

Experimental investigation of the effect of superplasticizer/surfactant aided aqueous dispersion of multi-walled Carbon nanotubes on workability and mechanical properties of cementitious composites

S. Alrekabi¹, A.B. Cundy¹, A. Lampropoulos¹, I. N. Savina²

¹ School of Environment and Technology, University of Brighton, UK

²School of Pharmacy and Biomolecular Sciences, University of Brighton, UK

Phone 0044-7453-869368, e-mail: s.alrekabi@brighton.ac.uk

Abstract

The present study is focused on the dispersion of carbon nanotubes (CNTs) assisted by superplasticizer/surfactant adsorption, and the impact of CNTs wettability agents on the rheological behaviour and mechanical properties of CNTs–cementitious composites. Two commercially available cationic superplasticisers (belonging to polycarboxylate and naphthalene families), and non-ionic agents including methylcellulose and Triton X-100 were used. In this study, the dispersion of CNTs in the aqueous phase was characterised using UV–vis spectra and the nanostructure of the fracture surface of CNTs–cementitious composite was studied using scanning electron microscopy (SEM). The compressive strength and workability of the mixtures were evaluated with and without dispersants/surfactants, through compressive strength tests after 3, 7, and 28 day of curing and flow table tests on the fresh mixture. The results indicated that surfactant molecules adsorbed onto the CNTs' surface facilitated the dispersion of CNTs by forming a large solvation shell from the hydrophilic moieties around a nanotube, leading to stabilization of CNTs in water. Also the wettability agents containing both active polar and non-polar groups improve the dispersion of CNTs within the composite, have no detectable negative influence on the cement hydration process, and significantly improve the workability of the CNTs–cementitious composites.

1 Introduction

Due to their unique properties carbon nanotubes (CNTs) have attracted considerable attention for a wide range of applications including the production of multi-functional cementitious composites[1]. However, the nano-scale dimensions of CNTs turn dispersion into a challenging task, since their high aspect ratios in combination with their high flexibilities and strong tube-tube contact interaction energies make them prone to entanglement [2-4]. Bundled nanotubes need to be effectively dispersed in water in order to enhance the mechanical characteristics of composite cementitious materials [5, 6]. Both mechanical and chemical approaches are widely used in nanotubes dispersion. Mechanical methods through sonication processes or high shear mixing in combination with dispersion agents can efficiently separate nanotubes from each other [6-9]. Chemical techniques are widely used in treatment and dispersion of carbon nanotubes and improve the bond with the host matrix, through covalent and non-covalent bonding. For the former, covalent bonding includes providing additional reactive groups (functionalizing groups) on the surface of carbon nanotubes [10, 11]. Different approaches have been used to generate covalent functional groups on the tubes' surface, including hydroxyl, carboxyl, and carbonyl groups [12]. For the latter, use of chemical surfactants with sonication techniques can introduce non-covalent bonding on the carbon tubes surfaces, thereby encouraging separation of the nanotubes within the solution[13]. Chemical surfactants are amphiphilic in nature, however their chemical structures contain hydrophobic and hydrophilic end groups[14].

Both hydrophobic and hydrophilic groups are adsorbed at the interface between the nanotubes and the solution [15], and increase the dispersibility of the nanotubes in water, forming more stable suspensions [16]. The adsorbed layer on the carbon nano tubes surfaces can counterbalance van der Waals attractions by inducing effective electrostatic repulsions or steric forces. The balance between these forces regulates the dispersion and stabilizes the nanotubes, and can prevent agglomeration[17].

Among mechanical and chemical dispersion methods, anionic (negatively charged), and cationic (positively charged) surfactant based-plasticizers have been used (with the aid of a sonicator) to disperse CNTs in water via covalent and non-covalent approaches, [5, 18]. Non-ionic (uncharged) agents such as ethoxylated alkyl phenol (Triton X-100) and methylcellulose (MS) have been widely used to disperse CNTs within CNT–polymer composites [19]. The limited op-

tions of dispersion agents which can be used for dispersion purposes within cementitious materials can be attributed to the nature and the chemistry of cement and the hydration process, since some types of dispersion agent can delay or stop the hydration process of the cement paste [11]. There are limited published studies on the optimization of the effect of agents on the dispersion of CNTs in nano-cementitious composites. Collins et al. [20] investigated the effect of different surfactants that are compatible in the production of concrete, in terms of dispersion, workability and strength of CNT aqueous and CNT–OPC paste mixtures. The result of this study indicated that the addition of cationic surfactant greatly enhanced the dispersion and maintained sufficient mixture fluidity. Cwirzen et al. [21] have dispersed CNTs (diameter 10 nm, length 2–4 μm) in water using polyacrylic acid polymers as a surfactant, and the results showed significant improvement of the compressive strength (up to 50%). Yazdanbakhsh et al. [6], and Trettin and Kowald [22], reported the impact of polycarboxylate-based superplasticisers as surfactants to produce cementitious CNT-reinforced composites. Compressive and bending tests results showed that the surfactant/superplasticisers with longer lateral chains led to a significant improvement in mechanical strength, which revealed better dispersion of CNTs and improved interfacial bonding between the nano tubes and the host matrix.

In this current work, various types of stabilization agents (i.e. surfactants based-plasticizers) [3, 23], Triton X-100, and (MS) have been examined to investigate their effect on the dispersion of CNTs in water. Fluidity of the fresh mixes and compressive strength tests of hardened cementitious composites have been conducted in order to investigate the effect of the examined agents.

2. Materials and methods

2.1 Materials

The mixtures of nano composites were prepared using the raw materials described below. Cement type I (OPC), meeting the requirements of British Standard BS EN 197-1 was used. Multiwall carbon nanotubes (MWCNTs), and functionalised multiwall carbon nanotubes (F-MWCNTs) were used as the nano additives, and their properties are shown in Table 1. Dispersion agents for the nano additive in water were; polycarboxylate ether (PCE), naphthalene (NPH)

base superplasticizer, Methylcellulose (MC), and Triton X-100 (TX-100). Table 2 shows the properties of the surfactants used in this study.

Properties	MWCNTs	F-MWCNTs
Diameter (nm)	8-15	8-15
Length (µm)	10-50	10-50
Purity (% by mass)	95	95
Bulk Density (g/cm³)	1.95	1.95

Table 1 Property of the used carbon based nano additives

Properties	PCE	NPH	MC	TX-100
Chemical Classification	Polycarboxylate	Naphthalene	Methylcellulose A, Methyl cellulose ether	Octyl phenol ethylene oxide condensate
Appearance and form	light low viscosity liquid	dark brown low viscosity liquid	White to Off-White Powder	colourless to light yellow, liquid
pH of 10 % content	6.7	7-9	6-8	6-8
Bulk density g/ml	1.075	1.2	1.31 g/cm ³	1.07
Ionic nature	Cationic	An ionic	Non-ionic	Non-ionic
Solubility	Soluble in water	Soluble in water	Soluble in water	Soluble in water

Table 2 Properties of admixtures/surfactants used to disperse MWCNTs, and F-MWCNTs.

2.2 Preparation of CNTs suspension

Aqueous dispersions were produced with 0.025 wt. % (by cement weight) of MWCNTs/F-MWCNTs and 100 ml of distilled water. Surfactant agents were used separately in different dosages based on previous literature and composites workability. Surfactants- PCE and PNS, were used in ratio of 0.8% by weight of cement [24-26], while MC and TX-100 were used in ratio of 1:2, 1:1.35 respectively [23, 27]. The dispersion of nanotubes in water was accomplished under high sonication intensity over a short time period using a sonicator with tip (i.e.

Sonic FB-705), which was set at an amplitude of 100 % of its maximum, and duration of 5 minutes. To avoid overheating of the suspensions the delivered energy was applied in cycles of 20 seconds. Ultraviolet–visible spectroscopy (UV–vis spectroscopy) was used to evaluate the dispersion ability of these surfactants.

UV–vis absorption spectra were recorded using a UV-Vis recording spectrophotometer (UV-20401pc) operating between 350 and 800nm, as only individual nanotubes absorb in this wavelength region [23]. Samples were taken after dispersion and diluted by a factor of 100, resulting in MWCNT /F-MWCTs contents that were suitable for UV–vis measurements. The blank used was the original of the PCE/ NPH/ MC/ TX-100 solution diluted by the same factor, and measured under the same conditions.

2.3 Production and testing of CNT-composites

A total of nine nano- cementitious cement composites were prepared with a water/cement ratio of 0.35 together with a control mixture (Table 3). All dry ingredients (cement, micro silica, and sand) were mixed using a Hobart mixer with a flat beater for 2 minutes. Then, water was added to the mix and the mixer was stirred for another 2 minutes. Finally, the MWCNTs/F-MWCNTs suspension was added at low speed for 1 minute and then fast speed for another 2 minutes. Following mixing, the resulting paste was poured into 50mm x 50mm x 50mm moulds. Specimens were demoulded after 24 hours and cured in water until the relevant testing age. They were then dried for 3 hours at room temperature before testing. The workability of nano cementitious pastes was assessed using a flow table test in accordance with ASTM C230/ 230m-1[28]. The initial and final diameters were recorded to calculate the mixture flow. The flow is defined as the diameter increment divided by the original diameter. Compressive strength tests at 3, 7, and 28 days after casting were conducted at a loading rate of 0.5 MPa/s using a Hydraulic Mechanical Testing System (MTS). The microstructures of MWCNT and cement hydration products were studied using scanning electron microscopy (SEM) (Zeiss; model of LEO 1455VP). Prior to SEM imaging, the fractured surface was sputtered with carbon.

Mix ID	Proportion (wt. % of cement)					
	OPC	Water	Silica sand	Sand	MWCNTs/F-MWCNTs %	Surfactant
PC						0.08
T-PCE						0.08
T-NPH						0.08
T-MC						0.05
T-TX-100	1	0.35	0.1	1.5	0.025	0.04
Ft-PCE						0.08
Ft-NPH						0.08
Ft-MC						0.05
Ft-TX-100						0.04

Table 3 Nano-cementitious composite mix design

3 RESULTS AND DISCUS SION

3.1 Characterisation of MWCNTs/F-MWCNTs suspensions

Figure 1 (a, b) shows that even after 5 minutes of high sonication intensity the nanotubes are poorly dispersed and highly aggregated in the absence of a surfactant agent. Within a few minutes of cessation of agitation the carbon nanotubes were completely settled. However, under the same conditions, adding surfactant (i.e. PCE/ NPH/ MC/ TX-100) led to the production of more stable homogeneous solutions. UV-vis absorption spectroscopy was used to characterise the concentration of dispersed nanotubes, as only individual carbon nanotubes are active in the UV-vis region [29]. UV-vis spectra were conducted for seven different concentration of nanotubes suspensions, as shown in the Figure 2, inset figures are optical photographs of various concentrations of nanotubes in surfactant suspensions (NPH is shown here). Figure 3 (a, b) shows the spectra of NPH-suspensions of carbon nanotube, and functionalised nanotubes, respectively. The absorbance spectra of surfactant-only solutions are used as a baseline correction for experimental analysis, and the UV-vis absorbance was chosen at the wavelength of 500nm as reported in many previous studies [23].

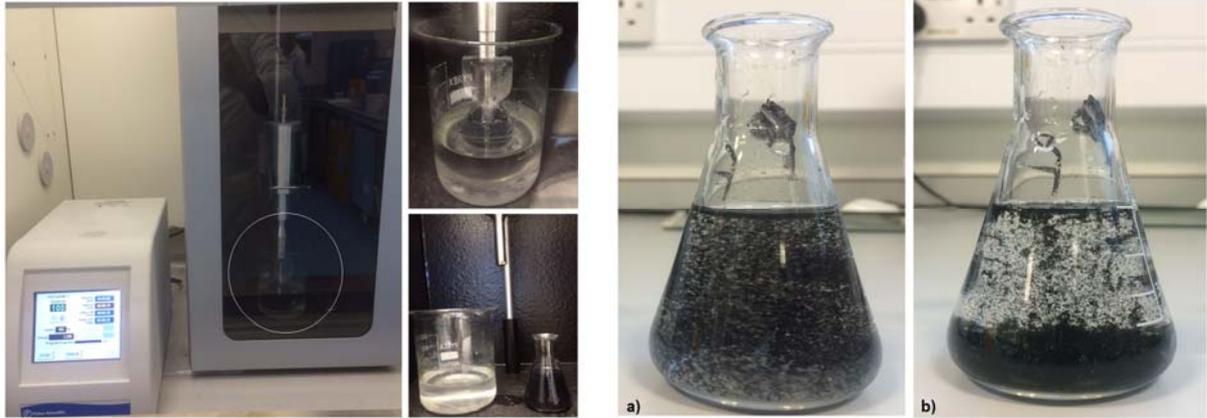


Figure 1: suspensions of nanotubes treated using sonicator (left side) sets at high sonication intensity without using dispersion agents, a) suspension directly after treatment, b) suspension few minutes after the agitation stopped

A positive relationship is observed between the absorbance and concentration of nanotubes for all suspensions, as shown in Figure 4). The absorbance depends on the concentration of well dispersed nanotubes, subsequently on the type of nanotubes and effectiveness of the used surfactant. However, with both types of nanotubes Tx-100 has the highest dispersion efficiency, leading to a significant improvement in the dispersion of both types of nanotubes. Superplasticisers based surfactants have approximately the same dispersion effectiveness, while the MC agent has less dispersion ability. A homogenous darkish dispersion was obtained for 0.047 g/L MWNTs, therefore various concentrations of MWNTs from 0.047 g/L to 0.004 g/L were selected for this work.

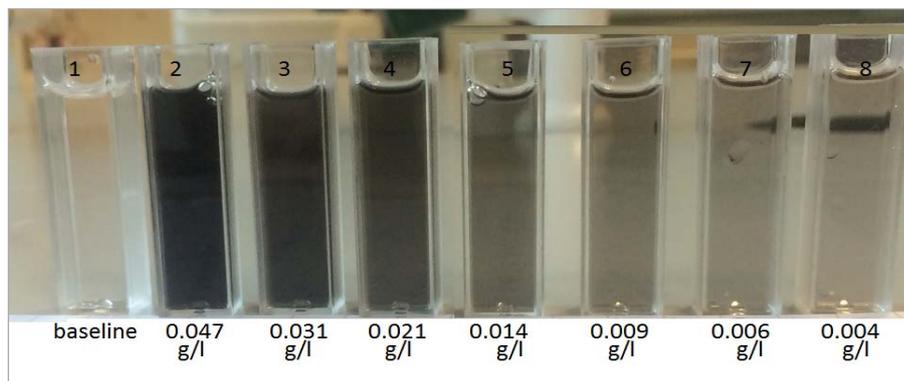


Figure 2: Seven concentrations of nanotubes- PCE, NPH, MC, TX-100 suspensions.

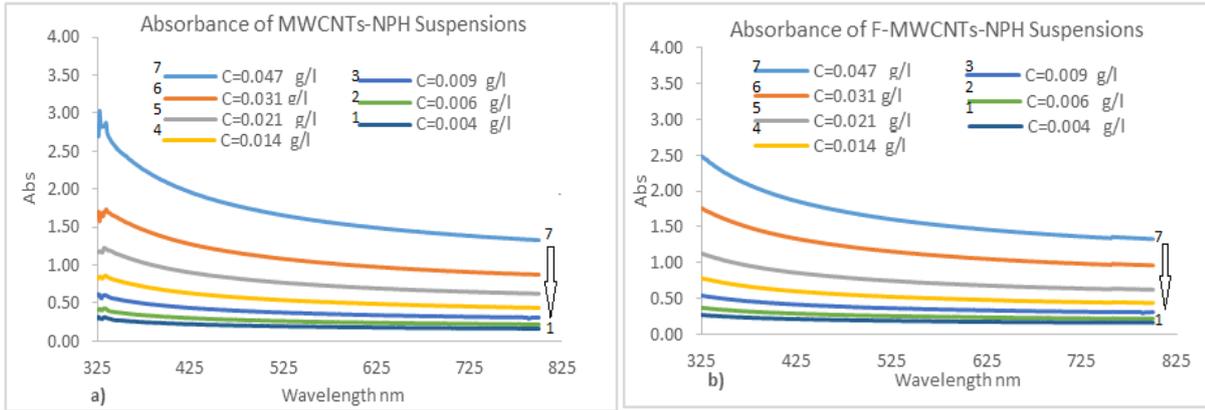


Figure 3: UV–vis spectra of nano tubes suspensions dispersed using NPH: a) MWCNTs, b) F-MWCNT

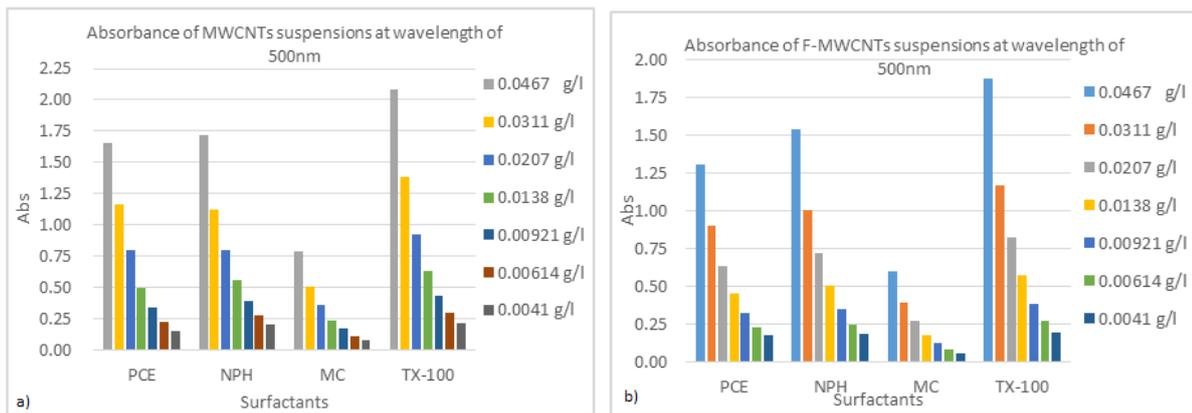


Figure 4: Absorbance of nanotubes suspensions recorded at wavelength of 500nm, suspensions containing different types of surfactants (PEC, NPH, MC, and Tx-100) and a) MWCNTs, b) F-MWCNTs

3.2 Fluidity of fresh nano composites

The effects of carbon nanotubes-surfactants/dispersion agents on the flow of nano cementitious composites are shown in Figure 5. The addition of surfactants based superplasticizers to cementitious paste generally increased the flow. For the reference paste (PC) the flow was 185 mm whereas the respective values for the pastes containing functionalised/MWCNTs were in the range of 180 mm to 205 mm. Flow values were found to be significantly higher (225 mm) in case of

paste containing nanotubes dispersed in non-ionic agents. Figure 6 illustrates the flow behaviour of the different pastes. These differences in flow are attributed to two main reasons. Firstly, the hydrophobic and hydrophilic nature of these agents contributes to a reduction in the viscosity of the mix and at the same time to the formation of a large volume of stable air bubbles [30]. Secondly the absorption of Carboxylic acid ($-\text{COOH}$) groups on the walls of the functionalised nanotubes improves the dispersion of the tubes in water [3]. Generally, the effect of surfactants on the dispersion of nanotubes and workability is dependent on the composition, the type, and the concentration of surfactants [23, 31]. Generally, Triton X-100 provides higher workability, which is further increased when functionalised nanotubes are used.

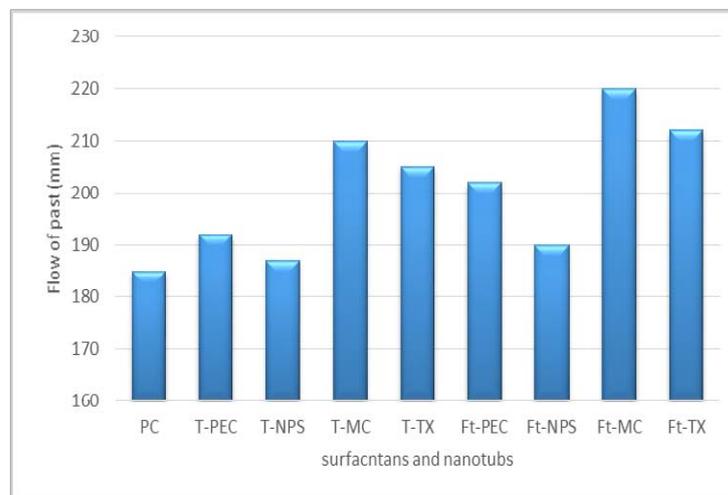


Figure 5: The effect of surfactant/nanotubes on workability of fresh pastes

3.3 Compressive Strength

The compressive strength results of nano cementitious composites are presented in Figure 7 (a, b) at 3, 7, 28 days after curing. It is observed that the use of surfactant-based superplasticisers in the dispersion of nanotubes resulted in a distinct improvement of the strength compared to the reference mix (PC). The strength of specimens containing as received MWCNTs, and F-MWCNTs dispersed using Naphthalene based superplasticizer was improved by 63% and 27% at early and late ages, respectively.

Although the non-ionic surfactant (MC, TX-100) has successfully dispersed the nanotubes in the water, the compressive strength of the specimens containing these suspensions is reduced. This can be attributed to the fact that these agents are incompatible with the cement hydration process leading to a delay in cement hydration

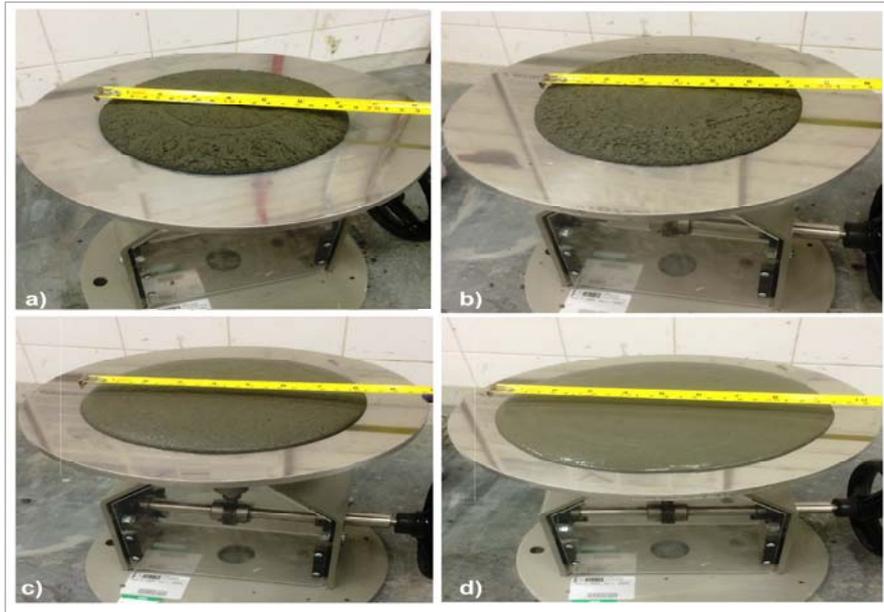


Figure 6: The flow behaviour of pastes containing different types of surfactants: a) Flow of control mix, b) Flow of paste containing nanotubes dispersed using NPH (which was slightly higher than that of paste containing PCE), c) Flow of paste containing CNTs dispersed using MC (approximately the same as that of paste containing TX-100), and d) Flow of paste containing Functionalised nanotubes dispersed using MC (which was slightly lower than pastes containing TX-100).

Typical scanning electron microscopy (SEM) images in Figure 8 show micrographs of the fractured surfaces of the hardened control mix, and mixes containing nanotubes dispersed using NPH. Figure 8 (a) shows the microstructure of the control mix, where the main constituents of the cement paste are $\text{Ca}(\text{OH})_2$, C–S–H gel, pores, cracks, and an amount of needle-like crystals emerging from the fracture surface, which were cement hydration crystals of Ettringite (AFt). CH can also be recognized. Figure 8 (b) shows that the nanotubes are dispersed uniformly without obvious agglomeration. CNTs were found to be embedded as individual fibres in the paste and acted as bridges between hydrates and across

cracks. This ensures good load-transfer efficiency from the cement matrix to the nanotubes.

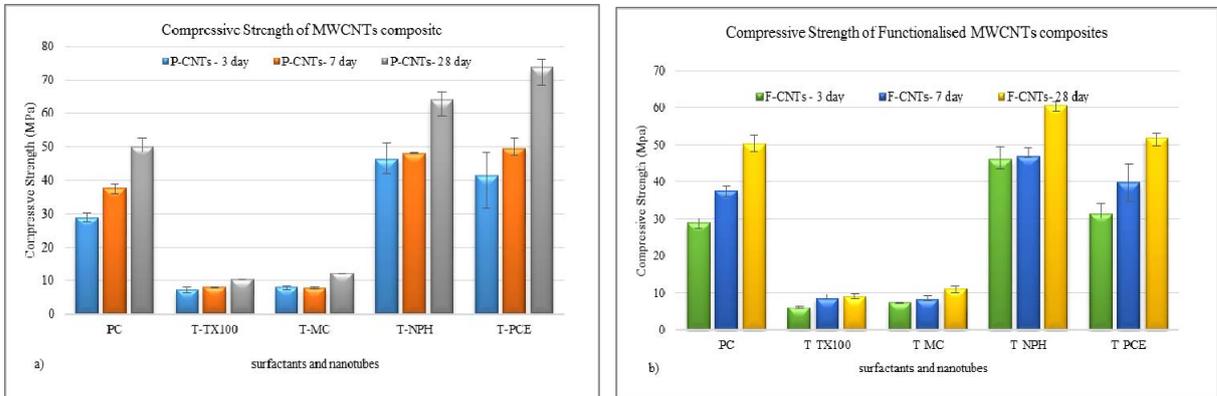


Figure 7: Compressive strength of cementitious composites with a) as received MWCNTs and b) composites containing Functionalised MWCNTs.

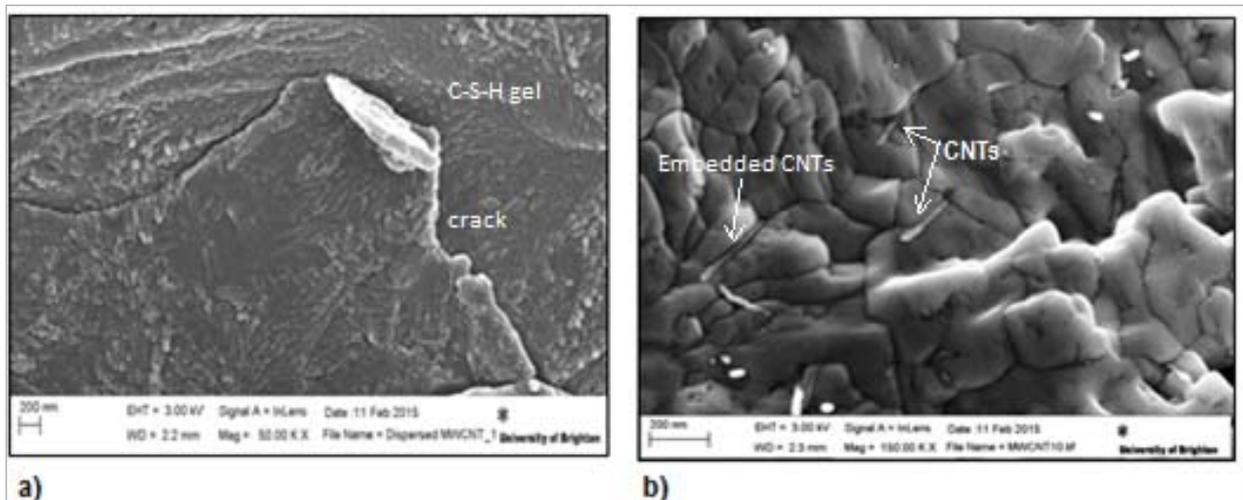


Figure 8: SEM images of hardened cementitious composites a) control mix b) mix containing MWCNTs dispersed using NPH.

4 Conclusion

This study presents the results of investigations on the dispersion, workability, and compressive strength of CNT-aqueous and CNT–cementitious composites.

Four different types of dispersants/surfactants (polycarboxylate, naphthalene sulfonate, methylcellulose, and Triton X-100) were used in this study. The outcomes of the work were:

- Based on UV-vis absorbance test results, non-covalent methods based on physical adsorption of anionic, non-ionic, and cationic surfactants generated homogeneous carbon nanotubes suspensions.
- Triton x-100 has the highest dispersion efficiency of the investigated surfactants, and significantly improved the dispersion of nanotubes in water. Mechanically, however, its use led to a significant reduction in the composite strength, which was attributed to the fact that the Tx-100 is incompatible with cementitious materials.
- Addition of carbon nanotubes did not affect the mix workability, while functionalised nanotubes slightly improved the fluidity, which can be attributed to the relevant functional groups (-COOH) acting to make the tubes more dispersible in water and thus aiding in improving the mix workability.
- Compressive strength was considerably increased in the case of MWCNTs/F-MWCNTs dispersed with the aid of Naphthalene base superplasticiser, for all examined ages.

Acknowledgment

The lead author would like to thank the Iraqi Ministry of Higher Education and Scientific Research, Iraqi Culture attaché in London, Babylon University in Iraq for award of a Doctoral scholarship.

References

- [1] Saptarshi Sasmal, B., Nagesh R. Iyer³, Can Carbon Nanotubes Make Wonders in Civil/Structural Engineering? Progress in Nanotechnology and Nanomaterials, 2013. Vol. 2(Iss. 4): p. PP. 117-129.

- [2] Hanus, M.J. and A.T. Harris, Nanotechnology innovations for the construction industry. *Progress in Materials Science*, 2013. 58(7): p. 1056-1102.
- [3] Liliana Olenic, S.P., Valer Almasan and Alexandru R. Biris, ed. *Electrochemical and Adsorption Properties of Catalytically Formed Carbon Nanofibers*. National Institute for Research and Development of Isotopic and Molecular Technologies Romania. 2010, SCIYO.COM: INTECH, Croatia. pp. 438.
- [4] Yu, J., et al., Controlling the dispersion of multi-wall carbon nanotubes in aqueous surfactant solution. *Carbon*, 2007. 45(3): p. 618-623.
- [5] Chen, S.J.C., F. G. Macleod, A. J. N. Pan, Z. Duan, W. H. Wang, C. M., Carbon nanotube–cement composites: A retrospect. *The IES Journal Part A: Civil & Structural Engineering*, 2011. 4(4): p. 254-265.
- [6] A. Yazdanbakhsh, Z.C.G., B. Tyson and R.K. Abu Al-Rub, Carbon Nano Filaments in Cementitious Materials: Some Issues on Dispersion and Interfacial Bond. 2009.
- [7] Li, G.Y., P.M. Wang, and X. Zhao, Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes. *Carbon*, 2004. 43(6): p. 1239-1245.
- [8] Jyoti Bharj, S.S., Subhash Chander, Rabinder Singh, Role of Dispersion of Multiwalled Carbon Nanotubes on Compressive Strength of Cement Paste. *World Academy of Science, Engineering and Technology International Journal of Physical, Nuclear Science and Engineering*, 2014. Vol:8 No:2.
- [9] Zhang, H., Z. Zhang, and C. Breidt, Comparison of short carbon fibre surface treatments on epoxy composites: I. Enhancement of the mechanical properties. *Composites Science and Technology*, 2004. 64(13–14): p. 2021-2029.
- [10] Coleman, J.N., et al., Small but strong: A review of the mechanical properties of carbon nanotube–polymer composites. *Carbon*, 2006. 44(9): p. 1624-1652.
- [11] ASHOUR, A.I., Aspect Ratio Effect of Functionalized/Non-Functionalized Multiwalled Carbon Nanotubes on the Mechanical Properties of Cementitious Materials. Master's thesis, Texas A&M University. Available electronically from [http : //hdl .handle .net /1969 .1 /ETD -TAMU -2011 -08 -10197](http://hdl.handle.net/1969.1/ETD-TAMU-2011-08-10197). 2011.
- [12] Abu Al-Rub, R.K., A.I. Ashour, and B.M. Tyson, On the aspect ratio effect of multi-walled carbon nanotube reinforcements on the mechanical

properties of cementitious nanocomposites. *Construction and Building Materials*, 2012. 35(0): p. 647-655.

- [13] Ouellette, L.L., CHEMICAL AND BIOLOGICAL SENSING WITH CARBON NANOTUBES IN SOLUTION, in Faculty of the Graduate School 2008, Cornell University.
- [14] Dong, B., et al., Dispersion of carbon nanotubes by carbazole-tailed amphiphilic imidazolium ionic liquids in aqueous solutions. *J Colloid Interface Sci*, 2011. 356(1): p. 190-5.
- [15] Chang-Yuan Hua, b., Ya-Juan Xuc , Shu-Wang Duoa,b, and Ming-Sheng Lia,b., Non-Covalent Functionalization of Carbon Nanotubes with Surfactants and Polymers. *Journal of the Chinese Chemical Society*,, 2009. 56: p. 234-239.
- [16] Díez-Pascual, A.M., et al., Nanoindentation in polymer nanocomposites. *Progress in Materials Science*, 2015. 67: p. 1-94.
- [17] Ardavan Yazdanbakhsh, Z.G., Bryan Tyson,, Distribution of Carbon Nanofibers and Nanotubes in Cementitious Composites. 2010.
- [18] Tyson BM, A.A.-R.R., Yazdanbakhsh A, Grasley Z. , Carbon nanotubes and carbon nanofibers for enhancing the mechanical properties of nanocomposite cementitious materials. *J Mater Civil Eng*, 2011. 23(7): p. 1028–35.
- [19] Bai, Y., et al., Adsorption of Triton X-series surfactants and its role in stabilizing multi-walled carbon nanotube suspensions. *Chemosphere*, 2010. 79(4): p. 362-7.
- [20] Collins, F., J. Lambert, and W.H. Duan, The influences of admixtures on the dispersion, workability, and strength of carbon nanotube–OPC paste mixtures. *Cement and Concrete Composites*, 2012. 34(2): p. 201-207.
- [21] Cwirzen, A., K. Habermehl-Cwirzen, and V. Penttala, Surface decoration of carbon nanotubes and mechanical properties of cement/carbon nanotube composites. *Advances in Cement Research*, 2008. 20(2): p. 65-73.
- [22] Trettin R, K.T., Nanotubes fur hochleistungsbetone (nanotubes for highperformance concretes). *Betonwerk und Fertigteil-Technik/Concr Precast Plant Technol*, 2005. 71(2): p. 20–1.
- [23] Rastogi, R., et al., Comparative study of carbon nanotube dispersion using surfactants. *Journal of Colloid and Interface Science*, 2008. 328(2): p. 421-428.

- [24] Li, G.Y., P.M. Wang, and X. Zhao, Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes. *Carbon*, 2005. 43(6): p. 1239-1245.
- [25] Burgos-Montes, O., et al., Compatibility between superplasticizer admixtures and cements with mineral additions. *Construction and Building Materials*, 2012. 31: p. 300-309.
- [26] Schröfl, C., M. Gruber, and J. Plank, Preferential adsorption of polycarboxylate superplasticizers on cement and silica fume in ultra-high performance concrete (UHPC). *Cement and Concrete Research*, 2012. 42(11): p. 1401-1408.
- [27] Wang, B.-M. and Y. Zhang, Synthesis and properties of carbon nanofibers filled cement-based composites combined with new surfactant methylcellulose. *Materials Express*, 2014. 4(2): p. 177-182.
- [28] ASTM C230 / C230M-14, Standard Specification for Flow Table for Use in Tests of Hydraulic Cement, ASTM International, West Conshohocken, PA, 2014, www.astm.org.
- [29] Ye, Y., et al., Concentration detection of carbon nanotubes in electrophoretic suspension with UV-vis spectrophotometry for application in field emission devices. *Applied Surface Science*, 2013. 284: p. 107-112.
- [30] Negim, E.-S., et al., Effects of Surfactants on the Properties of Mortar Containing Styrene/Methacrylate Superplasticizer. *The Scientific World Journal*, 2014. 2014: p. 10.
- [31] Fan, W., et al., A new class of organosilane-modified polycarboxylate superplasticizers with low sulfate sensitivity. *Cement and Concrete Research*, 2012. 42(1): p. 166-172.