EFFECT OF MULTIWALLED CARBON NANOTUBES AND NANO ALUMINIUM OXIDE ON FLEXURAL AND COMPRESSIVE STRENGTH OF CEMENT COMPOSITES

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ABSTRACT

This research investigates the behaviour of hardened cement paste incorporated with multiwalled carbon nanotubes (MWCNTs) and nano aluminium oxide (Nano-Al_2O_3). The percentages of MWCNTs and Nano-Al_2O_3 were fixed at 0.75% and 1.0% by weight of cement respectively. Dispersion of both MWCNTs and Nano-Al_2O_3 was carried out by ultrasonic energy method. At 28 days of curing in tap water, specimens of size 20mmx20mmx80mm were subjected to flexural test by three points loading and specimens of size 20mmx20mmx20mm were subjected to compression test. The results were then compared with the results of plain cement control specimens. Results showed remarkable improvements in mechanical properties of cement composites. Scanning Electron Microscopy was used to investigate the dispersion and microstructure bonding of MWCNTs in cement matrix.

Keywords: Multi-Walled Carbon Nanotubes (MWCNTS), Nano-Aluminium Oxide (Nano-Al_2O_3), Flexural Strength, Compressive Strength, Toughness Index.

I. INTRODUCTION

In Civil Engineering field, cement is being used as major construction material from centuries and it is the main ingredient of cement concrete along with the fine and coarse aggregates. The calcium silicate hydrate (CSH) gel formed due to hydration of cement is major factor for gaining strength of cement concrete. It has been found that on addition of some nano materials into the cement matrix, the nanoscale bonding can be developed between the CSH and nano materials. The nano pores in the cement matrix will be filled up by nano materials. The nanoscale bonding can hold the cement matrix stronger than the CSH itself and arrest the micro cracks and their propagation [1]. Some nano particles will act as pozzolana and hence there will be more cementitious products in the cement matrix [2]. Therefore mechanical properties of cement based material can be enhanced by adding the nano materials into cement composite.

Recently, carbon nano tubes (CNTs) have attracted tremendous scientific attention owing to their excellent physical and chemical properties. Due to their excellent mechanical properties, carbon nano tubes have been the subject of many investigations from the past decade where they have been used as inclusions in composite materials. Mechanically, CNTs exhibit elastic Young's modulus of more than 1 TPa. Their theoretical strength is 100 times that of steel, at only 1/6th the specific gravity [3]. CNTs are tubular structures made by rolling the of graphite sheets in layer. The CNTs consisting one layer of graphite sheet called single walled carbon nanotubes (SWCNTs) and more than one layers called multiwalled carbon nanotubes MWCNTs). Single-walled CNTs have a diameter of 1 to 3 nm, whereas multiwalled CNTs have a diameter ranging from 10 to 100 nm. The length of both types of CNTs ranges from 0.5 μm to 50 μm. CNTs have very high aspect ratios ranging from 1,000:1 to 2,500,000:1 and very small diameters. This property actually helps to bridge the cracks between cement compounds and restrict them from increasing and essentially create a new generation of a crack-free material [1]. After 28 days of curing, the cement composite reinforced with MWCNTs at 0.75% by weight of cement showed 43.75% increase in flexural strength [4]. Compressive strength and split tensile strength of cement paste reinforced with 0.5% of MWCNTs by weight of cement were increased by 15.0% and 36.0% respectively at 28 of days curing [1]. Compressive and split tensile strength were increased by 27.0% and 45.0% respectively in the cement composite incorporated with MWCNTs at 0.045% by weight of cement after curing for 28 days and permeability also decreased up to 17.0%[5].

Alumina component reacts with calcium hydroxide (pozzolanic action) produced from the hydration of calcium silicates. The rate of the pozzolanic reaction is proportional to the amount of surface area available for reaction. Nano aluminium oxide provides more surface area which promotes the proper pozzolanic reaction and hence there will be production of more cementitious materials in hydrated cement paste [6]. Therefore, it is possible to add Nano- Al_2O_3 of a high purity in order to improve the characteristics of cement mortars. The partial replacement of cement with Nano-Al_2O_3 particles improves the split tensile and flexural strength of concrete but decreases its setting time [7]. At 28 days of curing, the cement concrete specimens showed 55.0% and 18.0% increase in split tensile and compression strength respectively on addition of 1.0% Nano-Al_2O_3 by weight of cement [2] [7]. Abrasion resistance of cement matrix can be increased by incorporating the Nano- Al_2O_3 [8]. It is also noticed that water absorption of cement composite can be reduced by incorporating the Nano-Al_2O_3 [9]. It has been found that MWCNTs of higher aspect ratio results in better mechanical properties of cementitious composites [10]. Optimum levels of MWCNTs and Nano-Al_2O_3 in cement composite were found to be 0.75% and 1.0% respectively [4] [7].

II. EXPERIMENTAL PROGRAMME

2.1 Materials

The materials used in this investigation were ACC Ordinary Portland Cement of 43 grade, MWCNTs and Nano-Al_2O_3. MWCNTs and Nano- Al_2O_3 were obtained from Sigma-Aldrich.co USA. The properties of materials as per the supplier are given in the Table 1 to Table 3.

Table 1. Properties of Ordinary Portland Cement

Property	values
Density	1.4g/cc
Specific gravity	3
Initial setting time	30 minutes
Normal consistency	30%

Table 2. Properties of MWCNTs

Property	values
Diameter	10-30nm
Length	1-2μm
Purity	95%
Surface area	350 m^2/gm
Bulk density	0.05-0.17gm/cm^3

Table 3. Properties of Nano-Al_2O_3

Property	values
Diameter	15 $\pm$ 3nm
Surface area	165 $\pm$ 12 m^2/gm
Purity	99.90%
Bulk density	< 0.1gm/cm^3

2.2 Method

Preparation and testing of samples were carried out as per ASTM general standards. However, because of the economical considerations, small-size samples were prepared. Hence, the preparation and testing procedures had to be modified accordingly.

2.2.1 Dispersion of MWCNTs and Nano-Al_2O_3

MWCNTs are usually agglomerated due to van der Waal's bonding. Therefore dispersion of MWCNTs is a critical issue in processing the nano composite. Pre-dispersion of MWCNTs was carried out by sonication method in water using ethanol as dispersant [4]. Since Nano-Al_2O_3 is soluble in water, it was pre-dispersed in only water by sonication method.

2.2.2 Preparation of Specimens

Specimens were prepared in four series as per the composition given in the Table 4. After sonication, MWCNTs and Nano-Al_2O_3 were added into cement and mixed thoroughly to get homogeneous paste. Since the quantity of materials was very less due to smaller sizes of specimens, the manual mixing was adopted. W/C ratio was maintained at 0.4. The paste was filled into cleaned and oiled moulds of particular dimensions in layers with proper compaction and covered with the polythene sheets to avoid the surface cracks. After 24 hours specimens were demoulded and immersed in the water bath for curing.

Table 4. Showing the mix design of specimen series

Sl. No	Specimen Series	Specimen size for flexure test (in mm)	Specimen size for compression test (in mm)	Composition
1	PC	20x20x80	20x20x20	Cement only
2	A1	20x20x80	20x20x20	Cement+0.75% MWCNTs
3	A2	20x20x80	20x20x20	Cement+1.0% Nano-Al_2O_3
4	A3	20x20x80	20x20x20	Cement+0.75% MWCNTs+1.0% Nano-Al_2O_3

2.3 Testing

The mechanical performances of the nanocomposites were evaluated by performing flexure and compression test. After 28 day of curing, specimens of 20mm×20mm×80mm were subjected to flexural test by single point bending and specimen of size 20mmx20mmx20mm were subjected to compression test. The flexural tests were performed with a load cell frame testing machine with a 10 kN capacity with strain rate of 0.125mm/min. The deflections of the beam specimens were recorded at regular load intervals and corresponding load deflection curves were plotted. The compression tests were performed with a compression testing machine of capacity of 2000kN at loading rate of 0.1kN/sec. Scanning Electron Microscopy (SEM) was used to investigate the dispersion and microstructure bonding of MWCNTs in cement matrix.

III. RESULTS AND DISCUSSION

The objective of this present study is to compare the mechanical properties of cement composites like deflection criteria, flexural strength, toughness and compressive strength with those of plain cement control specimens.

Table 5. Details of test observations under the three points loading test

Sl. No.	Specimen Series	Ultimate load in N (Avg.)	Max. deflection in mm (Avg.)	Crack distance in mm (Avg.)	Percentage increase in ultimate load	Percentage increase in max. deflection
1	PC	360	0.37	33.33	------	-------
2	A1	500	0.46	33.5	38.88%	24.32
3	A2	443.3	0.41	33.66	23.13%	10.81
4	A3	580	0.53	33.5	61.11%	43.24

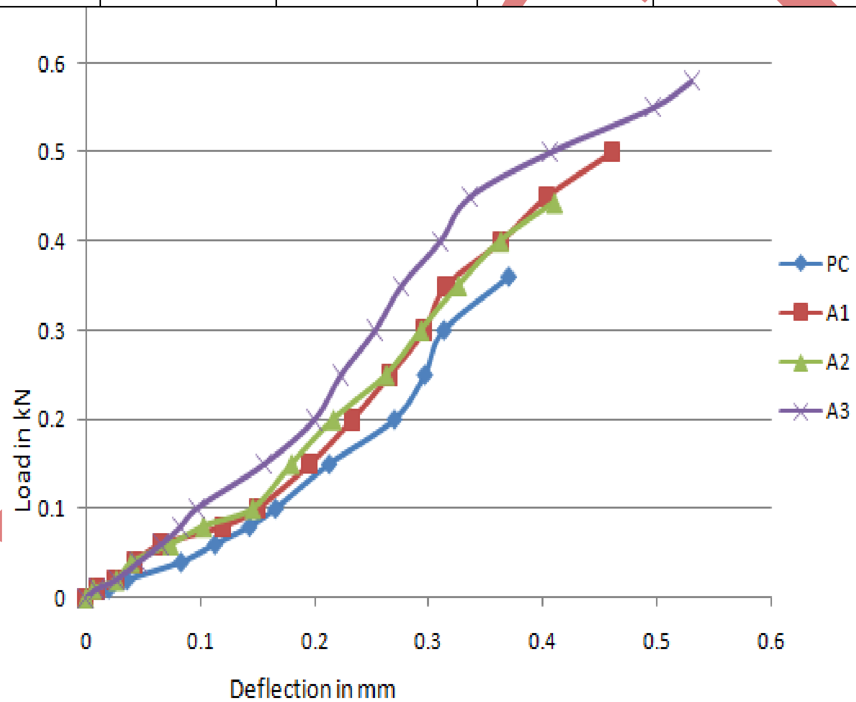


Fig 1. Load deflection curves of all specimen series

From Load Deflection curves it was observed that there was no particular distinct yield point for any cement composite series. This may be due to materials behavior was found to be more plastic. The cement composite beams reinforced with MWCNTs showed greater load carrying capacity with increased deflections in comparison with the beams having only cement and beams reinforced with Nano-Al_2O_3 particles. This may be due to bonding between the cement matrix and MWCNTs and hence inhibition of propagation of micro cracks.

The beams reinforced with nano-aluminium oxide showed higher load carrying capacity and greater deflection than the beams of only cement. The reason for this may be that nano aluminium oxide provided more surface area which promoted the proper pozzolanic reaction and hence there was production of more cementitious materials in hydrated cement paste.

The beams reinforced with both MWCNTs and Nano-Al_2O_3 showed till greater load carrying capacity and higher deflection. As said above, this may be due to that MWCNTs inhibited the propagation of micro cracks and Nano-Al_2O_3 helped in producing more cementitious products by its pozzolanic reaction.

3.1 Flexural strength of the cement composites

The flexural strength represents the highest stress experienced within the material at its moment of rupture. It is measured in terms of stress. Calculated flexural strength values indicate that the addition of multiwalled carbon nanotubes and nano aluminium oxide improved the flexural strength considerably. Compared to plain cement beams, flexural strength was increased by 39.6%, 24.3% and 62.0% in the cement composite beam series A1, A2 and A3 respectively.

Table 6. Shows the flexural strengths of cement composites under three point loading

Sl. No	Specimen Series	Ultimate load in N (Avg.)	Max. Deflection in mm (Avg.)	Crack Distance in mm (Avg.)	Flexural strength in N/mm^2	Percentage increase in flexural strength
1	PC	360	0.37	33.33	4.499	---
2	A1	500	0.46	33.5	6.281	39.6
3	A2	443.3	0.41	33.66	5.595	24.3
4	A3	580	0.53	33.5	7.286	62

The improvement in the flexural strength on addition of MWCNT may be due to proper bonding between the C-S-H of cement paste and MWCNTs and hence inhibition of propagation of micro cracks. But on addition of Nano Al_2O_3, improvement in the flexural strength may be due to that nano aluminium oxide provided more surface area which promoted the proper pozzolanic reaction and hence there was production of more cementitious materials in hydrated cement paste.

The beams reinforced with both MWCNTs and Nano-Al_2O_3 showed till greater flexural strength. As said above, this may be due to that MWCNTs inhibited the propagation of micro cracks and Nano-Al_2O_3 helped in producing more cementitious products by its pozzolanic reaction.

3.2 Toughness of the cement composites

Table 7. Shows toughness index of cement composites under three point loading

Sl. No	Specimen Series	Area under load deflection curve (N-mm)	Toughness index	Percentage increase in toughness index
1	PC	53.49	1	------
2	A1	104.6	1.95	95
3	A2	82.09	1.53	53
4	A3	162.88	3.04	204

The load deflection curves of beams of cement composite showed greater area under curves. This may due to increase in toughness by incorporating the nano particles (MWCNTs and Nano-Al_2O_3) in the cement composite. Compared with the plain cement beams, beams with MWCNTs and beams with Nano-Al_2O_3 showed 95% and 53% increase in toughness respectively. The beams reinforced with MWCNTs and Nano-Al_2O_3 showed 204% increment. Thus results showed that toughness index of composite beams incorporated with MWCNTs were greater than that of the beams incorporated with Nano-Al_2O_3. This may be due to the reason that the MWCNTs themselves are tougher. Beams reinforced with MWCNTs and Nano-Al_2O_3 showed till higher toughness. This may be due to that MWCNTs inhibited the propagation of micro cracks and Nano-Al_2O_3 helped in producing more cementitious products by its pozzolanic reaction. Higher toughness indicates the ability of the composite to undergo large deformations before failure and greater energy absorption.

3.3 Compressive strength of cement composite

Table 8. Showing ultimate compression strengths of cement composites

Sl. No.	Specimen Series	Ultimate compression load in kN (avg.)	Ultimate compression strength in N/mm^2	Percentage increase in ultimate compression strength
1	PC	11.533	28.53	-----
2	A1	15.533	38.84	36.13
3	A2	14.166	35.41	24.11
4	A3	18.066	45.16	58.31

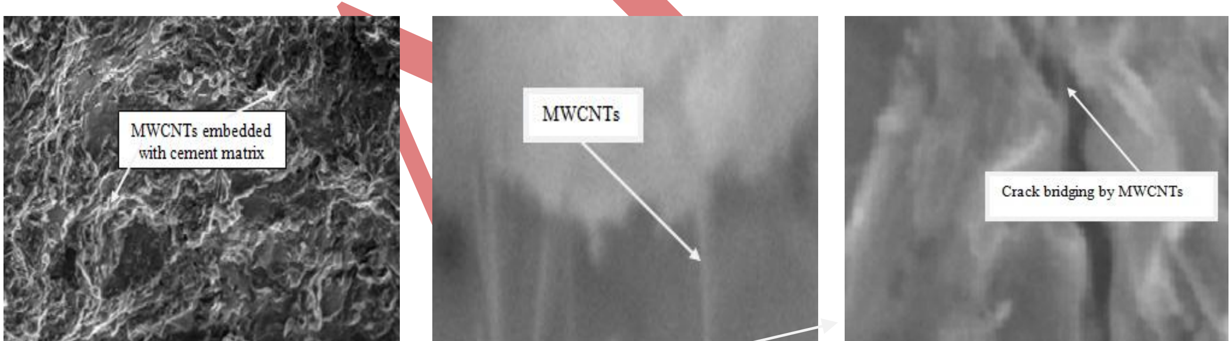
It was observed that there was increasing trend in the compression strength by addition of nanoparticles in the cement composite.

The specimen series A1showed 36.13% increase in the compression strength. Such increment may be due to high elastic modulus of MWCNTs and its bonding with the cement and hence arresting the propagation of micro cracks. The specimen series A2 showed 24.11% increase in compression strength. This may be due to pozzolanic action of Nano-Al_2O_3 which produced the more cementitious compound in the cement composite and also due to filling up of nano and micro pores by nanoparticles in the composite.

The specimen series A3 showed up to 58.31% increase in their strength may be due to high elastic modulus of MWCNTs and its bonding with the cement and hence arresting the propagation of micro cracks along with pozzolanic action of Nano-Al_2O_3 which produced the more cementitious compound in the cement composite and also due to filling up of nano and micro pores by nanoparticles in the composite.

3.4 Scanning Electronic Microscopic (SEM) analysis of cement composites incorporated with nanomaterials

SEM images of cement composites were obtained from Manipal Institute of Technology, Manipal. Fig.5 (a) shows SEM image of hardened cement paste incorporated with MWCNTs and Nano-Al_2O_3. In this image MWCNTs embedded with cement matrix can be seen and it is evident that MWCNTs were almost uniformly dispersed. Fig.5 (b) shows MWCNTs extruded from the cement matrix. Fig.5 (c) shows the bridging the micro cracks by MWCNTs. The bridging of micro cracks and bonding with the cement matrix by MWCNTs are the main reasons for enhancement of mechanical properties of cement composites.



(a) **(b)** **(c)**

Fig 5. (a) SEM image shows the MWCNTs embedded with cement matrix
Fig 5. (b) SEM image showing MWCNTs in cement matrix
Fig 5. (c) SEM image showing crack bridging by MWCNTs

IV. CONCLUSIONS

From this investigation it can be concluded that mechanical properties of hardened cement paste can be remarkably enhanced by incorporating the MWCNTs and Nano-Aluminium oxide. Results showed that ultimate load and deflection capacities were appreciably increased in the cement composites compared to plain cement control specimens. Flexural strength, compressive strength and toughness were also increased remarkably.

Enhancement of these mechanical properties may be due to reason that proper bonding between the cement matrix and MWCNTs and hence inhibition of micro cracks. Nano- Al_2O_3 improved the pozzolanic action by providing more surface area and produced the more cementitious product.

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