

Relationship between water Cement Ratio and Characteristic Properties of Multi Walled Carbon Nano Tube Reinforced Concrete

P.Mudasir, J.A.Naqash

Abstract: In this study effect of water-cement ratio (W/C) on the characteristic properties of multiwalled 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). Ratio of cement, sand and aggregates was also fixed at 1: 1.76:2.66 in all mixes. For maintaining workability 0.5% polycarboxylate based superplasticizer wbc was added in all mixes.. The workability of carbon nanotube 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%.

Key words: Multi walled carbon nanotubes, Water-Cement ratio, Concrete, Workability, Compressive strength, Split Tensile strength, Flexural strength, Porosity

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 $1000 \text{ m}^2\text{g}^{-1}$ [4,5,6]. They also show very high thermal conductivity of 1700–3000 W/mk and very low electrical resistivity of $5 \times 10^{-8} - 2 \times 10^{-6} \Omega\text{m}$, similar to copper [7]. CNTs exhibit a low density even at high aspect ratio.

They provide large interfacial contact area in matrix without much weight penalty like conventional fibers, hence reinforce concrete more efficiently [8, 9, 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 Waals 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. [16] observed decrease in workability of mortar mixtures 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. [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 Maker and chan [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. [19]. They also reported hydration of cement accelerates with increasing MWCNTs content. When Bharj et al. [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 et al. [21] with addition of 0.003% CNTs by weight to concretes. Tonder and Mafokoane [22] reported that at 28 days compressive strength increased by 13%, 20%, and 9%, while tensile strength increased upto 29%, 18%, and 25%, on adding 0.05%, 0.1%, and 0.2% MWCNT respectively, by weight, to concrete. On contrary

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Table I:Details of Mixes

Mixes	W/C Ratio	Cement kg/m ³	Effective Water kg/m ³	Coarse Aggregate kg/m ³	Fine Aggregate kg/m ³	SP % wbc	CNT % Wbc
REF 55	0.55	430	237	1145	760	0.5	-----
CNTC 55			237				1
REF 50	0.5		215				-----
CNTC 50			215				1
REF 48	0.48		206				-----
CNTC 48			206				1
REF 45	0.45		193				-----
CNTC 45			193				1
REF 40	0.4		172				-----
CNTC 40			172				1

when Madhavi et al. [23] added 0.015%, 0.03% and 0.045% MWCNTs by weight, to concretes and observed 2.75%, 16.38% and 26.69% enhancement of 28 day compressive strength and 30.84%, 45.37% and 66.3%, increment in split tensile strength respectively.

Analysis on the properties of CNT incorporated concrete is not over as little literature is available. Comprehensive studies about the influence of Water Cement ratio on the strength CNT reinforced concrete have never been discussed. Also influence of CNTs on split tensile strength and flexural strength have been rarely disused. Also no relationship between W/C and characteristic strengths of concrete is derived till now. Considering it as a difficulty for researchers the authors has taken an 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. First part of result and discussion compares characteristics properties of reference concrete and CNT reinforced Concrete. While in second part relationship between W/C ratio and characteristics properties of CNT reinforced Concrete is obtained.

II EXPERIMENTAL PROGRAMS

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 superplasticizer (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 and ratio of cement: sand: aggregates fixed at 1: 1.76:2.66 were produced to study the influence of W/C ratio on workability of carbon nano tube incorporated concrete (CNTC). 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 I. 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]. The denomination in table I include mixes produced with different W/C ratio where 'REF' represent reference concrete and 'CNTC' represent CNT reinforced concrete while numeric digits represent W/C ratio. Three 150mm cube specimens for compressive strength test, three 150×300mm cylindrical specimens for split tensile strength test and three 150×150×700mm beam specimen for flexure test at 28 days were prepared. After at 24h, specimens were demoulded and kept in water curing at room temperature 25±2°C for 28days.

III RESULTS AND DISCUSSION

A. Comparison between characteristic properties of reference concrete and CNT reinforced Concrete

Workability

The addition of CNTs caused drastic decrease in workability. Slump increased with increment of water and with $W/C \geq 0.50$, reference concrete attained self compacting state or flow concrete state. But at $W/C = 0.50$ CNTC didn't attained flow state like that of reference concrete because the some water was entrapped in agglomerates due to which slump was less than reference concrete. Its observed that the workability of CNTC reduced by 60% in comparison to reference concrete at a particular W/C ratio as observed from table II and figure 1. Also the variation of up to $\pm 2\text{cm}$ was observed in between the mixes with change of W/C as observed for table II. The decrease in workability of nano modified concrete 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. 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].

Table II: Result for slump

W/C	Ref slump	CNTC slump
0.55	122	75
0.50	118	72.5
0.48	115	69.5
0.45	112.5	68
0.40	100	65

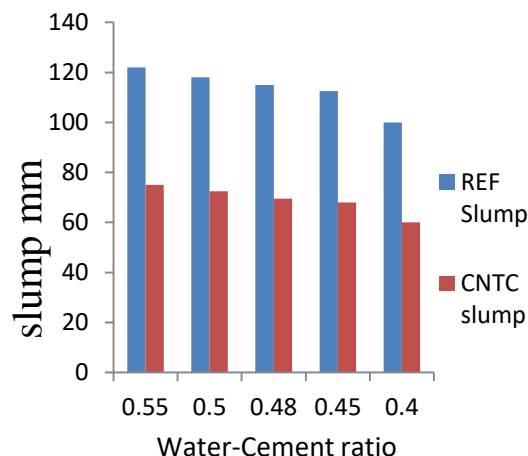


Fig 1. Slump increment with W/C ratio

Compressive, Split Tensile and Flexural Strength.

The compressive strength test was conducted as per IS 416-1959 on cubes of size $150 \times 150 \times 150$ mm. The split tensile strength test was conducted on 300×150 mm cylinder as per IS 5816-1999. The flexural strength test using three point loading method was performed as per IS 516:1959. The maximum failure load and its failure pattern are noted and results are presented in table III, table IV and table V respectively.

The strength test was performed on specimens with $W/C \geq 0.45$ because $W/C = 0.40$ is used for hydration of cement. At $W/C = 0.40$ Tri Calcium Aluminate i.e. C_3A 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.

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.

Table III: Detailed result of Compressive strength

W/C ratio	Ref concrete		CNT Concrete		% increase in strength
	Failure load kN	Mpa	Failure load kN	Mpa	
0.45	1013	45	1094	48	8
0.48	960	42	1029	45	7.20
0.50	855	38	913	40	6.87
0.55	805	35	862	38	7

Table IV: Detailed result of split tensile strength

W/C ratio	Ref concrete		CNT Concrete		% increase in strength
	Failure load kN	Mpa	Failure load kN	Mpa	
0.45	186	2.63	237	3.35	27
0.48	160	2.26	201	2.84	25.75
0.50	150	2.12	190	2.68	26.87
0.55	138	1.95	173	2.44	25

Table V: Detailed result of flexural strength

W/C ratio	Ref concrete		CNT Concrete		% increase in strength
	Failure load kN	Mpa	Failure load kN	Mpa	
0.45	15	6	15.75	6.3	5
0.48	14	5.6	14.54	5.81	3.87
0.50	13.5	5.4	14.10	5.64	4.5
0.55	12	4.8	12.36	5	3

As observed from tables III, IV and V the strength reduced with increase of W/C in both reference concrete as well as CNTC. But the strength of CNTC was higher than reference concrete as shown in figure 2, 3 and 4. 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. As 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

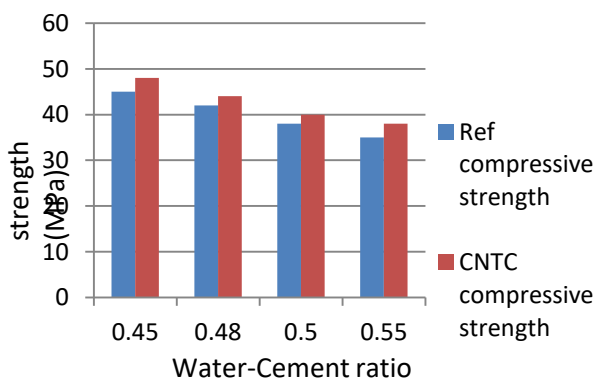


Fig 2. Comparison between compressive strength of Reference concrete and CNT reinforced concrete

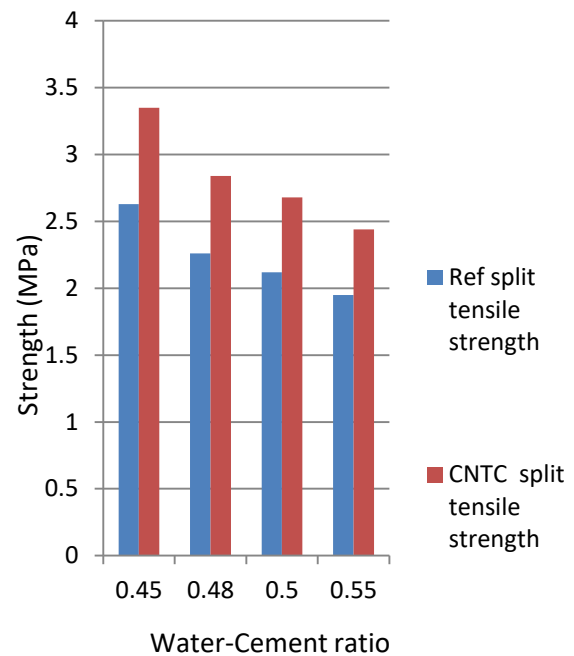


Fig. 3 Comparison between Split tensile strength of Reference concrete and CNT reinforced Concrete.

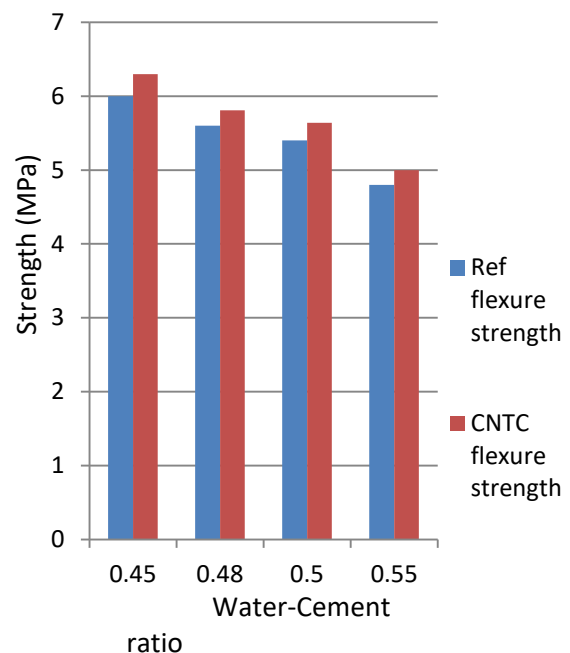


Fig. 4 Comparison between Flexural strength of Reference concrete and CNT reinforced Concrete.

B. Relationship between W/C ratio and Hardened properties of CNT reinforced Concrete

H.K.Kim et. al [33] derived relationship between compressive strength and porosity of CNT/cement composites and found R^2 was less than 0.6. From figure 5, 6 and 7 relationship between W/C and hardened properties (i.e compressive, split tensile, and flexural strength) of CNTC were fabricated.

By fitting experimental data in respective equations and tracing them values of constants terms of equations is obtained and are catalogued in table VI. In particular R^2 was as high as 0.9 in this study. High value of R^2 can be attributed to interaction between CNT and hydration product and bridging effect of CNT. Further investigation needs to be done in terms of varying CNT content, grade of concrete and length of fibers.

Table VI: Relationship equations

Equation	Variable obtained			R^2
	a	b	c	
$fck = Ax^2 + Bx + C$	943	-1046	328.1	0.9
$fct = Ax^2 + Bx + C$	95.53	-104.5	31.02	0.9
$fcr = Ax^2 + Bx + C$	19.48	-32.28	16.86	0.9

Where fck =compressive strength, fct =split tensile strength, fcr =flexural strength a, b, c =variable obtained by linear regression.

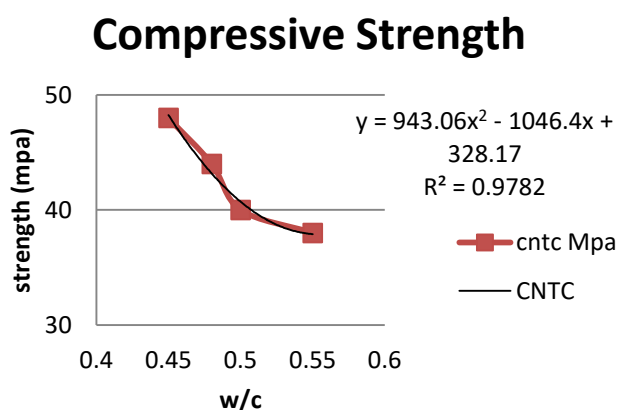


Fig. 5 Relationship between Compressive strength and Water cement ratio

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 $W/C \geq 0.40$.

Split Tensile Strength

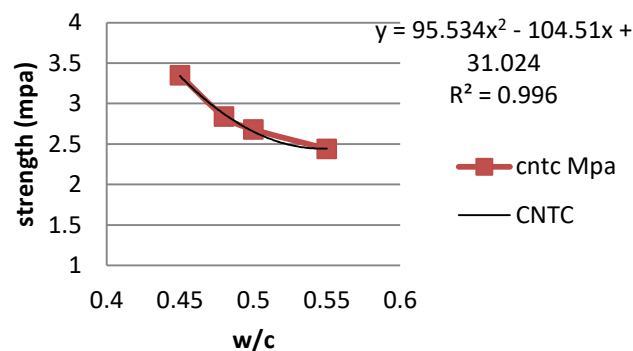


Fig. 6 Relationship between split tensile strength and Water-Cement Ratio

Flexural strength

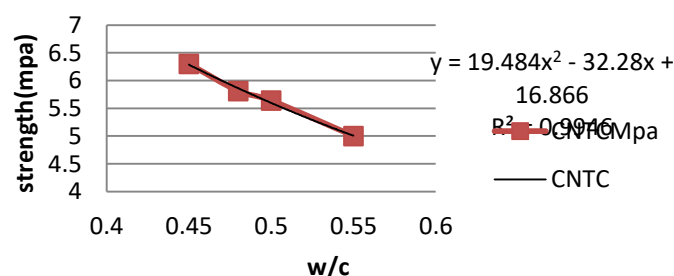


Fig. 7 Relationship between Flexural strength and Water-Cement Ratio

- 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.

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