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Experimental investigation on the effect of multiwalled carbon nanotubes and nano-SiO_2 addition on mechanical properties of hardened cement paste

Anand Hunashyal[1], Nagaraj Banapurmath[2], Akshay Jain[1], Sayed Quadri[1], Ashok Shettar[1]

[1]Department of Civil Engineering, B. V. Bhoomaraddi College of Engineering and Technology, Vidyanagar – 580031, Hubli, India
[2]Department of Mechanical Engineering, B.V. Bhoomaraddi College of Engineering and Technology, Vidyanagar – 580031, Hubli, India

Email address:

amhunashyal@bvb.edu (A. Hunashyal), nrbanapurmath@gmail.com (N. Banapurmath), noteakshay@gmail.com (A. Jain), ssquadri@bvb.edu (S. Quadri), asshettarabc@bvb.edu (A. Shettar)

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Abstract: This paper investigates the behaviour of hardened cement paste reinforced with multi-walled carbon nano-tubes (MWCNTs) and Nano-SiO_2 (NS). In these composites, the percentage of MWCNTs was fixed at 0.75% by weight of cement, while the percentage of NS was fixed at 0.5% by weight of cement. Dispersion of both MWCNTs and NS was carried out using ultrasonic energy method. The novel nano-composite specimens developed were tested for compression and flexure in order to evaluate their mechanical properties such as compressive strength, flexural strength, toughness and ductility. These results were then compared with the results of plain cement control beams. Scanning electron microscopy was conducted to examine the bond between the MWCNTs and the cement matrix.

Keywords: Plain Cement Beams, MWCNTs, SiO_2, Mechanical Properties, Flexural Strength, Toughness and Ductility, SEM

1. Introduction

Portland cement is one of the highest consumed building materials in the construction industry since centuries because of its ease of use and good binding property. Despite being widely used, cement-based materials have poor mechanical properties such as flexural strength, ductility, and toughness, and have low resistance to chemicals which reduces their durability. The cement paste is formed by mixing water with cement powder. This paste undergoes some chemical reactions to form the hydration products that become rigid after a certain time and heterogeneous in nature. The hydration of cement forms complex chemical compounds which bind the fine and coarse aggregate together and is responsible for the strength of concrete. Incorporating nanotechnology in the field of materials facilitates development of new hybrid materials besides increasing materials durability and providing materials with ultra-high performance. It also enables better usage of natural resources and getting the required materials properties with minimal usage [1]. It is well known that materials are the core elements of construction industry and these materials could be developed by using nanotechnology. Incorporating nano materials in cement can enhance its mechanical properties. Although high prices of nano-materials today could obstruct their broadened application in the current period, it is expected that these prices will fall in the near future [2]. One of the important drawback of incorporating nanomaterials in concrete is the self-aggregation of nano-particles which increases the particle size thereby producing un-reacted pockets leading to concentration of stress and at the same time reduces the benefits of nano-materials [3]. Characteristics of cement mortar with NS particles were explored and NS affecting the structure of the cement paste by pore filling leading to decrement of voids and increase in strength are reported [4]. It is reported that hydration of cement can be accelerated by addition of NS. When nano-silica is added to cement grains, $H_2SiO_4^{2}$_ forms and reacts with the available C_{a2+} which forms an additional calcium–silicate–hydrate (C–S–H) and these C–S–H particles are spread in the water between the cement particles and serve as seeds for the formation of more compact C–S–H phase. The formation of the C–S–H phase is no longer limited on the grain surface alone, as in the case of pure C_3S, but also takes place in the pore space. The formation of large numbers of seeds thereby causes an acceleration of early cement hydration. The aim of the application of ultra-fine additives like nano-silica in cementitious systems is to improve the characteristics of the plastic and hardened material. Micro and nano-scaled silica particles have a filler effect and fill up the voids between the cement grains [5]. With the right composition, the higher packing density results in a lower water demand of the mixture and it also contributes to strength enhancement due to the reduced capillary porosity. Besides this physical effect due to NS, there there is a pozzolanic reactivity which is much higher compared to silica fume. Thus, both the effects are very important in developing ultra-high performance concrete [6-11]. The SEM images reported in [4] showed that adding nano-particles to the cement paste makes the microstructure and the texture of the hydrate products more consistent, dense and solid in the case of well dispersion of the nano-particles. It also showed the absence of Ca (OH) $_2$ crystals. Furthermore, it was found that nano-particles fill the pores which enhanced the microstructure of the cement paste in order to increase the strength. But if the nano-particles are not dispersed properly due to their excessive amount addition, it will aggregate to generate weak zones and voids that decrease the strength and deteriorate the microstructure of the paste as mentioned. Nano-particles play an important role in promoting and activating the hydration process because they are highly active due to their large surface area. SEM analysis reported in [4] showed that adding NS to the cement paste provides dense microstructure with compacted hydration products and reduced Ca (OH) $_2$ crystals. SEM images [12] showed that adding nano-particles to the cement paste decreased the pores, increased C-S-H quantity, decreased $Ca(OH)_2$ crystals and thereby provided a denser structure.

The behaviour of composite round bars included multi-walled carbon nano-tubes (MWCNTs) and carbon fibers (CFs) using ultra-sonicator has been investigated [13] and the specimens were tested for their mechanical properties such as ultimate load, deflection criteria, stress–strain behaviour are reported. Abrasion resistance and compressive strength of concrete specimens containing SiO_2 and Al_2O_3 nano-particles [14] has been studied and the specimens were cured in different curing media and relation between compressive strength and abrasion resistance has been established. It was also found that addition of nano-silica enhanced mechanical properties. Replacement of 0.5% by wt of cement by nano-silica gave maximum strength with minimum usage of material. The split tensile and flexural strength was increased by addition of Al_2O_3 nano-particles, however the author emphasised on addition of needle like nano-particles for further enhancement in strength [14]. Hence needle like nano-reinforcements MWCNTs, were incorporated along with NS in the study. The effect of multi-walled carbon nano-tubes (CNT) on the strength characteristics of hydrated portland cement paste were studied and no much difference in the results obtained from 30 minutes of sonication compared to 4 hours of sonication [15-18].

In the recent years few researchers have illustrated enhancement in mechanical properties of singly reinforced nanocomposites [11,13-17]. However, the usage of two different nanoparticles which improves the strength of the cement paste by different mechanism is not done. This paper illustrates how usage of multiple nanoparticles namely nano-SiO_2 and MWCNTs can lead to further enhancement of strength. Nano silica improves the strength of the composite by reacting with cement paste and MWCNTs act as nano sized needle like reinforcements. The paper illustrates the necessity and importance of usage of multiple nanoparticles for the enhancement of mechanical properties of the cement composites.

2. Experimental Program and Specimen Preparation: Materials and Methods Adopted

This section provides information on the materials used for the research work such as cement, MWCNTs, silicon dioxide nano-materials and ethanol undertaken. Ordinary Portland cement of 43 grade manufactured by Coromandel InfoTech India limited was used for the present study in accordance with IS 8112-1989. It was tested as per IS-4031-1988 recommendation for hydraulic cement [18]. From the results the normal consistency and the specific gravity of cement were found to be 33% and 3.12 respectively. The initial and final setting times of cement were found to be 75 minutes and 260 minutes respectively.

The multi-walled carbon nano tubes (MWCNTs) were obtained from Sigma-Aldrich. The properties of the multi-walled CNTs used are presented in Table 1. The MWCNTs were of industrial grade with a purity of greater than 95 per cent.

Table 1. *Properties of MWCNTs.*

Sl. No.	Particulars	Specification
1	Manufacturer	Sigma-Aldrich Co., USA
2	Diameter	10–30 nm
3	Length	1–2 mm
4	Purity	95%
5	Surface area	350 m2/g
6	Bulk density	0.05–0.17 g/cm3

The NS was obtained from Sigma-Aldrich. The properties of NS used in this study are presented in Table 2.

Table 2. *Properties of NS.*

Sl. No.	Particulars	Specification
1	Manufacturer	Sigma-Aldrich Co., SA
2	Assay	99.5% trace metals basis
3	Form	Nano powder
4	Particle size	10-20 nm (BET)
5	Bp	2230 C (lit.)
6	Mp	>1600 C (lit.)
7	Density	2.2-2.6 g/mL at 25 °C
8	Bulk density	0.011 g/mL

Uniform dispersion of MWCNTs in the cement based matrix against their agglomeration due to Vander Waals' bonding is the first step in the processing of nano-composites. To disperse the MWCNTs, evenly in the cement based matrix 99.9% pure ethanol was used as a pre-dispersant.

Experimental testing was conducted to investigate the suitability and feasibility of using uniformly dispersed randomly oriented MWCNTs as reinforcement and uniformly dispersed NS for cement composites. Nano-level reinforcement was provided in the cement based matrices using MWCNTs and further strength development was supported by addition of NS. Four types of specimens were made for the present work which include plain cement specimens as control specimens for comparison, a set of specimens with 0.75% MWCNTs, one set of specimens with 0.5% NS, and one set of specimens containing both 0.75% MWCNTs and 0.5% NS. Flowchart shown in Figure 1 illustrates the experimental program. Compression tests on 20mm×20mm×20mm cubes were carried out to compare the compression strength of plain cement cubes and composite cubes developed. Three point flexure tests on 20mm×20mm×80mm beams [19] were carried out to compare the flexural responses of plain cement beams and composite beams.

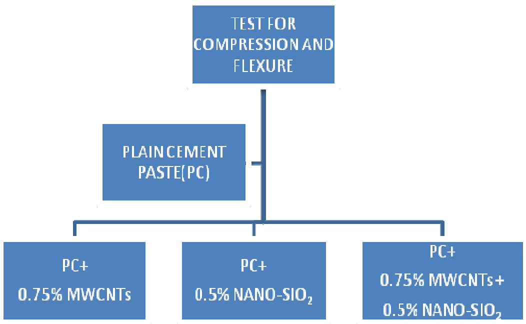

Figure 1. *Experimental program.*

Since MWCNTs are not visible with naked eyes, SEM was used to investigate the dispersion of MWCNTs in cement paste. Although the main objective of this study was to investigate the effect of addition of nano-silica and MWCNTs on the mechanical strengths, it was necessary to understand how the nano-tubes were holding the cement compounds after composites were tested for failure. Broken sample pieces were used for this purpose after mechanical testing was carried out (28-day test) for SEM. The SEM was performed at the department of materials engineering, IISc Bangalore, India.

Specimen preparation:

Ultrasonic dispersion methods are usually adopted for the dispersion of nanometer sized materials in a liquid, due to their relatively large surface-area-to volume ratios as well as the scale of action of the ultrasonic waves. The ultrasonic sonicator manufactured by SMPS Electronics, Mumbai having a frequency of Oscillation 30 + 3 MHz and power: 50 kW was used to disperse the MWCNTs. MWCNTs were sonicated in a glass beaker in ultrasonic bath. These nano-tubes were pre-dispersed in water by adding 1/2 of the total water to ensure that they were immersed completely into water. The beaker was vibrated by ultrasonic wave. Sonication process was carried out for 15 minutes, after that dispersant ethanol of quantity 5 % by weight of cement was added to the pre dispersed mixture and again sonicated for another 15 minutes with continuous stirring with glass rod at room temperature. Addition of ethanol acts as a pre dispersing agent and thereby bundled nano-tubes will get dispersed using the ultrasonic energy. Since the MWCNTs percentage is fixed same method was employed for all the specimens. Dispersion of NS is carried out by taking half of the water required to prepare the samples and adding NS to it, and the same was sonicated in two batches for 15 minutes each, aided with frequent stirring.

For the preparation of the cement composites, Ordinary Portland cement, dispersed with MWCNTs and NS were used. Moulds were cleaned, oiled, and kept on an even surface. Cement was weighed and stored in air-tight container. The w/c ratio of 0.4 was maintained. Prior to their addition to cement the nano-particles were stirred thoroughly and dispersed by the procedure explained above in the ultrasonic water bath. After the sonication, cement was added into the MWCNTs and NS dispersions and the materials were mixed thoroughly. The paste was placed into the moulds with proper compaction and polyethene sheets were wrapped around the fresh specimens which were subsequently de-moulded after 24 hours and immersed in water bath for 25 + 2°C for 28 days prior to testing.

Figure 2. *Ultrasonic Bath Dispersion of MWCNTs (left) and NS (right).*

3. Experimental Setup

The geometry of the flexural specimen and the 3 point bending test setup used is shown in Fig 3. The aspect ratio of the specimen was fixed as per ASTM D790-02 specifications [20]. The specimens of size 20mm×20mm×80mm were tested in under a 10kN capacity load frame at a constant strain rate of 0.125mm/minute. The whole set-up was displacement controlled. A seating load of 0.1kN to ensure simply supported end conditions and minimise lateral sway due to slip on the roller supports were adopted. Cement paste cubes of size 20mm×20mm×20mm were prepared and tested to measure compressive strength after 28 days of curing in water. The compressive strength of a specimen is expressed as the ultimate load required for breaking the specimen per unit area. The loading rate was set to 0.1kN/s. The specimen was sandwiched between two steel plates of thickness 5mm each to ensure uniform distribution of load.

Fig 3. *Image depicting the 10kN Load cell Frame adopted for 3-point bending test*

4. Results and Discussion

The objective of the present study was to analyze and compare the mechanical properties of singly reinforced nano-composites with doubly reinforced nano-composites by testing various properties such as compressive strength and flexural strength, toughness and ductility index of the composite under three point loading. The Table 3 consists of the abbreviations that are used for composites.

Table 3. *Specimen composition.*

Sl. No.	Specimen Particulars	Composition
1	PC	Plain cement
2	A1	Plain cement + 0.75% MWCNTs
3	A2	Plain cement + 0.5% SiO2
4	A3	Plain cement + 0.75% MWCNTs+ 0.5% SiO2

Flexural strengths were calculated using two deterministic approaches, one employing the Elastic theory of bending and another based on recommendations of ASTM D790 [20] (Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials). Whilst the Elastic theory gives due cognizance to the location of crack and hence acknowledges its influence on the flexural strength of the composite, the ASTM recommendation only focuses on the Failure load. The overall test results are discussed through Figures (4 -14) shown below.

The workability of the paste specimens decreased in the order PC>A1>A2>A3. With change in the composites proportions, the load carrying capacity increased and the corresponding deflection also increased (Figures 4-6). The hybrid composite showed maximum increment in the flexural strength almost double that of the strength of the plain cement matrix.

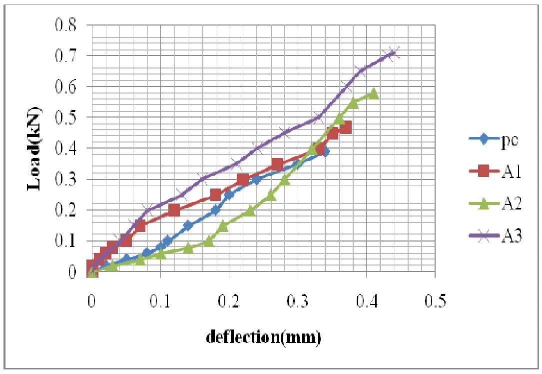

Figure 4. *Load deflection curves for all proportions under three point bending set up*

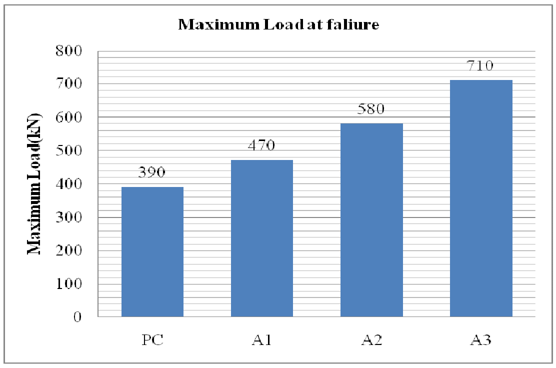

Figure 5. *Variation in ultimate load at failure for all proportions for three point bending set up.*

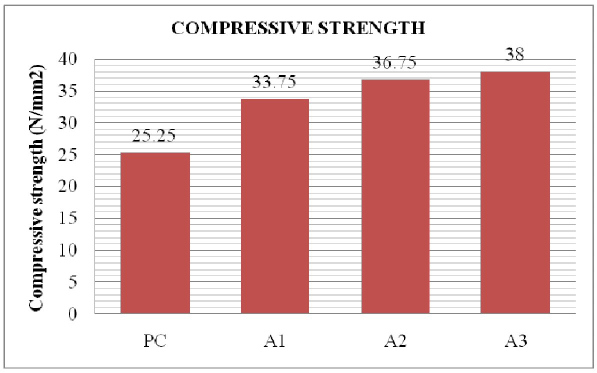

Figure 6. *Variation of compressive strength with addition of nano-particles*

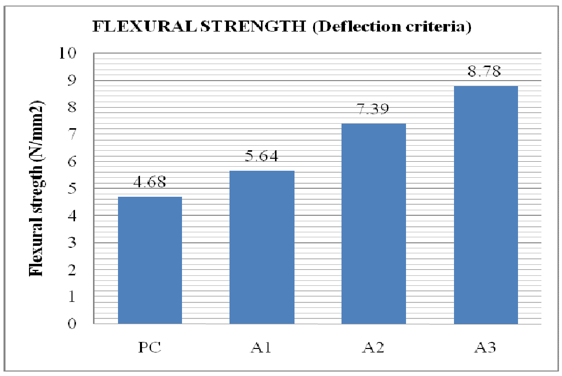

Figure 7. *Variation in flexural strength (based on theory of bending) for all proportions under three point bending set up*

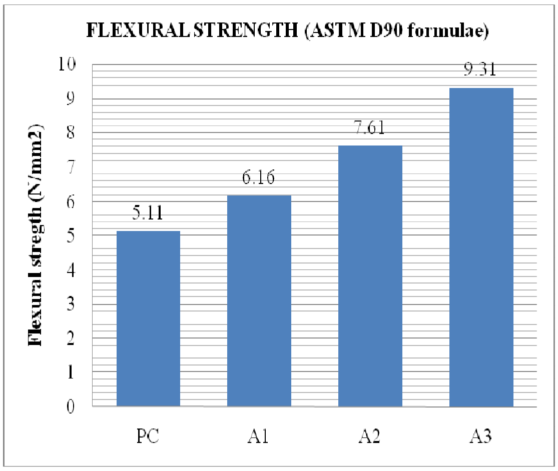

Figure 8. *Variation in flexural strength (based on ASTM D790 Formulae) for all proportions for three point bending set up.*

Figures 7 and 8 shows variation in flexural strength based on theory of bending and ASTM D790 formulae for all proportions under three point bending set up. From both Figures 7 & 8, the trend observed were completely different because elastic theory accounts for the magnitude of displacement at failure while the ASTM recommendation is inclined towards accounting for the slope of the stress-strain curve in the initial elastic region.

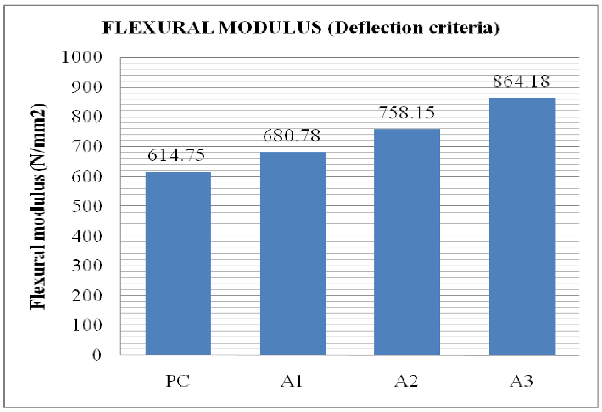

Figure 9. *Variation in flexural modulus (based on deflection criteria) for all proportions for three point bending set up*

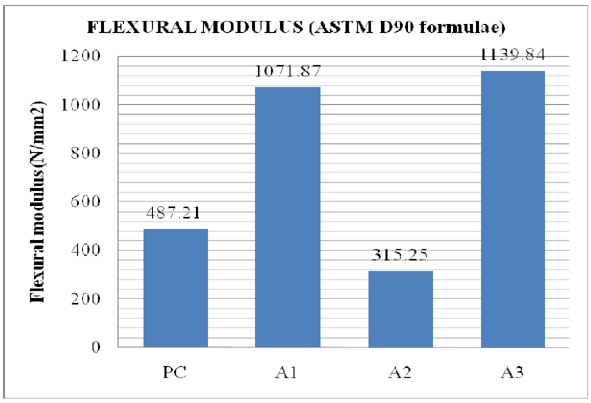

Figure 10. *Variation in flexural modulus (based on ASTM D790 Formulae) for all proportions for three point bending set up.*

Figures 9 and 10 shows variation in flexural modulus based on deflection criteria and ASTM D790 formulae for all proportions under three point bending set up. Determination of flexural modulus by ASTM formulae shows a sharp decrease for NS composite because the initial slope drawn to the load deflection curve is too less, which is not taken into account in determination of flexural modulus by theory of bending.

Higher toughness indicates the ability of the composite to take up large load and undergo large deformations before failure. The toughness represented by the area under the load deflection curve of the composite beams was increased significantly as evident from the load deflection curves in Figure 4. The highest toughness is achieved at the proportion of A3 having 152% increment in toughness index. Figures 11 shows variation in Toughness Index for all proportions for three point bending set up. The probable reason for the ductility of the composite specimens found to be slightly lower than the control specimens as see in Figure 12 may be because of the introduction of the foreign material inside the plain cement matrix. However there is no significant decrement as compare to PC. Figures 12 shows variation in ductility Index of all proportions for three point bending set up.

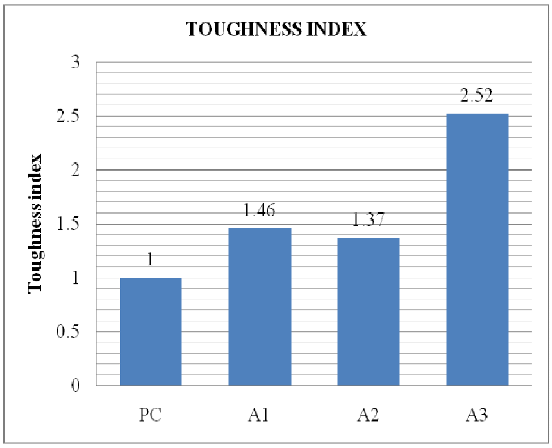

Figure 11. *Variation in Toughness Index for all proportions for three point bending set up.*

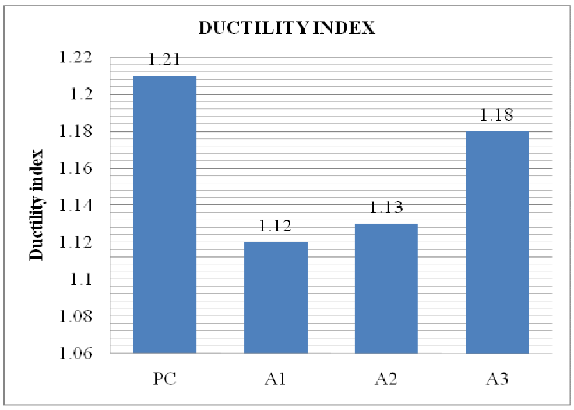

Figure 12. *Variation in Ductility Index for all proportions for three point bending setup.*

Inference from SEM study:

The SEM images obtained for novel nano-hybrid composites developed are shown in Figures 13 and 14. Figure 13 show the SEM images of nano composites containing NS, while Figure 14 shows the SEM images of nano composites containing nano-silica and MWCNTs. It is difficult to comment on the dispersion of nano particles by observing the SEM images. Fig. 14 shows the clustering of MWCNTs and NS in the hybrid composite. It can be seen from the fig.14 that there was a physical bonding between cement matrix and MWCNTs. However it would be difficult to conclude that there is a uniform dispersion of MWCNTs and NS in hardened cement paste by observing the images.

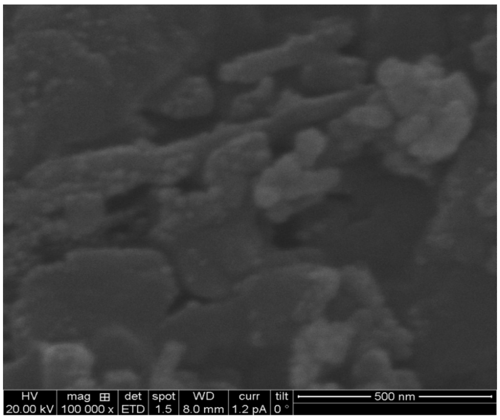

Figure 13. *SEM Image showing hardened cement paste modified with nano-silica.*

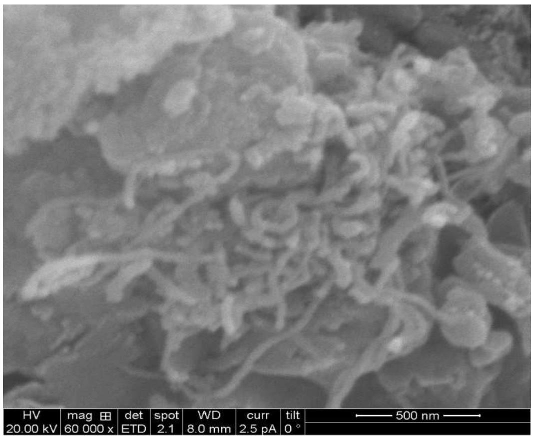

Figure 14. *SEM Image showing hardened cement paste modified with nano-silica and MWCNTs.*

5. Conclusions

Cement composite having enhanced mechanical properties was successfully developed using multiple nanoparticles. MWCNTs were used to reinforce cement paste at the nano-scale while NS was used to increase strength by forming additional CSH gel. Results of tests on the composite specimens have shown that

The addition of MWCNTs and NS almost doubled the flexural strength to in comparison with PC (the control beam).

The addition of nano particles that increase the strength of cement by different mechanisms can increase the load carrying capacity and the flexural strength, making the material having more toughness and improved mechanical properties.

The SEM data showed non uniform dispersion of CNTs in the cement matrix. Only few specimens gave good results due to dispersion issues of MWCNTs. Based on the results obtained, it was concluded that the way CNTs were sonicated was not good enough to disperse them in an effective manner. There is a necessity for further research in the dispersion techniques of MWCNTs adopted.

Although it is difficult to conclude if there existed any chemical bonding between cement compounds and MWCNTs, by SEM analysis, it was verified from this test that there was a physical bonding between cement matrix and MWCNTs.

It was encouraging to see that usage of multiple nano-particles could enhance the mechanical properties, and it can be concluded that similar experimentation with other nano-particles would lead to development of composites with enhanced mechanical strength.

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