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RESEARCH ARTICLE - CIVIL ENGINEERING

Effect of Different Parameters on Properties of Multiwalled Carbon Nanotube-Reinforced Cement Composites

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Abstract The exceptional mechanical properties of carbon nanotube (CNT) such as high strength, elastic modulus and aspect ratio. reflect its potential to be used as reinforcements in cementitious materials. Nanotubes can be distributed on much finer scale and can act as bridge across void spaces and cracks. This in turn improves the overall mechanical properties of the composite. However, there are certain issues that need to be considered while producing CNT cement composites. With this end in view, an attempt has been made to summarize the effect of different parameters on properties of CNT-reinforced cementitious composites through interpretation of results obtained from a comprehensive study. Different sizes and dosage rates of MWNT were used to conduct parametric study. In addition, untreated and surface-treated commercially available MWNTs were used to make composites. Sonication was done for dispersion of nanotubes within cement matrix. An appropriate mixing technique was suggested after conducting a parametric study by varying the amplitude and time of sonication. In some cases, polycarboxylate-based superplasticizer was used as surfactant to disperse MWNTs in aqueous medium. It was observed that surface treatment of nanotubes and utilization of superplasticizer as surfactant enhance their solubility within water. It was also found that proper dispersion and dosage rates of MWNT have significant effect on composite behavior. A suitable mix proportion in terms of MWNT dosage rate, MWNT size and plasticizer proportion has been found. Moreover, it was suggested that flow values of composite paste is a good indicator of stability of the mix.

Keywords Carbon nanotube · Cement · Multiwalled nanotube · Dispersion · Mix proportion

1 Introduction

Nanotechnology can be considered as the most promising area of research of the past decade in the field of material science. A nanometer (nm) is one billionth of a meter (10^{-9} m) and nanostructured material have at least one of the three dimensions <100 nm. Nanomaterials can improve material effectiveness due to their distinctive physical and chemical properties [1]. Carbon nanotube (CNT) constitutes a significant volume of nanotechnology-related research. The prime focus of such research activities involves commercial application of CNT. CNT was first discovered by Iijima [2] in 1991. CNT is a distinctive type of carbon which has high aspect ratio [3] as well as extremely high strength [4]. CNT also has very high modulus [5] and elasticity [6]. Due to these exceptional qualities, a wide variety of researches are being carried out on CNT ranging from field emission properties to self-sensing ability [7–9]. Such high strength, aspect ratio and elasticity also ensure the potential of nanotubes as an exceptional reinforcing material within the composite mix. The reinforcing performance of CNT is already proven in polymer-based materials [10,11]. In addition, finer distribution of CNT within the composite matrix is possible as compared to traditional reinforcing fibers due to their nanodimension. Incorporating various types of fibers within cement mortar and concrete is quite common for improving ductility, flexural performance and energy absorption capacity [12,13]. Therefore, research on

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developing proper nanotechnology for cement and concrete through addition of nanofiber like CNT is of great interest.

Mechanical properties of concrete, strength in particular, depend on concrete microstructure and mass transfer at nanolevel [14]. Moreover, it is already established that the chemistry and physical behavior of hydration products can be manipulated through nanotechnology because of their nanodimensions [15]. Addition of CNT can, therefore, enhance both strengths (flexural and compressive) and overall density of cement composites, as well as decrease failure strain. Several researches have already observed improved mechanical properties of cementitious composites through addition of both SWNT (single-walled nanotubes) and MWNT (multiwalled nanotubes). Makar et al. [15] showed that hydration of cement can be accelerated at early age by adding SWNT within cement paste. Nanotubes can also influence the morphology of hydration products [16]. Moreover, nanotubes can provide more spaces for hydration reactions to occur if properly dispersed and eventually encourage the formation of hydration reaction products. Higher compressive strength (19 %) and flexural strength (25 %) than that of Portland cement composite at 28 days was observed by Li et al. [17] through addition of treated MWNT by an amount of 0.5 %. Manzur and Yazdani [18] in 2010 also observed enhancement of compressive strength by adding two different sizes (outside diameters) of untreated MWNT within cement matrix. The compressive strength enhancement was ranged between 15 and 25 %. However, sample size was smaller in that study. Later, in another study in 2015, Manzur and Yazdani [19] proposed an optimum mix ratio for treated MWNT-reinforced cement composites based on compressive and flexural strengths of larger sample size. About 15 % increment in compressive strength and 19.5 % increment in flexural strength was observed for the best-performing mix. Size effect of CNT on compressive strength of cement composites was also showed by Manzur et al. [20]. It was also observed that flowability of composite mix can have significant effect on composite strength [21]. Agullo et al. [22] obtained early high strength of cement mortar by adding low concentration of MWNT. However, they found less compressive strength than that of plain cement mortar at 28 days. Cwirzen et al. [23] found about 10 % increase in flexural strength than normal cement mortar by adding MWNT. Konsta et al. [24] showed that addition of short and long MWNT within cement composites enhanced the flexural strength and Young's modulus. It is also found that dispersion of nanotubes plays a significant role in producing CNT cement composites. Several studies [25,26] showed that using acid-treated nanotubes resulted in better dispersion and eventually better performing cementitious composites. Utilization of polycarboxylate-based water reducing agent as surfactant has also been found as an effective way to disperse nanotubes homogenously within cement matrix [27,28]. It is, therefore, obvious that nanotube addition within cement composites has multifold effect and resulted in quite variable outcomes. Such variability of CNT cement composites is also described comprehensively in an article by Parveen et al. [29]. It is observed that increase in strengths of cementitious composites by adding nanotubes largely depend on mixing techniques, treatment of nanotubes, nanotube size, nanotube concentration, etc. Hence, it is evident from past researches that performance of nanotube-reinforced cement composites depends on several important parameters and mixing issues. Consequently, a clear and concise idea on effect of various parameters on properties of nanotube-reinforced cement composites is of immense importance in order to carry out future researches. With this end in view, an attempt has been made in this article to interpret and summarize the results obtained through a comprehensive study [18–21] conducted by the authors over a period of time for discussing the effect of mixing process, surface treatment of nanotubes, workability of mix, size (outside diameter) and amount of nanotubes.

2 Experimental Program

The experimental program was conducted in two phases [30]. MWNTs were used as reinforcing agent. The first phase of the study was conducted to explore the effect of MWNT dosage rate, MWNT size and different mix proportions on compressive strength of MWNT cement composites. Seven different sizes (based on outside diameter) of commercially available MWNT were used as reinforcement. Different mixing methods using ultrasonication for uniform dispersion of MWNT within cement matrix were examined to suggest a suitable mixing technique [18]. Surface-treated MWNT with acid solution was also utilized as reinforcement and compared with the untreated MWNT-reinforced composites. Based on the first-phase test results, the better-performing mix proportion and a particular size of MWNT were chosen for further investigation in the second phase [19,20]. In this article, discussions on both phases of the study are presented together in brief with particular emphasis on various factors that have considerable influence on strength of MWNT-reinforced cement composites.

3 Material Used

Ordinary Type II Portland cement was utilized in this study. Grading of the used sand conform to ASTM C109 [31] test requirements. Seven different sizes (based on outside diameter) of commercially available (supplied by Cheap Tubes Inc.) untreated MWNT was used initially. The length of nanotubes was ranged between 10 and 30 µm since MWNT with larger length (10–100 µm) is relatively difficult to disperse within cement matrix [24]. Moreover, such longer MWNT is expensive than that of shorter length. Commercially available surface-treated MWNT with acid solution was also used in the later phase of the study. Surface-treated MWNT was collected from the same supplier. MWNT was treated by oxidizing in nitric and sulfuric acid mixture. Such acid treatment adds polar impurities like hydroxyl or carboxyl end groups to the outer surface of MWNT which in turn produces more soluble nanotubes in water. Tables 1 and 2 show the properties of untreated and treated MWNT, respectively. Figure 1 shows the TEM image of untreated MW2 and treated MWT5, respectively. Designations of MWNTs are as per Tables 1 and 2.

4 Mixing Process

Commercial grade MWNT was procured in powder form. Uniform distribution of nanotubes in cement composite is essential to ensure reinforcing behavior of fibers. However, mixing of MWNT is difficult using conventional process since large surface area of nanotubes result in extremely high van der Waals forces and causes agglomeration. Such agglomeration of MWNT is very difficult to break with manual stirring or any other low-energy mechanism. Figure 2 shows an unstable mix of MWNT in water done by manual stirring which clearly shows that manual mixing cannot produce enough energy to break the agglomeration. Therefore, ultrasonic vibration was utilized to split agglomeration of nanotubes and distribute them across the cement grains. A MISONIX 4000 sonicator was used for this purpose in the

Table 1 Untreated MWNT properties

Types of MWNT and properties	OD (outside diameter) nm	Length µm	Purity (wt %)	SSA (specific surface area) m^2/g	EC (electrical conductivity) s/cm
MW1	>50	10–20	>95	>40	$>10^{-2}$
MW2	20–30	10–30	>95	>110	$>10^{-2}$
MW3	10–20	10–30	>95	>233	$>10^{-2}$
MW4	<8	10–30	>95	>500	$>10^{-2}$
MW5	8–15	10–30	>95	>233	$>10^{-2}$
MW6	20–40	10–30	>95	>110	$>10^{-2}$
MW7	30–50	10–20	>95	>60	$>10^{-2}$

Table 2 Treated MWNT properties

Types of MWNT and properties	OD (outside diameter) nm	Length µm	Purity (wt %)	SSA (specific surface area) m^2/g	EC (electrical conductivity) s/cm	COOH content (wt %)
MWT2	20–30	10–30	>95	>110	$>10^{-2}$	1.23
MWT3	10–20	10–30	>95	>233	$>10^{-2}$	2.00
MWT4	<8	10–30	>95	>500	$>10^{-2}$	3.86
MWT5	8–15	10–30	>95	>233	$>10^{-2}$	2.56

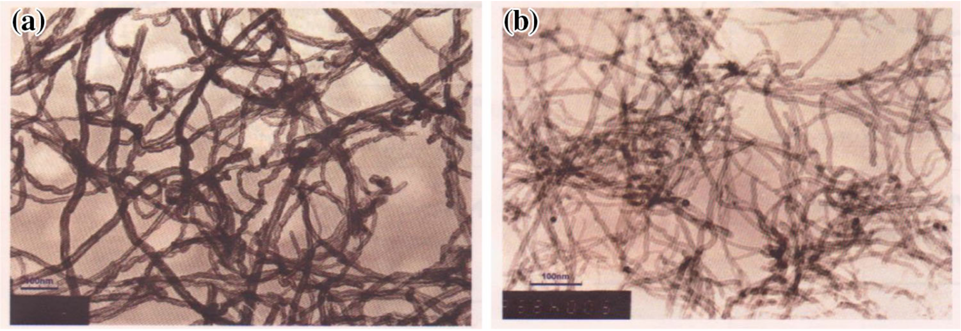

Fig. 1 TEM image of **a** untreated MW2, **b** treated MWT5

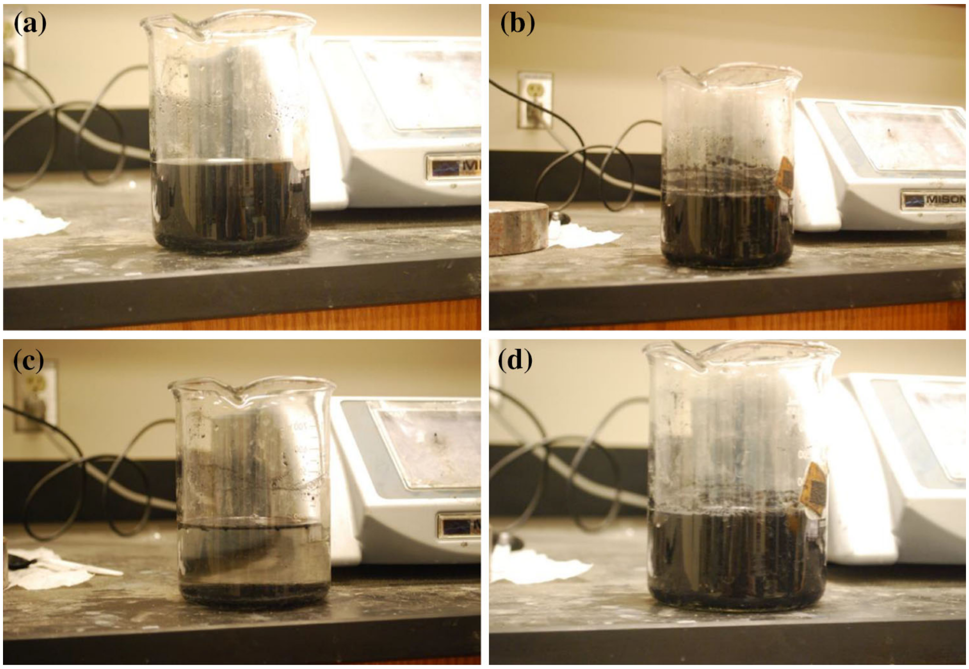

Fig. 2 **a** Suspension state of MWNT just after mixing by manual stirring; **b** suspension state of MWNT 15 min after mixing by manual stirring; **c** suspension state of MWNT just after mixing through 40 min sonication; **d** suspension state of MWNT after 120 through 40 min sonication

experiment, and a suitable mixing technique was developed [18,30]. In order to develop the suitable mixing technique, 0.3 % of MW1 by weight of cement was added through the sonication process in water. The amount and type of MWNT was kept constant for the base study of mixing technique. Sonication steps, amplitude and timing were varied. The best-performing technique in terms of composite strength was then utilized for the rest of the study. Such procedure was found to produce a stable suspension (Fig. 2). A typical procedure of dispersing nanotubes followed in this study consisted of two steps. In the first step, MWNT was suspended in water through sonication. In the second step, the MWNT dispersed water was used as mixing water with 1 part of cement and 2.75 parts of sand by mass to produce cementitious composite following ASTM C109 procedure [31]. A rotary mixer with flat beater was used for mixing sand, cement and MWNT-suspended water. After mixing the cement and water for 30 s, the sand was added keeping the mixer rotating and mixed for 3.5 min. Figure 3 [18] shows the 7- and 28-day compressive strengths of MWNT-reinforced cement composites prepared by three of several mixing methods investigated in the study. Mixing 3 process achieved the highest compressive strength both at 7 and 28 days among all mixing techniques. Composites produced by following Mixing 3 process yielded about 70 and 30 % higher compressive strength than that of samples produced by Mixing 1 process at 7 and 28 days, respectively. Mixing 1 process produced the lowest composite strength. Results of Mixing 2 process is showed to provide an idea on how amplitude and time of sonication can affect the composite strength. In Mixing 1 process, the whole amount of nanotubes was added to the water and then sonicated for 5 min at a constant amplitude of 50 %. After completing the sonication, samples were made using MWNT dispersed water as mixing water. In Mixing 2 process, sonication was done for 15 min after adding all required amount of nanotubes. The amplitude was varied between 50 and 70 %. In Mixing 3 process, nanotubes were added in sequence and was sonicated for 5 min for each addition. Once sonication of all required amount of nanotubes was done, the entire mixture of water and nanotubes was sonicated for another 15 min. The total sonication time was kept fixed at 40 min for this mixing process. The amplitude was varied between 50 and 75 %. It was found that both Mixing 2 and Mixing 3 process produced similar compressive strengths at 7 days. However, Mixing 3 process

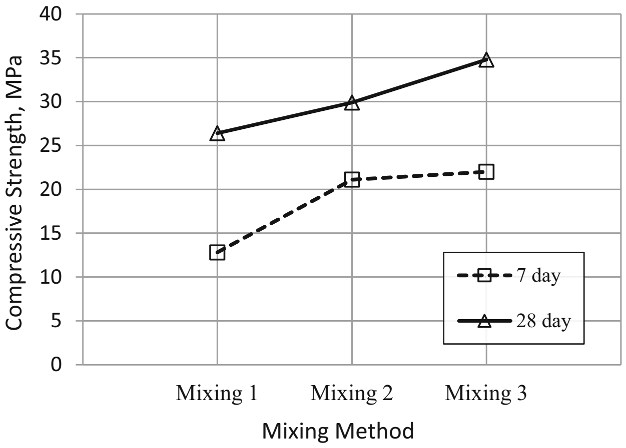

Fig. 3 Compressive strength of MWNT-reinforced cementitious composites for various mixing techniques

yielded 16 % higher 28-day strength as compared to Mixing 2 process. It is, therefore, obvious that appropriate mixing technique is needed to follow for ensuring proper dispersion of nanotubes with cement mix.

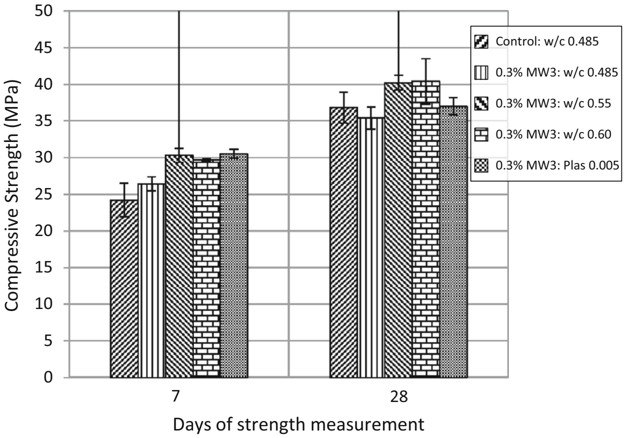

Fig. 4 Compressive strength for different mix proportions of 0.3 % MW3-reinforced composites

5 Effect of Mix Proportion, Concentraion and Size of Untreated MWNT on Composite Strength

Compressive strength of the samples was determined according to ASTM C109 [31]. Cubic specimens of 50 mm in dimension were made. MWNT were mixed with water by sonication following Method 3 process. Rotary mixture was used to mix cement, sand and sonicated water as mixing water. Cubic samples were made using the prepared mix and kept in the mold for 1 day in the moisture room. After 1 day, samples were removed from the mold and immersed in lime water until tested. Compressive strength of samples was measured at 7 and 28 days. Flow values were determined using the flow table as per ASTM C1437-01 [32].

Samples were prepared using different w/c ratios, dosage rates and sizes of untreated MWNT in the first phase [30]. Control samples without nanotubes were also made for comparison. Plasticizers were used in some mix proportions to increase the workability of the mix but not as surfactant for nanotubes. Plasticizer proportion of 0.005 in terms of weight of cement was used. The w/c ratios, ranged from 0.485 to 0.65, were used. The dosage rates of MWNT were varied between 0.10 and 0.50 % by weight of cement. Similar pattern of variation in compressive strength was observed for MWNT cement composites with the change in mix proportion. For example, composites with MWNT dosage rate of 0.1–0.3 % exhibited comparable compressive strengths when all other parameters (w/c ratio, MWNT size, plasticizer addition, etc.) of mix proportion were kept constant. On the other hand, when MWNT size was varied keeping other parameters constant, composites reinforced with smaller size nanotubes yielded the maximum compressive strength for a given mix proportion [20]. In this section, compressive strength test results of MW3-reinforced composites are described in details. Comparisons between strengths of composites having different sizes of MWNT for a given mix proportion are also made for assessing the effect of nanotube size.

Figure 4 shows the strength variation of 0.3 % MW3 cement composites with the variation in mix proportions. Three different w/c ratios of 0.485, 0.55 and 0.60 were utilized. Composites with w/c ratios of 0.55 and 0.60 produced almost equal 28-day compressive strength which was 10 % higher than that of control samples. Samples having w/c ratio of 0.55 and 0.60 obtained 25 % and 23 % higher 7-day compressive strength than control samples, respectively. Plasticizer addition increased the 7- and 28-day compressive strengths by 26 and 7 %, respectively, as compared to the control samples. Compressive strengths of 0.2 % MW3-reinforced samples having different mix proportions were also evaluated. The maximum strength was obtained for the mix with w/c ratio of 0.60. The 7- and 28-day compressive strengths of those mixes were found to be 24.5 and 11 % higher than that of control samples, respectively. Composites with w/c ratio of 0.55 also achieved 20 % higher 7-day compressive strength than control samples, but the 28-day strength was similar to the strength of the control samples. Similar trend of relative higher 7-day compressive strength than 28-day strength as compared to control specimens was observed for all nanotube-reinforced composites. The reason behind such higher early strength is the influence of nanotubes on the morphology of cement hydration products particularly at early age. As already mentioned, nanotubes has accelerating effect on hydration process since they provide more space for hydration reaction to occur and consequently, encourage the formation of reaction products.

Composites with w/c ratio of 0.485 produced the lowest compressive strength both at 7 and 28 days for all MWNT-reinforced composites. Composites with 0.2 % MW3 and w/c ratio of 0.485 exhibited slightly higher 7-day strength (1.0 %) and 3 % lower 28-day strength, as compared to the control samples. In case of 0.3 % MW3 composites with w/c ratio of 0.485, 9 % higher 7-day compressive strength and 4 % lower 28-day strength was observed. It was evident that the mix proportion with w/c ratio of 0.60 yielded maximum compressive strength both at 7 and 28 days. Therefore, a comparison among compressive strengths of composites having different MW3 dosage rates but constant w/c ratio of 0.60 is shown in Fig. 5. Composites with dosage rate of 0.2 and 0.3 % had almost equal 7- and 28-day compressive strength which were about 23 and 11 % higher than the control samples, respectively. Samples with 0.1 % MW3 produced a little lower 7- and 28-day compressive strength than that of 0.2 and 0.3 %

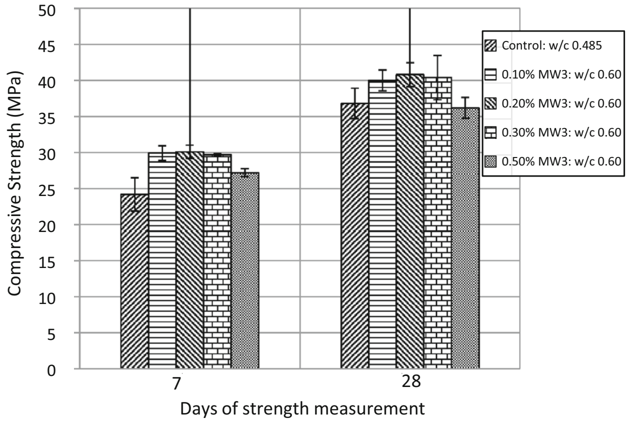

Fig. 5 Compressive strength of control and MW3-reinforced samples with w/c: 0.60

dosage rates. Composite samples with 0.5 % dosage rate of MW3 obtained the lowest compressive strength, both at 7 and 28 days, among all MW3-reinforced composites. Such reduction in strength with relatively higher dosage rate of 0.5 % is mainly due to two reasons. Firstly, less water remains available in these samples as more water adhere to nanotubes surfaces and eventually hinders proper hydration. Secondly, more MWNT get clumped and water get entrapped within them which also affect the hydration of cement. In contrast, more aqueous solution in higher water content samples provides more spaces for MWNT to disperse uniformly through sonication. As a result, more stable dispersion is achieved that eventually ensured higher compressive strength. Similar increase in compressive strength was also observed by Musso et al. [33] when w/c ratio was increased from 0.40 to 0.56 for CNT cement composites.

It was also found from the study that composites with w/c ratio of 0.485 resulted in lowest flow values. Table 3 shows the flow values of different MW3-reinforced composites. It is apparent from the flow values that as MWNT concentration increases, the workability of the mix decreases for a given mix proportion in most cases. This kind of behavior was expected as higher amount of MWNT adhere more water on their surface causing workability to reduce. Although addition of plasticizer resulted in higher workability of the mix, no increase in 28-day compressive strength was found as compared to control sample for higher dosage rate of MWNT. Similar trend was also observed for other six different sizes of MWNT-reinforced composites. In majority of cases, composites with w/c ratio of 0.60 produced the maximum compressive strength for a given dosage rate of MWNT. It was also observed that dosage rate of 0.3 % achieved the highest compressive strength in most cases. However, 0.1% and 0.2 % dosage rates also produced similar compressive strength as of 0.3 % dosage rate. Composites with MWNT dosage rate higher than 0.3 % achieved less compressive strength than control samples in all instances. Therefore, it is apparent that amount of MWNT and proper selection of mix proportion are of immense importance for producing robust MWNT-reinforced composites.

As already mentioned, size of nanotubes has significant effect on strength of CNT cement composites [20,30]. Therefore, a comparison between compressive strengths of composite samples having different sizes of nanotubes as reinforcement is summarized and discussed in this study. Figure 6 [20] shows the effect of nanotube size on 7- and 28-day compressive strength of composites having 0.3, 0.2 and 0.1 % MWNT and w/c ratio of 0.60. It is apparent from Fig. 6 that size of nanotubes can affect the compressive strength of

Table 3 Flow values of control and MW3-reinforced composites with different mix proportions

Type of sample	Amount of MWNT (% of wt of cement)	w/c ratio	Plasticizer proportion (in terms of cement wt.)	Flow values (%)
Control	–	0.485	–	32
Composite	0.3	0.485	–	13
Composite	0.2	0.485	–	8
Composite	0.1	0.485	–	15
Composite	0.5	0.60	–	37
Composite	0.3	0.60	–	48
Composite	0.2	0.60	–	52
Composite	0.1	0.60	–	55
Composite	0.3	0.55	–	40
Composite	0.2	0.55	–	42
Composite	0.1	0.55	–	45
Composite	0.3	0.485	0.005	42
Composite	0.2	0.485	0.005	35
Composite	0.1	0.485	0.005	53

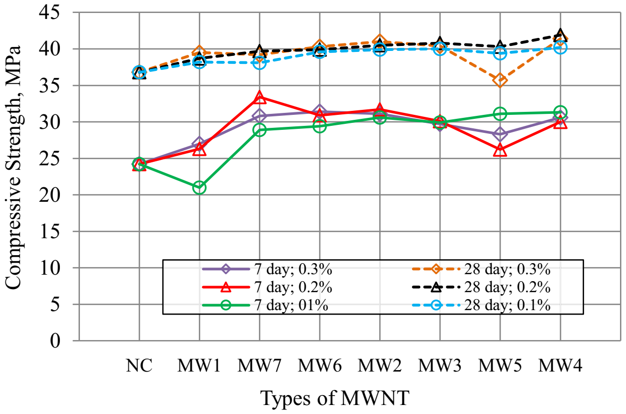

Fig. 6 Compressive strength of composites having 0.3, 0.2 and 0.1 % of different types of MWNT and w/c of 0.60

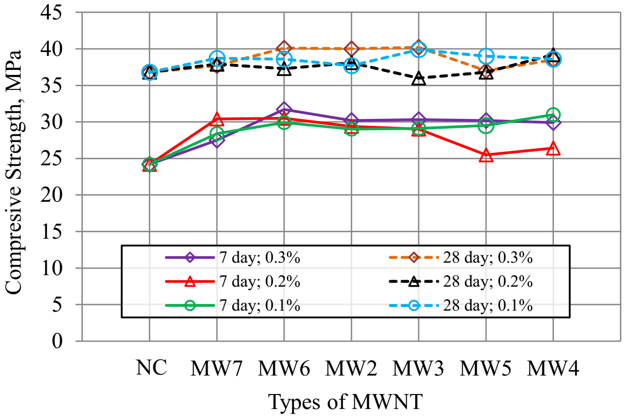

Fig. 7 Compressive strength of composites having 0.3, 0.2 and 0.1 % of different types of MWNT and w/c ratio of 0.55

composites. In general, an upward trend was found with the decrease in MWNT size. The maximum 28-day compressive strength was achieved by MW4 addition which was the smallest in size (with the least outside diameter). However, MW2 and MW3 also produced similar 28-day compressive strength as compared to MW4. For 0.3 % dosage rate, MW1 and MW7 produced the lowest compressive strength at 28 days which was around 5 % less than that of MW4-reinforced composite [20]. For 0.2 % dosage rate, the difference between the two extreme cases (the highest and lowest compressive strength) was found to be about 8 % [20]. And, in case of 0.1 % dosage rate, the maximum compressive strength was 5 % higher than the lowest one [20]. In case of 7-day compressive strength, no definite pattern was observed. However, similar to 28-day strength, MW1 produced the lowest 7-day compressive strength. Therefore, it can be said that smaller MWNT produces relatively higher compressive strength since the maximum compressive strength was achieved by smallest nanotubes (MW4)-reinforced composite, both at 7 and 28 days. Such beneficial effect of smaller nanotubes is attributed to the greater surface area of smaller nanotubes that enhance the effectiveness of them as nucleating agent and consequently, facilitates the growth of hydration products. In addition, smaller nanotubes fill the nanosized pores within the cement matrix more effectively in turn resulting in more compact composites. Variation in compressive strengths of samples reinforced with different sizes of nanotubes for mix proportion with w/c ratio of 0.55 is shown in Fig. 7 [20]. Similar pattern, exhibited by samples with w/c ratio of 0.60, is also observed in this case.

6 Treated vs Untreated MWNT

Since behavior of MWNT-reinforced cement composites is greatly influenced by uniform distribution of nanotubes across the cement grains, effort should be made to make nanotubes more soluble to aqueous solution. It has been found that surface treatment of MWNT with a mixture of nitric and sulfuric acids could make them more soluble. Such acid treatment develops hydroxyl or carboxyl end groups on outer surface of nanotubes and hinders the agglomeration. Since it was evident from the initial study [20,30] that MWNT having OD smaller than 30 nm produced composites with relatively higher compressive strength, MWWT larger than 30 nm OD was not utilized for comparison between treated and untreated nanotubes. Hence, acid-treated MWT2, MWT3, MWT4 and MWT5 were used to make samples in this phase. Compressive strength of 0.3 % MWT2-, MWT3-, MWT4- and MWT5-reinforced composites at 7 and 28 days were measured. All mixes had w/c ratio of 0.60. The highest compressive strength was achieved by MWT4-reinforced composites at 28 days (about 13 % higher than the control samples). For MWT3 addition, the increase was slightly greater than 12 %. The highest 7-day compressive strength was achieved by MWT3 addition which was about 40 and 2.5 % higher than that of control samples and MWT4 composites, respectively. Figures 8 and 9 show the compressive strengths of composites reinforced with treated and untreated nanotubes having different sizes and dosage rates at 7 and 28 days, respectively. In both the figures, untreated MWNT is termed as “UT” and treated MWNT is designated as “T”. It was found that in all cases, addition of treated MWNT resulted in better compressive strength than that of untreated ones both at 7 and 28 days. The average increase in 7- and 28-day compressive strength was about 12.5 and 5 %, respectively, as compared to untreated MWNT-reinforced samples for 0.3 % dosage rate. For 0.2 % dosage rate, the mean increase of about 15 and 1 % were observed at 7 and 28 days, respectively. For 0.1 % dosage rate, the mean increment of 9 % at 7 days and 2 % at 28 days were observed. Thus, it became apparent that acid treatment of MWNT resulted in more stronger composites.

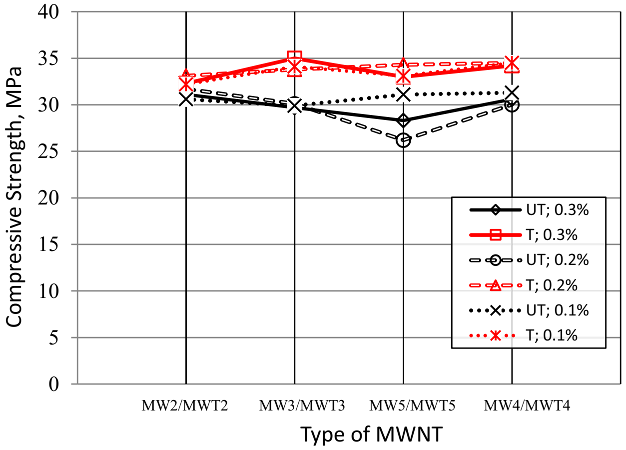

Fig. 8 Comparison of 7-day compressive strength of different untreated and acid-treated MWNT-reinforced composites for 0.3, 0.2 and 0.1 % concentration

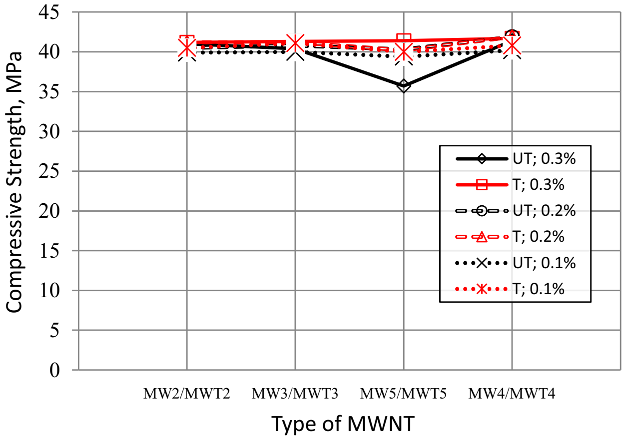

Fig. 9 Comparison of 28-day compressive strength of different untreated and acid-treated MWNT-reinforced composites for 0.3, 0.2 and 0.1 % concentration

7 Significance of Mix Flowability and Plasticizer as Surfactant

In the second phase of the study, samples were prepared using treated 0.3 % MWT3 to obtain a tentative optimum mix proportion [30]. Composite samples were made using six w/c ratios ranging from 0.50 to 0.70, and Fig. 10 [19] shows the compressive strengths of these composites. Similar to initial phase of study, composites with higher w/c ratio yielded relatively higher compressive strength than that of composites having lower water content. Composites having w/c ratio of 0.60 and 0.62 produced the highest compressive strength. Total eight sets were prepared for each mix proportion. Flow value was also determined for each sample. Figure 11 [21] shows 28-day compressive strength of different sets of composites having similar w/c ratio of 0.60 and corresponding flow values. Considerable fluctuation in flow values was observed. Samples with higher flow values obtained higher compressive strength [21]. However, an interesting observation was made regarding flow values and compressive strength of the samples. It was observed that flow values tend to follow the compressive strength of the corresponding samples. Higher flow values represent less viscous mixes that result from the uniform dispersion of MWNT within the cement matrix. Inadequate dispersion of nanotubes makes the mix glutinous as more nanotubes remain adhered to each other. Such agglomeration of nanotubes needs to be broken; otherwise, it creates weaker zones within the composite. This in turn produces weaker composites with lesser compressive strengths. Therefore, it can be inferred that flow values can be considered as a good indicator of the stability of a nanotube-reinforced cement mix [21].

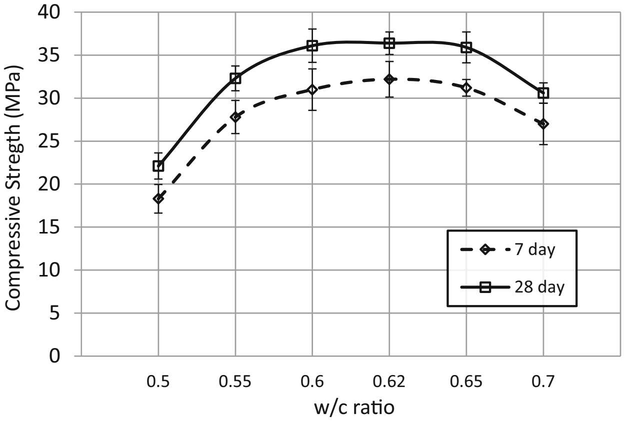

Fig. 10 Compressive strengths of composite samples with 0.3 % treated MWT3 with different w/c Ratios

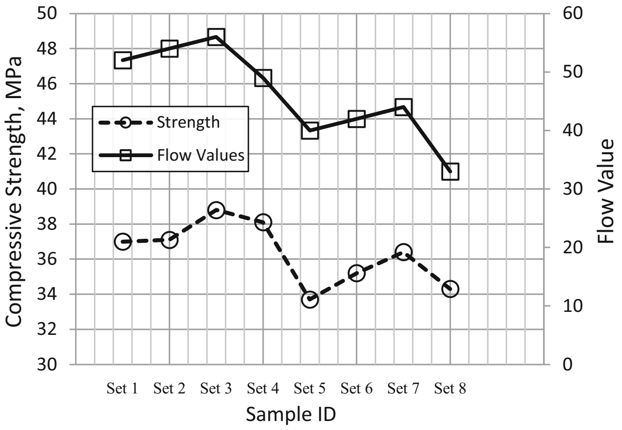

Fig. 11 28-day compressive strength and corresponding flow values of 0.3 % treated MWT3-reinforced composites with w/c ratio of 0.60

It is also clear from Fig. 11 that sonication of MWNT in water alone was not successful to ensure stable mixes in all cases. Surfactants that are usually used to sonicate nanotubes in ceramic industry hinder the cement hydration process. However, polycarboxylate-based superplasticizer has been

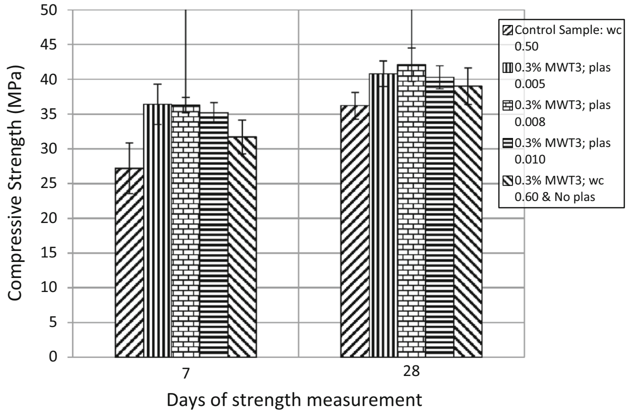

Fig. 12 Compressive strengths of control samples and composite samples with different plasticizer proportions as surfactant

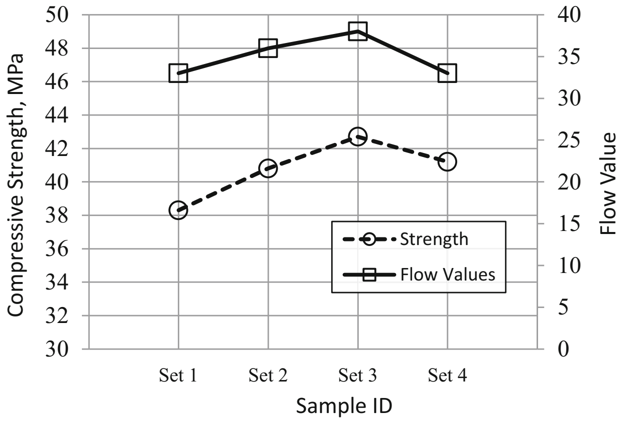

Fig. 13 28-day compressive strength and corresponding flow values of 0.3 % treated MWT3-reinforced composites with w/c ratio of 0.50 and plasticizer proportion of 0.008 as surfactant

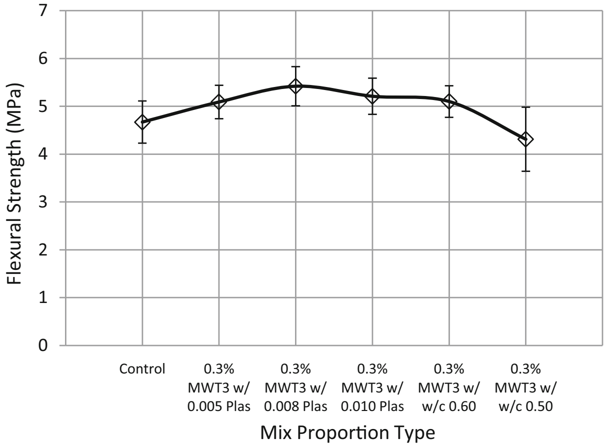

Fig. 14 Flexural strengths of control and composite samples with 0.3 % treated MWT3 having different mix proportions

found in some studies [27,28] as an effective surfactant to disperse nanotubes within cement without affecting the hydration process. Hence, polycarboxylate-based superplasticizer ADVA Cast 575 was used as surfactant to disperse MWNTs. Samples were prepared with different proportion (in terms of weight of cement) of plasticizer addition as surfactant. Treated MWNT (MWT3) was used, and the concentration was kept constant at 0.3 %. Plasticizer proportions were ranged between 0.005 and 0.010 [19,30]. Water/cement ratio of 0.50 was used for samples having plasticizer as surfactant. Four sets (each set contained six samples) of samples were prepared for each plasticizer addition as surfactant. Figure 12 [19] shows the 7- and 28-day compressive strength of control and composite samples having different plasticizer proportion as surfactant. Maximum 28-day compressive strength (about 8 % higher than that of MWT3-reinforced composites with w/c ratio of 0.60 and no plasticizer) was obtained by samples with plasticizer proportion of 0.008 as surfactant [19]. As compared to control samples, composites with plasticizer proportion of 0.008 achieved about 16 % higher strength [19]. It was also observed that these samples had similar flow values which means that relative stable mix was achieved through such technique (Fig. 13) [21]. Consequently, compressive strength values also had less variation for these samples. Besides, similar to previous case, flow values tend to follow the compressive strength of the corresponding mix. Plasticizer addition as surfactant is thus proven to be beneficial for producing nanotube-reinforced cement composites since it stabilizes the dispersion of MWNT and eventually results in higher compressive strength. Therefore, it is obvious that proper distribution of nanotubes is one of the key parameters that must be given proper attention to develop robust composites.

The effect of plasticizer as surfactant on flexural strengths of MWNT-reinforced composites was also investigated [19,30] as per ASTM C348-02 [34] and summarized in this article. Similar to compressive strength tests, plasticizer proportions of 0.005 to 0.010 were used. The w/c ratio of these samples was kept constant at 0.50. Control samples were made with w/c ratio of 0.50 for comparison. Composites were also made with w/c ratio of 0.60 and 0.50. Nanotube dosage rate of 0.3 % was used. Samples were tested at 28 days after proper curing. Figure 14 [19] shows the flexural strength of different 0.3 % MWT3-reinforced samples. It was observed that, composites with plasticizer proportion of 0.008 exhibited the maximum flexural strength which was about 16 % higher than that of control samples [19]. Composite samples with w/c ratio of 0.60 produced about 9 % higher flexural strength than control samples [19]. The lowest flexural strength was achieved by composites having w/c ratio of 0.50. Such pattern of behavior is analogous to the compressive strengths of the composites. However, nanotube-reinforced composites exhibited relative better performance in flexure as compared to compressive strength tests. This is because behavior of cementitious composites under flexure is mainly influenced by crack bridging and fiber pullout actions of nanotubes in addition to enhanced hydration products produced by addition of nanotubes.

8 Conclusions

The prime objective is to present and discuss the influence of various factors that should be given proper consideration while producing nanotube-reinforced cementitious composites in a single article. A comprehensive experimental investigation was carried out, and the results obtained from the conducted tests have been summarized and analyzed to identify several parameters that have significant effect on behavior of nanotube-reinforced composite in this article. It has been observed that both compressive and flexural strengths of cementitious composites can be increased by MWNT addition. However, such strength augmentation depends on mixing technique of nanotubes within cement matrix and proportions of different constituents of the mix. Dispersion of MWNT plays a significant role in producing robust nanotube-reinforced composites. Proper sonication time and amplitude are required to ensure uniform dispersion. Additionally, more aqueous solution is required for stable dispersion of nanotubes if no surfactant is used. Hence, mix proportion with higher w/c ratio is recommended to make nanotube-reinforced cement composites. However, it should be noted that too much aqueous solution has detrimental effect on cement composites. It is also found that using polycarboxylate-based superplasticizer as surfactant reduces the water requirement for dispersion of nanotubes and eventually produces composites with higher strengths. This is due to the fact that polycarboxylate-based superplasticizer greatly enhances the solubility of MWNT by hindering the tendency of their agglomeration. Therefore, polycarboxylate-based superplasticizer can be recommended to be used as surfactant for proper dispersion of nanotubes. Moreover, addition of superplasticizer as surfactant also reduces water requirement for the mix.

It is also evident from the discussion that amount of MWNT has significant effect on strength of composites. It is apparent that a tentative optimum mix proportion in terms of MWNT dosage rate, plasticizer proportion and water/cement ratio exists to produce stronger composites. A water/cement ratio of 0.6 and MWNT concentration between 0.1 and 0.3 % can be recommended to produce composites when no surfactant is utilized. On the other hand, if polycarboxylate-based superplasticizer is used as surfactant, plasticizer proportion of 0.008 in terms of weight of cement is recommended to be used along with w/c ratio of 0.50. It can also be concluded that size of nanotube has influence on strength of composites. Based on the findings, MWNT with outside diameter smaller than 30 nm can be suggested. Surface-treated MWNT with sulfuric and nitric acid solution were also used to investigate the effect of such treatment on composite properties. In all cases, composites with treated MWNT yielded higher compressive strength than that of untreated ones. So, treated MWNT is recommended to be used with cement mix. Another interesting observation is that flowability of mixes can be used as an indicator of the quality of the mix regarding dispersion of nanotubes. Lower flow values for the similar mix proportion, in general, indicate viscous mix resulting from relative non-uniform dispersion of nanotubes. Flow value of a mix is easy to measure and can be considered as a quick and less costly way of getting an idea on stability of the nanotubes dispersion within cement matrix.

Past researches on nanotube-reinforced cement composites exhibited quite variable results, and in several cases insignificant improvement in strengths were observed. The mixing technique and recommended mix proportions discussed in this study are capable of producing MWNT-reinforced composites with enhanced compressive and flexural strengths. However, tests were conducted under controlled condition of laboratory and further investigation is required on practical application of nanotube-reinforced cementitious composites.

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