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An Experimental Study of pH Value and Flexural Strength of Cement Sand Mortar with Surface Untreated Multi-Walled CNTs

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Abstract

Background/Objectives: The paper describes the study carried out on test specimens of cement mortar composite admixed with multi-walled carbon nanotubes (CNTs) in order to investigate the physical property changes under nano-level hydration. **Methods/Statistical Analysis:** In this study, the standard engineering tests such as pH value identification, flexural strength test and compression strength tests were carried out for both control and test specimens which were cast and cured as per Indian Standard specifications. Test specimens of cement mortar composite consisted of ordinary Portland cement and river sand added with 0.2% (by weight of cement) pristine multi-walled CNTs ultrasonicated but without any surface treatment. **Findings:** The pH value of ultrasonicated multi-walled CNTs dispersed in de-ionised (DI) water was first determined and found to be 6.85. The pH of control mix without multi-walled CNTs was 12.64 and the pH of test mix with multi-walled CNTs was 12.37. The percentage addition of multi-walled CNTs was very small and hence the reduction in alkalinity was found to be equally small. Flexural strength of test specimens showed 23%, 31.41% and 31.46% increase at 7, 28 and 45 days respectively over control specimens. Compressive strength of test specimens showed 6.1% increase at 28 days over control specimens. **Application/Improvements:** In view of improvement in flexural strength in mortar, addition of multi-walled CNTs to concrete elements may help in improving their performance under dynamic loading. Further improvements are required to study the effect of an increased percentage addition of multi-walled CNTs without any surface treatment and without any surfactant in cement sand mortar (1:3).

Keywords: Cement Sand Mortar, Compressive Strength, Flexural Strength, Multi-Walled CNT, pH Value

1. Introduction

Pore modification with finer particles such as flyash and silica fume has increased durability and compressive strength of concrete but not necessarily the tensile strength of the composite. While concrete of grade greater than M75 have been easily achieved by use of such pore modification conversion of free lime into useful additional binding chemicals. The flexural strength of concrete was found to be 8 to 11 percent of the compressive strength of the concrete for higher ranges of concrete strength[1]. On the other hand, fibres were used for strengthening[2,3] and also improvement of defects was achieved using fibres[4].

Incorporation of nano-scale material to cement composite necessarily involves study at atomic level. A nano-composite is a multiphase solid material where one of the phases has one, two or three dimensions within 100 nanometers (nm), or structures having nano-scale repeat distances between the different phases that make up the material. As such, CNTs have unique properties for considering them as a reinforcing material and also along with chemical and bacteria[5,6] respectively.

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Hydraulic cements, such as those constituted by calcium silicate, calcium aluminate and calcium sulpho aluminate have an intrinsic maximum tensile strength of about 20 MPa. Brittle nature and consequent tendency of cracking are the primary drawbacks of all cement based structural materials[7]. Intrinsic properties of cementitious composite are stiffness and hardness[8]. At atomic level, calcium silicate hydrate (CSH) gel provides strength and cohesion by bonded silicate chains. Significance of silicate chain is that upon its breakage, C-S-H gel would provide a low tensile strength, although surface force between nano-sized CSH gels provides cohesion property of CSH gel[9,10]. Tensile strength of binder and cohesive force between C-S-H gels determine the stiffness which in turn contributes to mechanical strength. On the other hand, presence of nano-, micro-, meso- and macro-sized crack affects durability.

Reinforcing materials also had various improvements from steel rods, fibers to various chemical agents; that is from macro- to micro-scale. Recently, carbon nano tubes are identified as a reinforcing material to cementitious composite. CNTs were first invented by Ijima in 1991 but its application as a reinforcing material in cementitious composite was investigated only a decade ago[11]. When compared to other traditional fibers, carbon nanotubes are considered better in increasing the amount of CSH gel and reducing the porous phase[12].

Crack propagation involves energy releases. If higher amount of energy is required to break bonds, then the strength of the material as a whole rises up i.e., higher aspect ratio, where significantly higher energies for crack propagation than would be the case for a lower aspect ratio fiber[13]. Among the two classifications of CNT viz. single-walled CNTs and multi-walled CNTs, the latter is a better performer with respect to cementitious composite and more rigid as their sections are larger than that of the single-walled CNTs[14]. Also, two other important advantages of multi-walled CNTs over single-walled CNTs are their low production costs and availability in large quantities. Further, earlier studies revealed the interaction of multi-walled CNTs with the cementitious composite resulted in better strength performance[11]. Other researchers have used multi-walled CNTs in their studies and developed the application of multi-walled CNTs to cementitious composite[15-18]; including other applications[19,20]. It is only logical that the studies should be further extended into mortar phase.

2. Experimental Investigation

2.1 Materials

Ordinary Portland cement of 53 grade conforming to IS: 12269[21] was used. Chemical composition is shown in Table 1 and Table 2 and physical properties of the cement is shown in Table 3 and Table 4. The fine aggregate used was standard sand conforming to IS:650[22] as shown in Table 5.

Table 1. Chemical composition of OPC 53 grade cement

$CaO-0.7SO_3$/ $2.8SiO_2+1.2Al_2O_3+0.65Fe_2O_3$	Al_2O_3 / Fe_2O_3	Insoluble Residue (% by mass)
0.90	1.02	2.24

Table 2. Chemical composition of OPC 53 grade cement, contd.

Magnesia (% by mass)	Sulphuric Anhydride (% by mass)	Total Loss on Ignition (% by mass)	Total Chlorides (% by mass)
1.33	2.65	2.23	0.019

Table 3. Physical properties of OPC 53 grade cement

Fineness (m^2/kg)	Standard Consistency (%)	Setting Time (min)		Soundness	
		Initial	Final	Le-Chat Expansion (mm)	Autoclave Expansion (%)
290	31.0	190	290	1.0	0.060

Table 4. Physical properties of OPC 53 grade cement, contd.

Compressive Strength (MPa)		
72 +/- 1hr.(3 days)	168 +/- 2 hr.(7 days)	672 +/- 4 hr.(28 days)
35.0	44.5	53

Table 5. Properties of Fine Aggregate

Type of sand	Ennore sand
Particle size	33.33% of smaller than 2mm and greater than 1 mm 33.33% of smaller than 1 mm and greater than 500 microns 33.33% of below 500 microns but greater than 90 microns
Specific gravity	2.64

Table 6. Properties of multi-walled CNTs obtained from M/s Reinste Nano Ventures Pvt. Ltd.

Carbon purity	Min. 95%
Number of walls	3-15
Outer diameter	5-20 nm
Inner diameter	2-6nm
Length	1-10micro meter
Apparent density	0.15 - 0.35 g/cm^3
Loose agglomerate size	0.1 - 3mm

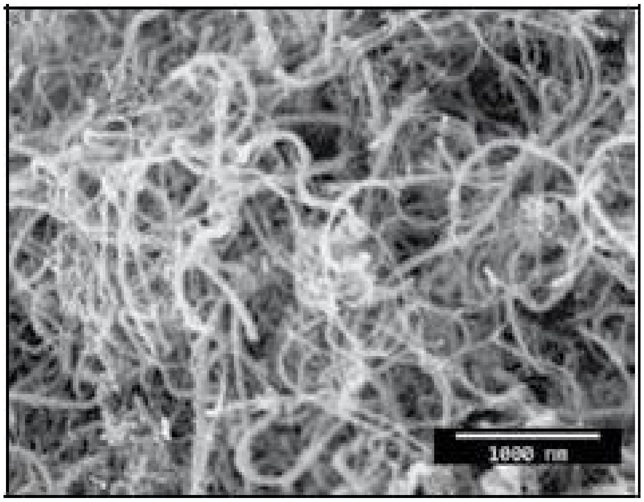

Figure 1. SEM image of multi-walled CNTs.

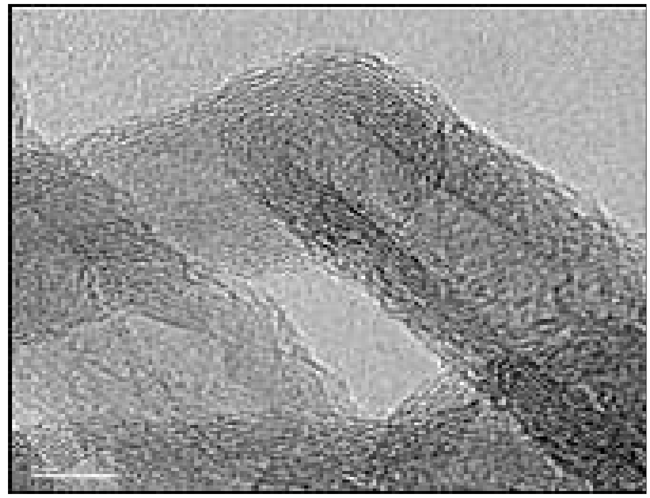

Figure 2. TEM image of multi-walled CNTs.

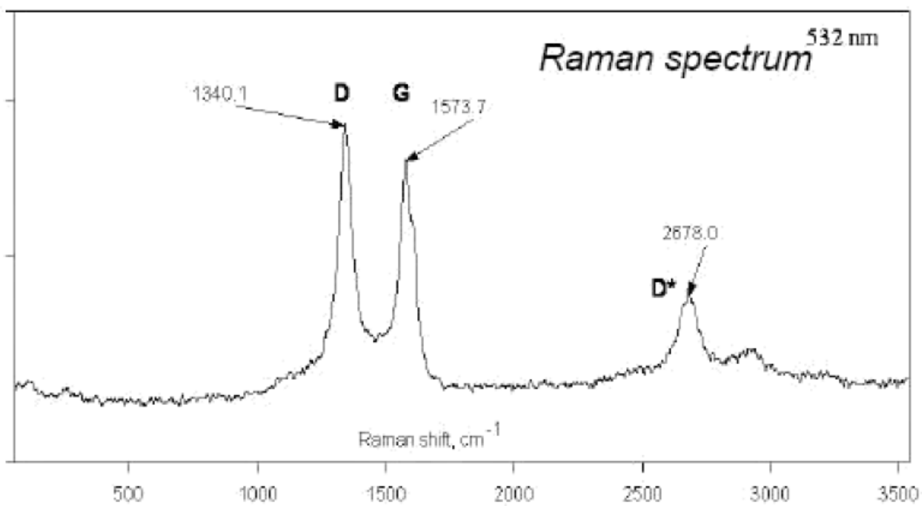

Figure 3. Raman spectroscopy.

Pristine multi-walled carbon nanotubes obtained from M/s Reinste Nano Ventures Pvt. Ltd., were used. Properties of multi-walled CNTs are shown Table 6. Microstructure and morphology of multi-walled carbon nanotubes using SEM, TEM and Raman as provided by the suppliers are shown in Figure 1, Figure 2 and Figure 3 respectively. These are in conformity with those used by other researchers.

2.2 Preparation of Specimens

Mix proportion of cement sand mortar was chosen as 1:3. Water cement ratio of 0.4 was adopted as indicated by the normal consistency of cement. CNT added was 0.2% (by weight of cement). No dispersing agent or surfactant was added.

At first, multi-walled CNTs were dispersed in de-ionised (DI) water with ultrasonication at 25 kHz was carried out for 4 hours with regular intervals of 30 seconds to avoid overheating. The DI water quantity used was the amount of water required for preparing prism specimens with a ratio of 0.4.

2.2.1 Flexural Strength Specimens

Prismatic specimens of sizes 40mm x 40mm x 160mm were prepared as per normal procedure. Initially, dry mixing of sand and cement with a mixing time of 2mins was done. Then, wet mixing was carried out with the addition of water with a mixing time of 2mins, till a uniform colour of mix was obtained. The prepared mix was then put in the prism mould prepared out of 12mm thick acrylic. Compaction was achieved through vibration with 12000 rpm vibrator for 5mins. The specimens were smooth finished and kept for setting. Demoulding was done after 24hrs and cured under water at room temperature which varied between 26°C to 30°C. Cement mortar without multi-walled CNTs of flexure strength (CMF) specimens were marked as CMF1, CMF2, …CMF24 and Cement mortar with multi-walled CNTs of flexure strength (CNMF) specimens were marked as CNMF1, CNMF2, …CNMF24.

2.2.2 Compressive Strength Specimens

Cube specimens of size 70.6 mm with a cross sectional area have prepared as per normal procedure. The specimens were smooth finished and kept for setting. Demoulding was done after 24 hrs and cured under water at room temperature which varied between 26°C to 30°C. Cement mortar without multi-walled CNTs of compressive strength (CMC) specimens were marked CMC1, CMC2 and CMC3 and Cement mortar with multi-walled CNTs of compressive strength (CNMC) were marked as CNMC1, CNMC2, and CNMC3.

2.3 Testing

2.3.1 pH Value

Using a pH meter, the pH value of (i) Green mortar (ii) Ultrasonicated liquid dispersed with multi-walled CNTs (iii) Cement sand mortar mixed with multi-walled CNTs. The results are given in the Table 7.

2.3.2 Flexural Strength

Flexural strength of the specimens was carried out using a two point flexure bending test as shown in Figure 4. From the flexural test, maximum breaking load and maximum deflections were obtained and flexural strength was calculated using the formula below; the recorded and calculated values were tabulated in Table 8 and Table 9.

$$\text{Flexural strength} = \frac{3F(L_{span} - L_{load})}{2bt^2}$$

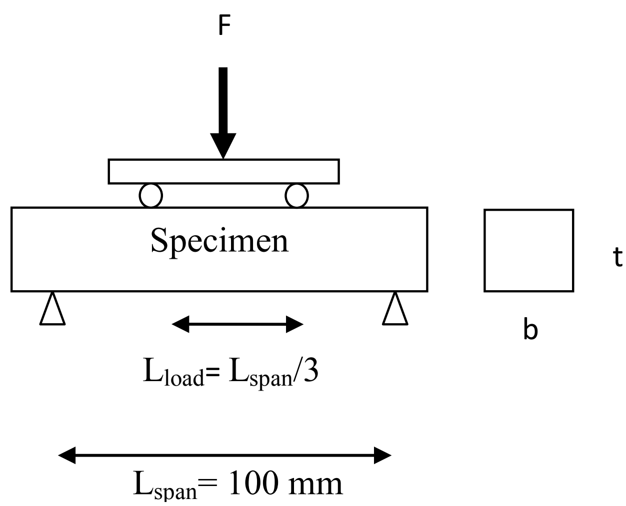

Figure 4. Flexural strength test.

Table 7. pH values

Medium	pH Value
(i) pH value of green mortar	12.64
(ii) ultrasonicated liquid dispersed with multi-walled CNTs	6.85
(iii) cement sand mortar mixed with multi-walled CNTs	12.37

Table 8. Breaking load, Flexural strength and Deflection Specimen: Prismatic beams of 40 mm x 40 mm x 160 mm cast with plain cement sand mortar Values are tabulated accordingly: Breaking load F (kN) as column 1, Flexural strength (MPa) as column 2 and Deflection (mm) as column 3.

CMF sample data									
sample	7 days			28 days			45 days		
	1	2	3	1	2	3	1	2	3
CMF1	4.34	6.78	1.20	6.50	10.16	3.10	6.52	10.19	3.10
CMF2	4.52	7.06	1.40	6.40	10.00	2.90	6.51	10.17	3.00
CMF3	4.80	7.50	1.60	6.60	10.31	3.20	6.42	10.03	3.00
CMF4	4.75	7.42	1.60	6.51	10.17	3.10		-	
CMF5	4.62	7.22	1.50	6.46	10.09	3.00		-	
CMF6	4.63	7.23	1.50	6.45	10.08	3.00		-	
CMF7	4.73	7.39	1.60	6.50	10.16	3.10		-	
CMF8	4.60	7.19	1.50	6.41	10.02	2.90		-	
CMF9	4.80	7.50	1.60	6.52	10.19	3.10		-	
CMF10	4.80	7.50	1.30	6.53	10.20	3.20		-	
CMF11	4.65	7.27	1.50	6.51	10.17	3.10		-	
CMF12	4.69	7.33	1.60	6.50	10.16	3.10		-	
CMF13	4.75	7.42	1.60	6.52	10.19	3.10		-	
CMF14	4.46	6.97	1.30	6.40	10.00	3.00		-	
CMF15	4.61	7.20	1.50	6.41	10.02	3.00		-	
CMF16	4.60	7.19	1.50	6.41	10.02	2.90		-	
CMF17	4.65	7.27	1.50	6.45	10.08	3.00		-	
CMF18	4.70	7.34	1.60	6.48	10.13	3.10		-	
CMF19	4.72	7.38	1.60	6.46	10.09	3.00		-	
CMF20	4.61	7.20	1.40	6.42	10.03	3.00		-	
CMF21	4.80	7.50	1.60	6.60	10.31	3.20		-	
CMF22	4.75	7.42	1.60	6.56	10.25	3.20		-	
CMF23	4.52	7.06	1.40	6.40	10.00	3.00		-	
CMF24	4.55	7.11	1.30	6.60	10.31	3.00		-	
Average		7.27	1.49		10.13	3.05		10.13	

Table 8. Breaking load, Flexural strength and Deflection Specimen: Prismatic beams of 40 mm x 40 mm x 160 mm cast with plain cement sand mortar added with multi-walled CNTs Values are tabulated accordingly: Breaking load F (kN) as column 1, Flexural strength (MPa) as column 2 and Deflection (mm) as column 3.

CNMF sample data									
sample	7 days			28 days			45 days		
	1	2	3	1	2	3	1	2	3
CNMF1	5.68	8.88	2.30	8.51	13.30	5.10	8.52	13.31	5.2
CNMF2	5.62	8.78	2.20	8.19	12.80	4.90	8.51	13.30	5.30
CNMF3	5.57	8.70	2.20	8.78	13.72	5.20	8.54	13.34	5.30
CNMF4	5.61	8.77	2.20	8.75	13.67	5.30		-	
CNMF5	5.59	8.73	2.50	8.77	13.70	5.20		-	
CNMF6	5.65	8.83	2.30	8.12	12.69	5.20		-	
CNMF7	5.70	8.91	2.40	8.00	12.50	5.30		-	
CNMF8	5.60	8.75	2.30	8.10	12.66	4.80		-	
CNMF9	5.62	8.78	2.30	8.22	12.84	4.90		-	
CNMF10	5.71	8.92	2.20	8.50	13.28	5.10		-	
CNMF11	5.68	8.88	2.10	8.70	13.59	5.00		-	
CNMF12	5.62	8.78	2.20	8.80	13.75	5.10		-	
CNMF13	5.71	8.92	2.10	8.90	13.91	5.20		-	
CNMF14	5.66	8.84	2.30	8.23	12.86	5.20		-	
CNMF15	5.88	9.19	2.20	8.56	13.38	5.30		-	
CNMF16	5.91	9.23	2.20	8.55	13.36	4.90		-	
CNMF17	5.50	8.59	2.30	8.45	13.20	4.90		-	
CNMF18	5.20	8.13	2.40	8.55	13.36	5.10		-	
CNMF19	5.89	9.20	2.40	8.66	13.53	5.10		-	
CNMF20	5.78	9.03	2.50	8.79	13.74	5.20		-	
CNMF21	5.55	8.67	2.60	8.77	13.70	5.20		-	
CNMF22	5.99	9.36	2.30	8.88	13.88	5.20		-	
CNMF23	6.20	9.69	2.20	8.20	12.81	5.30		-	
CNMF24	6.25	9.77	2.20	8.50	13.28	5.30		-	
Average		8.93	2.29		13.31	5.13		13.32	

where, F is breaking load values taken from Table 8 and Table 9 respectively. L_{span} is the span between supports taken as 100mm and L_{load} is the spacing between load points taken $^{1}/_{3}{}^{rd}$ span as from Figure 4.

2.3.3 Compressive Strength

Compressive strength of specimens was carried out using a compressive testing machine of 100 kN capacity and the results were tabulated in Table 10.

in an approximate increase of about 30% in cement sand mortar (1:3).

However, the average deflection at 28 days was found to be about 40%. This is to be expected as the mix got altered and become more flexible by addition of multi-walled CNTs.

It is seen from Table 10, the average 28 days compressive strength of samples with and without multi-walled CNTs was found to be 56.48 MPa and 53.22 MPa respectively. The corresponding ratios work out to 4.24 and 5.25 respectively indicating an improvement of 20%.

Earlier researchers worked on surface treated multi-walled CNTs and addition of surfactant have showed flexural strength of 8.37+/- 2.1% and compressive strengths of 62.13+/-2.3%[15] while in another study an increase of 10% in flexural strength[16] was observed; also improvement was observed in modulus of rupture using pristine multi-walled CNTs[17] and in very recent study, an addition of 0.025% of treated multi-walled CNTs showed 86% and 27% improvement in tensile strength and compressive strength respectively[18].

Table 10. Compressive strength values

CMC sample data at 28 days			CNMC sample data at 28 days		
Sample	Load (kN)	Compressive Strength (MPa)	Sample	Load (kN)	Compressive Strength (MPa)
CMC1	265	53.02	CNMC1	280	56.02
CMC2	264	52.82	CNMC2	283	56.62
CMC3	269	53.82	CNMC3	284	56.48
Average		53.22			56.48

3. Results and Discussions

3.1 pH Values

The pH value of ultrasonicated CNTs dispersed in water was 6.85. The pH value of control mix without CNTs was 12.64 and the pH value of mix with CNTs was 12.37.

Multi-walled CNTs being chemically acidic, it is expected that their addition would reduce the alkalinity of cement sand mortar. However, the results show that the reduction was only marginal (12.64 and 12.37). Hence, corrosion protection provided to reinforcement in RCC by the alkaline medium of cement is not likely to be affected.

3.2 Flexural Strength

The percentage increase in flexural strength was 22.87% in 7 days (average of 24 specimens), 31.41% in 28 days (average of 24 specimens) and 31.46% in 45 days (average of 3 specimens). It may be concluded that addition of 0.2% (by weight of cement) multi-walled CNTs will result in an approximate increase of about 30% in cement sand mortar (1:3).

4. Conclusions

Addition of 0.2% multi-walled CNTs without any surface treatment and without any surfactant in cement sand mortar (1:3) resulted in

(i) Slight decrease in alkalinity from 12.64 to 12.37

(ii) Increase in flexural strength of about 30% in 28 days

(iii) Decrease in the ratio of compressive strength to flexural strength showing an improvement of 20%.

Further investigations are required to study the effect of an increased percentage addition of multi-walled CNTs without any surface treatment and without any surfactant in cement sand mortar (1:3).

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