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Effect of diameter of MWCNT reinforcements on the mechanical properties of cement composites

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Abstract. Application of nanotechnology can be used to tailor made cementitious composites owing to small dimension and physical behaviour of resulting hydration products. Because of high aspect ratio and extremely high strength, carbon nanotubes (CNTs) are perfect reinforcing materials. Hence, there is a great prospect to use CNTs in developing new generation cementitious materials. In the present paper, a parametric study has been conducted on cementitious composites reinforced by two types of multi walled carbon nanotubes (MWCNTs) designated as Type I CNT (10-20 nm outer dia.) and Type II CNT (30-50 nm outer dia.) with various concentrations ranging from 0.1% to 0.5% by weight of cement. To evaluate important properties such as flexural strength, strain to failure, elastic modulus and modulus of toughness of the CNT admixed specimens at different curing periods, flexural bending tests were performed. Results show that composites with Type II CNTs gave more strength as compared to Type I CNTs. The highest increase in strength (flexural and compressive) is of the order of 22% and 33%, respectively, compared to control samples. Modulus of toughness at 28 days showed highest improvement of 265% for Type II 0.3% CNT composites. It is obvious that an optimum percentage of CNT could exists for composites to achieve suitable reinforcement behaviour and desired strength properties. Based on the parametric study, a tentative optimum CNT concentration (0.3% by weight of cement) has been proposed. Scanning electron microscope image shows perfect crack bridging mechanism; several of the CNTs were shown to act as crack arrestors across fine cracks along with some CNTs breakage.

Keywords: carbon nano tubes; nano materials; nanotechnology; flexural strength; toughness; ductility

1. Introduction

In the past decade, nanotechnology research can be thought as the most encouraging area in the field of material science. Of late, many types of carbon nano filaments have raised attention of research community in construction industry due to their unique chemical, mechanical and electrical properties and remarkable performance in reinforcing cementitious materials (Wang *et al*. 2006, Marrs *et al*. 2007). A high aspect ratio and exceptionally high strength of 60 GPa is the characteristic of CNTs (Manzur and Yazdani 2016). It also has very high elastic modulus around 1 TPa and ductility of 12% (Jean 2002). Such exceptional properties confirms the potential of CNTs as an excellent reinforcing agent within the cement matrix. Therefore, exploration on developing suitable nanotechnology using CNTs in mortar is of significant interest in the past decade. Mechanical properties of mortar, particularly flexural and compressive strength, depends on mass transfer and microstructure at nano level (Aiu 2006). Moreover, it is established that hydration products can be modified through nanotechnology. Addition of CNTs can, therefore, enhance strength properties apart from improved density of composites, as well as lower ductility values.

Whereas extensive studies on carbon nano tubes has been focused on their integration in polymers, less consideration has been given on using nano tubes in cement mortar. Further, limited research of nano tube effectiveness in augmenting flexural strength or toughness has been done. Within recent past, several investigators obtained improved mechanical properties of cementitious composites by incorporating CNTs. Khater and Gawwad (2015) investigated the effect of firing temperatures on alkali activated geopolymer mortar incorporated with MWCNTs and showed reduction in mechanical strength with temperature.

Manzur and Yazdani (2016) investigated the effect of different sizes and dosage rates of MWCNTs on the properties of cement composites, and recommended a CNT concentration between 0.1-0.3%. In another study, Al-Rub *et al*. (2012) studied the influence of CNT aspect ratio on the mechanical properties of composites. It was found that 28 days strength in flexure with short and long CNTs was improved by 269% and 65%, respectively. Hallad *et al*. (2017) obtained 88% increase in flexural strength by adding both carbon micro fibers and MWCNTs as compared to the control samples. Manzur and Yazdani (2010) investigated the effect of two different MWCNT sizes on compressive strength and found 15-25% increase in compressive strength. Later, Manzur and Yazdani (2015) in a similar study with treated MWCNTs recommended a CNT concentration by weight of cement for strength aspects. For

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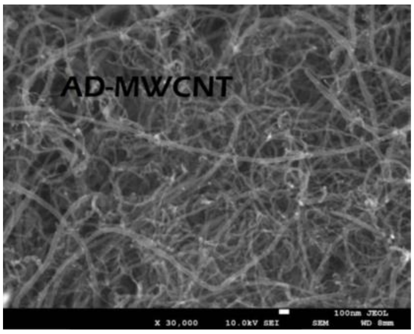
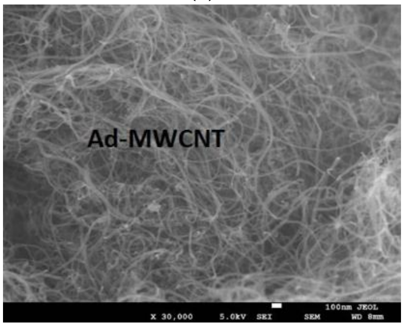


(a)



(b)

Fig. 1 SEM images of (a) Type I and (b) Type II CNTs

optimum mix ratio, increase in compressive and flexural strength was found to be 15% and 19.5%, respectively. Archontas and Pantazopoulou (2015) investigated the microstructural behaviour and mechanics of nano modified cementitious materials and found that fracture toughness was increased by 15%. Yazdani and Mohanam (2014) investigated the effect of short CNTs and long carbon nano fibers (CNFs) on the mechanical strengths of cement mortars. The results showed an increase of 50% and 150% in flexure and compressive strengths compared to plain mortar. Recently, Mohsen *et al*. (2017) investigated the ideal CNT content for improving mechanical strength of cementitious composites. It was found that batches with CNT content lower than 0.25% shows lower mechanical strengths, whereas, batches with CNT contents higher than 0.25 wt% gave marginally higher strengths. In one of the study, Tyson *et al*. (2011) studied the effect of adding untreated CNTs and CNFs in mortar mechanical properties; i.e., elastic modulus, flexural strength, ductility and toughness at 7, 14 and 28 days. It was found that the strength, ductility, and toughness can be enhanced with the CNT content in lower concentrations. Influence of CNTs on various properties like physical, mechanical, electrical and piezoresistive sensitivity of cementitious materials was critically presented by Rashad (2017). A comprehensive review on the properties of cement composites using nano particles was presented by Paul *et al*. (2018). In a recent review paper Shi *et al*. (2019), highlights the research progress on CNT/CNFs added cement composites. Nevertheless, the majority of studies focused on the strength of cement composites reinforced with one particular size of CNTs, and little research was carried out on properties such as ductility, elastic modulus and toughness. It is, therefore imperative to confirm thoroughly

Table 1 Physical properties of MWCNT

Physical properties	Type I CNT	Type II CNT
Colour	Black	Black
Purity (%)	>99	>99
Average Outer Dia. (nm)	10 -20	30 -50
Average Length (μm)	1-5	10-20
Amorphous carbon (%)	<1	<1
Surface Area (m^2/g)	370	400
Average aspect ratio	200	375

the effect of various parameters such as nanotube diameter, nanotube content, curing period, etc. on the mechanical properties of CNT composites in order to accomplish better results.

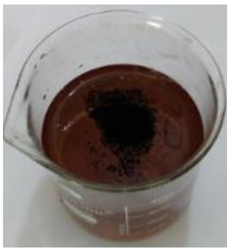
With this goal in mind, an effort has been made in this study to compare the strengths and stress strain properties of flexural specimens added with two types of CNTs (based on outside diameter) to highlight its usefulness as an additive in cement mortar. For uniform dispersion of CNTs, ultrasonic energy along with polycarboxylate based superplastisizer was utilized. Three point flexural bending experiments were conducted to study the load deflection characteristics of specimens prepared using Type I and Type II CNTs after curing periods of 7, 14, and 28 days. Four other mechanical properties, viz., compressive strength, ductility, modulus of elasticity and toughness are determined. To the author's understanding, the present study represents only few studies to date that presents experimental data for the stated properties particularly at various curing periods. After the flexural testing, the samples were cut from the ends to the size of cubes 40 mm×40 mm×40 mm from the uncracked portion of the sample for compressive strength tests. Five dosage rates of 0.1%, 0.2%, 0.3%, 0.4% and 0.5% by weight of cement were used to prepare the specimens. Control samples were also made for comparisons. High resolution electron microscopy was performed to substantiate the outcome of the CNT admixed mortar with microstructure at the fracture surfaces.

2. Experimental work

2.1 Materials

OPC 43-grade (Ultra Tech) and standard sand supplied by Tamil Nadu Minerals Ltd., Chennai were used in the study. MWCNTs manufactured by Ad-Nano Technologies Pvt. Ltd, Karnataka were used as procured in casting CNT composites. Catalytic Chemical Vapour Deposition (CCVD) process was used to produce these CNTs. Fig. 1 shows the Scanning Electron Micrograph (SEM) of MWCNTs. The morphological structure shows CNTs are randomly distributed and are jumbled. In the morphological structure, CNTs are also shown to be in different sizes and lengths. The physical properties of both Type I and Type II CNTs as supplied by the manufacturing company are shown in Table 1. A polycarboxylate based superplasticizer, supplied by Chemcon Tecsys, trade name "CONXL-PCE DM 09" was

(a) Mixing water with super plasticizer



(b) Mixing water with SP and MWCNTs

(c) Sonication for dispersion of MWCNTs

(d) Sonicated water after 30 minutes of sonication

Fig. 2 Different stages of sonication

used to help in uniform mixing of CNTs in water.

2.2 Dispersion of MWCNTs

Separate batches for Type I CNTs were prepared at five different percentages (0.1 through 0.5wt% of cement). For Type II CNTs, identical batches were made at same concentrations by cement weight. For all the specimens, w/c ratio was kept same as 0.5. For each batch, three replicates were cast and tested after curing periods of 7, 14, and 28 days, respectively. The mean value as well as standard error of the mean for the specimen were computed after respective curing periods. In this study, measured quantity of MWCNTs was first mixed with mixture of water and superplastisizer (0.4% of SP by weight of cement was added to water). Bath sonicator was employed for 30 minutes to achieve uniform dispersion of CNTs in water. The various stages of sonication are shown in Fig. 2 (a)-(d). Before the application of CNTs dispersed water in the mix, three trials were made with regards to sonication time (10 min, 20 min and 30 min), respectively. The resulting dispersed CNT solution was filled in test tubes to assess qualitatively its stability. The colour of dispersed solution was observed for next 8 hours. It was revealed that for 30 min sonication time, CNTs in the test tube remains stable and did not settle down indicating effective and uniform dispersion of CNTs. Therefore, 30 min sonication time was adopted to prepare all mixes.

2.3 Mixing and sample preparation

After the completion of sonication process, required quantity of sonicated water with a water cement ratio of 0.5 was poured into the mixture of cement and sand with a ratio of 1:3. The resulting mixture were then mixed together for 7 min in a multispeed planetary blender. The mix proportions and sonication time are given in Table 2.

The moulds conforming to IS: 10078-1982 was used to prepare the specimens. Specimens were cast by pouring mixture into the moulds of size 160 mm×40 mm×40 mm. The moulds were lightly oiled inside before use. The samples were kept in moulds under moist condition for 24 h, and finally immersed in water for flexural strength tests after 7, 14 and 28 days. Control specimens were also prepared using the same procedure.

Table 2 Details of the test specimens

Specimen constitution	CNT (% wt. of cement)	Super plasticizer (% wt. of cement)	Sonication time (min.)
Control Specimen (Plain)	0.0	0.4%	0
Type I 0.1% CNT	0.1	0.4%	30
Type I 0.2% CNT	0.2	0.4%	30
Type I 0.3% CNT	0.3	0.4%	30
Type I 0.4% CNT	0.4	0.4%	30
Type I 0.5% CNT	0.5	0.4%	30
Type II 0.1% CNT	0.1	0.4%	30
Type II 0.2% CNT	0.2	0.4%	30
Type II 0.3% CNT	0.3	0.4%	30
Type II 0.4% CNT	0.4	0.4%	30
Type II 0.5% CNT	0.5	0.4%	30

2.4 Flexural testing

A three point bending testing frame was used for flexural testing. It consist of load cell and LVDT to measure the displacement. Two roller supports of 10 mm diameter, 100 mm apart were used during testing. The third roller having same diameter and at same distance from first two supports was used to transmit the load 'P' on the opposite side of the sample as shown in Fig. 3. Rate of loading was kept as 50±10 N/s during testing. Flexural testing machine along with specimen after failure are shown in Fig. 4. For calculating mechanical properties, deflections corresponding to each load were measured and recorded. Finally, Euler-Bernoulli elastic beam theory was applied to evaluate corresponding stresses and strains.

$$\boldsymbol{\sigma} = \frac{\boldsymbol{Ld}}{\boldsymbol{4I}}\boldsymbol{P} \quad \text{and} \quad \boldsymbol{\varepsilon} = \frac{\boldsymbol{12d}}{\boldsymbol{L^2}}\boldsymbol{y} \tag{1}$$

where σ and ε denotes respectively the flexural tensile stress and the strain at the bottom most layer of the flexural specimen at each load increment, L denotes the simply supported span of the specimen (100 mm), d is the half-depth of the specimen cross-section (20 mm), I is the moment of inertia of the beam cross-section, P is the applied load, and y is the deflection at mid-span. Following formula is used to calculate the flexural strength as per IS: 4031 (Part 8) - 1988.

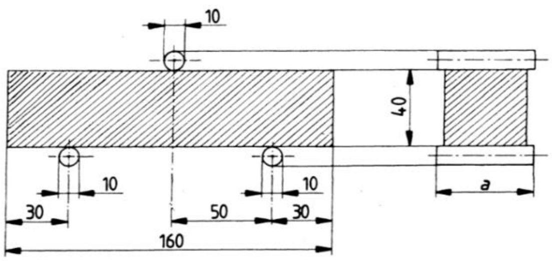
$$\boldsymbol{R} = \frac{\boldsymbol{6M}}{\boldsymbol{B^3}} \tag{2}$$

Where,

$R =$ Flexural strength of the specimen

$M =$ Maximum bending moment under central point loading

$B =$ Side of the prism square cross section



(All dimensions are in mm)

Fig. 3 Flexural strength testing as per (IS: 4031 (Part 8) - 1988)

Fig. 4 Flexural specimen after failure

2.5 Compression testing

After the flexural strength tests, the samples were cut from the ends to cube dimensions, 40 mm each from the uncracked portion of the sample as per IS: 4031 (Part 8) - 1988). Each prism was tested for compressive strength test by placing an area 40 mm×40 mm between two hard metal plates in compression testing machine of 45 KN capacity provided by AIMIL, Bangalore. The load was applied at the rate of 200 kg/cm^2/min.

2.6 Electron microscopy images

Since carbon nano tubes are not visible with naked eyes, Scanning Electron Microscope (SEM) was employed to study the relations of nanotubes with cement hydration products. To elucidate and substantiate the results from mechanical testing, it was essential to know how the CNTs were holding the hydration products after these samples were tested to failure. With this objective, broken samples after 28 days was subjected to SEM analysis. The SEM was performed at University Sophisticated Instruments Facility (USIF) centre, AMU, Aligarh, India. SEM from JOEL, Japan was used for analysis and interpretation of the variations in the microstructure of the composite matrix.

3. Results and discussion

For each batch at 7, 14, and 28 days, various properties were evaluated, viz., flexural strength, compressive strength, ductility, modulus of elasticity, toughness and stress strain characteristics. Figs. 5 to 9 showed results with average values in comparison to control specimens. For each specimen, the mean values and the standard error of the mean are shown by bar charts. The third and first quartile represents top and bottom error bars.

3.1 Flexural strength

Fig. 5 depicts the flexural strength of mortar specimens with various wt% of CNTs at 7, 14 and 28 days of immersed water curing. This strength enhancement follows an uptrend up to 0.3 wt% CNT content beyond which a falling trend was observed. In few cases, the inclusion of CNTs indicate a decrease in strength compared to control samples. The improvement in strength may be attributed to the use of CNT which behaves not only as filler to improve microstructure but also as an activator to promote high chemical reactivity due to greater surface area of CNTs. Typically, CNTs reduce the number of fine pores within C-S-H gel, and fortify the nano structure of cementitious composites. Further, reduction in strength for CNT specimens in excess of 0.3% is primarily due to two reasons. Firstly, less water remains available in such specimens as more water stick to CNT surfaces and ultimately obstructs proper hydration. Secondly, more nano tubes get agglomerated causing water to entrap within clumped CNTs resulting insufficient hydration of cement. The highest increase in flexural strength (22%) was shown at 7 days for Type II 0.3% CNT specimens when compared to control specimens. The same values for Type I 0.3% CNT specimen shows an improvement of 15% compared to its counterpart. The increase in flexural strength at 28 days for the specimens with Type II 0.3% CNT and Type I 0.3% CNTs was found to be 17% and 11%, respectively. A higher increase in strength at early ages indicates that presence of CNTs initiates quick hydration at early ages (0-7 days). The

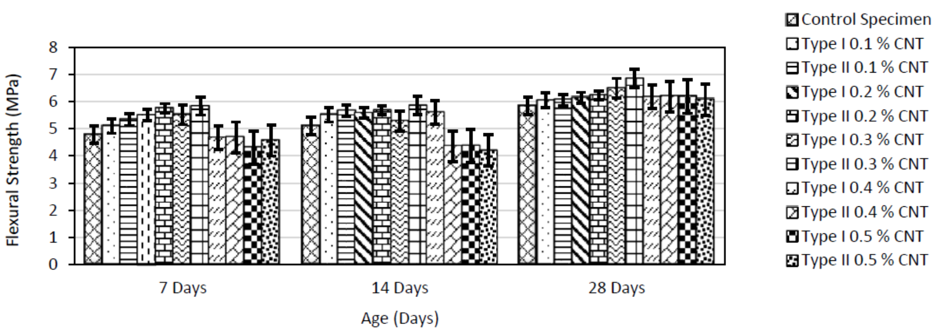


Fig. 5 Average flexural strength values for various CNT specimens

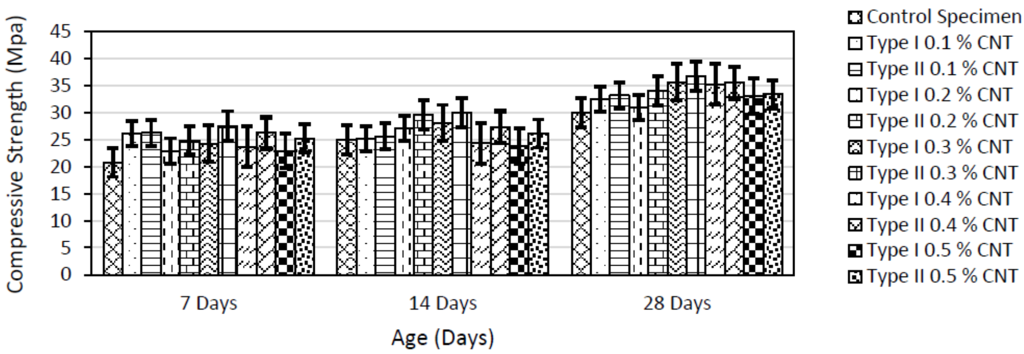


Fig. 6 Average compressive strength values for various CNT specimens

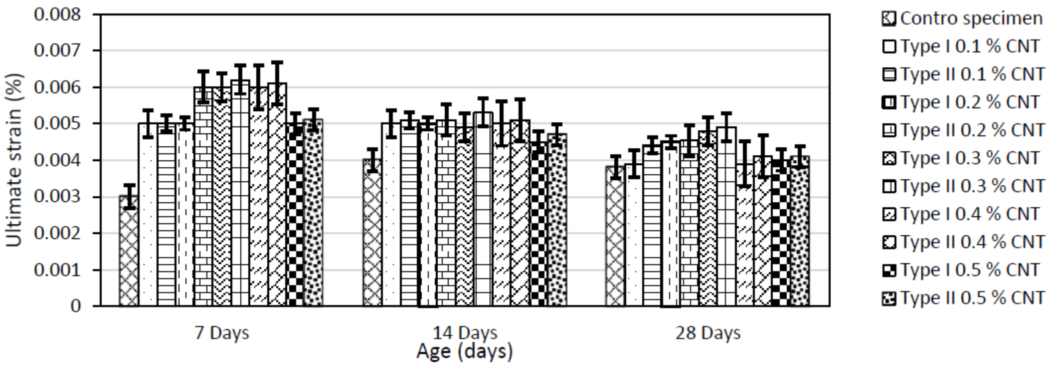


Fig. 7 Average ductility values for various CNT specimens

reason behind quick hydration at early ages is that inclusion of CNTs in the matrix increased the hydration reaction of C_3S. The morphology of both C_3S and C_3A hydration compounds were found to be affected by the addition of nano tubes (Rashad 2017). The nano tubes seemed to be acted as nucleating sites for the C_3S hydration compounds, wherein the CNTs becoming quickly coated with C-S-H gel. The formation of Ca $(OH)_2$ during the initial period of hydration increases. Thus, heat of hydration increased leading to higher strength at early ages. From the foregoing discussion it can be concluded that optimum concentration of CNTs is found to be 0.3 wt% of cement for obtaining high strength mortars. Overall, Type II CNT specimens perform better in strength contribution as compared to Type I CNT specimens. This could be due to the fact that at high aspect ratio, the crack bridging mechanism is more effective, leading to higher strengths.

3.2 Compressive strength

Compressive strength of mortar specimens for various wt% of CNTs at different ages are shown in Fig. 6. It is found that at all curing periods, compressive strength increases up to 0.3 wt% CNTs. The maximum 7 days strength under compression was found for composites with Type II 0.3% CNT specimens. The maximum increase in compressive strength was about 33% than the control specimens. Same trend is obtained for increase in compressive strength at 14 days. At 28 days, a lesser increase in strength (22%) was obtained compared to control specimens. The mechanism for increase in strength at low CNT contents is alike to the strength enhancement mechanism as discussed in the previous section. Beyond 0.3% CNT addition, a falling trend is observed in compressive strength. As amount of CNT was increased, more aqueous solution was required for proper sonication and additional water stick to the CNT surface due to larger surface area of CNTs. Consequently strength reduction is observed due to less workability. Also higher dosage rate of CNT has greater tendency to agglomerate and therefore, uniform dispersion is difficult to achieve. In turn, CNT fail to fill nano space within cement grains which is very important for achieving proper reinforcement behaviour. So there exists an optimum concentration of CNT that could result in desired properties of the cementitious specimens. Manzur *et al*. (2014) obtained similar results in their study for finding optimum percentage of CNTs in mortars. It is also observed that Type II CNT composites produced higher strengths as compared to Type I CNT composites at almost all percentages of CNT admixed mortar specimens.

3.3 Ductility

Ductility (strain to failure) of mortar specimens with different wt% of CNTs at various curing ages are shown in Fig. 7. At 7 days of immersed curing, majority of the CNT composite specimens show an increasing trend in ductility (upto 0.3% CNT) when compared to the control flexural beams. The maximum enhancement in ductility with an increase of 107% was obtained for Type II 0.3% CNT specimens. On the other hand, at 14 days of immersed curing, significant changes were observed in the behaviour of CNT composites. Most of the CNT composites shows significant drop in the ductility, to be less than the ductility

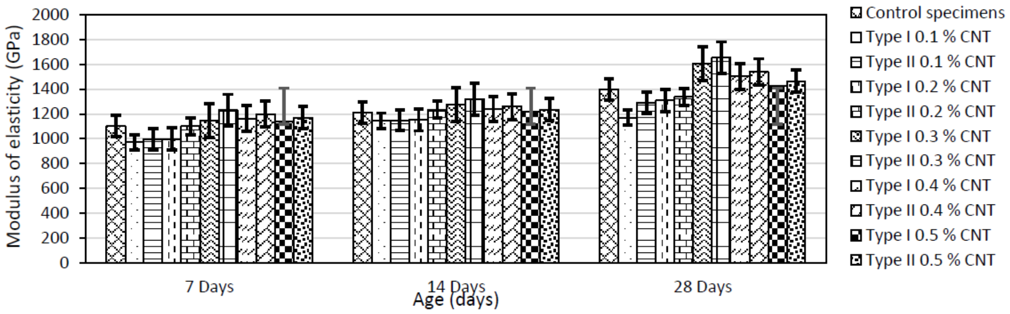


Fig. 8 Average elastic modulus values for various CNT composites

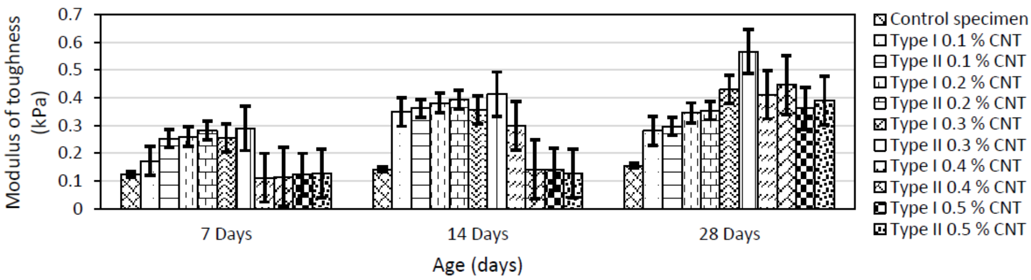


Fig. 9 Average modulus of toughness values for various CNT specimens

at 7 days, in general. After 14 days, it was again observed that Type II 0.3% CNT composites showed 33% increase in ductility with respect to the control samples. After 28 days, majority of the CNT composites show ductility to reduce in comparison to 7 and 14 days, where again Type II 0.3% CNT composites performed better in ductility. The degree of ultimate strain capacity mainly depends on the aspect ratio and the percentage of CNTs apart from age of curing. Composites containing nano tubes with high aspect ratio (Type II CNTs) exhibited more ductility than their counterpart Type I CNTs with less aspect ratio. Higher aspect ratio of CNTs makes them more effective as reinforcement because of their greater interaction with the cementitious matrix.

3.4 Modulus of elasticity

The modulus of elasticity values with different wt% of CNTs for various ages are shown in Fig. 8. Most of the CNT admixed mortar specimens show a rising trend in elastic modulus in comparison to the control specimens after 7 days of curing. The highest improvement was shown for Type II 0.3% CNT specimens with an increase of 12% when compared to control samples. After curing period of 14 days, majority of the flexural specimens showed elastic modulus values close to the control ones. After 28 days, all the samples again showed rising trend compared to control specimens, and Type II 0.3% CNT composites has the maximum increase of 19%. The elastic modulus of cement mortar is normally found to be greater for higher concentration (upto optimal level) of CNTs as shown in Fig. 8. The mechanism of enhancement in elastic modulus is similar to the strength enhancement mechanism as discussed before. These CNTs react with $Ca(OH)_2$ resulting in matrix densification, thus reducing the porosity. Therefore, when under load application on flexural samples, a steeper stress-strain slope was obtained for Type II CNT composites (Fig. 10) due to lesser deformation of the denser cement matrix. However, higher concentration of CNTs can adversely influence the elastic modulus as shown in Fig. 8.

3.5 Toughness

The modulus of toughness is calculated by using MATLAB by simply integrating the area under the stress strain diagram. The toughness shows the same common trends: a beneficial effect upto 0.3% CNT content and a worsening effect beyond that for all curing periods. Fig. 9 shows modulus of toughness values for all CNT composites increases from age of 7 through 28 days. At 7 days, majority of the CNT admixed specimens show an increase in modulus of toughness with respect to the control specimens. The maximum improvement was shown by the Type II 0.3% CNT specimens with a substantial increase of 125% as compared to the control beams. Beyond 0.3% CNT concentration, several of the CNT specimens showed decrease in toughness followed by their improvement. Because of large enhancement in flexural strength of Type II 0.3% CNT at 28 days, it has shown the maximum increase in toughness as 265%.

Hence, from the stated outcome for the CNT specimens, one can see that in majority of the cases, the modulus of elasticity and toughness increased from 7 to 28 days (see Figs. 8 and 9). The reverse is observed for the ductility (see Fig. 7). These results are in close agreement with Konsta *et al*. (2010), which can be attributed to: (a) arresting micro crack propagation due to reduced nano tube free volume of the cement matrix with Type II CNTs and (b) more effective filling of small voids by Type II CNTs, which lead to enhanced packing density of the paste. Figs. 8 and 9 clearly shows that modulus of elasticity and toughness increases as the CNT content increases. In general, this trend is more

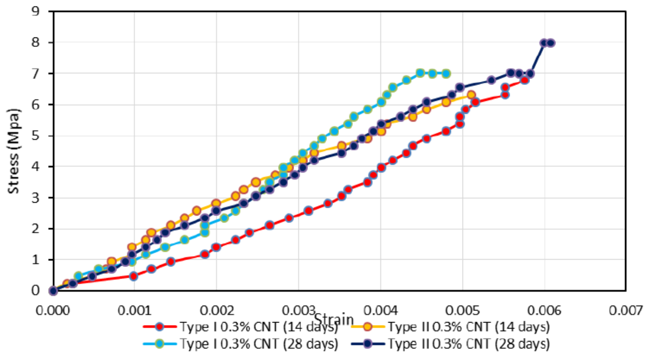


Fig. 10 Stress-strain curves for few beams of the Type I 0.3% CNT and Type II 0.3% CNTs at 14 and 28 days.

likely with Type II CNTs upto 0.3% concentration. Beyond a certain limit, increase in CNT concentration showed decrease in corresponding values. Although this observation is vital from economic aspect; the lesser the percentage of CNTs in the matrix the lesser the cost of CNT composites, for desirable mechanical properties one may ensure uniform distribution of nano tubes in the composite matrix. As Type II CNT has higher surface area when compared to Type I CNT, it is anticipated that mechanical properties with Type II CNT will get maximum benefit in terms of strength improvement.

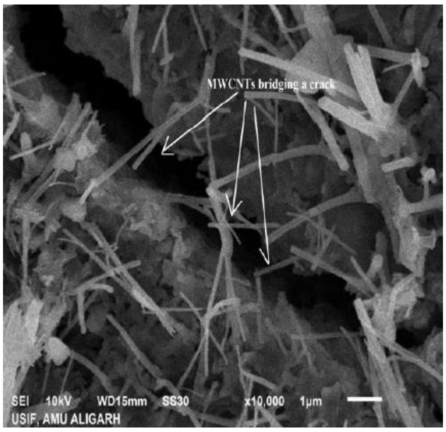
3.6 Stress strain behaviour

Fig. 10 shows a sample stress strain curves for few CNT flexural beams. Based on the observation, multi peaks behavior is noticed which can be correlated to pull out mechanism of CNTs from fine cracks in the composite matrix. This phenomenon is of vital importance for ductility and toughness of the CNT composites. Fig. 11(a) shows crack bridging phenomenon by the nano tubes within the cement matrix. The micrograph clearly shows that many nano tubes are bridging the micro crack. Pull out as well as breakage of nano tubes can also be seen from image. In fact, the nano tube breakage denotes a good bonding between the CNTs and the adjacent cement matrix, whereas, pull out of CNTs from the matrix are mainly responsible for multi peaks behaviour.

Deviation in the outcomes of the same mix of a sample was observed even though each sample of a lot are alike and prepared from the same mix proportions. Uniform distribution of the CNTs by sonication process does not have a guarantee for its uniform distribution within the matrix, hence the stress variation in the flexural specimens will be non-uniform that leads to variable flexural behaviour of the samples. Contrary to non-uniform dispersion of CNTs in the matrix, formation of weak hydration products could be the reason behind flexural strength reduction in some beams.

3.7 Electron microscopy images

The main objective of performing SEM analysis was to comprehend how the CNTs are holding the hydration products after testing of CNT specimens. The broken samples post mechanical testing after 28 days were crushed to a fine powder and taken to the USIF centre at AMU. The broken samples were subjected to SEM analysis under various magnifications, ranging from 3000× to 2000× Fig. 11 (a)-(c) show selected SEM images of the samples. Fig. 11(c) shows how the nano tubes were distributed in the cement matrix. Agglomeration of nano tubes seen in the image specify inadequate dispersion of CNTs in the matrix. Some agglomerated CNTs were shown entangled with each other without any connection to the matrix. Improper dispersion of nano tubes, as shown in Fig. 11(c), might be responsible for hindering the bonding between the hydration products. From obtained mechanical testing



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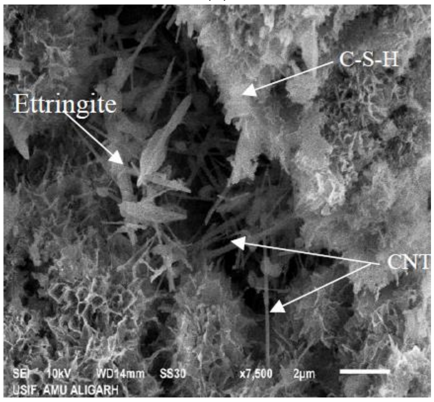

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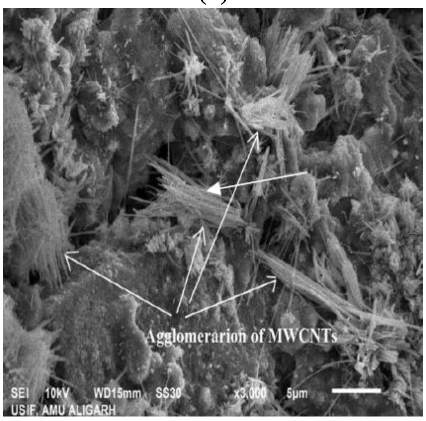

(c)

Fig. 11 (a) SEM micrographs of mortars with 0.3 wt% (b) 0.4 wt% and (c) 0.5 wt% of Type II CNTs at 28 days results in earlier sections, this seems to be the justification that CNTs at higher dosage rates (0.4%-0.5%) did not actively take part in holding the matrix and ultimately improving its properties. For example, mechanical strengths tests showed strength enhancement of CNT composites, when the CNT percentage was upto 0.3%. However, flexural and compressive strength of 0.4% and 0.5% CNT specimens showed degradation in strength to be less than that of 0.3% CNT specimens. It shows that when the concentration of nano tubes was less, good dispersion was accomplished, causing improvement in strength. Fig. 11(a) shows some CNTs bridging a micro crack as well as pull out, indicating that CNT was assisting to hold the cementitious matrix at low concentrations. Fig. 11(b) shows both CNTs and small needle like ettringite formations, which could describe the deprivation in mechanical properties in samples with higher content of CNTs. From SEM micrographs, it was tough to distinguish any sort of chemical bonding between hydration products and CNTs and it should be investigated in future study by using TEM or EDS technique.

4. Conclusions

From the various studies performed on nano composites, the following conclusions are drawn:

- Larger increase in flexural and compressive strength was observed in Type II CNT specimens having CNT concentration of 0.3% by weight of cement. The maximum increase in the previously stated strengths with respect to the control samples at 7 days were 22% and 33%, respectively. At 28 days, the same values for strength enhancement were found to be 17% and 22%, respectively. CNT composites with nano tube content in excess of 0.3% shows a decreasing trend in strength. It is also observed that Type II CNT composites produced higher strengths as compared to Type I CNT composites at almost all percentages of CNT admixed specimens which can be due to high aspect ratio of Type II CNTs which makes them more effective as reinforcement due to their larger interaction (higher specific surface area) with the cementitious matrix.
- In this study, 0.1%-0.5% CNT by weight of cement were tested to see how well these CNTs perform within cement mortar. From the outcomes of the study, one can limit the CNT percent fractions in order to find the optimum concentration for successfully reinforcing cement mortar. The study findings propose that a CNT content of 0.3 wt% might be an optimal concentration for achieving better dispersions and desirable strength enhancement at an affordable cost.
- It was found from the study that nano tube admixed cement composites hardened relatively rapidly as compared to normal cement mortar. A higher increase in strength at early ages (07 days) verifies the fact that hydration process accelerates in the presence of CNTs. The reason behind accelerated hydration may be attributed to increased formation of $Ca(OH)_2$. Thus heat of hydration increased leading to higher strength at early ages.
- The addition of Type II 0.3% CNTs at early age (7 days) increased the ductility by 107% than the control specimens, which is crucial for structural applications where higher ductility is required. The highest increase in modulus of toughness value (265 %) was again found for Type II 0.3% CNTs at 28 days.
- The SEM micrograph of high CNT content specimens showed agglomeration of CNTs in the cement matrix, and this seems to be the reason for the degradation of strength in higher CNT composites. However, embedment of CNTs in the matrix bridging micro cracks was also detected. Based on the outcomes, it was concluded that the sonication method was not good enough for effective dispersion of CNTs in the matrix. Future studies on the change in microstructural properties using TEM or EDS are needed to fully understand the detailed morphology of CNT and cement compounds.

References

Aiu, M. (2006), "The chemistry and physics of nano-cement", *Strain*, 28.

Al-rub, R.K.A., Ahmad, I.A. and Bryan, M.T. (2012), "On the aspect ratio effect of multi-walled carbon nanotube reinforcements on the mechanical properties of cementitious nanocomposites", *Constr. Build. Mater.*, **35**, 647-655.

Archontas, N.D. and Pantazopoulou, S.J. (2015), "Microstructural behavior and mechanics of nano-modified cementitious materials", *Adv. Concrete Constr.*, **3**(1), 15-37.

Brock, M., Rodney, A. and David, P. (2007), "Multiwall carbon nanotubes enhance the fatigue performance of physiologically maintained methyl methacrylate-styrene copolymer", *Carbon*, **45**(10), 2098-2104.

Hallad, S.A., Nagaraj, R.B., Anand, M.H., Ashok, S.S., Narasimha, H.A., Mruthunjaya, A.K. Lohit, R.B. and Manjunath, U. (2017), "Experimental investigation for graphene and carbon fibre in polymer-based matrix for structural applications", *J. Appl. Res. Technol.*, **15**(3), 297-302.

Jean-Paul Salvetat-Delmotte, Angel Rubio (2002), *Salvetat*, **40**. http://www.sciencedirect.com/science/article/pii/S000862230200012X.

Khater, H.M.M. and Hamdy, A.A.G. (2015), "Characterization of alkali activated geopolymer mortar doped with MWCNT", *Epitoanyag-J. Silicate Bas. Compos. Mater.*, **67**(2), 38-47.

Konsta-Gdoutos, M.S., Zoi, S.M. and Surendra, P.S. (2010), "Highly dispersed carbon nanotube reinforced cement based materials", *Cement Concrete Res.*, **40**(7), 1052-59.

Manzur, T. and Yazdani, N. (2010), "Strength enhancement of cement mortar with carbon nanotubes", *Tran. Res. Record: J. Tran. Res. Board*, **2142**(1), 102-108.

Manzur, T. and Yazdani, N. (2015), "Optimum mix ratio for carbon nanotubes in cement mortar", *KSCE J. Civil Eng.*, **19**(5), 1405-1412.

Manzur, T. and Yazdani, N. (2016), "Effect of different parameters on properties of multiwalled carbon nanotube-reinforced cement composites", *Arab. J. Sci. Eng.*, **41**(12), 4835-4845.

Manzur, T., Yazdani, N. and Emon, A.B. (2014), "Effect of carbon nanotube size on compressive strengths of nanotube reinforced cementitious composites", *J. Mater.*, **2014**, 1-8.

Mohsen, M.O., Taha, R., Taqa, A.A. and Shaat, A. (2017), "Optimum carbon nanotubes' content for improving flexural and compressive strength of cement paste", *Constr. Build. Mater.*, **150**, 395-403.

Paul, S.C., van Rooyen, A.S., van Zijl, G.P. and Petrik, L.F. (2018), "Properties of cement-based composites using nanoparticles: A comprehensive review", *Constr. Build. Mater.*, **189**, 1019-1034.

Rashad, A.M. (2017), "Effect of carbon nanotubes (CNTs) on the properties of traditional cementitious materials", *Constr. Build. Mater.*, **153**, 81-101.

Shi, T., Zexin L., Guo, J. Gong, H. and Gu, C. (2019), "Research progress on CNTs/CNFs-modified cement-based composites - a review", *Constr. Build. Mater.*, **202**, 290-307.

Tyson, B.M., Al-Rub, R.K.A., Yazdanbakhsh, A. and Grasley, Z. (2011), "Carbon nanotubes and carbon nanofibers for enhancing the mechanical properties of nanocomposite cementitious materials", *J. Mater. Civil Eng.*, **23**(7), 1028-1035.

Wang, J., Fang, Z., Gu, A., Xu, L. and Liu, F. (2006), "Effect of amino-functionalization of multi-walled carbon nanotubes on the dispersion with epoxy resin matrix", *J. Appl. Polym. Sci.*, **100**(1), 97-104.

Yazdani, N. and Mohanam, V. (2014), "Carbon nano-tube and nano-fiber in cement mortar: effect of dosage rate and water-cement ratio", *Int. J. Mater. Sci.*, **4**(2), 45-52.

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