

Experimental Investigation on the Effect of Ultrasonication on Dispersion and Mechanical Performance of Multi-Wall Carbon Nanotube-Cement Mortar Composites

S. Alrekabi, A. Cundy, A. Lampropoulos, I. Savina

Abstract—Due to their remarkable mechanical properties, multi-wall carbon nanotubes (MWCNTs) are considered by many researchers to be a highly promising filler and reinforcement agent for enhanced performance cementitious materials. Currently, however, achieving an effective dispersion of MWCNTs remains a major challenge in developing high performance nano-cementitious composites, since carbon nanotubes tend to form large agglomerates and bundles as a consequence of Van der Waals forces. In this study, effective dispersion of low concentrations of MWCNTs at 0.01%, 0.025%, and 0.05% by weight of cement in the composite was achieved by applying different sonication conditions in combination with the use of polycarboxylate ether as a surfactant. UV-Visible spectroscopy and Transmission electron microscopy (TEM) were used to assess the dispersion of MWCNTs in water, while the dispersion states of MWCNTs within the cement composites and their surface interactions were examined by scanning electron microscopy (SEM). A high sonication intensity applied over a short time period significantly enhanced the dispersion of MWCNTs at initial mixing stages, and 0.025% of MWCNTs wt. of cement, caused 86% and 27% improvement in tensile strength and compressive strength respectively, compared with a plain cement mortar.

Keywords—Dispersion, multiwall carbon nanotubes, mechanical performance, sonication conditions.

I. INTRODUCTION

ALTHOUGH concrete is the most common construction material used worldwide, it suffers from low tensile strength and strain capacity [1]. Therefore, different types of reinforcement are widely used to overcome the brittleness of concrete and to improve ductility. Recently there is an enormous development on the use of fibres in concrete in order to control the growth of cracks in cementitious composites. However, it is known that concrete failure is a multi-scale process, and during crack propagation phase, cracks develop from nano scale to micro and then to macro scale. This crack propagation could be prevented by controlling cracks at the nano scale [2], [3].

Since 1991, when carbon nanotubes (CNTs) were presented for first time by Sumio Iijima [4], CNTs have attracted

considerable attention as nano sized reinforcement fibres for a whole range of promising nano composites applications, due to their remarkable mechanical and chemical properties [5]. The dispersion of carbon nanotubes is one of the major challenges that need to be considered in order to achieve the ideal isotropic reinforcing effect. CNTs tend to adhere to each other to form large bundles or agglomerates as a result of the high van der Waals attraction between them [6]-[8]. Many past studies have focused on dispersion of CNTs within CNTS-cementitious composites using superplasticisers (high-range water-reducing admixtures) as dispersion agent, usually in combination with sonication treatment. This can effectively disperse CNTs in mixing water, moreover surfactants can significantly increase the sonicator dispersion efficiency and reduce the time and energy required to achieve the dispersion [9]-[11].

Studies by Li et al., showed that the compressive and flexural strength of cement mortar containing CNTs (0.5 wt% of cement) dispersed using ultrasonic bath over 30-min, were increased by 18.9% and 25.1%, respectively [12], [13]. Mechanical properties of cement pastes reinforced using multiwall carbon nanotubes (MWCNTs) with different lengths were tested by Konsta-Gdoutos et al. [14], [15]. In these studies, the dispersion was achieved by applying ultrasonic energy in compensation with surfactant. Even when small amount of MWCNTs (from 0.02 wt. % to 0.1 wt. % of cement) was used, flexural strength and Young's modulus were improved by 25–40% and 35–45%, respectively. Tyson et al. [16] and Abu Al-Rub et al. [17], in their studies, CNTs and carbon nanofibres (CNFs) in concentration of 0.1 wt. % and 0.2 wt. % of cement weight were dispersed using sonic probe for 20–30 min. These treatment conditions have reported to effectively enhance the ductility, modulus of elasticity, and modulus of toughness.

From all past studies, it can be observed that ultrasonication is one of the most important techniques for the dispersion of carbon based nano additives. However, ultrasonication process in aided of surfactant can contribute to exfoliation and dispersion of agglomerated CNTs/Fs [18]. Extensive sonication treatment leads to reduction of the length of CNTs, defects on the wall of the tubes, and subsequently deterioration of the mechanical performance [10], [19]. In this study, various sonication conditions have been examined. The effect of sonication conditions on the mechanical properties of

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cementitious composites containing MWCNTs in terms of dispersion, workability, compressive and direct tensile strength has been evaluated.

II. EXPERIMENTAL WORK

A. Materials

Ordinary Portland Cement (OPC), meeting the requirements of British Standard BS EN 197-1 [20] was used as the cementitious material. Commercially available multiwall carbon nanotubes (MWCNTs) were used with the properties presented in Table I. Polycarboxylate super-plasticizer (SP) was used as an agent for dispersing CNFs and in order to improve workability.

TABLE I
PROPERTY OF CARBON NANOTUBES

Diameter (nm)	Length (mm)	Purity (% carbon by mass)	Bulk Density (g/cm ³)
8-15 (outer diameter)	10-50	95	1.95

B. Sonication Conditions and Dispersions

In this study, moderate and high sonication conditions were employed to disperse the agglomerated MWCNTs; the sonicator (i.e. Sonic FB-705) was set at; 50% (60µm) and 100% (120µm) amplitude and the input power was fixed at 50 and 150 Watts, respectively. To examine the effect of sonication intensity, the sonicator was run at: i) 50% amplitude with four different sonication times (10, 20, 30, and 40 minutes) ii) at 100% amplitude with sonication times of 3 minutes and 5 minutes, with energy applied to the CNTs suspension in 20 second intervals to prevent overheating. Sonication settings and mix design parameters are presented in Table II. The dispersion of MWCNTs was achieved using a sonic probe and SP. SP to MWCNTs ratio of 1/40 was used in the current study. Transmission electron microscopy (TEM) images and UV-vis absorbance values were used to quantify the dispersion degree of MWCNTs in water. This was also used to characterise the extent of dispersion in the water as higher absorbance values indicate more dispersed CNT suspensions [7].

C. Preparation of CNTs- Composites

After dispersion, a total of nineteen mixes of cement specimens were prepared, included a reference sample of plain cement paste (CO). All prepared samples were labelled as “CT-1 (10, 20, 30, 40), CT-2 (10, 20, 30, 40), CT-3 (10, 20, 30, 40), CT-1 (3, 5), CT-2 (3, 5), and CT-3 (3,5),” respectively, first letter “C” represents the cement composites the second letter “T” represents “CNTs”, the third letters “1”, “2”, and “3” refer to the dosages of CNTs (0.01%, 0.025%, and 0.05% by cement weight, respectively), fourth letters of “3”, “5”, “10”, “20”, “30”, “40”, indicate the sonication time in minutes, shown in Table II.

The composites were produced at three different concentrations of MWCNTs; 0.01%, 0.025%, and 0.05% by weight of cement. Mixing procedures were carried out in the following sequence: all dry ingredients (cement and sand) were mixed together for 2 min using an electrical multispeed stirrer

with a flat beater, then the remaining mixing water was added and mixed at low speed for 1 min, finally the CNTs suspension was added and mixed at high speed for a further 4 min. Fig. 1 summarizes the steps of the mixing procedure.

TABLE II
SONICATION TIMES AND MIX DESIGN PARAMETERS

ID	CNT %wt.	SP/CNT	CNT/W %	Sonic probe amplitude %	Sonication Time (min)
CT-1	0.010	0.4	0.028	50	10,20, 30, 40
CT-2	0.025	1	0.07	50	10,20, 30, 40
CT-3	0.050	2	0.14	50	10,20, 30, 40
CT-1	0.010	0.4	0.028	100	3, 5
CT-2	0.025	1	0.07	100	3, 5
CT-3	0.050	2	0.14	100	3, 5

Workability of nano cementitious pastes was assessed using mini-slump test of dimensions; top diameter 20 mm, bottom diameter of 40 mm, and high 57 mm. The mould was placed on a flat and horizontal plate and filled with the cement paste; the top surface was evenly levelled and compacted using spatula, next, the mould vertically and slowly removed to minimise the lateral disturbance. The average reading of the diameter of spread sample at four locations around the outline was recorded. Next, the paste was cast and vibrated for compaction in stainless steel cubic moulds (25 x 25 x 25) mm, and wooden dog-bone molds for the characterization of compressive and tensile strength respectively. All specimens were de-moulded after one day from the casting then cured in water until testing. For each mix, three identical specimens were tested under tension and compression. Furthermore, scanning electron microscopy (SEM) was performed using (Zeiss; model of LEO 1455VP) to characterise the nano composites.

III. RESULTS AND DISCUSSION

A. Characterisation of MWCNTs Suspensions

After exposure to ultrasonication, the precipitate of MWCNTs is diminished due to the exfoliation process. UV-vis spectra for the suspensions subjected to variant sonication treatments, clearly show that as the applied sonication intensity is increased, absorbance values are increased. This can be traced back to the increased number of individual nanotubes. The UV-vis spectra presented in Figs. 2 (a) and (b) show that absorbance is clearly dependent on the ultrasonic treatment conditions (i.e., sonicator setting and treatment duration). Higher absorbance values were recorded when suspensions were treated for 40 and 5 minutes, and sonicator set at 50 % and 100 % amplitudes (moderate and high sonication intensity) respectively. However, by further increasing the ultrasonication time with both sonication conditions, no increase the absorbance values (i.e. obvious reduction on the sedimentation amount) was recorded.

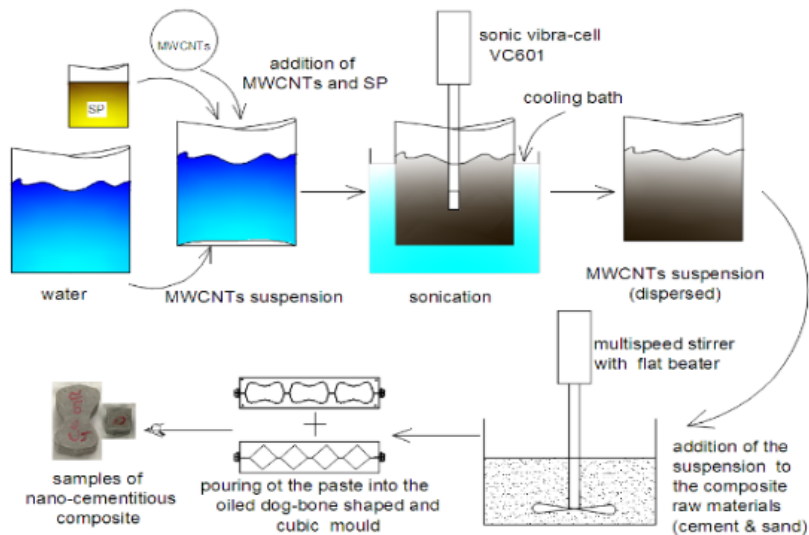


Fig. 1 Fabrication steps of MWCNTs cementitious composites

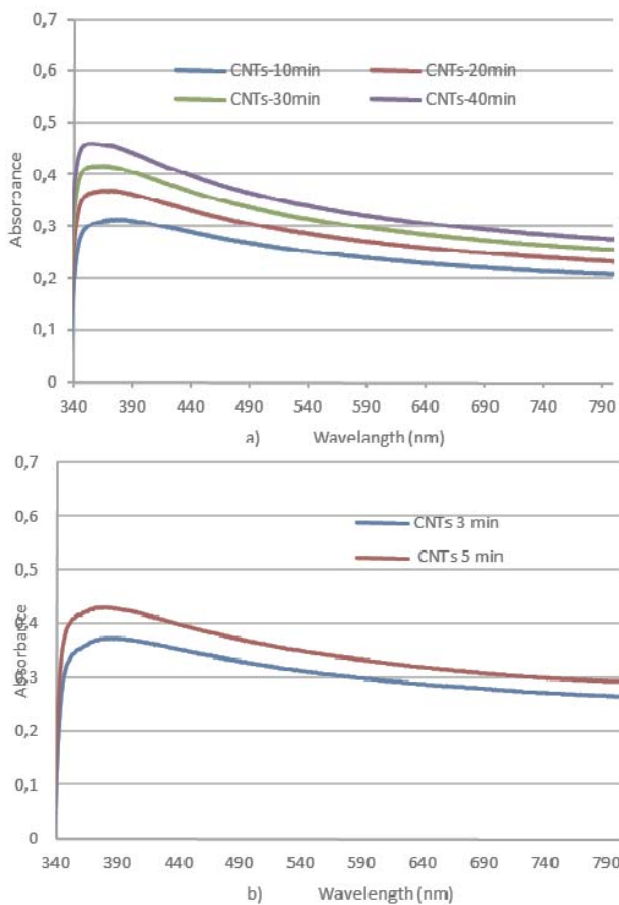


Fig. 2 UV-vis spectrum of MWCNTs suspension treated in different sonication time a) 50% amplitude at 10, 20, 30, and 40 minutes, (b) 100% amplitude at 3 and 5 minutes.

TEM images, Figs. 3 (a) and (b), show the representative TEM images of MWCNTs with moderate and high sonication intensity. Based on these images, the diameter of the individual

nano tubes is uniformly increased from 15nm to 25-30nm as the duration of the sonication is increased, leading to significantly improve the dispersion. Whereas prominent black areas (circulated in Fig. 3 (a)) are visualized in suspension sonicated for 10 minutes using moderate sonication intensity, indicated that poor dispersion do not disperse the interlocking structure of bundles of nanotubes.

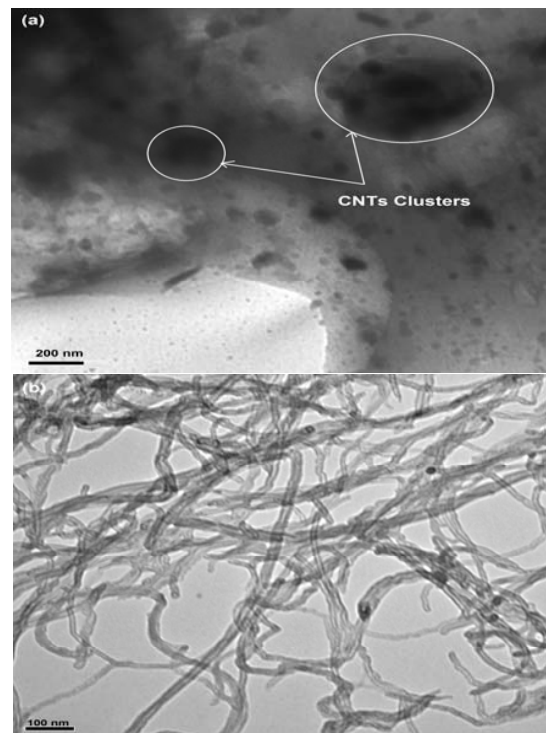


Fig. 3 TEM images of MWCNT suspensions (a) agglomerated CNTs (b) individual CNTs dispersed under extensive sonication

B. Characterization of MWCNTs/Cementitious Composites

Min-slump tests results are presented in Fig. 4. Based on these results, the workability is not affected by the quantity of MWCNTs in the mix. However, the consumed quantity of SP during the dispersion process did not affect amount required to maintain the quality of nano cementitious pastes, which alleviate the difficulties associated with slump loss of paste containing MWCNTs. Furthermore, high-magnification SEM images, Fig. 5, show CNTs embedded in cement hydration products which, due to its nano structured morphology, seems to bond well to nanotubes. Moreover, the embedded CNTs also act as fillers filling the pores in between the hydration products (i.e. calcium silicate hydrate (C-S-H), calcium hydroxide (CH) and calcium sulfoaluminate hydrate (ettringite) which can lead to a denser microstructure and higher strength compared with the reference matrix. These observations are in good agreement with past SEM investigations [6]-[7].

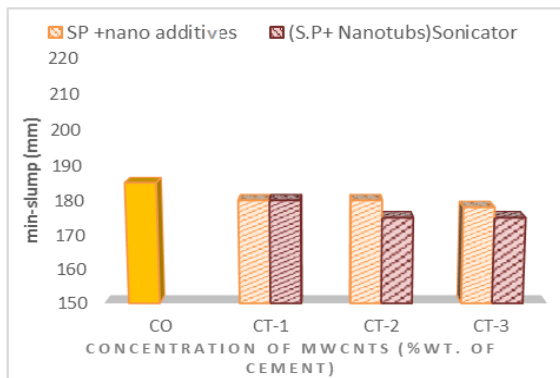


Fig. 4 Min slump spreads of fresh plain past (CO) and pastes containing different percentages of MWCNTs dispersed using; only superplasticizer SP, and SP and sonicator

C. Mechanical Properties Analysis

1. Compressive Strength

The compressive strength of cementitious composites was examined after 28 days under a constant compressive loading rate of 0.5 MPa. Mean compressive strength values and standard deviations are summarized in Table III and Fig. 6. Compressive strength was enhanced by 10 %, 21%, and 13 % as the MWCNTs content was increased to 0.01, 0.025, and 0.05 %wt. of cement when moderate sonication intensity for 10 minutes was used. The respective enhancement for vigorous sonication intensity for 5 minutes was found to be 16.5%, 27%, and 26%. Further sonication durations did not considerably affect the compressive strength (or indeed caused a slight decrease in compressive strength), as shown in Fig. 6. This could be attributed to the fact that further treatment (up to 40 minutes under moderate sonication intensity) can lead to shortening of the nanotubes, which is in good agreement with the finding of Zou et al. [1].

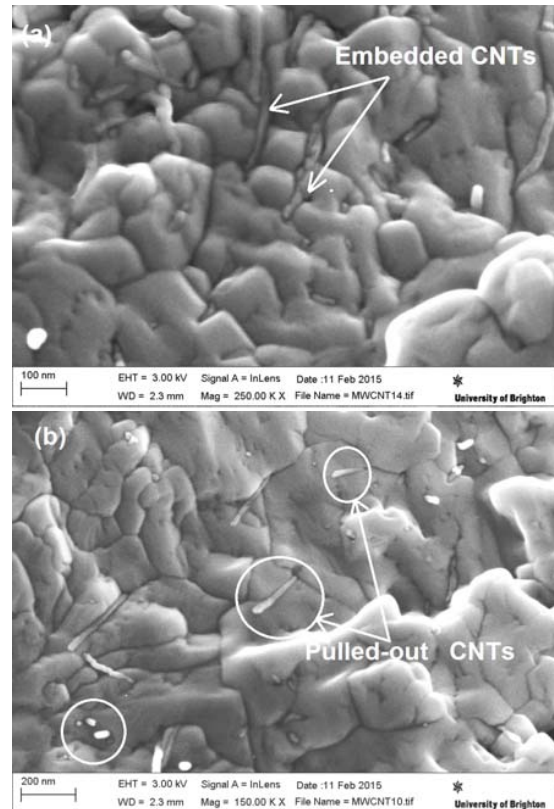


Fig. 5 Typical SEM micrographs of the cement/CNFs composites shown (a) CNTs embedded within the composite (b) pull out and fracture carbon nanotubes

2. Direct Test of Tensile Strength

Fig. 7 and Table III present and summarize the mean values and standard deviation of the direct tensile tests of the dog-bone shaped specimens (Fig. 8). Tensile tests were conducted using a universal testing machine (Instron, model 1340) under displacement control using 0.005 mm/s rate. Tensile strength was found to be significantly improved as the sonication time is increased for both moderate and high sonication intensity. This is can be attributed to the improvement of the composite microstructure, the occurrence of interfacial interaction between nanotubes and cement.

Due to the suspensions dispersed using high sonication intensity applied within two different, shorter, sonication times (3 and 5) minutes were led to improve the tensile strength by 29% and 83%, 35% and 86%, 42% and 87% for specimens containing MWCNTs of 0.01%, 0.025%, and 0.05% %, respectively. These results indicated that MWCNTs suspensions dispersed at high rates of ultrasonic intensity during short time (i.e. 5 minutes) illustrate significantly improved tensile strength at all MWCNTs contents, and the nanotubes successfully bridged across the cracks and the guarantees the load-transfer in case of tension.

TABLE III
COMPRESSIVE AND TENSILE STRENGTH OF MWCNTs/CEMENTITIOUS COMPOSITES AFTER 28 DAYS OF CURING

Mix	CNTs /OPC %	Sonication time (min)	Sonication condition	Compressive Strength			Tensile Strength		
				Mean (MPa)	Standard Deviation	% improvement (I_c)	Mean (MPa)	Standard Deviation	% improvement (I_c)
CO	-	0	Moderate sonication intensity	46.63	2.58	0.00	1.82	0.26	0.00
CT-1	0.01	10		51.47	5.44	10.39	2.59	0.23	42.42
CT-1	0.01	20		50.85	2.20	09.06	2.71	0.24	48.71
CT-1	0.01	30		51.69	1.56	10.80	2.95	0.27	62.09
CT-1	0.01	40		51.88	2.68	11.27	3.06	0.86	68.13
CT-2	0.025	10		56.53	3.54	21.24	3.1	0.62	70.11
CT-2	0.025	20		52.68	3.11	12.98	3.03	0.36	66.48
CT-2	0.025	30		51.05	3.81	9.48	3.32	0.33	82.42
CT-2	0.025	40		51.93	2.97	11.36	3.35	0.17	84.07
CT-3	0.05	10	High sonication intensity	60.25	1.99	29.20	2.89	0.37	58.93
CT-3	0.05	20		55.36	4.26	18.72	2.95	0.31	62.09
CT-3	0.05	30		52.67	2.17	12.96	3.26	0.23	79.39
CT-3	0.05	40		53.03	1.29	13.72	3.23	0.05	77.23
CT-1	0.01	3		52.50	2.54	12.60	2.35	0.16	29.12
CT-1	0.01	5		54.26	2.62	16.36	3.33	0.12	82.86
CT-2	0.025	3		59.70	0.89	28.03	2.46	0.26	35.21
CT-2	0.025	5		59.37	3.48	27.33	3.39	0.31	86.08
CT-3	0.05	3		59.08	1.17	26.70	2.58	0.30	41.83
CT-3	0.05	5		58.85	0.64	26.21	3.41	0.10	87.36

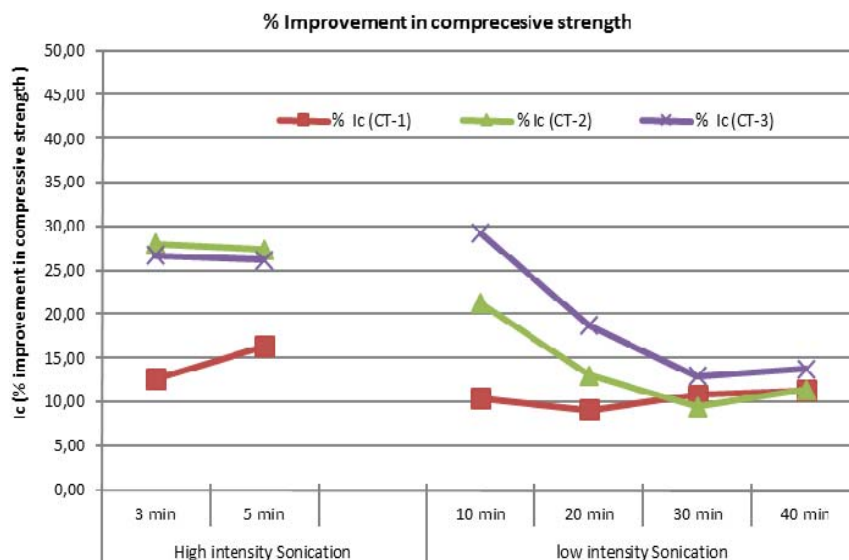


Fig. 6 Relative increase in compressive strength of MWCNTs cementitious composites

IV. SUMMARY AND CONCLUSION

Determining effective dispersion technique of MWCNTs in water is a key issue for developing practical applications of MWCNTs as reinforcing agents for structural application. Therefore, different approaches have been examined in this study in order to evaluate the dispersion of MWCNTs in water under different sonication conditions. Dispersion efficiency was evaluated using UV-vis spectroscopy and TEM. Microstructure of the examined mixes was also analyzed alongside with the mechanical (compressive and direct tensile strengths) properties of MWCNTs cement composites.

Results obtained in the present work can be summarized as:

1. Different sonication conditions were examined. When moderate sonication intensity was used, longer duration of treatment is required in order to disentangle the nanotubes. However, at the same time this may lead to reduction of the aspect ratio of MWCNTs by breaking the tubes. Higher intensity can rapidly improve the dispersion level of the suspension. Further study is required to identify the effect of sonication conditions on the integrity of carbon nanotubes.
2. Intensive sonication intensity applied in combination with high dosage of SP (i.e. SP to CNTs ratio 1/40), led to significant increment of the concentration of individually

dispersed tubes in water. This sonicator setting can facilitate the dispersion of MWCNTs making this technique suitable for large scale applications.

3. SEM images indicated that MWCNTs have been uniformly distributed and embedded as individual tubes in

the examined areas leading to improved crack resistance and interaction with the cement matrix.

4. Tensile and compressive strength were considerably improved when high sonication intensity was applied for 5 minutes. This enhancement was attributed to the improved dispersion of the nanotubes in the mix.

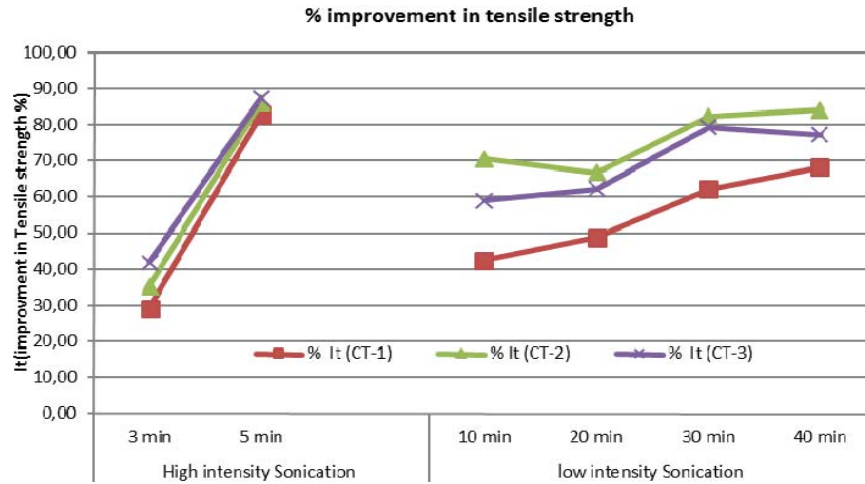


Fig. 7 Relative increase in tensile strength of MWCNTs cementitious composites

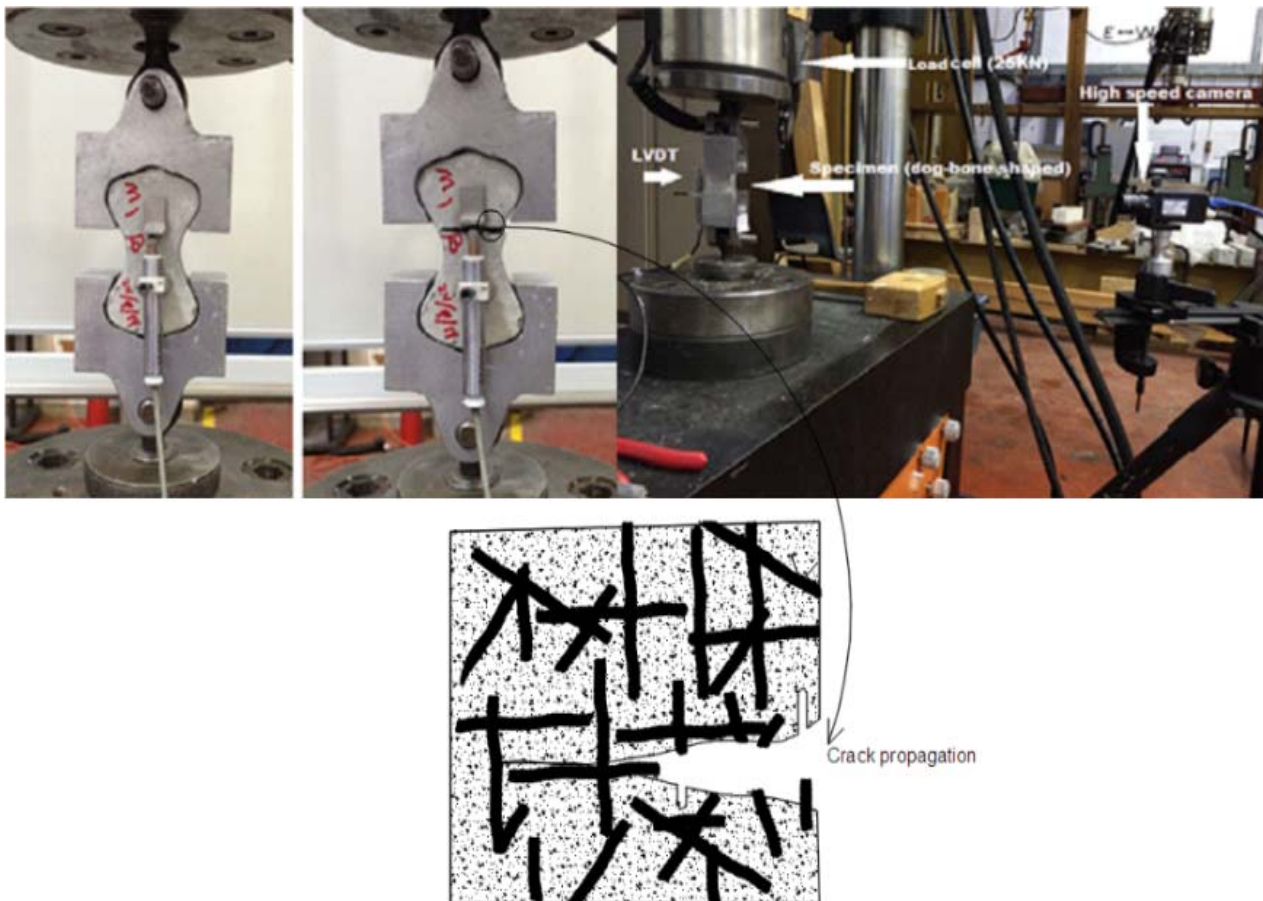


Fig. 8 Uniaxial tensile tests setup: Specimen preparation before and after test

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