

## IMPORTANCE OF FLOW VALUES IN QUALITATIVE EVALUATION OF CARBON NANOTUBE REINFORCED CEMENTITIOUS MATRIX

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**Abstract:** In the field of nanotechnology, Carbon nanotube (CNT) has the prime focus as one of the most important areas of research. A major difficulty of producing CNT-cement composites is the attainment of uniform dispersion of CNT. CNT has a tendency to agglomerate creating zones of weakness in composite materials. In this study, a parametric study was carried on surface treated multiwalled carbon nanotubes (MWNT) reinforced cementitious composites having different mix proportions and an attempt was made to establish a relation between compressive strengths and flow values of composites samples. It was observed that the effect of flow values on compressive strength was most pronounced at 28 day. Composites made with surfactant exhibited less fluctuation in flow values and corresponding compressive strengths. A higher flow value of MWNT added composites, having same mix proportion, represents more uniform distribution of MWNT within the cement grains and more stable mix. Furthermore, less variation in flow values represents more stable dispersion technique to distribute CNT within cement matrix.

**Keywords:** Carbon nanotubes; surface treated; dispersion; compressive strength; flow values

### 1.0 Introduction

Utilization of nano-particles in improving material characteristics has already gained recognition and is being applied in many fields ranging from computer hard drives, cosmetics, sports goods to oil refining technology. Nano-materials exhibit distinctive chemical and physical properties that can result in the improvement of material effectiveness (Li *et al.* 2004). With the emerging nanotechnology, one can build material block atom by atom. This will largely enhance and control the physical properties of materials. There is particular interest in developing nanotechnology for cement and concrete. The mechanical properties of CNT depict their immense potential for use as reinforcements in composite materials. CNT have already proven its rein-

forcing performance in polymer based materials (Marrs *et al.* 2007; and Coleman *et al.* 2006).

Adequate dispersion of nanotubes is extremely important to produce cement composites with improved mechanical properties. Insufficient sonication fails to break the agglomeration of nanotubes and results in inadequate reinforcement of nanotubes within the cement. In addition, if the nanotube bundles remain intact, they no longer remain in the nano scale range. Also, lack of proper dispersion of MWNT make the paste more viscous affecting workability of the mix adversely. The cumulative outcomes of these effects reflect on the strength of the composite, which is much less than the strength of normal cement mortar.

In this study, the relation between flow values and compressive strengths of composite samples is presented and discussed. Compressive strengths were determined both at 7 and 28 days. It was observed that the effect of flow values on compressive strength was most pronounced at 28 day. Composites with higher flow values resulted in relatively higher compressive strengths at 28 day having the same mix proportion. Relations between compressive strengths and flow values were also developed for composites made with plasticizer addition not as surfactant. Similar trend was also found in this case. Composites made with surfactant exhibited less fluctuation in flow values and corresponding compressive strengths. Moreover, relatively higher compressive strengths were obtained by these composites having plasticizer as surfactant. Closely spaced flow values were observed and relatively higher compressive strengths were obtained. This type of behavior indicates that more stable mix can be achieved through plasticizer addition as surfactant. Therefore, flow values can be considered as a good measure of the quality of cement mix reinforced by nanotubes.

## 2.0 Material Used and Mixing of Nanotube

Ordinary Type II Portland cement was used as cementitious material in this study. Special graded sand according to ASTM C109 (ASTM C109/C109M, 2008) test requirement was utilized. Surfaces treated MWNT having outside diameter (OD) 10-20 nm was used and is designated as M. In this method of surface treatment, the MWNT was first oxidized in a mixture of nitric and sulfuric acids and then the acid treated MWNT was heated and sonicated. This acid treatment results in more soluble nanotubes than pristine CNT by adding polar impurities like carboxyl end groups to the outer surface of MWNT. The properties and composition of M are shown in Table 1. Fig. 1 shows the TEM images of M. ADVA Cast 575 was used as plasticizer in the experiments to improve the workability of the mix and as surfactant.

Commercially available M were collected in powder form. Due to Van der Waals forces resulting from large surface area of nanotubes, they tend to adhere together. Manual

stirring of MWNT within water is not suitable to suspend nanotubes as this process is not capable of producing required energy to break the agglomeration of nanotubes. Ultrasonic vibration was utilized to exfoliate and distribute the MWNT bundles across the cement grains. A MISONIX 4000 sonicator was used for mixing the M within cement matrix. In a typical procedure of this study, nanotubes suspension was prepared by sonicating them into water (Manzur *et al.* 2010). This water was then used as mixing agent to prepare the composite mortar. In case of utilization of surfactant, required amount of plasticizer used as surfactant was first mixed with water and sonicated for two minutes. Then the nanotubes were added to that plasticizer mixed water and sonicated. Plasticizer was used as surfactant since some recent studies (Konsta *et al.* 2010; Gay *et al.* 2010; and Yazdanbakhsh *et al.* 2010) showed that polycarboxylate based water reducing agent can be used as surfactant to disperse nanotubes within aqueous solution. Utilization of such super plasticizer as surfactant to distribute nanotubes within cement matrix, not only ensure adequate dispersion of nanotubes but also increase workability of cement paste that is necessary to produce strong composites. Fig. 2 shows SEM image of a crushed samples at 28 day.

Table 1: Properties of M

Type of MWNT & Properties	M
OD (outside diameter)	10-20 nm
Length	10-30 $\mu\text{m}$
Purity	>95wt%
Ash	<1.5wt%
SSA (Specific Surface Area)	>233m <sup>2</sup> /g
EC (Electrical Conductivity)	>10 <sup>-2</sup> s/cm
COOH Content (wt%)	2.00

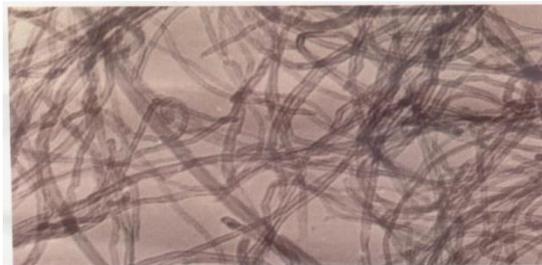


Figure 1: TEM image of treated M

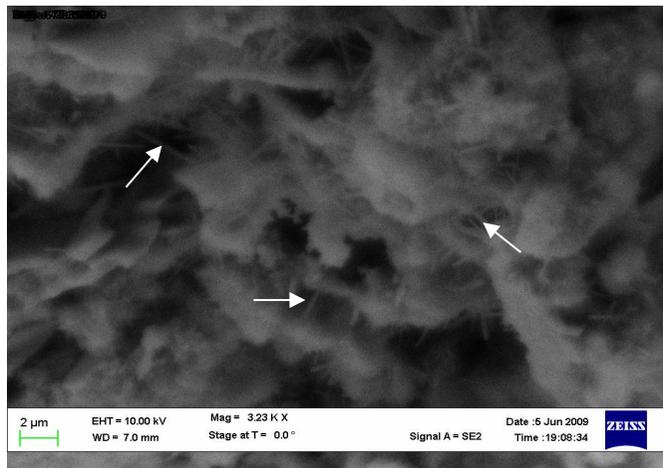


Figure 2: Distribution of CNTs through sonication within cement matrix

### 3.0 Experimental Setup and Preparation of Samples

Compressive strength was determined according to ASTM C109 (ASTM C109/C109M, 2008). Cube specimens of 50 mm size were prepared with 1 part mass of cement and 2.75 parts mass of sand. Samples were mixed using a rotary mixer with flat beater. Nanotubes were first dispersed in water and mixed by hand stirring. Then sonication was done by the sonicator. Cement and sand were then mixed in the mixer with M dispersed water. The mixes are then poured into oiled cubic molds (50x50x50 mm) and were surface-smoothed and covered with wet clothes. The cubes were then kept in the mold for one day in the moisture room and then were demolded and immer-sed in lime water until tested. Compressive strengths of the samples were evaluated at the ages of 7 and 28 days. An MTS machine was used. The rate of load application was 1400 N/sec as per ASTM and the result was obtai-ned through a data acquisition system. Flow values were determined using the flow table as per ASTM C1437-01 (ASTM C1437-07, 2008).

Composite samples reinforced by 0.3% M were made with different mix proportions. Initially, composites having w/c ratio of 0.60 were used as this mix proportion obtained the maximum compressive strengths in earlier ex-periments (Manzur *et al.* 2010). A total of eight sets of composite samples were made using this water content. There were six samples in each set. Composites having w/c ratio of 0.50, 0.55, 0.62, 0.65 and 0.70 were also made. For each case, 3 to 5 sets of samples were made and in each set there were 6 samples. Composites with w/c ratio of 0.50 had least workability and eventually prevented the fluid cement from completely filling the mold, re-sulting in large bubbles being trapped in the cement. These bubbles and cor-responding voids produced samples with uneven sides and surfaces that si-gnificantly reduced the compressive strengths. Therefore, composite samples were also produced with plasticizer addition to increase

the workability. The w/c ratio was kept at 0.50 in all cases of plasticizer addition. Three different proportions of plasticizer were used with respect to the weight of cement. Composite samples were then made using ADVA Cast 575 superplasticizer as surfactant. Three different proportions of plasticizer, ranging from 0.005 to 0.010, were used in terms of weight of cement.

#### 4.0 Significance of Flow Values on Composites' Strength Properties

The compressive strengths of composites with w/c ratio of 0.60 were presented in Fig. 3. It is obvious that compressive strengths had significant fluctuation both at 7 and 28 days. Similar variation was also observed for composites having other w/c ratios. Therefore, an attempt was made to establish a relation between compressive strengths and flow values for composites samples, both at the age of 7 and 28 day.

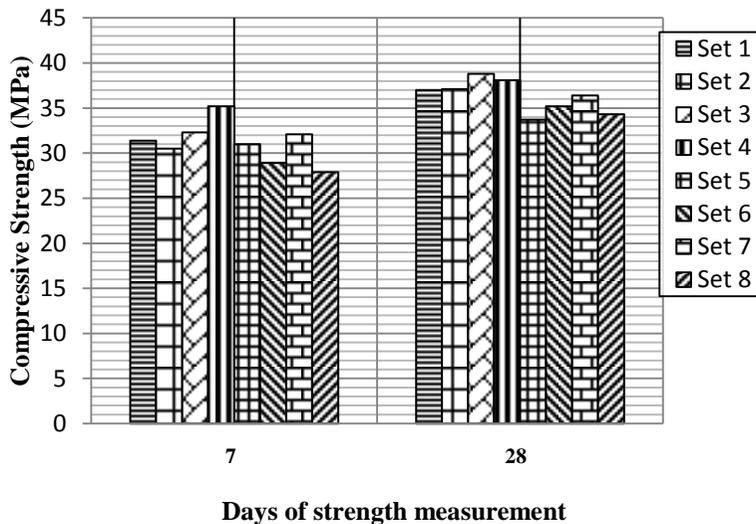


Figure 3: Compressive strength of composite samples with w/c ratio of 0.60

Fig. 4 and 5 show the relation between the average compressive strengths (with standard deviation) of different sets and corresponding flow values of composites having w/c ratio of 0.60 at the age of 7 and 28 day, respectively. As already mentioned, a total of 48 samples were made in 8 sets. Flow values were measured for each set of the samples. It is apparent that the effect of flow values on compressive strength was most pronounced at 28 day. Composites with higher flow values resulted in relatively higher compressive strengths at 28 day. The maximum 28 day compressive strength of 38.8 MPa was obtained for the highest flow value of 56%. It was also found that the mean compressive strength of these composites having flow values greater than 49% was 37.8 MPa. Composites having flow values less than 49% had mean compressive strength of 34.9

MPa at 28 day in this case. The lowest compressive strength was 33.7 MPa for a flow value of 40%. Similar trend was also found for 7 day compressive strengths but not as prominent as in the case of 28 day. In most cases, it was found that the 7 day compressive strengths of composites were higher than that of control samples even when the corresponding compressive strengths at 28 day were less as compared to control samples. Since nanotubes accelerate the early hydration process, there will be less influence of flow values on compressive strengths of composites at early age.

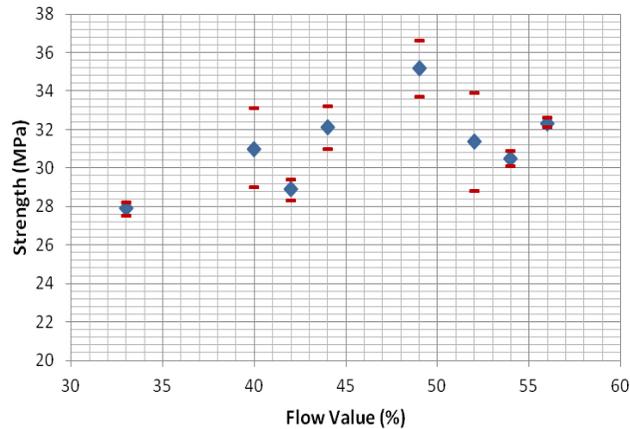


Figure 4: Compressive strengths vs flow values of composites with w/c ratio of 0.60 at 7 day

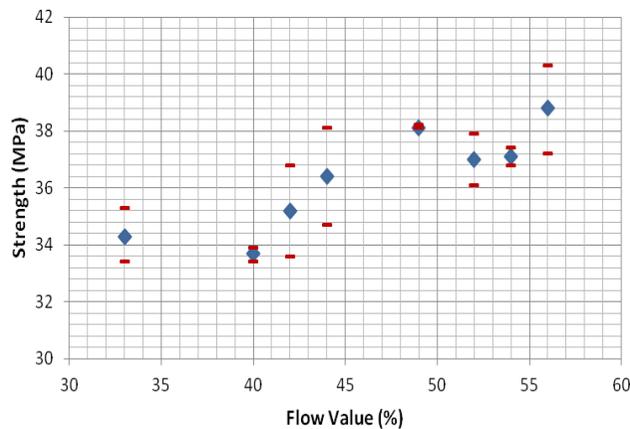


Figure 5: Compressive strengths vs. flow values of composites with w/c ratio of 0.60 at 28 day

The relation between compressive strengths and flow values for composites with w/c ratio of 0.55 are shown in Fig. 6 and 7. Both at 7 and 28 days, the maximum compressive strengths were obtained by the composite having the maximum flow values.

Similar phenomenon was also observed in cases of composites having other w/c ratios. Relations between compressive strengths and flow values were also developed for composites made with plasticizer to increase the workability of mix. Fig. 8 and 9 show the relation between flow values and compressive strengths of composites with plasticizer proportion of 0.010. Higher compressive strengths at 28 day were achieved by composites with higher flow values. Therefore, it becomes clear that the higher compressive strengths particularly at 28 day were obtained for higher flow values for all composites irrespective of mix proportions. Relations between compressive strengths and flow values of composites having plasticizer proportion of 0.008 as surfactant are presented in Fig. 10 and 11. Closely spaced flow values were observed in both the cases. Flow values were ranged between 33 and 38%. It is also apparent that the compressive strengths had less fluctuation, both at 7 and 28 days, as compared to composites without using plasticizer as surfactant. Using plasticizer as surfactant hinders the agglomeration of nanotubes and ensures proper dispersion. The w/c ratio was kept as 0.50. Adequate dispersion ensures effective filling of nano space within the cement matrix by nanotubes that eventually results in more compact composite and ensures better reinforcing.

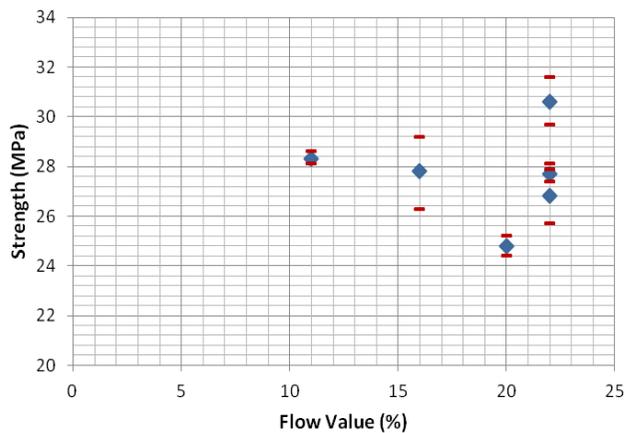


Figure 6: Compressive strengths vs. flow values of composites with w/c ratio of 0.55 at 7 day

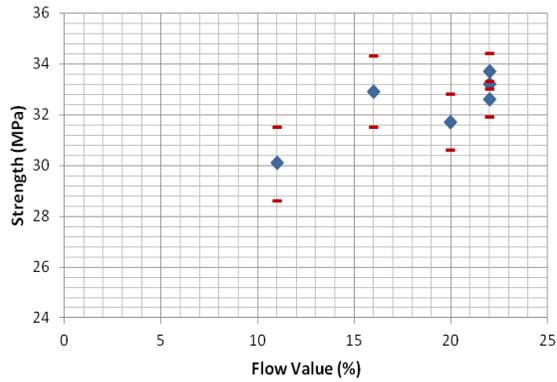


Figure 7: Compressive strengths vs. flow values of composites with w/c ratio of 0.55 at 28 day

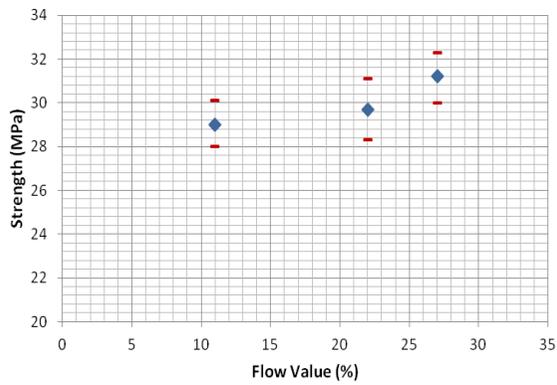


Figure 8: Compressive strengths vs. flow values of composites with w/c ratio of 0.50 and plasticizer proportion of 0.010 at 7 day

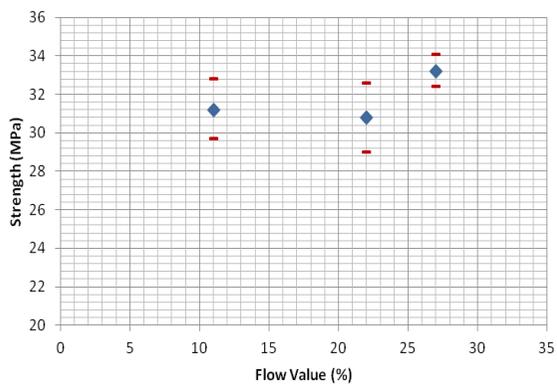


Figure 9: Compressive strengths vs. flow values of composites with w/c ratio of 0.50 and plasticizer proportion of 0.010 at 28 day

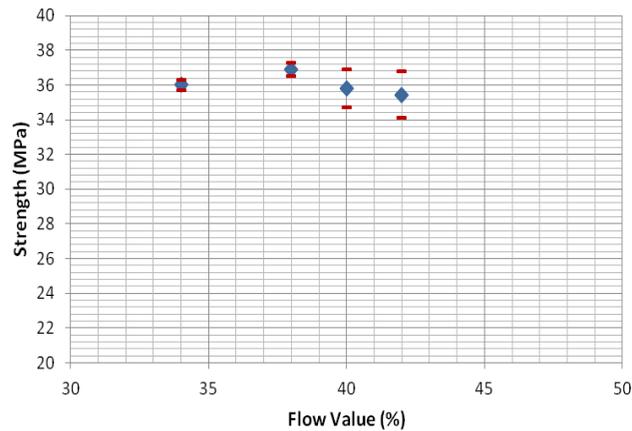


Figure 10: Compressive strengths vs. flow values of composites with plasticizer proportion of 0.008 as surfactant at 7 day

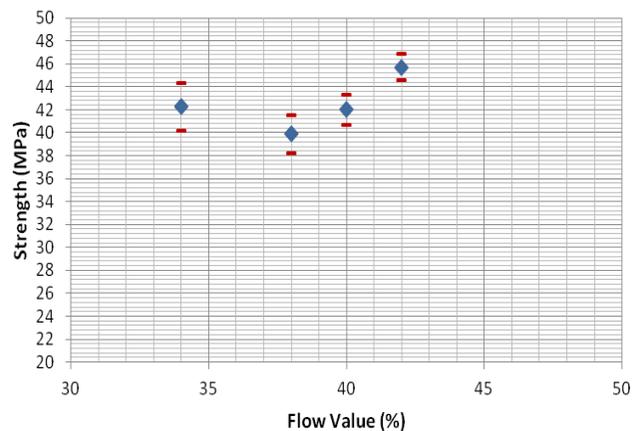


Figure 11: Compressive strengths vs. flow values of composites with plasticizer proportion of 0.008 as surfactant at 28 day

## 5.0 Conclusions

It is obvious that higher flow values represent better dispersion of nanotubes within the cement matrix. Inadequate distribution of nanotubes makes the mix viscous resulting in low flow values. As a result workability decreases significantly. At the same time, inappropriate dispersion of nanotubes means more nanotubes remain adhere to each other. If the agglomeration of nano-tubes is not broken properly, they create zones of weakness within the ce-ment paste. The eventual outcome is the weaker composites with lesser compressive strengths. Therefore, flow values can be considered as a good

measure of the quality of cement mix reinforced by nanotubes. A higher flow value of nanotubes reinforced composites, having same mix proportion, represents more uniform distribution of nanotubes within the matrix and more stable mix. Utilization of plasticizer as surfactant makes the nanotubes more soluble to aqueous solution and ensures better quality of dispersion. Closely spaced flow values and higher compressive strengths are indications of more stable mix that can be achieved through plasticizer addition as surfactant.

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