTs also increases hydration rate of cement as observed by Cui et al., (2015) [19]. They also reported hydration of cement accelerates with increasing MWCNTs content.

When Bharj et al., (2015) [20] added 0.1% MWCNTs, by weight, to concretes, and observed increment of 7, 14, 28 and 35 days compressive strength. 90 days compressive strength of was also enhanced by Hamzaoui (2012) et al., [21] with addition of 0.003% CNTs by weight to concretes. Van Tonder and Mafokoane (2014) [22] reported that at 28 days compressive strength increased by 13%, 20%, and 9%, while tensile strength increased up to 29%, 18% and 25%, on adding 0.05%, 0.1% and 0.2% MWCNT.
different W/C ratio were characterized bearing 1% on CNT reinforced concrete. For this cause concretes with and its influence on fresh and hardened properties of 25.75% and flexural strength increased by 3.87% at 0.5 addition of CNT showed compressive strength for CNTC relationship between water absorption and w/c ratio was evaluated by immersing cubes in water and hardened properties compressive, split tensile and test and compaction factor test was conducted while for previous works done, as very little work is done on influence of CNTs on split tensile strength and flexural strength have been rarely disused. Also no relationship between W/C and porosity of CNT reinforced concrete is derived till now. Considering it as initiative to investigate role of water-cement (W/C) ratio and its influence on fresh and hardened properties of CNT reinforced concrete. For this cause concretes with different W/C ratio were characterized bearing 1% on pristine multi walled CNTs by weight of cement (wbc). The Optimal amount of CNT was selected on the basis of previous works done, as very little work is done on 1% CNT wbc in concrete. For fresh state slump cone test and compaction factor test was conducted while for hardened properties compressive, split tensile and flexural strength test was conducted. Water absorption was evaluated by immersing cubes in water and relationship between water absorption and w/c ratio was obtained. In comparison to above cited researchers 1% addition of CNT showed compressive strength for CNTC increased by 7.20%, split tensile strength increased by 25.75% and flexural strength increased by 3.87% at 0.5 W/C.

II. MATERIALS AND METHODS

A. Materials
For concrete production Ordinary Portland Cement of Type I, crushed aggregates of 20mm nominal size and coarse sand of Zone II grade according to IS8112:2013 and IS 383: 2016 were used. Multi walled carbon nano tubes (CNTs) of 97% purity and diameter of 5-15nm were used. For maintaining workability Super Plasticizer (SP) based on polycarboxylate was used.

B. Dispersion procedure of multi walled CNTs
Multi walled carbon nano tubes were procured in powder form and to deagglomerate CNT clusters sonication was conducted. The CNTs were first dispersed in 30% of mixing water and continuously stirred for 10 minutes. The optimum ratio by weight CNT/Water was 1:35. Sonication time was 20 minutes for each sample from whole mixture.

C. Concrete composition and mixing
Five concretes with W/C of 0.40, 0.45, 0.48, 0.50 and 0.55 were produced to study the influence of W/C ratio on workability of carbon nano tube incorporated concrete (CNTC). Ratio of cement: sand: aggregates used was 1:1.76:2.66. In addition to cement, sand and aggregates, 1% CNT by weight of cement was added to CNTC and concrete without CNT was produced for comparison and termed as reference concrete. Compositions details are shown in Table 1. For concrete production aggregates was thoroughly washed and dried. The cement, sand, and aggregates were dry mixed for 2 minutes and then remained 70% of mixing water was added. Simultaneously dispersed CNT solution was also added. The plasticizer (SP) was already mixed in 70% of remained water. The whole mixing was carried for 5-7 minutes. After mixing the slump was measured using slump cone test according to IS 1199:1959 (Reaffirmed 2004). In table 1 the denomination ‘0.4REF’ represent reference concrete having W/C 0.4 and ‘0.4CNTC1’ represent CNT reinforced concrete having 0.4 W/C ratio and 1% CNT content. Three 150mm cube specimens for compressive strength test, three 150 × 300 mm cylindrical specimens for split tensile strength test and three 100 × 100 × 500 mm beam specimen for flexure test at 28 days were prepared. After 24 hours specimens were demoulded and kept in water curing at room temperature 25±2°C for 28 days.

### Table 1: Details of Mixes.

<table>
<thead>
<tr>
<th>Mixes</th>
<th>W/C Ratio</th>
<th>Cement kg/m²</th>
<th>Effective Water kg/m³</th>
<th>Coarse Aggregate kg/m³</th>
<th>Fine Aggregate kg/m³</th>
<th>SP% wbc</th>
<th>CNT% Wbc</th>
</tr>
</thead>
<tbody>
<tr>
<td>55REF</td>
<td>0.55</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>55CNTC1</td>
<td>0.55</td>
<td>430</td>
<td>237</td>
<td>1145</td>
<td>760</td>
<td>0.5</td>
<td>—</td>
</tr>
<tr>
<td>50REF</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>50CNTC1</td>
<td>0.5</td>
<td></td>
<td>215</td>
<td>1145</td>
<td>760</td>
<td>—</td>
<td>1</td>
</tr>
<tr>
<td>45REF</td>
<td>0.45</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>45CNTC1</td>
<td>0.45</td>
<td></td>
<td>193</td>
<td>1145</td>
<td>760</td>
<td>—</td>
<td>1</td>
</tr>
<tr>
<td>40REF</td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>40CNTC1</td>
<td>0.4</td>
<td></td>
<td>172</td>
<td>1145</td>
<td>760</td>
<td>—</td>
<td>1</td>
</tr>
</tbody>
</table>

D. Sorptivity
Sorptivity of concrete was evaluated by water absorption. Water absorption test was conducted by immersing and saturating 150×150×150mm concrete cubic specimens in potable water for 24 hours. The concrete cube specimens were allowed to drain for a minute before wiping off visible surface water using a damp cloth. The saturated specimens were then oven-dried at a temperature of 105°C for 24 hours. The water absorption was calculated using the following expression:

\[
\text{Absorption}\% = \frac{M_s - M_d}{M_d} \times 100
\]

where Ms and Md are the mass of the saturated and dry concrete cube specimens, respectively.
III. RESULTS AND DISCUSSION

A. Workability

The addition of CNTs caused drastic decrease in workability as shown in Fig. 1. Slump increased with increment of water and 0.50REF attained self compacting state or flow concrete state with compaction factor equal to 1. But 0.5CNTC1 had compaction factor equal to 0.81 as catalogued in Table 2. All mixes of CNTC’s were workable as per IS 1199:1959. From Table 3 it's observed that the workability of CNTC reduced by 65% in 0.48CNTC in comparison to 0.48REF. The overall decrease in compaction factor and slump of CNTC in comparison to REF can be attributed to high specific surface area and surface tension property of nano particles [24, 25]. Due to surface tension and hydrophobic nature the water get cling around the nano particles, thereby reducing their specific surface area. Also as per literature dispersion of CNT in matrix plays vital role in modification of functionalities of concrete. If they are not well dispersed water gets entrapped in agglomerated state.

<table>
<thead>
<tr>
<th>W/C</th>
<th>REF</th>
<th>CNTC1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>0.86</td>
<td>0.68</td>
</tr>
<tr>
<td>0.45</td>
<td>0.92</td>
<td>0.72</td>
</tr>
<tr>
<td>0.48</td>
<td>0.95</td>
<td>0.77</td>
</tr>
<tr>
<td>0.50</td>
<td>1</td>
<td>0.81</td>
</tr>
<tr>
<td>0.55</td>
<td>1</td>
<td>0.82</td>
</tr>
</tbody>
</table>

B. Sorptivity

The water absorption increased with increasing W/C show in Fig. 2 (a). Least absorption 0.43% was observed in 0.4CNTC1 while 0.4REF has 0.45% which was 0.02% more in comparison to 0.4CNTC1. Highest absorption 0.58% was observed in 0.55REF which reduced by 0.03% in 0.55CNTC1. Hence water absorption increased with increasing W/C while it decreased with addition of CNT content at that particular W/C as represented in Table 4. Hence water absorption of CNTC was less than REF. From Fig. 2 (b) relationship between water absorption and water-cement ratio CNTC was fabricated. By fitting experimental data in respective equations and tracing them values of constants terms of equations $R^2$ was as high as 0.9 in this study. The absorbed water remains in capillary pores and absorption increases with increment of porosity. The pores get developed due to entrapment of air in the matrix. Low porosity in CNTC mixes can be attributed to the filler and nucleation effect of CNTs. As quantity of CNT increased more entanglement was formed which entrapped more air hence led to more porosity. On contrary Carriço et al., (2018) [27] stated 12% reduction absorption with addition of 0.1% CNTSS (ie CNTs supplied in aqueous suspension, by the manufacturer and stabilized using a polyethylene-based dispersant). The reason for reduction was attributed to filler and nucleation effect of CNTs. Contradiction in results is due to high quantity of CNTs present in this research. Even though CNTs provide high filler and nucleation effect but dispersion also play vital role.

<table>
<thead>
<tr>
<th>W/C</th>
<th>REF</th>
<th>CNTC1</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>0.45</td>
<td>0.43</td>
<td>0.02</td>
</tr>
<tr>
<td>0.45</td>
<td>0.5</td>
<td>0.48</td>
<td>0.02</td>
</tr>
<tr>
<td>0.48</td>
<td>0.52</td>
<td>0.49</td>
<td>0.03</td>
</tr>
<tr>
<td>0.5</td>
<td>0.56</td>
<td>0.53</td>
<td>0.03</td>
</tr>
<tr>
<td>0.55</td>
<td>0.58</td>
<td>0.55</td>
<td>0.03</td>
</tr>
</tbody>
</table>

As the specific surface area of nano particles reduces due to agglomerates, therefore full interaction CNTs with matrix and improvement in desired properties is not attained [26]. Amount of CNT also plays vital role in dispersion and workability of concrete [16, 27].

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**Error in Table 2 and Table 3:**

The values in Table 2 and Table 3 need to be corrected for consistency with the described results. The table values should reflect the actual data that supports the text. The given values do not align with the text and need to be updated accordingly.

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**Fig. 2.** (a) Comparison of Water absorption for concretes with W/C of 0.4-0.55.
The compressive strength test was conducted as per IS 516-1959 on cubes of size 150 × 150 × 150 mm. The split tensile strength test was conducted on 300mm×150mm cylinder as per IS 516-1959. The flexural strength test was performed using three point loading method was performed as per IS 516:1959 on three 100×100 × 500mm beam specimens. The maximum failure load was noted and results are presented in Table 5, 6, 7 respectively.

### Table 5: Detailed result of Compressive strength.

<table>
<thead>
<tr>
<th>W/C ratio</th>
<th>Failure load kN</th>
<th>Mpa</th>
<th>Failure load kN</th>
<th>Mpa</th>
<th>% increase in strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45</td>
<td>1013</td>
<td>45</td>
<td>1094</td>
<td>48</td>
<td>8</td>
</tr>
<tr>
<td>0.48</td>
<td>960</td>
<td>42</td>
<td>1029</td>
<td>45</td>
<td>7.20</td>
</tr>
<tr>
<td>0.50</td>
<td>855</td>
<td>38</td>
<td>913</td>
<td>40</td>
<td>6.87</td>
</tr>
<tr>
<td>0.55</td>
<td>805</td>
<td>35</td>
<td>862</td>
<td>38</td>
<td>7</td>
</tr>
</tbody>
</table>

The strength test was performed on specimens with W/C=0.45 because W/C=0.40 is used for hydration of cement. At W/C=0.40 Tri Calcium Aluminate i.e. C₃A is formed which is responsible for early strength development. The excess water (i.e. water greater than 0.40) remains in capillary pore and evaporates. This phenomenon is called capillary porosity and is responsible for decrease in strength which will be investigated in next research.

### Table 7: Detailed result of flexural strength.

<table>
<thead>
<tr>
<th>W/C ratio</th>
<th>Failure load kN</th>
<th>Mpa</th>
<th>Failure load kN</th>
<th>Mpa</th>
<th>% increase in strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45</td>
<td>15</td>
<td>6</td>
<td>15.75</td>
<td>6.3</td>
<td>5</td>
</tr>
<tr>
<td>0.48</td>
<td>14</td>
<td>5.6</td>
<td>14.54</td>
<td>5.81</td>
<td>3.87</td>
</tr>
<tr>
<td>0.50</td>
<td>13.5</td>
<td>5.4</td>
<td>14.10</td>
<td>5.64</td>
<td>4.5</td>
</tr>
<tr>
<td>0.55</td>
<td>12</td>
<td>4.8</td>
<td>12.36</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>

It is observed as slump increases with W/C ratio strength decreases as stated above. So W/C = 0.50 is ideal for slump as well as for strength. At this W/C compressive strength for CNTC increased by 7.20%, split tensile strength increased by 25.75% and flexural strength increased by 3.87%. So the strength achieved at W/C = 0.48 in reference concrete is achieved at W/C = 0.50 in CNTC.

Since the strength reduced with increase of W/C both in REF as well as CNTC. But the strength of CNTC was higher than reference concrete as shown in Figs. 3, 4 and 5. The increment in strength of CNTC is attributed to incorporation of CNTs as they have tensile strength from 20 Gpa to 100Gpa which in turn increases strength of matrix. They act as filler the spaces between hydration products is filled which increases strength [28, 29]. Due to nucleation they provide strong links between hydration products which accelerate C-S-H formation [30]. Due to bridging effect propagation of micro cracks resists and subsequent growth to the macro scale [31].

The decreases in strength of CNTC with increment of W/C can also be attributed to porosity caused by evaporation of entrapped water from agglomerates [32]. As W/C increases excess water get entrapped and evaporates causing porosity, thus decreasing the strength. But due to formation of strong links between hydration products, the strength of CNTC is higher than reference concrete as observed in this research.

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**Fig. 2.** (b) Relationship between Water-Cement and Water absorption for concretes with W/C of 0.4-0.5.

**Fig. 3.** Comparison between compressive strength of Reference concrete and CNT reinforced concrete.
IV. CONCLUSION

The workability improved with increases W/C ratio as slump increased. But at W/C =0.50 reference concrete attained flow state.

The workability of CNTC was reduced by 60% due to entrapment of water molecules in agglomerates.

As strength reduced with increase of W/C ratio in both reference concretes as well as CNTC, but the strength of CNTC was higher than reference concrete.

The decrease in strength of compositions is due to capillary porosity as it increases at W/C ≥0.40.

W/C=0.50 is ideal for slump as well as strength. At this W/C compressive strength for CNTC increased by 7.20%, split tensile strength increased by 25.75% and flexural strength increased by 3.87%.

The decrease in strength due to capillary porosity is balanced by CNTs in case of CNTC, as CNTs provide bridging effect.

V. FUTURE SCOPE

CNTs can be efficiently used for freeze thaw resistance, strain sensing and piezo resistivity. CNTs can make concrete self sensing concrete. CNT reinforced concrete can be used to concrete sensors to detect cracks.

Conflict of Interest. No.

REFERENCES


