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Increasing flexural strength and toughness of cement mortar using multi-walled Carbon nanotubes

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ABSTRACT

In this study the effect of using multi-walled carbon nanotube (MWCNT) on flexural and compressive strengths, ultimate displacement and energy absorption capability of standard cement mortar considering different weight percentages of nanotubes as well as different dispersion methods has been investigated. Influential point in adding nanotubes to the composites is their proper dispersion, which is considered by comparing the results of two different dispersion methods. According to the test results and scanning electron microscope (SEM) images, the method using functionalized MWCNTs together with ultrasonication is pointed as an appropriate dispersion method. Using nanotubes resulted in significantly increase in the flexural strength and specially toughness of cement mortar which represents the ability of properly dispersed nanotubes in bridging and closure of the micro cracks. Finally, the observed results has been assessed with a statistical analysis and validated with acceptable significance levels.

Keywords: *Carbon nanotube; Cement mortar; Dispersion; Toughness; Flexural strength.*

INTRODUCTION

Addition of fibers to concrete improves concrete properties such as tensile, flexural and impact strengths, energy absorption capability and fire resistance, and increases the life time of the concrete structures in comparison with those of conventional concrete.

In recent years, extensive research has been conducted to study and improve the mechanical behavior of cement and concrete mixtures using micro fibers. Due to the micro scale research, consideration of nanometer fibers using nanotechnology and studying their effects on concrete properties is of great importance.

Cement and concrete composites have suitable potential for the addition of carbon nanotubes (CNTs). It is expected that using CNTs as a reinforcing material have more advantages in comparison with microfibers.

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This is because of: First, they have significantly greater strengths than other fibers, which should improve overall, mechanical behavior. Second, carbon nanofibers have much higher aspect ratios, requiring significantly higher energies for crack propagation around a tube as compared to across it than would be the case for a lower aspect ratio fiber. Third, the smaller diameters of these fibers mean both that they can be more widely distributed in the cement matrix with reduced fiber spacing and that their interaction with the matrix may be different from that of the larger fibers. Nanofibers, with their diameters being close in size to the thickness of the calcium silicate hydrate (C-S-H) layers of hydrated cement, could show very different behavior, including different bonding mechanisms [1].

As concrete is loaded, initially, short and discontinuous microcracks are created in a distributed manner. These microcracks coalesce to form large macroscopic cracks, known as macrocracks. Fibers are incorporated into cementitious matrices to control cracking by bridging the cracks during loading and transferring the load. The incorporation of fibers and CNTs at the nanoscale will allow the control of the matrix cracks at the nanoscale level. Effectively dispersed CNTs can improve the fracture properties of cement matrices by bridging the nanoscale cracks and have a beneficial effect on the early strain capacity of the nanocomposites [2].

Fibers with smaller diameter and more specific surface have more frictional resistance to being pulled out of concrete matrix under applied loads. According to recent issues and characteristics of nanoparticles and nanofibers to increase strength, control cracks, prevent brittle failure and reduce porosity, studies on nanofibers in order to fully understand and improve various properties of the fiber reinforced concrete seems useful.

So far, few studies in the field of nano fiber concrete compared to polymer composites have been done. CNTs high aspect ratio, high resistance to corrosion and low specific weight make them a very promising reinforcing material. Until now, carbon nanotubes were incorporated into normal, high and ultra-high performance concrete which has led to improved mechanical properties [3].

Konsta-Gdoutos et al. [2] investigated the changes in the nanostructure, fracture properties, and autogenous shrinkage of cement paste reinforced with highly dispersed nanofibers such as carbon nanotubes (CNTs) and carbon nanofibers (CNFs). The results suggest that nanofibers not only improve the fracture properties of cement matrix, by controlling cracks of the matrix at the nanoscale level, they also improve the early age strain capacity of the cementitious matrix producing a high performance nanocomposite.

Influence of the carbon nanotubes on the micromechanical properties of the ultra-high performance concrete has been studied by Kowald et al. [3]. The results show that the CNTs affect the proportions of the hydration products.

Vera-Agullo et al. [4] have used several nanomaterials (carbon nanofilaments, nanosilica and nanoclays) in different cementitious matrices. The physico-chemical behavior of these nanomaterials at three different levels has been analyzed: cement paste, mortar and concrete. It has been found that almost all of the nanomaterials used in that study accelerate the hydration process (if properly dispersed). Carbon nanofilaments accelerate the hydration process and increase the early age compressive strength. And they improve the flexural strength at 28 days.

Metaxa et al. [5] investigated the reinforcing effects of the well dispersed multiwall carbon nanotubes (MWCNTs) in cementitious matrices. According to this study, increased fracture resistance properties represent excellent reinforcing capability of MWCNTs. The results show that incorporation of very low amounts of well dispersed CNTs (0.025-0.048 wt.% of cement) can significantly increase the strength and the stiffness of the cementitious matrix. Compared to plain cement matrix, the nanocomposites appear to have a higher amount of high stiffness C–S–H and reduced nanoporosity. Due to small diameters of MWCNTs (20–40 nm) they appear to specifically reduce the amount of fine pores. This phenomenon leads to the reduction of the capillary stresses, resulting in a beneficial effect on the early strain capacity of the nanocomposites.

A major problem for providing high quality cementitious nanocomposites containing CNTs is to achieve a uniform and homogenous mixture. So that CNTs could be dispersed well in all parts of the mixture and not to make bundles. Several methods have been used to disperse CNTs by different researchers. For example, Musso et al. [6] studied the influence of carbon nanotubes structure on the mechanical behavior of cement composites. In order to minimize the size of aggregated MWCNTs, MWCNTs were all dispersed in acetone by means of an ultrasonic probe. After 4 hours, the sonication was stopped and the acetone was allowed to evaporate. In another study, the developments in CNT-cement composites production have been investigated by Makar et al. [7]. Single walled carbon nanotubes were dispersed by sonication in isopropanol. And then cement added to the beaker containing the CNT while maintaining continuous sonication. After four hours, the sonication was stopped and the isopropanol was allowed to desiccate. Li et al. [8] used carboxylation of nanotubes for dispersion of the MWCNTs. MWCNTs at first modified by using a H2SO4 and HNO3 mixture solution and then were added to cement matrix composites. It was found that there are interfacial interactions between carbon nanotubes and the hydration products of the cement, which will produce a high bonding strength between the reinforcement and cement matrix. Ibarra et al. [9] dispersed nanotubes in water with gum arabic powder to improve the dispersion of the nanotubes. Some electrical properties of MWCNT-cement composites were studied by Wansom et al. [10]. A polycarboxylate superplasticizer was added to the mixing water, followed by the MWCNTs. The solution was stirred by hand for 2 min and then ultrasonicated for 5 min until the MWCNTs appeared to be well dispersed in the solution. The results of a research by Cwirzen et al. [11] showed that stable and homogenous dispersions of MWCNTs in water can be obtained by using surface functionalization combined with decoration using polyacrylic acid polymers.

As can be seen reaching to a homogenous dispersion of CNTs in the cement mortar composites is the key issue and plays an important role in improvement of the properties of the cement mortar containing CNTs. This phenomenon is of high importance when using CNTs of high length for most practical applications, such as reinforcing purposes.

While this research is to investigate the flexural and compressive strength and energy absorption capability of cement mortar containing different percentages of carbon nanotubes, different ways of dispersing carbon nanotubes inside cement mortar have been evaluated as well and for the interpretation of the results, the scanning electron microscopy (SEM) images have also been used.

EXPERIMENTAL

In this study, flexural strength and energy absorption capabilities of standard cement mortar containing multi wall carbon nanotubes (MWCNT) in comparison with those of conventional cement mortar have been investigated. The effects of different weight percentages of nanotubes and the methods of their dispersion inside the mixture have also been considered.

For flexural strength evaluation, center point loading on cement mortar beams have been conducted. Basic cement mortar specimens were prepared using ordinary Portland cement according to ASTM C348. Specimens containing MWCNTs are obtained by adding 0.5 and 0.7 wt.% of cement nanotubes to the cement mortars. In the specimens containing MWCNTs with the constant water to cement ratio of 0.485 to reach the flow of 110±5 % referred to ASTM C348, superplasticizer was used. The characteristic properties of the MWCNTs used are shown in Table 1.

Table 1. Properties of multiwall carbon nanotubes (MWCNTs).

Type	Outer Diameter (nm)	Length (µm)	Purity (%)	SSA (m2/g)	-OH Content (wt%)
Funcionalized	8-15	~50	>95	>233	3.70
Non-Functionalized	8-15	~50	>95	>233	---

For the proper dispersion of nanotubes inside the cement mortar and studying the effect of mixing method, two methods of applying surfactant and functionalized nanotubes have been used. In a series of specimens, aqueous solution containing functionalized nanotubes sonicated for 60 min without the use of surfactant. In the second series after the addition of surfactant and functionalized nanotubes to water, the solution sonicated for the same time as first series of specimens. A series of specimens containing non-functionalized MWCNTs have also been prepared to compare the results with the previous ones. After dispersion phase the cement mortars was mixed and test prisms of 40 by 40 by 160 mm (according to ASTM C348) were molded. Prisms are cured one day in the molds in moist room and stripped and immersed in lime water until tested.

Different specimens with different weight percentages of nanotubes and different methods of dispersion (Table 2) were prepared and tested by center point loading. Three point flexural tests were conducted at the rate of 0.05 mm/min (deformation controlled testing). Then compressive strength tests were carried out on the portions of the mortar prisms tested in flexure already, in accordance with ASTM C349. Furthermore, SEM images have been provided to see and compare the dispersion of nanotubes in the different cementitious composites in order to support the test results.

Table 2. MWCNT content and dispersion methods.

Specimen	MWCNT Content(wt %)	Type of MWCNT	Surfactant	Sonication (min)
CM1	---	---	---	---
CM2	0.5	Functionalized	Not Used	60
CM3	0.5	Functionalized	Used	60
CM4	0.7	Functionalized	Not Used	40
CM5	0.5	Non-Functionalized	Not Used	60

RESULTS AND DISCUSSION

One way to disperse nanofibers inside cement mortar is the use of surfactants. Organic surfactants which are used for suitable dispersion of CNTs have soapy property. Their usage leads to producing foams during mixing of cement mortars leading to an increase in volume and porosity of the mortar and a decrease in density. As expected, increasing porosity results in a reduction of mechanical strengths such as compressive and flexural. Moreover inappropriate dispersion of nanotubes in the mixture and their tendency to clump together into agglomerates or flocs can actually disrupt the expected function of nanotubes. Another method of carbon nanotubes dispersion into the mix is their functionalization which seems to be more effective in the preparation of cement mortars and concrete mixes. In this method, functional groups (such as hydroxyl or carboxylic acid) are formed on the nanotubes and result in to more dispersion of them due to the repulsion of like charges.

Results of the three point flexural tests are shown in Figure 1(a-e). Flexural and compressive strengths of the specimens and also the area under the load-deflection curve of the flexural tests which represents the total energy absorbed, i.e. toughness are shown in Table 3. Each of the values listed in this table represents the mean value obtained from tests on three specimens. Figures 2 to 4 are corresponding to the SEM images of plain cement mortar specimens, cement mortar specimens containing 0.5 wt.% of cement functionalized nanotubes without using surfactants and cement mortar specimens containing 0.5 wt.% of cement functionalized nanotubes with using surfactants respectively. According to Figure 1 and Table 3, all specimens containing functionalized nanotubes show higher flexural strength, ultimate displacement and toughness than those of conventional cement mortar. A statistical Analysis was carried out on the results of mechanical tests which show that there is statistically significant difference in the means and it is not due to chance or sampling error but it is due to their different content and different preparing method with the given probability (Table 4). The significance (p-value) calculated from the T-Test analysis is the likelihood of obtaining a given result by chance. So it is a statistical assessment of whether observations reflect a pattern rather than just chance.

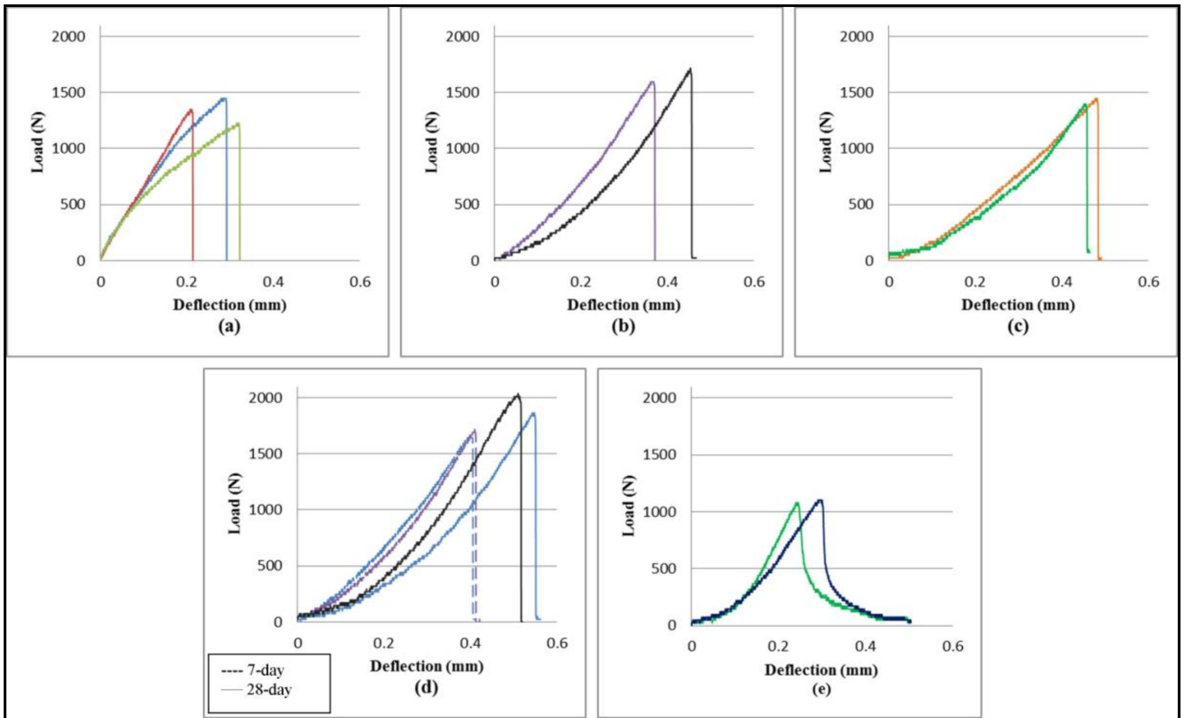

Fig. 1. Load-Deflection curves of the three point flexural test: (a) CM1 specimens, (b) CM2 specimens, (c) CM3 specimens, (d) CM4 specimens, (e) CM5 specimens.

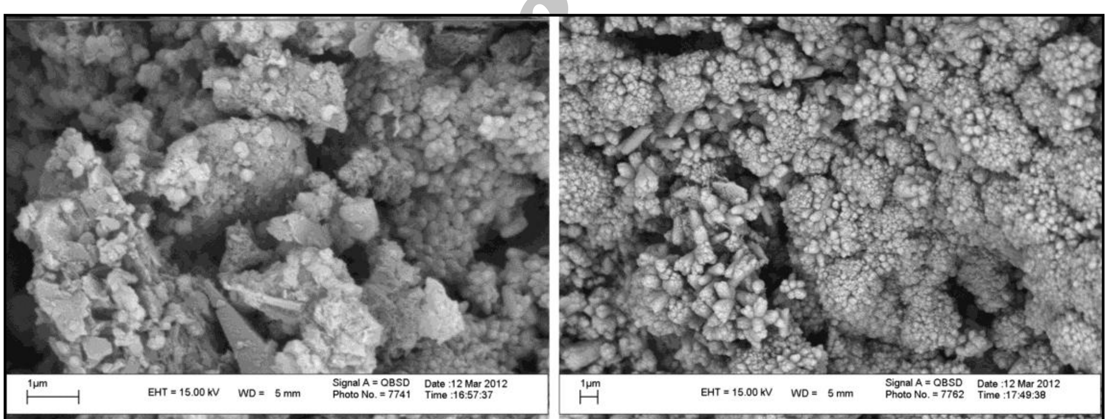

Fig. 2. SEM images of CM1 specimens (without MWCNTs).

Table 3. Flexural and compressive strengths and toughness of the specimens

Specimen	Flexural Strength (MPa)		Toughness (N.mm)		CompressiveStrength (MPa)
	7-day	28-day	7-day	28-day	90-day
CM1		3.75		212.0	
CM2		4.64		276.1	20.56
CM3	4.74	3.98		269.5	10.32
CM4		5.46	291.5	387.7	27.93
CM5		3.06		155.4	

Mean 28-day flexural strength of standard cement mortar CM1 specimens is equal to 3.75 MPa. The lowest flexural strength within the specimens containing functionalized nanotubes is 3.98 MPa and belongs to CM3 specimens, which represents 6% increase. CM2 specimens with 4.64 MPa flexural strengths and 23% increase are next. The highest flexural strength belongs to CM4 specimens with 5.46 MPa which shows an increase of 45%. Mean toughness of standard cement mortar CM1 specimens is equal to 212 N mm. Mean toughness of CM3, CM2 and CM4 specimens are respectively 269.5, 276.1 and 387.7 N.mm which show an increase of 27%, 30% and 83%. According to Table 4 the increased flexural strength and toughness of CM4 specimens in comparison with plain cement mortar respectively with 99% and 97.7% confidence level is due to the MWCNTs. As it can be seen the effect of the addition of nanotubes in cement mortars on its toughness is more than its effect on the flexural strength. This can be related to the proper function of nanotubes in bridging micro cracks and increasing the ultimate displacement. According to Table 3, the minimum compressive strength is for CM3 specimens with 10.32 MPa and the maximum value with 27.93 MPa is obtained in CM4 specimens. Comparison of the 7 and 28-day flexural strength and toughness of CM4 specimens indicated 15% increase in flexural strength and 33% in toughness from age 7 to 28 days.

In the extent of this study, increasing the amount of nanotubes led to an increase of flexural strength, toughness and ultimate displacement, although the trend of this increase is not linear and the results can also be affected by dispersion method. In specimens CM2 and CM3, both containing 0.5% by weight of cement functionalized nanotubes, observed differences in compression and flexural strength and toughness is related to the applied dispersion methods of nanotubes in cement mortar. As shown in Tables 3 and 4 concerning CM2 and CM3 specimens, with more than 99% confidence level, the use of surfactant has led to decrease of compressive strength as expected. Also the decrease of flexural strength because of the same reason is significant at the 0.074 level. SEM images provided from specimens containing functionalized carbon nanotubes dispersed under ultrasonication represents appropriate dispersion of these nanotubes, even without the use of surfactants. This can be referred to the properties of functional groups in repulsion of like charges (Figure 3). Inappropriate dispersion and large agglomerates and bundles of MWCNTs due to the foam formation in the mixture of cement mortar containing surfactant are visible in Figure 4.

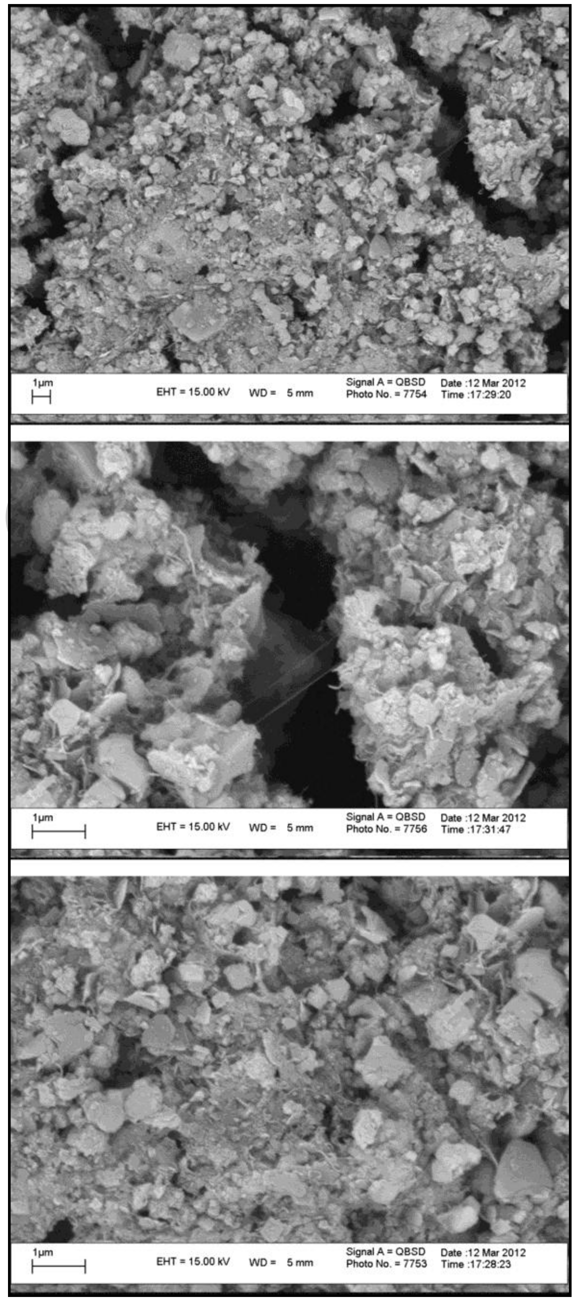

Fig. 3. SEM images of CM2 specimens (containing 0.5wt% functionalized MWCNTs and 60min sonicated without using surfactant).

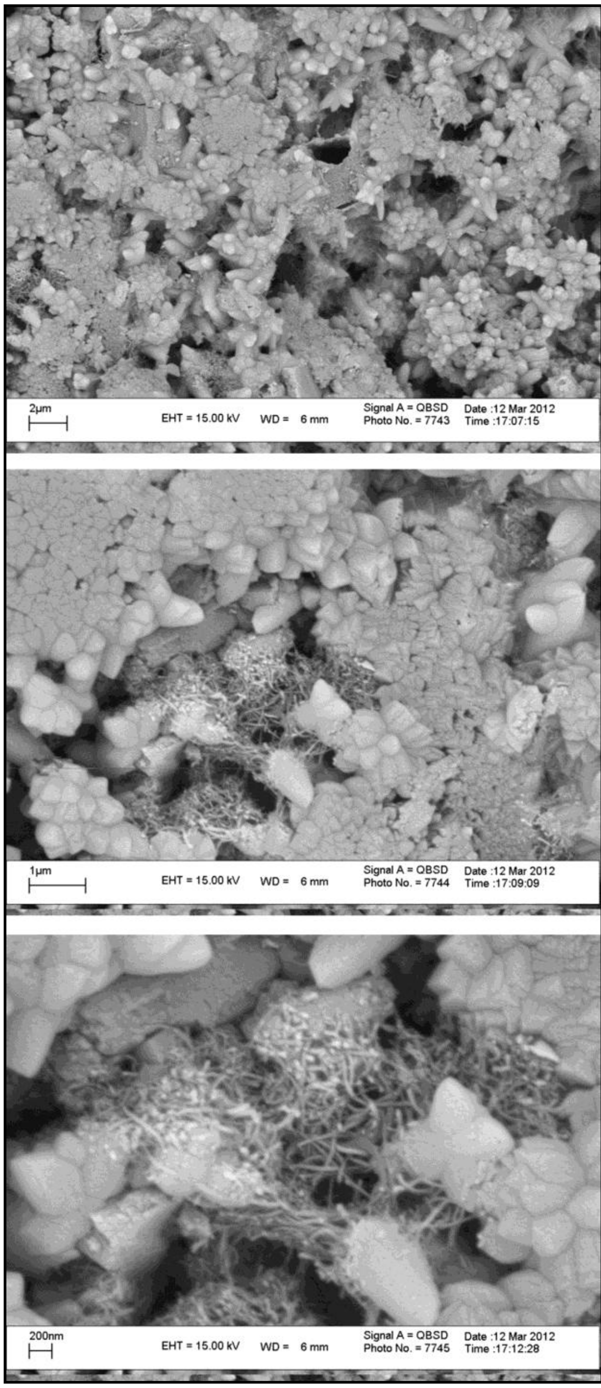

Fig. 4. SEM images of CM3 specimens (containing 0.5wt% functionalized MWCNTs and 60min sonicated using surfactant).

Simultaneously comparison of the flexural strength and the toughness of all specimens are depicted on Figure 5. Maximum energy absorption is observed in CM4 specimens containing 0.7 wt.% of cement functionalized nanotubes in comparison with those of other specimens. In these specimens with regard to the proper dispersion, increasing the amount of nanotubes leads to the rise of the toughness and compressive and flexural strengths. As it can be seen, flexural strength and toughness of the specimens containing 0.7 wt.% of cement MWCNTs at the age of 7 days is even more than those of other specimens at the age of 28 days.

Table 4. Statistical analysis results

Independent SamplesT-Test			
		t	**Significance (2-tailed)**
Toughness (28-day)	CM1	4.342	0.023
	CM4		
	CM2	4.709	0.042
	CM4		
	CM2	5.309	0.045
	CM5		
Flexural Strength (28-day)	CM1	5.83	0.010
	CM4		
	CM2	8.853	0.013
	CM5		
	CM2	3.475	0.074
	CM3		
Ultimate Displacement (28-day)	CM1	5.913	0.010
	CM4		
Compressive Strength (90-day)	CM2	9.571	0.002
	CM3		
	CM2	7.358	0.005
	CM4		

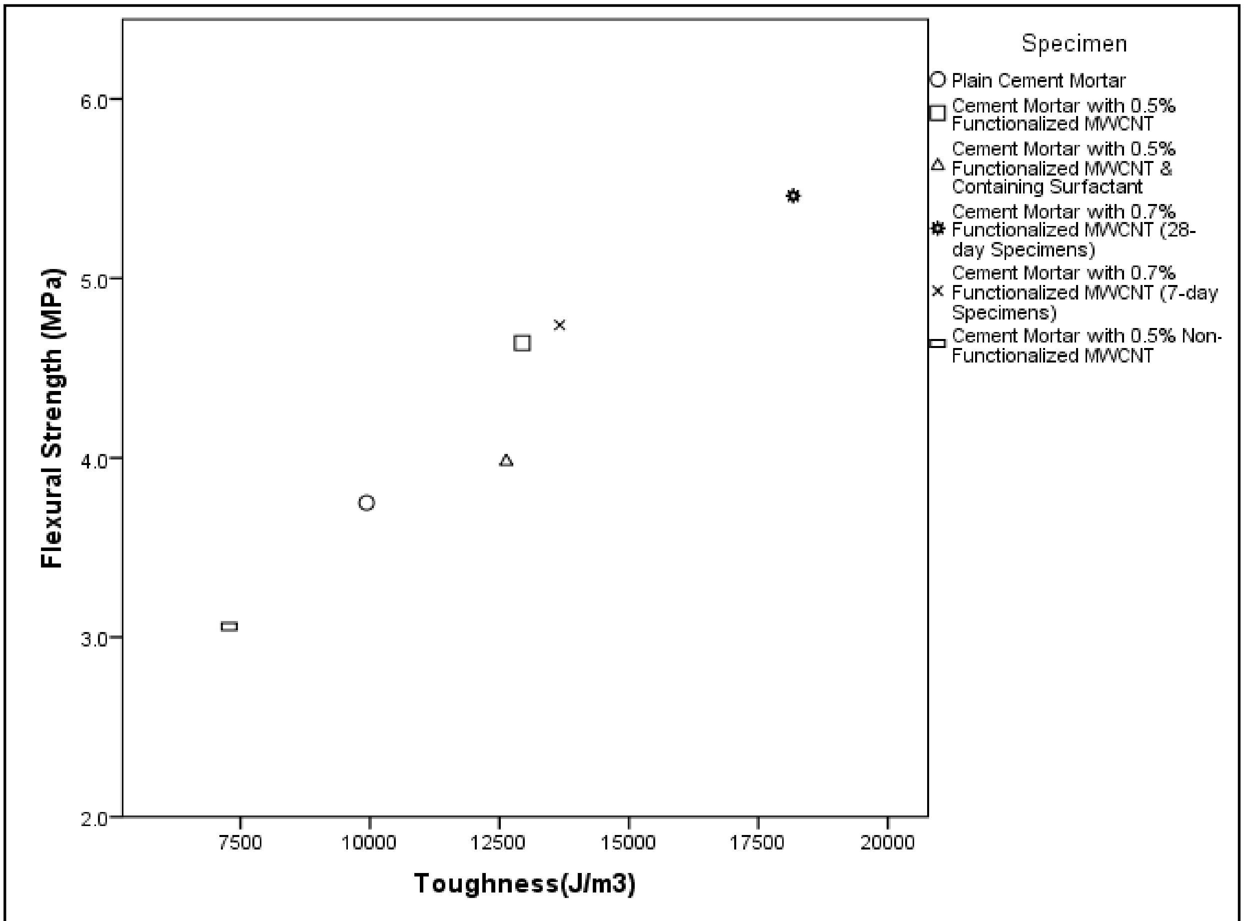

Fig. 5. Mean value of flexural strength and toughness of all specimens.

CONCLUSIONS

In this study the effect of using different weight percentages of MWCNTs on the mechanical properties of cement mortars including flexural and compressive strengths, ultimate displacement and energy absorption capability was investigated. And the results were confirmed by the statistical analysis with the acceptable confidence level. The following conclusions can be drawn:

- Using different dispersion methods led to different results.
- In the dispersion of nanotubes using surfactants, soapy property of organic surfactants led to foam production while mixing the mortar. Foam formation can result in an increase in volume and porosity of the mortar and a decrease in compressive and flexural strengths. Furthermore, it caused inappropriate dispersion of nanotubes leading to formation of flocs which disrupted the expected function of nanotubes.
- According to SEM images, the dispersion of nanotubes without surfactants and utilization of functional groups property besides ultrasonication led to appropriate dispersion and consequently compressive and flexural strengths and toughness significantly improved.
- In the extent of this study, using MWCNTs can improve the mechanical properties of the cement mortar which can be amplified with an increase in both the age of specimen and the percentage of used nanotubes.
- According to the results, the amplification effect of MWCNTs on the toughness is more than that on the flexural strength which finally could be considered in the seismic behavior.

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