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A Study on Carbon Nanotube (CNT) in Cement Mortar

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Abstract:
The incorporation of the Nano-materials in the cementitious components has been researched in the recent past and the research showed the significant increase in the mechanical properties of the cementitious composites such as the Flexural capacity, Ductility, reduction in the porosity and resistance for the micro-crack formation. The commonly used Nano material are Nano silica, Titanium Dioxide.,. The utilization of the CNTs in the cementitious composites has been done in the recent past due to the desirable mechanical properties of the CNTs. The CNT incorporation in cementitious composites has some difficulties. The researchers are undergoing on overcoming the difficulties. In this article the literatures are reviewed about the incorporation of the CNTs in the cementitious composites.

Keywords: Cementitious Composites, Carbon Nanotubes, Flexural Capacity, Porosity, Microstructure.

I.INTRODUCTION

Plain mortar is a brittle material has extremely weak tensile strength. This problem has been a primary concern for structural applications. In these days, various Nanomaterials are being widely used to control cracking in cementitious composites. Among them Fibre-Reinforced Polymer (FRP) is being used mostly. The post-cracking behaviour of FRP depends on the crack-bridging capability of the fibers. A wide variety of fibers have been used in the last two decades, including steel, glass, carbon, and synthetic materials. These fibers, which are usually randomly incorporated in the concrete matrix, may not withstand the tensile strength as effectively as steel reinforcing bars, but they are more closely spaced and are better at controlling cracks. The efficiency of FRP highly depends on both the mechanical properties and the geometry of the fibers employed. Recently, a fascinating type of Carbon Nano Materials has raised some researchers interests owing to its remarkable mechanical properties and excellent performance in reinforcing polymer based materials. The Carbon Nanotube was discovered in 1991 and was being proved as the strongest known material that can be made, fracture at strain up to 10–30%. With typical Young's modulus of 1 TPa, CNTs fail at stress up to 100–300 GPa. CNTs are classified as either Single walled carbon nanotubes (SWNTs) or Multi-walled carbon nanotubes (MWNTs). A SWNT is like a planar sheet of carbon atoms, known as graphene, seamlessly wrapped into a tube with thickness equal to a single atom and diameter ranging from 0.4 nm to 3 nm. MWNTs appear as multiple concentric SWNTs, with diameter of 1.4–100 nm. Fig. 1 shows the schematics of SWNTs and MWNTs. The length of CNTs can be up to centimetres, which gives an aspect ratio exceeding 107, while the density of CNTs is generally reported as less than 1500 kg/m^3. With the concurrent benefits of high aspect ratio and low mass density, CNTs can reinforce concrete more effectively than conventional fibers by providing an enormously large interfacial contact area with the matrix without much weight penalty. The combination of CNTs and conventional polymer-based fibers and films is among the highly developed areas of research. The results proved that CNTs tremendously increased the strength and energy-absorbing capacity of polymers. On the other hand, the investigation of CNT/concrete composites is at a relatively novel stage, and limited amount of work regarding the effectiveness of CNTs in enhancing the tensile strength or toughness of concrete has been published. The CNT/cement composite under compression and found that SWNTs and MWNTs increased the strength of plain cement paste demonstrated that MWNTs surface-treated by H2SO4 and HNO3 substantially improved the compressive strength and the flexural strength of Portland cement. These results suggest that CNTs have potential for being used as reinforcement for concrete. However, there is still a significant need for further studies in this area to completely understand the structural behaviour of CNT reinforced cement. Since laboratory testing of CNT/cement composite placed a number of challenges on thoroughly assessing the behaviour of the composite, this study focused on the applicability of finite element method (FEM) as an alternative. There has been a debate among scientists and researchers on whether continuum mechanics approaches could be utilized in studying materials on the Nano level. Based on numerous studies, there has been an agreement that the theory of continuum mechanics could be utilized in a situation where a global mechanical property is of interest such as determining Young's modulus or global deformations of CNTs or CNT-based composites. However, if the interest is in studying the local behaviour of the material such as obtaining local stresses or strains in the vicinity of a single atom or even a group of atoms, then molecular dynamic (MD) simulations or experimental methods should be used. It should be noted also that in this study, the authors were mainly interested in studying the global behaviour of CNT/cement composites and how would introducing deficiencies in the averaged bond strength between CNT and the surrounding cement matrix would affect the global behaviour. Therefore, no attempts were made in this paper to investigate the local bond characteristics of CNT and cement on the atomic level. In addition, the study also addressed correlating the mechanical properties obtained from a nano-scale finite element (FE) model with the macro behaviour of a structural element built with CNT/cement composite.

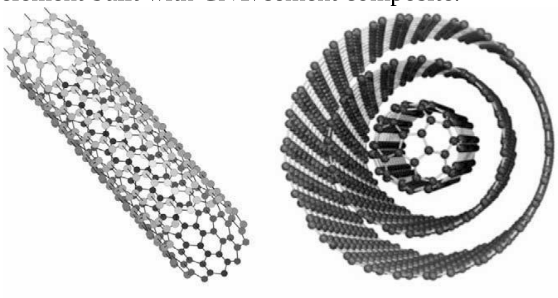

Figure.1. Schematics of Carbon Nanotubes a) Single Walled b) Multi Walled

II.LITERTURE REVIEW

Baomin Wang (2014) conducted the research on the incorporation of the surface modified Multi-Walled Carbon Nanotubes in cementitious composites. His article stated that the MWCNTs have a nano-scale hollow structure at a high aspect ratio, with excellent mechanical properties. The mechanical properties and microstructure of the cement composites containing MWCNTs have been investigated. It is found that incorporation of MWCNTs in the cement paste could mildly improve flexural and compressive strength. This enhancement is excellent in mechanical properties of MWCNTs. Then the article stated the significance of dispersion of MWCNTs and its role in improving the microstructure. The MWCNTs incorporation in cement paste also resulted in a reducing the pore size distribution and lesser the porosity, therefore the composites have higher density. The interfacial interactions between surface-modified MWCNTs and cement hydration products increase bonding strength, and increase the load-transfer efficiency from cement matrix to the reinforcement.

Aida Nasiri (2014) reviewed the properties of common traditional cement slurry reveals its undesirable qualities such as high water/cement ratio, poor elasticity and settlement of weighting agent, less tensile capacity., The addition of MWCNTs as nanofluids produced properties suitable for fluid loss, free water, thickening time, compressive strength and elastic constants. Maximum compressive strength was obtained from the cement specimens with 1% CNTs due to the cross-linking of CNTs with hydration products, which leads to improved resistance to microcrack formation. However, at higher ratios of CNT loading, the CNTs were agglomerated around the cement grains, leading to their partial hydration, which decreases the bond strength of cement pastes. The increasing proportion of MWCNTs improves the elastic modulii of cement mainly by increasing the Poisson's ratio, so that the samples can withstand more stresses without being broken down. With MWCNTs added to the mixture, the increase in surface energy of the mixture increased the rate of hydration reactions in the mortar; an early initial setting time was also obtained, thus reducing the thickening time of the cement slurries. It was observed that the use of MWCNTs decreases the porosity of cement. Therefore, the composites become more compacted and pore water is immobilised, which will leads to reduction of freewater. Moreover, by bridging and blocking the pores in the cement cake, the added CNTs will control fluid loss.

Adil Tamimi (2016) studied the use of silica fumes and surface functionalized CNTs in the production of mortar. His study revealed that adding 0.15% CNTs to the cementitious material improved the compressive strength by 8%. Initially dispersed CNTs in water solution resulted in a compressive strength improvement of 8.5%. It showed that adding 15% silica fume with 0.15% CNTs has increased the compressive strength of all the samples from 7% to 13%. The application of non-dispersed, non-functionalized CNTs resulted in the lesser increase, and initially dispersed CNTs in a water solution the highest increase in the compressive strength. Increasing silica percentage to 30% had a negative impact on the compressive strength of the sample with CNT and CNT-H_2O, however, use of functionalized CNTs resulted in an increase of 16–20%. The silica fume can effectively disperse CNT in the composite; it should be added in conjunction to functionalized CNTs to effectively enhance the mechanical properties of the composite. The flexural strength of the samples increased by 50% and 35% when compared with the control sample (no CNT) when using surface functionalized CNTs (CNT-COOH and CNT-OH) and non-surface functionalized CNTs, respectively. The increase in flexural strength with CNT-COOH could be related to the presence of carboxylic acid groups on the surfaces of carbon nanotubes that bring about a chemical interaction between the carboxylic acid and the calcium silicate hydrate (C–S–H) or $Ca(OH)_2$. The interaction leads to a strong covalent force on the interface between the CNT reinforcement and matrix in the composites, there by bridging microcracks as seen through SEM analysis. The SEM results revealed that although all the CNTs were not dispersed properly and formed clumps, they were able to fill the voids in the mortar, and thereby improved the compressive strength.

Rashid K. Abu Al-Rub (2012) showed the improvements in the flexural strength and ductility for all of the nanocomposites at age of 28 days curing when compared to the plain cement samples. It was observed that nanocomposites with low concentration of long MWCNTs give comparable mechanical performance to the nanocomposites with higher concentration of short MWCNTs. Moreover, it was found that the short MWCNT at 0.2% concentration by cement weight has better results than other specimens at age of 28days.Those observations could be due to that short CNTs result in a relatively better dispersion of filaments within the cement paste, reduction in the filament-free volume of the cement paste, and effective filling of nano-sized voids. At early ages (age of 7 days) all specimens showed higher ductility than the plain cement(control) samples. It was noticed that at age of 28 days, for the same concentrations of 0.1% and 0.04%,the long MWCNTs composites showed higher strength and less ductility than the corresponding short MWCNTs composites which can be due to breakage of long CNTs during the sonication process that in turn led to a relatively better dispersion of the CNTs. The nanocomposite specimens showed multi-peaks in the stress–strain response, which indicates multiple pull-out actions of the MWCNT from the hydrated cement matrix. However, this multi pull-outs behaviour, from the stress–strain diagrams, could not improve significantly the strength or the ductility of the CNTs/cement composites in all cases; this could be due to the low bonding between the CNTs and the cement matrix or due to the formation of low-stiffness hydration products in the cement paste matrix due to the existence of the CNTs. The SEM images clearly show successful crack-bridging by the MWCNTs and pull-outs and breakage. The CNTs breakage implies a good bonding between the CNTs surfaces and the surrounding cement paste. The TEM images show clear embedment of CNTs within the cement hydration products, and bridging of neighbouring hydration products by long MWCNTs indicating that MWCNTs with higher aspect ratios are more effective reinforcements if well-dispersed. Extensive studies are needed on the effects of the existence of the CNTs within cement paste on the chemical reactions and hydration process of cement. Improvements on dispersing techniques are also needed in order to effectively utilize long MWCNTs in cement composites. Also, novel multiscale computational modelling of CNT/cement composites that can be used carefully for investigating the effects of aspect ratio and various reinforcing mechanisms by CNTs is highly desirable.

Yakovlev (2017) found that the main effect of the modification of cement binding matrices using complex Nano-dispersed systems comprising MWCNT and Nanosilica was ensured with the directed influence on the hydration processes and the subsequent crystallization of new products. Scanning electron microscopy and X-ray microanalysis confirmed with IR spectra have revealed that adding multi-walled carbon nanotubes dispersion together with Nano-dispersed silica provides the structuring of the binding matrix along with the perfect dense shell of hydrated new products on the surface of solid phases. The structured interfacial layers form the special frame cells in the modified cement matrix which ensures the formation of extremely filled system predetermining the strengthening of the structure of the modified binding matrix due to the formation of the spatial packaging. Consequently, the main factor increasing the characteristics of cement concrete modified with carbon nanotubes and nanosilica was the structural modification of calcium hydrosilicates concerning both the composition and the morphology of new products. To quantify the effect of the addition of the CNT on the characteristics of the material on micro-mechanical level proved to be a challenging task, though. While it is possible to inspect the surface of a concrete sample with a resolution in a range of 1 micron, the necessary process of preparation of the samples for the nano-indentation probably obliterates all detectable effects of the CNTs, as shown by a SEM.

Yu Hu (2014) found the dispersion technologies of CNTs in aqueous solution, fabrication, mechanical properties, microstructure, porosity and pore size distribution of MWCNTs-OPC composites with common MWCNTs and MWCNTs-COOH. Effective dispersion of CNTs in aqueous solution was achieved by using commercially available surfactants and Ultrasonication process. The MWCNTs in cement paste can be dispersed uniformly without obvious agglomeration phenomenon. Meanwhile, the MWCNTs with a carboxyl group can be distributed thoroughly in aqueous solution by using only ultrasonication except a surfactant.

Anand M Hunashyal (2012) discovered the novel nano-hybrid cement composite was successfully developed in this work using multi-scale fiber reinforcement. The Carbon microfibers were used to reinforce cement paste at the micro scale while MWCNTs were chosen at the nanoscale. The results of three-point bending tests on the notched hybrid specimens have shown that the combinations of MWCNTs and carbon microfiber increase the flexural strength to 242.85% in comparison with PC (the control beam). This indicates that the reinforcement both at nano and micro level have increased the flexural strength. Also it is observed that there is no significant increase in ductility index toughness the observations by SEM confirmed the homogeneous dispersion of the MWCNTs provides the good bonding between the Nano and micro fibers and the cement hydration products, and the synergistic effect of MWCNTs and the microfibers in controlling cracking at different scales. It is also found that the increase in the weight loss of the samples with an increase in MWCNT composition. This is due to the very high thermal conductivity of MWCNTs which thus causes a faster evaporation of water and decomposition of other chemical constituents.

H.K. Kim (2014) presented the results of his investigation on the enhanced effect of CNTs on mechanical and electrical properties of cement composites by incorporation of silica fume. Cement composites with three different amounts of CNTs addition (0%, 0.15%, and 0.3% by weight of cement) were designed, and for each mixture, silica fume in amounts of 0%, 10%, 20%, and 30% by weight of cement was applied. A qualitative analysis using SEM images was carried out to observe the surface morphology and microstructure of cement composites with different amounts of silica fume and CNTs addition. The effects of silica fume addition on the flow, porosity and compressive strength of CNT/cement composites were then stematically investigated. The following conclusions have been drawn from this investigation. In the cement matrix without silica fume, CNTs were not easily dispersed and tended to agglomerate with large size. In this case, the CNT additions had an insignificant effect on the compressive strength and electrical resistance of the cement composites. However, when small amounts of silica fume were added to the cement matrix, some agglomerated CNTs were intermixed with silica fume particles and mechanically broken into smaller sizes. This results in the increase in compressive strength and the decrease in electrical resistance of the CNT/cement composites. As the amount of silica fume addition was further increased, the agglomerated CNTs separated (almost) completely and dispersed densely in silica fume fields. However, with this increase of individual CNTs, the dispersed CNTs re-agglomerated and formed CNTs clumps this would adversely affect the compressive strength of CNT/cement composites. The appropriate amounts of silica fume and CNTs were needed to achieve an effective dispersion of CNTs in the cement matrix, which in turn is expected to enhance the mechanical and electrical properties of CNT/cement composites.

Saeed Sahranavard (2014) found the effects of functionalised MWCNTs on the mechanical properties of High Performance Mortar were studied. The experimental results show that the influence of MWCNTs on HPM is affected by the type of loading and test conditions – the compressive strength and impact resistance of RHPM were respectively 25.58%and1400% higher than the values obtained for the control sample, but the flexural strength increase due to the addition of MWCNTs in quasi-static three-point loading was just2%.The dramatic effect of MWCNTs on the impact resistance of HPM and its significant effect on compressive strength are due to the structure of the MWCNTs, their bridging action in the mortar matrix and their effect on improving the hardness of calcium silicate hydrate crystals, all causing increased rigidity and strength of the RHPM. However, in quasi-static three-point loading, MWCNTs are affected by the high force rate and are pulled out from the HPM matrix very quickly, therefore losing their bridging effect and rendering them ineffective at significantly improving flexural strength. SEM images revealed that MWCNTs can act as bridging agents and can limit cracking in HPM microstructures. This work has shown that the application of a small amount of MWCNTs has a significant effect on the properties of HPM. Therefore, despite their high cost, these materials are useful for enhancing the mechanical properties of HPM.

Rafat Siddique (2014) discovered the Carbon Nanotubes (CNTs) have excellent properties which generates the wide range of applications in medical, electrical, particularly in construction fields. Lots of research has been carried out and the results showed excellent potential applications in various sectors. With the inclusion of CNTs as fillers, significant effect on mechanical properties of mortars has been discovered. From the SEM micrographs it has been observed that the CNTs were dispersed uniformly in the cement mortar and there was no aggregation of CNTs. Good interaction between carbon nanotubes and the fly ash cement matrix with CNTs has been observed which acts as filler resulting in a denser microstructure and higher strength when compared to the reference fly ash mix without CNTs. The increase in compressive strength of fly ash mixes has been observed with increase in carbon nanotubes content with the highest strength achieved with CNT content of 1% by weight. Also, under high strain loading rate the compressive strength increases with the inclusion of CNTs. The flexural strength found to be increased with the inclusion of CNTs when compared to the plain cement paste but with higher aspect ratio of CNTs, flexural strength found to be dependent on concentration of CNT. Also CNTs were found to be better than carbon fibers in enhancing flexure strength. Young‘s modulus found to be higher than plain cement paste when the samples were reinforced with CNTs.6 The porosity and the total pore volume of concrete/pastes made with the inclusion of CNTs found to decrease, leading to a denser microstructure than that of the control mix and also the shrinkage values were also found to be lower than that of control mixes.

Sanjeev Kumar (2013) found the increase in compressive and splitting-tensile strength was in cement-CNT composites having CNT content of 0.5% by weight of cement. The increases in the previously mentioned strengths with respect to control mix were 15% and 36%, respectively, at 28 days of curing. Cement-CNT composites with 0.75% CNT showed almost the same compressive and splitting-tensile strengths as that of the control mix. The control mix and all cement-CNT composites showed considerable strength (mechanical) gain from 7 days of curing to 28 days of curing. The rate of change of compressive and splitting-tensile of all cement-CNT composites with respect to curing age was seen to be very similar to that of the control mix. This indicates that the strength gain of composites is primarily because of cement hydration and the fact that CNTs are not reacting with cement compounds. A small increase in compressive and splitting-tensile strengths was observed as the sonication time increased from 30 min to 4 h for specimens tested after 90 days of curing. However, specimens tested at other curing ages did not show consistent results. Based on the results obtained, it was concluded that increased sonication period did not cause a significant change in the mechanical strengths of the composites.

The SEM data showed nonuniform dispersion of CNTs in the cement matrix, and this appears to be the reason for the lower strengths of the composites with higher CNT content. However, the embedding of CNT in the cement matrix bridging microcracks was observed. 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. Detailed morphology of CNT and cement compound strand was studied using TEM. Although it is difficult to conclude if there existed any chemical bonding between cement compounds and CNT, it was verified from this test that there was a physical bonding between cement matrix and CNT. The diameter of the cement compound strand was almost the same as that of CNT.

III. CONCLUSION

The following salient conclusions were drawn after the detailed literature review.

- The incorporation of CNTs in the Cementitious Composites increases the mechanical and durability properties of the Composites to certain extend.
- The addition of the untreated SWCNT in cementitious composites upto 0.15% increases the compressive strength upto 13%. The functionalized SWCNTs show a increase upto 20 % for the same amount of CNT incorporation.
- The addition of MWCNTS upto the 0.1% showed a excellent crack bridging characteristics which reduces the crack formation and porosity.
- The dispersion methods show the significant increase in the mechanical and durability property increase.
- The incorporation of MWCNTs in the cementitious composites shows a tremendous increase in the Flexural capacity of the composite.
- The Surface treated CNTS addition upto 0.75% increase the strength by 36%.
- The micro level analysis shows the addition and proper dispersion of the CNT in cementitious composites bridges he microcracks and resists the formation of the cracks.

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