Cement & Concrete Composites 34 (2012) 201–207

Contents lists available at SciVerse ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

The influences of admixtures on the dispersion, workability, and strength of carbon nanotube–OPC paste mixtures

Frank Collins *, John Lambert, Wen Hui Duan

Department of Civil Engineering, Monash University, Australia

ARTICLE INFO

Article history:
Received 15 December 2010
Received in revised form 20 September 2011
Accepted 21 September 2011
Available online 12 October 2011

Keywords:
Carbon nanotube
Cement
Dispersion
Workability
Strength

ABSTRACT

Carbon nanotubes (CNT) have excellent mechanical properties and have the potential, if combined with Ordinary Portland Cement (OPC), traditionally a brittle material in tension, to become a nano-composite with superlative mechanical properties. However, highly attractive van der Waals forces between CNTs create coherent agglomerates that prove difficult to disperse within the cement matrix and reduce the fluidity of the fresh mixture. Good dispersion of CNTs, while maintaining good workability of fresh OPC–CNT paste mixtures, is a prequalification before CNT-cement nanocomposites can be considered as a future building and construction material with enhanced mechanical properties. This paper reports the results of investigations of the dispersion, workability, and strength of CNT aqueous and CNT–OPC paste mixtures, with and without several generically different dispersants/surfactants that are compatible as admixtures in the manufacture of concrete. These include an air entrainer, styrene butadiene rubber, polycarboxylates, calcium naphthalene sulfonate, and lignosulfonate formulations. Aqueous mixtures were initially assessed for dispersion of CNTs, followed by workability testing of selected OPC–CNT-dispersant/surfactant paste mixtures. A broad range of workability responses were measured and the CNT dispersion within hardened pastes was qualitatively assessed by SEM analysis.

1. Introduction

Carbon nanotube (CNT) fibers have superlative mechanical properties and have future promise when combined with Ordinary Portland Cement (OPC) as a nanocomposite. The first evidence of tubular shaped carbon nanotubes was observed under transmission electron microscope by Radushkevich and Lukyanovich [1] and Monthioux and Kuznetsov [2]. CNTs are macromolecules of carbon atoms in a periodic hexagonal arrangement with a cylindrical shell shape and categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). The structure of a SWNT can be conceptualized by wrapping a graphene sheet into a seamless cylinder while MWNT consists of multiple graphene sheets rolled in on themselves to form a tube shape. CNTs can have diameters ranging from 1–100 nm and lengths up to millimetres. However, because of high attractive van der Waals forces between CNT particles [3], considerable surface area, and high length/diameter ratio, with lengths of tens of microns and diameters from 2 to 100 nm [4], it can be difficult to ensure uniform dispersion of CNTs within the OPC paste. Insufficient dispersion of CNTs is cited a key diminishing factor in performance of composites incorporating CNTs [5,6]. Poor dispersion of CNTs leads to the formation of many defect sites in the nanocomposite and limits the efficiency of the CNTs in the matrix.

Many past studies have focused on dispersion of CNTs within CNT–polymer composites, however there are few published studies on dispersion of CNTs within OPC pastes. Many of the surfactants that can effectively disperse CNTs in polymer liquids are incompatible with cement hydration; they can retard or prevent hydration, entrap substantial air in the paste, or undergo reactions with water-reducing admixtures, resulting in reagglomeration [7].

When mixed in water, OPC–CNT paste mixtures are highly viscous and difficult to place, even when only 2% CNT (weight of cement) has been admixed within cement paste prepared with a 0.8 w/c ratio [8]. When embedded as fillers, CNTs with poor dispersion act as crack initiators, thereby impairing the elastic properties of the resultant composite [9].

Kowald [10] incorporated 0.5% MWNTs (% cement weight) and measured 12% increase in compressive strength, however the consistency of the paste (i.e. the ability of freshly mixed cement paste to flow) was substantially reduced and pressures up to 125 MPa were applied for more than 45 min for adequate compaction.

Methods for dispersing CNTs have included mechanical ultrasonication to disperse CNTs [11], or changing the surface tension of the wetting liquid [12], or functionalization of the CNT surface

---

* Corresponding author. Address: Department of Civil Engineering, Monash University, Building 60, Wellington Road, Clayton, Victoria 3800, Australia. Tel.: +61 3 9905 5989.

E-mail address: frank.collins@monash.edu (F. Collins).

0958-9465/$ - see front matter Crown Copyright © 2011 Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconcomp.2011.09.013

[9,13,14] to change the surface energy of the nanotubes. However, chemical functionalization of the CNT surface has the potential for damage to the CNTs following this treatment [11,15]. Although previous dispersion investigations have been undertaken on OPC–CNT-surfactant paste mixtures [16–20], none link the simultaneous need for aqueous dispersion of both CNTs and OPC particles; a key factor when considering future applications that involve future placement and fabrication of CNT–OPC mixtures.

This paper reports the results of preliminary investigations of the dispersion and rheology of CNT–OPC paste mixtures, with and without dispersants/surfactants. The work was conducted over the following stages:

(i) Initial screening of aqueous solutions containing CNTs and several generically different types of admixtures that were designed to disperse OPC particles.
(ii) Based on the results of (i), a short-list of OPC–CNT-admixture combinations were selected for consistency and compressive strength testing.
(iii) Hardened samples from (ii) were fractured and the fracture surface was assessed by SEM for distribution of CNTs within the cement paste.

2. Materials and experimental program

2.1. Materials

Ordinary Portland Cement (OPC), conforming to the requirements of Australian Standard AS3972 as a Type GP cement, was used as the binder material [21]. The chemical composition and properties of the binder is summarized in Table 1. The multiwalled CNTs (MWCNTs) used in the experiments were sourced from Nanotech Port Corporation (Shenzhen, China). The physical properties of the MWCNTs used in the investigation are summarized in Table 2, and are distinguished by diameters within the ranges of 10–20 nm (MWCNT-1020), 10–30 nm (MWCNT-1030), and 60–100 nm (MWCNT-60100), with corresponding lengths of 5–15 μm for each MWCNT type.

The chemical admixtures used in this investigation are dispersants and surfactants used for manufacture of Portland cement concrete and conform to the requirements of Australian Standard AS1478.1 Admixtures for Concrete [22]. The following types of dispersants/surfactants were chosen because of the known compatibility when utilized in cement pastes:

- Air Entraining Agent based on alkylbenzene sulfonic acid (AEA).
- Styrene butadiene rubber co-polymer latex (SBR).
- Aliphatic propylene glycol ether including ethoxylated alkyl phenol (SR).
- Polycarboxylate (PC#1 and PC#2).
- Calcium naphthalene sulfonate (CNS).
- Naphthalene Sulphonic Acid Derivative (NSAD).
- Lignosulfonate (WDRA).

Table 1
Chemical composition and properties of OPC.

Constituent/property (%)	OPC
SiO_2	19.90
Al_2O_3	4.70
Fe_2O_3	3.38
MgO	1.30
CaO	63.93
Na_2O	0.17
TiO_2	0.245
K_2O	0.446
MnO	0.079
P_2O_5	0.063
SO_3	2.54
LOI	2.97
Fineness, m^2/kg	360
Specific gravity	3.15

Table 2
Summary of CNT properties.

Parameter	MWCNT-1020	MWCNT-1030	MWCNT-60100
Purity	>95%	>95%	>95%
Diameter	10–20 nm	10–30 nm	60–100 nm
Length	5–15 μm or 1–2 μm	5–15 μm or 1–2 μm	5–15 μm or 1–2 μm
Amorphous carbon	<3%	<3%	<3%
Ash (catalyst residue)	<0.2%	<0.2%	<0.2%
Special surface area	40–300 m^2/g	40–300 m^2/g	40–300 m^2/g
Thermal conductivity	~2000 W/m k	~2000 W/m k	~2000 W/m k

2.2. Sedimentation within aqueous solutions

All solutions were generated initially by magnetically stirring 50 ml of water with 0.05 gm of CNT in the presence of 0.5–1.5 ml of chemical admixture (based on the Suppliers' recommendations for use in general concrete manufacture). The initial magnetic stirring was in all cases only partially effective in dispersing the CNT. The phials were sealed and immersed in a Branson ultrasonic bath (Unisonic SXP12D 0.9 A, 40 V 2 by 150 W disk transducer unit) and were ultrasonicated for 12 min. Samples were observed for the visual effectiveness of dispersion and transferred into 40 ml phials for storage and longer-term study. Visual observations of sedimentation were taken over 1–30 days and initial conclusions were drawn as to the most effective additives based on solution stability. Samples showing little initial sedimentation were chosen for subsequent mini-slump testing of OPC–CNT-Admixture pastes.

2.3. Mini-slump and compressive strength testing

Paste mixtures were made to assess consistency arising from the following variables:

(i) Variation of CNT diameter and length (MWCNT 60100, MWCNT 1020, and MWCNT 1030).
(ii) Proportion of CNT (0%, 0.5%, 1%, and 2% weight of cement).
(iii) Water to cement ratio (0.4, 0.5, and 0.6).
(iv) Addition of admixtures (selected after aqueous sedimentation trials).
(v) Agitation by ultrasonic methods.

Mixing of the CNT–OPC-Admixture pastes was conducted within a 10 l stainless steel mixing bowl. The total quantity of material used for any given batch ranged from 0.5 to 1.0 kg. Mixing was conducted by machine mixing at 98 rpm in a *Kenwood KNM20* planetary mixer. The sequence of mixing consisted of: 2 min mixing followed by 2 min cessation of mixing, followed by further mixing for 2 min.

Consistency was assessed by the mini-slump test [23], of dimensions: top diameter 19 mm, bottom diameter 38 mm, and height 57 mm (Fig. 1). The mold was placed firmly on a flat and horizontal plastic sheet and filled with paste and compacted with a spatula. When the mold was full, the top surface was levelled, and the excess paste removed. The mold was removed vertically, ensuring minimal lateral disturbance, and to avoid sample disturbance the slumped sample was left to harden over 24 h. The diameter of the hardened base was measured at five locations

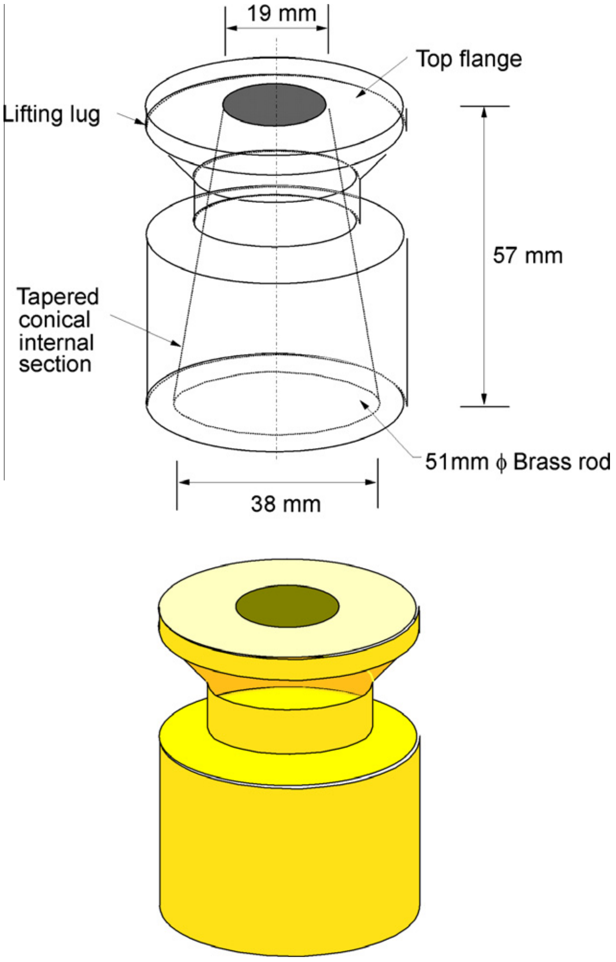

Fig. 1. Set-up for mini-slump test [24].

around the outline and the mean was used to calculate the area of the base.

Paste cylinders, measuring 50 mm diameter by 100 mm length, were tested for compressive strength at 28 days. Following mixing of paste, the molds were filled and compacted on a vibrating table for 30 s. The samples were then covered with polythene film to ensure minimal air circulation over the sample. Following elapse of 24 h, the samples were removed from the molds and each end of the sample was machine linished to ensure smoothness and perpendicularity. Following linishing, the final length of the sample was close to 100 mm, ensuring a length to diameter ratio of almost 2.0. Samples were fog room cured at 23 °C and 100% relative humidity (RH) until testing for compressive strength. Compressive strength testing was conducted in a Baldwin loading machine that has an accuracy of ±1% for loads greater than 2 kN. Rubber caps, consisting of 3 mm thick natural rubber with a nominal Shore A Durometer hardness of 50, were placed at each end of the samples prior to testing. A total of three cylinders were made for each data set.

2.4. Scanning electron microscopy

Selected hardened paste samples from the mini-slump trials were investigated under SEM to examine the dispersion of CNTs within the matrix. All paste mixtures were composed with water/cement ratio of 0.5, CNT type was MWCNT 1030, and all mixtures contained 0.5% CNT (% weight of cement). The mixture types were as follows:

(i) OPC + CNT
(ii) OPC + CNT + air entrainer
(iii) OPC + CNT + polycarboxylate2

At 28 days the hardened samples were broken to expose the CNT's crossing the fracture surface. The samples were sputter-coated with 15 μm thick gold layer and were examined using an Oxford Instruments JEOL JSM-840A scanning electron microscope. The microscope was operated at 5–15 kV.

3. Results and discussion

3.1. Sedimentation in aqueous solutions

Although there are methods to quantify dispersion (e.g. image analysis and UV–vis spectroscopy), the purpose of the visual observations of aqueous solutions containing carbon nanotubes, with and without dispersants, was to identify those mixtures that showed very clear contrasts, for the purpose of selecting mixtures for subsequent cement paste mixes. There was little ambiguity of the opaque black CNT agglomerations that separated from the mixture, settling underneath a very clear and transparent supernatant. At present we are currently undertaking UV–vis spectroscopy on further aqueous mixtures where there is not such a clear contrast in the visual observations. Fig. 2 shows a selection of aqueous solutions containing CNTs, with and without dispersing admixtures. Control solutions containing solely CNT + water developed agglomerations almost immediately and showed negligible dispersion despite magnetic stirring and ultrasonication (Sample 1, Fig. 2).

Addition of air entrainer (AEA) showed good visible dispersion, following magnetic stirring and ultrasonication (Sample 2, Fig. 2), with the mixture showing a uniform opaque black color that remained stable up to 9 days. However, when ultrasonication was not applied, limited initial dispersion of CNT particles occurred, and following 9 days the CNT agglomerates had settled to the bottom of the phial, leaving a clear supernatant (Sample 3, Fig. 2).

SBR provided poor dispersion, as evidenced by CNTs flocculation into large clumps (Sample 4, Fig. 2). Sample 5 (Fig. 2), based on glycol ether (Type SR), also showed poor dispersion, with agglomerates quickly settling to the base of the phial and forming a clear supernatant. The polycarboxylates (Samples 6–8, Fig. 2) showed mixed results. Sample 6, containing polycarboxylate1, responded to ultrasonication and provided a uniformly black solution, however following 9 days, a black precipitate of CNTs was visible at the base of the phial (Sample 7, Fig. 2), although limited dispersion was evident. In contrast, polycarboxylate2 dispersed the CNTs to a uniformly black opaque solution that remained unchanged when observed at 9 days (Sample 8, Fig. 2). The differences in dispersion performance between polycarboxylates 1 and 2 are currently under further investigation and could relate to

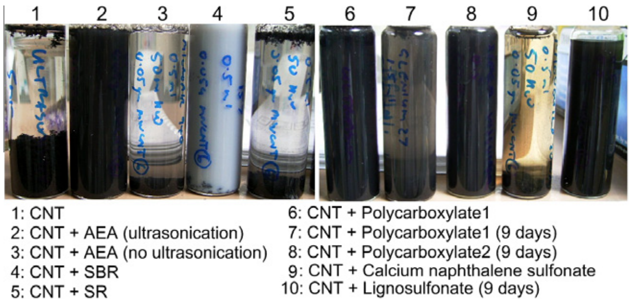

Fig. 2. Selected samples, following sedimentation trials of CNT in aqueous solutions.

several reasons, including: (i) molecular weight (MW) and MW distribution; (ii) the nature of the polycarboxylate chain (linear or branched); (iii) level of functionalization, and whether free polar carboxylate functionalities are present. Samples containing admixtures based on calcium naphthalene sulfonate (Sample 9, Fig. 2) responded poorly, with black agglomerates of CNTs forming shortly after ultrasonication. The lignosulfonate-based admixture provided reasonable dispersion, displaying a uniformly dark emulsion that remained unchanged when observed at 9 days (Sample 10, Fig. 2).

Further work, in addition to visual observation, such as laser particle size analysis or UV adsorption profiles and their variation with time, would quantify these visual observations. Nevertheless, visual observations of the sedimentation performance in aqueous solutions showed clear differences in dispersion of CNT and were used at this stage for the purpose of screening a number of feasible admixtures for subsequent cement paste consistency trials. Based on the results of sedimentation trials, the following admixture types were selected for further testing within OPC–CNT paste mixtures:

(i) Air entrainer.
(ii) Polycarbonate#2.
(iii) Lignosulfonate.

3.2. Mini-slump and compressive strength of CNT–OPC mixtures

3.2.1. Effect of CNT dosage

The mini-slump test results for the OPC paste control samples (i.e. 0% CNT), with w/c's of 0.4, 0.5, and 0.6, are summarized in Fig. 3a. The results show expected mini-slump consistency increasing with increasing w/c [23,24]. When CNTs are added in small proportions (0.5%, 1%, and 2% by mass of OPC), significantly reduced consistency was evident. At w/c = 0.4, addition of 0.5% CNT causes the consistency to reduce 19.5% and, at 1% and 2% CNT dosages, the paste samples displayed minimal mini-slump spread (i.e. 38 mm is the lower limit of the test). At w/c = 0.5, the slump diameter reduced by 14.5% when 0.5% CNTs was added, however considerably greater losses were measured at higher CNT dosages: 32.8% and 48.9% when 1% and 2% CNTs were mixed respectively. At w/c = 0.6, similarly high losses in consistency were measured, with up to 38.3% loss of consistency measured at the 2% CNT dose.

The compressive strength of companion test cylinders made from the same batch of paste as utilized for the mini-slump tests showed interesting trends (Fig. 3b):

(i) The OPC paste control samples (i.e. 0% CNT) showed expected strength differences between pastes comprising w/c's of 0.4, 0.5, and 0.6.
(ii) Despite ultrasonication, all samples had decreasing compressive strength when dosed with increasing CNT. The samples with w/c of 0.4 demonstrated the most significant changes: 2% CNT dosed samples had only 24% of the compressive strength of the control samples. It should be noted that samples with w/c of 0.4 displayed minimal consistency following all doses of CNT and entrapped voids would have reduced the strength. However, all samples, regardless of w/c, show similar trends, and it is likely that agglomerations of CNT within the hardened cement paste have lead to local stress raisers that have impaired the strength. The agglomerations were visible as black streaks of nanotubes were noticeable within the fresh paste samples following mixing and ultrasonication, as shown in Fig. 4.

3.2.2. Effect of length/diameter (l/d) of CNT

The effect of l/d on the mini-slump of OPC–CNT pastes with w/c = 0.5 and CNT dose 0.5% (% weight OPC) is summarized in Table 3. The l/d of CNT samples ranged from 150–250 (MWCNT-1030) to 750–1500 (MWCNT-1020). There was little variation in measured mini-slump values corresponding with changes in l/d: the mini-slump reducing between 13–15.2% from the OPC control paste mixture. The compressive strength showed little variation between samples when comparing l/d of CNT's (Table 3). Subsequent paste tests therefore utilized the one type of CNT, MWCNT-1030.

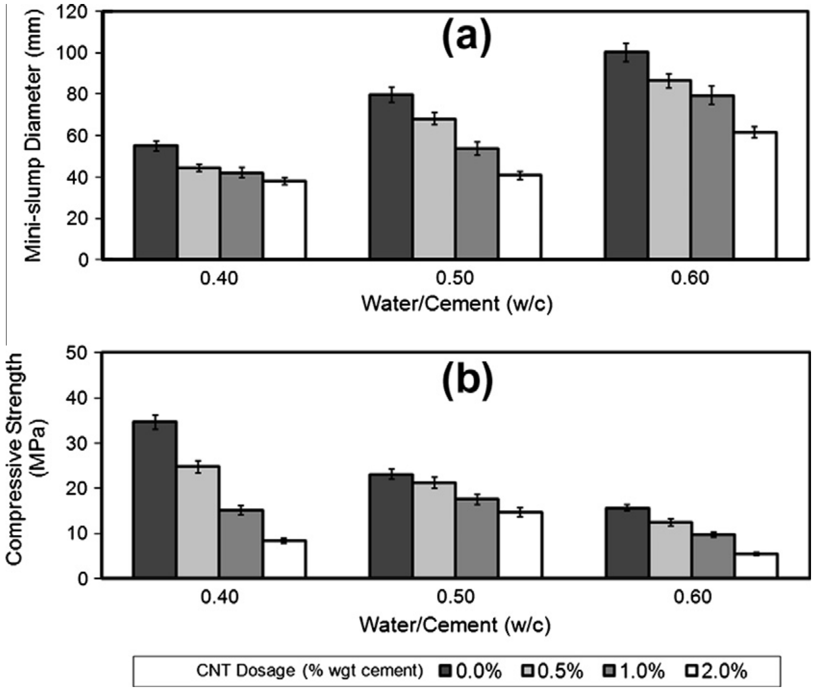

Fig. 3. Effect of CNT dosage and water/cement on: (a) measured mini-slump diameter; (b) Compressive strength. Note: the error bars represent the coefficient of variation at each measurement point.

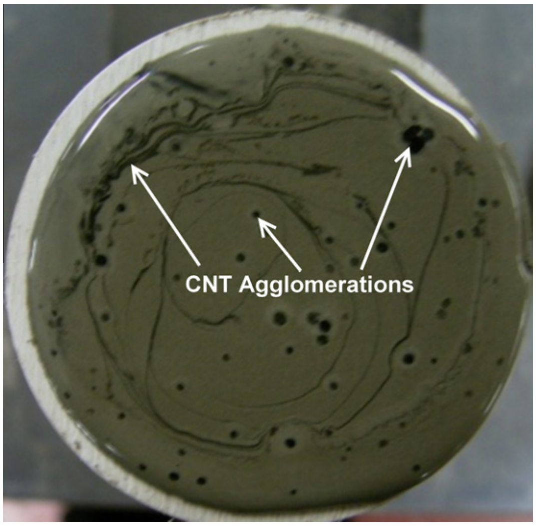

Fig. 4. Fresh paste sample showing agglomerations of CNTs (w/c = 0.5, 0.5% CNT (% weight cement).

3.2.3. Effect of air entrainer (AEA)

The OPC control paste mixtures showed expected improved mini-slump with addition of AEA, while ultrasonication produced lower consistency, most likely due to egress of entrained air from the paste agitation. However, when the water-CNT-AEA premix was added to the OPC paste, significantly reduced minislump diameter of 20.8% (Table 3) was measured and, following ultrasonication, higher loss was evident (28.9%). Although air entrainment promotes better dispersion of CNTs in aqueous solutions, as evidenced earlier in Fig. 2, addition of AEA significantly reduces OPC–CNT paste consistency.

Without CNT's, the polar group of the AEA attaches to the cement particles, while the non-polar end forms a hydrophobic outer surface where stable air bubbles displace water within the paste: a stable air-cement-air "bridge" yields improved cohesion and relatively free motion in shear, with the stabilized air bubbles acting like compressible bearings. However, CNTs compete with cement for the non-polar group within the AEA, leading to formation of CNT-air-cement-air-CNT and/or CNT-air-CNT "bridges" that are far more cohesive and more conducive towards forming agglomerates than cement–water-AEA mixtures. The resultant mixtures have reduced shear motion and lower consistency, as demonstrated by the mini-slump test results. Likely agglomeration of CNT's is reflected in the compressive strength results (Table 3), demonstrating 10.9% lower strength of OPC–CNT–AEA mixtures when compared with OPC–AEA control samples, while ultrasonication produced 14.6% lower strength.

3.2.4. Effect of lignosulfonate (WRDA)

Lignosulfonate additions to fresh OPC paste (without CNT) provide expected improvement in consistency and similar compressive strength, as shown in Table 3. However companion mixtures containing 0.5% CNT had 30.1% lower consistency and 28.4% lower strength. There is competition between the OPC and CNT for lignosulfonate. In aqueous solutions, CNTs are highly attracted to lignosulfonates [25]. Besides the hydrophobic attraction of the alkyl chains to the CNTs, the high number of aromatic rings within the lignosulfonate chemical structure also provides many active attaching sites onto the sidewalls of CNTs. Lignosulfonates are adsorbed so that the sulfonate groups in their molecules point away from the CNT surface, conferring a negative charge to the CNTs, thereby providing repulsion between adjacent particles and dispersion in water. Nevertheless, it is clear that significantly higher doses than the supplier's recommended limits of lignosulfonate are needed to provide sufficient dispersion. However, at high dosages, Lignosulfonate have a reported history of delaying the setting time of Portland cement mixtures to the detriment of reasonable setting times (for hardening) and early-age strength development [26], and therefore use of lignosulfonate in our studies was discontinued.

3.2.5. Effect of polycarboxylate (PC)

Polycarboxylate addition to the OPC paste mixtures was considerable and the mixture was free-flowing when the water/cement ratio was 0.35 or greater (Table 3). The effect of CNT addition on the consistency of OPC–PC mixtures is only 4.7%, and the minislump was considerably better than control OPC mixtures that had much higher w/c. The compressive strength of mixtures containing CNT was 25% higher that control OPC mixtures with w/c

Table 3
Summary of minislump and compressive strength of OPC paste mixtures showing the effects of CNT, ultrasonication, and chemical admixtures.

Mixture	w/c	% Admixture[a,b]	% CNT[a]	l/d (CNT)	Ultrasonication	Minislump diameter (mm)[c]	Compressive strength (MPa)[c]
OPC	0.4	0	0	Control	No	55.1 (5.1)	34.6 (7.3)
OPC	0.5	0	0	Control	No	79.8 (4.6)	23.1 (6.2)
OPC	0.6	0	0	Control	No	100.2 (4.9)	15.6 (6.7)
OPC/CNT	0.5	0	0.5	150–250	No	68.2 (5.3)	21.3 (7.8)
OPC/CNT	0.5	0	0.5	500–1500	No	67.6 (5.0)	21.6 (5.5)
OPC/CNT	0.5	0	0.5	750–1500	No	69.4 (4.5)	20.5 (6.1)
OPC/CNT	0.5	0	0.5	150–250	Yes	70.1 (4.3)	69.4 (5.8)
OPC/AEA	0.5	0.4	0	Control	No	82.0 (5.2)	22.7 (5.3)
OPC/AEA	0.5	0.4	0.5	Control	Yes	75.1 (4.7)	22.5 (6.2)
OPC/CNT/AEA	0.5	0.4	0.5	150–250	No	63.2 (4.0)	20.4 (5.9)
OPC/CNT/AEA	0.5	0.4	0.5	150–250	Yes	56.7 (3.1)	19.4 (6.3)
OPC/WRDA	0.5	0.3	0	Control	No	97.00 (4.5)	24.2 (5.7)
OPC/WRDA	0.5	0.3	0	Control	Yes	108.7 (5.3)	25.1 (4.8)
OPC/CNT/WRDA	0.5	0.3	0.5	150–250	No	55.75 (4.3)	17.3 (5.5)
OPC/CNT/WRDA	0.5	0.3	0.5	150–250	Yes	53.1 (5.8)	16.2 (6.2)
OPC/PC	0.5	0.1	0	Control	No	97.7 (4.5)	22.4 (5.7)
OPC/PC	0.35	0.8	0	Control	No	123.9 (4.1)	42.0 (6.8)
OPC/PC	0.35	0.8	0	Control	Yes	136.3 (4.6)	43.3 (6.5)
OPC/CNT/PC	0.35	0.8	0.5	150–250	No	118.4 (3.5)	52.84 (5.9)
OPC/CNT/PC	0.35	0.8	0.5	150–250	Yes	121.3 (4.7)	53.2 (5.6)

[a] % Weight of cement.

[b] Chemical admixture notation: AEA (Air Entraining Agent); WRDA (Water Reducing Admixture based on Lignosulphonate); PC (Polycarboxylate).

[c] Numbers in brackets are the % coefficient of variation.

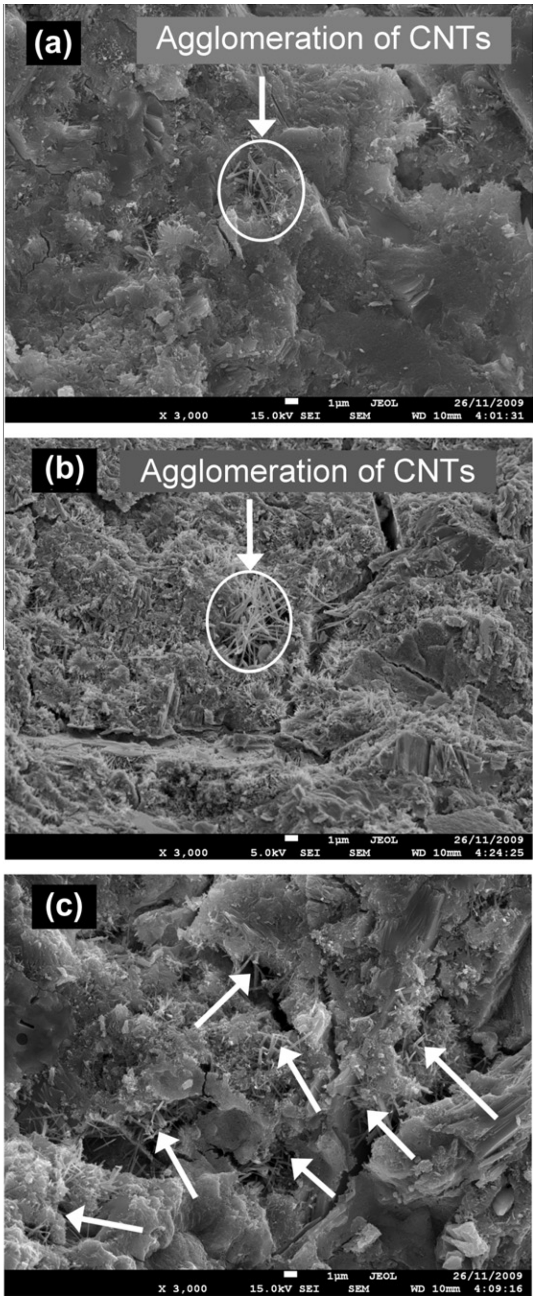

Fig. 5. SEM images taken from 28 day CNT–OPC hardened paste samples. Effect of admixtures on dispersion of CNT's: (a) No Admixture; (b) Air Entrainer; and (c) Polycarboxylate.

of 0.35. This indicates the improved dispersion of the CNTs throughout the OPC paste by addition of polycarboxylate is a key factor towards improvement of strength. Polycarboxylates were the best performed admixture in the earlier sedimentation trials in aqueous solutions and have shown significantly better OPC paste consistency at low dosage levels when compared with air entrainment and admixed lignosulfonate options. Dispersion is partly due to electrostatic repulsion owing to the carboxylate groups, but primarily to the steric repulsion associated with the long lateral ether chains [27,28]. Polycarboxylates have active non-polar groups to disperse CNTs (non-polar) while the polar groups disperse cement and water, thereby creating stable dispersions while contributing higher consistency. While maintaining low w/c of 0.35, the CNT–OPC mixtures show promise towards the future development of high strength nanocomposites.

3.3. SEM results

Fig. 5 shows SEM images taken from 28 day CNT–OPC hardened paste samples. All paste mixtures were composed with water/cement ratio of 0.5, 0.5% CNT (% weight cement), and CNT type MWCNT-1030 (10–30 nm diameter and 1–2 μm length). The images are typical of the SEM observations that compare the dispersion of CNT's within the following CNT–OPC mixtures: (a) no admixture; (b) air entrainer (AEA); and (c) polycarboxylate2. The sample containing no dispersing admixture had obvious agglomerations of CNTs, despite prior ultrasonication, as shown in Fig. 5a. There were no signs of distribution of CNTs throughout the paste samples: thick clusters of CNT agglomerates were visible. Adjacent to CNT agglomerates were areas of OPC paste that had no embedded CNTs. Fig. 5b, showing a mixture containing AEA, also showed little dispersion of CNT, although some CNTs were visible across cracks. Despite the encouraging results from the prior aqueous sedimentation trials, the AEA disperses smaller agglomerates of CNTs rather than distributing CNTs more generally within the matrix. This is confirmed by lower measured strength in the OPC–CNT–AEA samples. In contrast, the polycarboxylate surfactant provided reasonably uniform dispersion of CNTs within the paste (Fig. 5c). The white arrows shown in Fig. 5c represent several locations of CNTs dispersed within the sample, while agglomerations were not visible. The improvement in compressive strength can be attributed to the better dispersion of CNTs throughout the paste by virtue of the polycarboxylate.

4. Conclusions

This paper reports the results of investigations of the dispersion and consistency and strength of CNT-aqueous and CNT–OPC paste mixtures, with and without several generically different dispersants/surfactants for OPC-based mixtures, including air entrainer, styrene butadiene rubber, polycarboxylate, calcium naphthalene sulfonate, and lignosulfonate. The outcomes of the work were:

(i) As per previous studies, CNTs in aqueous solutions agglomerate despite mechanical agitation by magnetic stirring and ultrasonication.
(ii) Air entrainer dispersed CNTs in aqueous solutions, however sedimentation occurred within days following mixing. Mechanical agitation by ultrasonication greatly reduced sedimentation when observed at 9 days following mixing.
(iii) Following ultrasonication, polycarboxylate and lignosulfonate admixtures provided good dispersion of CNTs in aqueous solutions, even 9 days following mixing, as evidenced by little visible sedimentation. Styrene butadiene rubber and calcium naphthalene sulfonate admixtures facilitated rapid agglomeration of CNTs and were therefore not considered further in this study.
(iv) Addition of CNTs to OPC paste mixtures significantly reduces consistency and strength. SEM analysis confirmed the presence of agglomerates of CNT and these have most likely contributed as stress raisers leading to lower compressive strength.
(v) While the air entraining admixture and the lignosulfonate showed initial promise in dispersing CNT in water, when included in OPC paste mixtures, the CNTs competed with OPC for reaction with the admixture, resulting in reduced consistency and strength.
(vi) CNT–OPC paste consistency was greatly improved in the case of polycarboxylate admixture addition, with highly flowable mixtures achieved when w/c was as low as 0.35. At w/c of 0.35, the compressive strength of OPC–CNT–PC

was 25% higher than companion OPC mixtures, indicating the improved dispersion of CNT (visible when observed by SEM analysis) has been a key contributing factor toward strength improvement. The active non-polar groups within the polycarboxylate molecule disperse CNTs (non-polar) while polar groups disperse cement and water, thereby creating stable dispersions.

Consistency and strength are key factors toward future adoption of OPC–CNT composite pastes, mortars, and concrete mixtures. Many past studies have focused on dispersion of CNTs within CNT–polymer composites, however there are few published studies on dispersion of CNTs within OPC pastes. This study has shown that, with addition of polycarboxylate to the OPC–CNT mixture, it is possible to achieve good dispersion of CNT at low w/c, while maintaining good consistency and improved compressive strength.

Acknowledgements

The authors wish to acknowledge the financial support provided to the project by a Monash University Engineering Small Grant. The support and efforts provided by Tim Williams from the Monash Centre for Electron Microscopy, Jeff Doddrell and the Department of Civil Engineering concrete laboratory technical staff, is greatly appreciated.

References

[1] Radushkevich LV, Lukyanovich VM. O strukture ugleroda, obrazujucegosja pri termiceskom razlozenii okisi ugleroda na zeleznom kontakte (about the structure of carbon formed by thermal decomposition of carbon monoxide on iron substrate). Zurn Fisic Chim 1952;26:88–95.
[2] Monthioux M, Kuznetsov VL. Who should be given the credit for the discovery of carbon nanotubes? Carbon 2006;44(9):1621–3.
[3] Ko F, Gogotsi Y, Ali A, Naguib N, Ye H, Yang G. Electrospinning of continuous carbon nanotube-filled nanofiber yarns. Adv Mater 2003;15(14):1161–5.
[4] Coleman JN, Khan U, Blau WJ, Gunko YK. Small but strong: a review of the mechanical properties of carbon nanotube–polymer composites. Carbon 2006;44:624–52.
[5] Bai JB, Allaoui A. Effect of the length and the aggregate size of MWNTs on the improvement efficiency of the mechanical and electrical properties of nanocomposites – experimental investigation. Compos Part A – Appl Sci 2003;34(8):689–94.
[6] Odegard GM, Gates TX, Wise KE, Park C, Siochi EJ. Constitutive modeling of nanotube-reinforced polymer composites. Compos Sci Technol 2003;63:1671–87.
[7] Yazdanbakhsh A, Grasley Z, Tyson B, Abu Al-Rub RK. Carbon nanofibers and nanotubes in cementitious materials: some issues on dispersion and interfacial bond. ACI Special Publication 2009;267:21–34.
[8] Makar J, Margeson J, Luh J. Carbon nanotube/cement composites – early results and potential applications. In: Banthia N, Uomoto T, Bentur A, Shah SP, editors. Proceedings 3rd international conference on construction materials: performance, innovations and structural implications. Vancouver: UBC Press; 2005. p. 1–10.
[9] Vaisman L, Wagner HD, Marom G. The role of surfactants in dispersion of carbon nanotubes. Adv Colloid Interface Sci 2006;128–130:37–46.
[10] Kowald T. Influence of surface-modified carbon nanotubes on ultra-high performance concrete. In: Schmidt M, Fehling E, editors. Proceedings international symposium on ultra high performance concrete. Kassel: Kassel University Press GmbH; 2004. p. 195–202.
[11] Hilding J, Grulke EA, Zhang ZG, Lockwood F. Dispersion of carbon nanotubes in liquids. J Disper Sci Technol 2003;24(1):1–41.
[12] Dalton AB, Collins S, Munoz E, Razal JM, Ebron VH, Ferraris JP, et al. Super-tough carbon-nanotube fibres. Nature 2003;423(6941):703.
[13] Thostenson ET, Chou T-W. Aligned multi-walled carbon nanotube-reinforced composites: processing and mechanical characterization. J Phys D Appl Phys 2002;35:77–80.
[14] Bae J, Jang J, Yoon SH. Cure behaviour of the liquid-crystalline epoxy/carbon nanotube system and the effect of surface treatment of carbon fillers on cure reaction. Macromol Chem Phys 2002;203(15):2196–204.
[15] Liu L, Barber AH, Nuriel S, Wagner HD. Mechanical properties of functionalized carbon nanotube/PVA nanocomposites. Adv Funct Mater 2005;15:975.
[16] Shah SP, Konsta-Gdoutos MS, Metaxa ZS, Mondal P. Nanoscale modification of cementitious materials. In: Bittnar Z, Bartos PJM, Nemecek J, Šmilauer V, Zeman VJ, editors. Proceedings NICOM3 nanotechnology in construction, vol. 3. Bilbao, Spain: Springer-Verlag Berlin Heidelberg Publishers; 2009. p. 125–30.
[17] Luo J, Duan Z, Li H. The influence of surfactants on the processing of multi-walled carbon nanotubes in reinforced cement matrix composites. Phys Status Solidi A 2009;206(12):2783–90.
[18] Li GY, Wang PM, Zhao X. Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes. Carbon 2005;43:1239–45.
[19] Li GY, Wang PM, Zhao X. Pressure-sensitive properties and microstructure of carbon nanotube reinforced cement composites. Cem Concr Compos 2007;29(5):377–82.
[20] Cwirzen A, Habermehl-Cwirzen K, Penttala V. Surface decoration of carbon nanotubes and mechanical properties of cement/carbon nanotube composites. Adv Cem Res 2008;20(2):65–73.
[21] Standards Australia International. AS 3972 Portland and blended cements; 1997.
[22] Standards Australia International. AS1478.1 Chemical admixtures for concrete, mortar and grout. Part 1, Admixtures for concrete; 2000.
[23] Kantro DL. Influence of water reducing admixtures on properties of cement paste – a miniature slump test. Cem Concr Agg 1980;2(2):95–102.
[24] Collins FG, Sanjayan JG. Early age strength and workability of slag pastes activated by NaOH and Na_2CO_3. Cem Concr Res 1998;28(5):655–64.
[25] Liu Y, Barber AH, Sun J. Noncovalent functionalization of carbon nanotubes with sodium lignosulfonate and subsequent quantum dot decoration. J Phys Chem C 2007;111(3):1223–9.
[26] Rixom R, Mailvaganam N. Chemical admixtures handbook for concrete. 3rd ed. London: E & FN Spon; 1999.
[27] Yamada K, Takahashi T, Henahara S, Matsuhira M. Effects of the chemical structure on the properties of polycarboxylate-type superplasticizer. Cem Concr Res 2000;30(2):197–207.
[28] Uchikawa H, Sawaki D, Hanehara S. Influence of kind and added timing organic admixture on the composition, structure and property of fresh cement paste. Cem Concr Res 1995;25(2):353–64.