Quantification of the re-agglomeration of carbon nanofiber aqueous dispersion in cement pastes and effect on the early age flexural response

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Abstract

The effects of the chemical environment of cement composites on the quality and stability of carbon nanofiber (CNF) aqueous dispersion and changes in relative agglomeration state of CNFs from the aqueous solution to the hydrated cement paste were studied. Several dispersion methods and CNF loadings (0.02-1.0% per mass of cement) were examined. Evidence of secondary agglomeration of formerly dispersed CNFs and growth of non-dispersed primary agglomerates in the hydrating and hydrated cement paste was shown, regardless of the dispersion method, dispersing agent to CNF mass ratio, and CNF loading. The polycarboxylate-based high range water reducer (P-HRWR) dispersing agent resulted in a smaller number of large agglomerates ($> 200 \mu\text{m}$) and a smaller agglomerate-to-agglomerate average distance (0.79-0.55 mm for CNF loadings of 0.2-1.0%) when compared to the other DAs ($> 1 \text{ mm}$). The flexural performance of the CNF/cement pastes was influenced by the size and spatial distributions of the CNF agglomerates and the nanoscale reinforcing behavior of the agglomerates. The cement pastes prepared with the P-HRWR and a CNF loading above 0.2% per mass of cement showed improvements in the flexural strength and toughness despite the presence of microscale agglomerates (65% and 125%, respectively at the 1.0% CNF loading).

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1. Introduction

Despite reports of successful preparation of carbon nanofiber/nanotube (CNF/CNT) cement composites [1, 2], controlling the microstructure of such composites to reliably achieve the desired material properties remains a challenge. Widely-differing effects in the composite mechanical and electrical properties have been observed. In some cases, significant improvements were obtained, while in other cases, deterioration of the composite properties were seen [2-6]. The dispersion and distribution of the CNFs/CNTs in the cement matrix is key to the ability to control the properties of the resulting composites. The most common approach to incorporate CNFs/CNTs in cement composites is to first disperse the CNFs/CNTs in the mix water using a cement-compatible water-soluble surfactant with the assistance of ultrasonication and then mix the resulting suspension with the cement powder [2]. Despite much research to disperse CNTs, and to a lesser extent CNFs, in cement-based matrices [2, 3, 5, 7-14], a uniform distribution of the CNTs/CNFs at the individual fiber level throughout the cement matrix has proven difficult. Cement particle size [12, 13] and stability of OH-functionalized CNT dispersions in a calcium hydroxide rich environment [6, 11] have been reported as potential obstacles. Nonetheless, most of the research has focused on the dispersion quality of CNTs/CNFs and optimization of the dispersion process [7, 10, 15-17] in the mix water used to prepare the cement composites. The effect of the chemical environment generated during cement hydration on the stability and homogeneity of the dispersion has, however, been largely ignored. Yet, the stability and homogeneity of the dispersion is key to ensure uniform dispersion within the cement matrix and is expected to be influenced by the pH and ionic composition of the hydrating cement paste. Furthermore, to the best of the authors' knowledge, there has been no effort that directly addresses and quantifies the relation between the dispersion/agglomeration state of the CNFs/CNTs in the mix water and hydrating cement environment and their subsequent final dispersion/agglomeration and arrangement in the hydrated cement paste. A homogeneous dispersion of CNFs/CNTs in the *mix water* may not be a guarantee of a uniform dispersion in the cement matrix [2, 5, 18]. In addition, qualitative indications of the CNF dispersion within the cement paste have varied definitions among different studies. From a meta-analysis, what one study described as 'well' dispersed, another described as a 'moderate' or 'relatively poor' dispersion, while similar mechanical results have been obtained (Table S1). Thus, understanding the behavior of CNFs/CNTs in aqueous environments, including the

hydrating cement environment, and the relationship between the relative dispersion/agglomeration state of CNFs/CNTs in solutions and subsequent behavior in cement composites is critical for the development of reliable CNF/CNT cement composites.

This paper deals with CNFs in Portland cement pastes and reports on the effect of dispersion methods and CNF loading on (i) the disaggregation and relative agglomeration state of CNFs in solutions, including the stability of the dispersion in the highly alkaline environment reflective of cement composites, and (ii) their subsequent agglomeration state and distribution in cement pastes. The early age flexural response of the CNF cement pastes as affected by the CNF dispersion and re-agglomeration process in the cement paste is presented. Early age properties were studied as the addition of carbon nanomaterials has been shown in the literature to accelerate the hydration process and to have a relatively greater influence on the 7-day strength than the 28-day strength [19, 20]. Several approaches to assist dispersion, including surfactants, acid functionalization, ultrasonication, or a combination of these methods, were investigated. A staggered experimental approach was used in which CNF suspensions in the chemical environment developed during cement hydration were first studied to select the dispersion conditions to be employed in the fabrication of the CNF/cement pastes for subsequent characterization and mechanical testing. The relative agglomeration states of CNFs in solutions and cement pastes were assessed macroscopically and microscopically using both qualitative and quantitative analysis. This research provides new insights into the incorporation and mechanical reinforcement of CNFs in hydrated calcium-silicate-based matrices.

2. Experimental

2.1. CNFs and dispersing agents

Commercially available, vapor grown, Pyrograf[®]-III PR-19-LHT CNFs (Applied Sciences, Inc., Cedarville, OH, USA) were used. Per the manufacturer specifications, the CNFs ranged from 70-200 nm in diameter and 30,000 to 100,000 nm in length and had a bulk density of *ca.* 1.95 g/cm³. The CNFs were used as received and after surface treatment with nitric acid (HNO₃). Surface treatment with HNO₃ consisted of the immersion and ultrasonication of the CNFs in 67-70% TraceMetal[™] Grade HNO₃ (Fisher Chemical, Waltham, MA, USA) using a liquid to solid ratio of 28.5 mL/g for a total of three hours. The resulting suspension was repeatedly washed in

deionized water and filtered until the pH of the wash water was neutral. The filtered CNFs were then dried in an oven at 105°C for 24 hours.

Three non-covalent dispersing agents (DAs) were evaluated: a sulfonated naphthalene condensate high-range water reducer (HRWR)–*Rheobuild*[®] 1000 (BASF, Ludwigshafen, Germany); a polycarboxylate-based HRWR–*Glenium*[®] 7500 (BASF, Ludwigshafen, Germany); and an air-entraining admixture–*MicroAir*[®] (BASF, Ludwigshafen, Germany). Although previous investigations have identified the polycarboxylate-based HRWR (P-HRWR) as the most effective for the dispersion of carbon nanomaterials in cement composites, there has been some indication that it might not be adequate to obtain stable dispersions in the chemical environment developed during cement hydration [11, 17]. The different DAs were thus selected for comparison based on their different mechanisms of action and known compatibility with cement hydration [21]. The naphthalene-based HRWR (N-HRWR) is an anionic surfactant that works through electrostatic repulsion by providing particles with a highly negative surface charge through its adsorption onto their surface, causing their mutual repulsion [22]. The polycarboxylate-based HRWR (P-HRWR) is a polymer surfactant that works through a dual mechanism of electrostatic repulsion and steric stabilization in which the long molecules of the organic polymer wrap around the particles to prevent their aggregation by physically precluding them to approach each other [22, 23]. The air-entraining (AE) admixture is a modified resin acid compound-based anionic surfactant that lowers the surface tension of water [21]. HRWR agents are frequently used in concrete technology to improve the workability of cement systems, and AE admixtures are common practice to increase freeze-thaw and scaling resistances. The widely used anionic surfactant, sodium dodecyl benzene sulfonate (SDBS), was not considered as a suitable dispersing agent for the present study because it has been shown in the literature to result in more agglomeration in aqueous solution and lower mechanical properties of the cement paste compared to surfactants similar to the P-HRWR [17] and because of its reported lower dispersive effectiveness for larger diameter CNTs [24].

2.2. Preparation of CNF suspensions

CNF suspensions were prepared to determine the best dispersion conditions with regards to DA type, DA concentration, and sonication time and technique (bath vs. probe sonication) in the chemical environment generated during cement hydration. CNF suspensions were also prepared

to monitor the stability of the dispersions as a function of pH in dynamic conditions close to those obtained during cement mixing.

Effect of DA type. The ability of the different DAs to achieve homogeneous and stable dispersions was evaluated for two types of aqueous environments: (i) a water solution representative of the mix water typically used in the preparation of cement composites – *mix water* and (ii) a solution that simulated the typical chemical environment of hydrating Portland cement pastes – *pore water*. A fixed DA to CNF mass ratio of 5:1 was used based on preliminary results and consistent with the limited data found in the literature that suggested DA to carbon nanomaterial mass ratios ranging from 4:1 [3, 15, 25] to 8:1 [16] for effective dispersion. A total of six (6) *mix water* and four (4) *pore water* suspensions were then prepared (Table 1) with the various DAs and as received or HNO₃ treated CNFs at a concentration of 7.2 g/L. All suspensions were sonicated in a bath sonicator (Aquasonic model 250D, VWR Scientific Products) for 30 minutes to aid in the disaggregation of the CNFs. A mild sonication bath was chosen as it has been reported to be an ideal option for high quality dispersion while avoiding damaging of the CNFs during sonication [26]. The *pore water* solution simulated the pore water of Portland cement pastes at an age of two (2) hours with a composition as reported in [27]. Early cement pore water solution composition (shortly after mixing) was chosen since it represents the environment in which the cement paste is considered to still be in the liquid phase. Occurrence of CNF agglomeration at this stage will most likely remain at later stages of hydration during the hardening process. The simulated *pore water* solution was prepared with Milli-Q water and 20.2 g/L potassium hydroxide (KOH), 1.2 g/L sodium hydroxide (NaOH), and 21.4 g/L calcium sulfate hemihydrate (CaSO₄·½H₂O), resulting in a measured pH and conductivity of ~13.3 and ~43.9 mS/cm, respectively. Results from this study were used to guide investigations of the parameters that were thought to affect CNF dispersion in the chemical environment generated during cement hydration, including DA concentration and sonication time and technique.

Table 1. Carbon nanofiber (CNF) suspensions prepared with different dispersing agents (DAs) using a DA to CNF mass ratio of 5:1 and CNF concentration of 7.2 g/L.

Nanofiber condition	DA type	Mix water (W) suspension	Pore water (PW) suspension
As received	None	W/CNF	PW/CNF
HNO ₃ treated	None	W/T-CNF	---
As received	N-HRWR	W/N-HRWR/CNF	PW/N-HRWR/CNF
As received	AE	W/AE/CNF	PW/AE/CNF
As received	P-HRWR	W/P-HRWR/CNF	PW/P-HRWR/CNF
HNO ₃ treated	P-HRWR	W/P-HRWR/T-CNF	---

Effect of DA concentration. In the case of P-HRWR, the effect of DA to CNF mass ratio on the dispersion quality and stability in the chemical environment generated during cement hydration as simulated by the *pore water* solution was investigated. A total of seven (7) DA to CNF mass ratios (1:1, 3:1, 5:1, 7:1, 10:1, 15:1, and 50:1) were examined. The ratios selected were a function of the CNF concentration and meeting the manufacturer dosage recommendation of a DA to water mass ratio of less than 5% and a DA concentration of about 1% per mass of cement in the fabrication of cement composites. *Pore water* suspensions were prepared with CNF concentrations of 0.7 g/L, 7.2 g/L, and 35.7 g/L. These CNF concentrations were chosen because they effectively corresponded to a low, medium, and high loading of CNFs in cement pastes (i.e., 0.02%, 0.2%, and 1.0% CNFs per mass of cement for cement pastes with a w/c ratio of 0.28). To facilitate visual detection of the dispersion quality, a larger quantity of solution was used at the low CNF concentration. Table 2 summarizes the different DA to CNF mass ratios tested along with the corresponding DA to solution mass ratios associated with each CNF concentration. It should be noted that the design space was a function of the DA-solution-carbon nanomaterial ratio triangle (i.e., DA to carbon nanomaterial, DA to solution, and solution to carbon nanomaterial mass ratios) and was constrained by the amount of DA that could practically be used in cement without affecting the hardening process (i.e., DA to water mass ratio less than 5%). The DA to CNF mass ratios for the dispersion of the CNFs were thus bounded by an upper value, limiting the range of possible DA to CNF mass ratios. Specifically, at high CNF concentrations, only DA to CNF mass ratios lower than 4 could be achieved. All suspensions were sonicated in a bath sonicator (Aquasonic model 250D, VWR Scientific Products) for 30 minutes.

Table 2. Dispersing agent (DA) to CNF mass ratios and corresponding DA to solution mass ratios for different CNF concentrations.

DA/CNF mass ratio	DA/solution mass ratio ^a		
	0.7 g CNF per liter	7.2 g CNF per liter	35.7 g CNF per liter
1:1	0.0007	0.007	0.036
3:1	0.0021	0.021	0.107 ^b
5:1	0.0036	0.036	--- ^b
7:1	0.0050	0.050	--- ^b
10:1	0.0071	0.071 ^b	--- ^b
15:1	0.0110	--- ^b	--- ^b
50:1	0.0360	--- ^b	--- ^b

^a Based on a w/c of 0.28.

^b Significantly higher dose than the manufacturer's recommended limit for use in cement.

Effect of sonication time and technique. The effects of bath sonication time and sonication technique (i.e., indirect sonication vs. direct sonication) on the stability of the CNF suspensions in the *pore water* solution were examined. *Pore water* suspensions of CNFs (7.2 g/L) with different DA amounts (i.e., DA to CNF mass ratios of 1:1, 3:1, 5:1, 7:1, and 10:1) were prepared at three different bath sonication times (i.e., 30 mins, 1 hour, and 2 hours). Probe sonication (direct sonication) was also performed for comparison with bath sonication (indirect sonication) using a 500W probe sonicator (Fisher Scientific Model 505 Sonic Dismembrator) operating at 50% power amplitude with a 20 second pulse for a total time of 15 mins [5, 28].

Effect of cement addition and solution pH. *Mix water* suspensions of CNFs (7.2 g/L) at different DA to CNF mass ratios (i.e., 1:1, 3:1, 5:1, 7:1, and 10:1) were prepared and sonicated in a bath sonicator (Aquasonic model 250D, VWR Scientific Products) for 30 minutes. To account for the dynamic conditions obtained during cement mixing, cement powder was added to the suspensions in 0.34 g increments per 100 mL of suspension to cover a solution pH range from *ca.* 5 (i.e., pH of the *mix water*–DA solution) to 12.5–13 (i.e., pH of cement slurry). The stability of the dispersion as a function of pH was visually monitored.

2.3. Fabrication of CNF/cement pastes

CNF loadings of 0.02%, 0.08%, 0.2%, 0.5%, and 1.0% per mass of cement were used to fabricate the CNF/cement pastes. These loadings were chosen to represent the wide range of CNF concentrations from low to high that has been investigated in the literature. Type I Portland cement (Holcim Inc., Waltham, MA, USA) was used as the cementitious material. A water-to-cement (w/c) ratio of 0.28 was employed to reduce the CNF migration and transport out of the cement paste in the bleed water based on a previous study by the authors [18] that showed that at w/c ratio greater than 0.3, a visible porous layer of agglomerated CNFs was formed at the free surface of the specimens. The different CNF loadings were added to the cement pastes as suspensions of CNFs in *mix water*–DA solutions. A fixed DA to *mix water* mass ratio was used for all mixes to allow for appropriate controls (i.e., same amount of DA) and comparisons across all cement pastes and CNF loadings. The DA to *mix water* mass ratio was selected after the study of aqueous dispersion and to accommodate incorporation of a wide range of CNF loading. Cement pastes with 0.2% as received CNFs per mass of cement were prepared using N-HRWR, P-HRWR, and AE as the DAs for the CNFs. In addition, pastes with 0.2% as received CNFs in water, HNO₃ treated CNFs in water, and HNO₃ treated CNFs in water with P-HRWR were also prepared. Cement pastes with 0.02%, 0.08%, 0.5%, and 1.0% as received CNFs per mass of cement were prepared using only P-HRWR as the DA. Cement pastes with the three different DAs and no CNFs and a cement paste with no DA and no CNFs were used as controls. A total of ten (10) CNF/cement pastes and four (4) control cement pastes were thus prepared (Table S2).

A small multi-speed stand mixer (KitchenAid Artisan 5-quart, Whirlpool Corporation, Benton Charter Township, Michigan, USA) was used for mixing the cement pastes. The cement powder was first poured in the mixer and blended for three minutes. The CNF suspension (or water with and without DAs and no CNFs) was then slowly added to the cement powder, and the resulting mixture was blended for an additional six minutes. The cement pastes were poured into 2.54 cm × 2.54 cm × 68.58 cm (1 in × 1 in × 27 in) beam molds and compacted by hand as mechanical vibration would cause re-agglomeration. The test specimens were then cured at room temperature in 100% relative humidity for 7 days prior to testing. The beams were cut into 11.43 cm (4.5 in) long specimens for flexural strength testing.

2.4. Characterization

2.4.1. Dispersion/agglomeration state in aqueous solutions

The dispersion homogeneity and presence of CNF agglomerates in the different aqueous suspensions were evaluated using a combination of visual observations and optical microscopy analysis. Optical microscopy analysis was selected to quantify dispersion because of its wide use in the literature to characterize CNF/CNT solutions [5, 12, 16, 17] and its ability to characterize solutions containing spherical and non-spherical particles, whereas other methods such as dynamic light scattering have known issues with analyzing solutions with non-spherical particles [29, 30]). In addition, optical microscopy was the only technique whereby a comparison of agglomeration size and shape between aqueous solutions and opaque solid hydrated cement pastes could be made. The stability of all suspensions was visually monitored over time (i.e., immediately, 30 mins, and 3 hours after sonication). Optical microscopy analyses were performed using a Zeiss Axiovert 200M motorized inverted microscope (Carl Zeiss MicroImaging, Inc., Thornwood, NY, USA). Drops of the suspensions were placed on a glass slide and covered with a cover glass for microscopy experiments. Interference of moving particles due to Brownian motion was alleviated by allowing sufficient time for the particles to settle (i.e., 5-10 minutes) and by recording several images of each drop taken at different locations. For each suspension, a minimum of 15 representative drops was examined and 10 representative micrographs were collected for each drop. All images were taken at a magnification of 400X.

ImageJ, a Java-based open source digital image processing software (National Institute of Health, Bethesda, Maryland, USA) was used to analyze the optical micrographs. A minimum of 150 images were analyzed for each CNF suspension. A similar cumulative area of the projected CNF particle system was used for all suspensions, resulting in an investigated total area of *ca.* 1.2 mm² per suspension type. A binary image was created from each micrograph by applying a threshold to the image that was set manually to an appropriate limit. The threshold limit was chosen so that all CNFs present in the image were captured and that background pixels did not interfere with the analysis. After conversion to a binary image, the images were cropped such that all images covered the same area and the interference from the reduced illumination around the edge of the images was eliminated. The agglomeration state of CNFs in each *mix water* solution was then evaluated by plotting the number of CNF particles per mm² areal coverage

versus the area of the projected CNF particles of each area class. The relative size of the CNF agglomerates was determined using the Feret's statistical diameter method, which consists of measuring the distance between two parallel tangential lines of the projection of a three-dimensional object on a 2D plane [31].

2.4.2. Dispersion/agglomeration state in cement pastes

The relative agglomeration state of CNFs in the cement matrix was evaluated through image mapping of the polished surface of representative thin cross-sections of each cement paste. Image mapping was performed on the specimens using the optical mapping tool of a New Wave UP-213 laser ablation system (Electro Scientific Industries, Inc., Portland, Oregon, USA). For each cement paste, a total of 1350 images (27.6×20.6 pixels each) were collected at a 30X magnification and assembled into a single image, which represented the entire cross-section of the specimen. A combination of thresholding techniques and visual inspection was used to create a binary image showing only agglomerates of CNFs in the cement pastes. Careful identification of the agglomerates was performed with adequate checks using SEM and EDS mapping to confirm the presence of carbon. The resulting images were analyzed using the ImageJ software and in-house developed Matlab codes to determine the size distribution, area fraction, and spatial distribution of the CNF agglomerates, and histograms were used to quantitatively assess the relative agglomeration state of the CNFs in each cement paste. The area fraction was defined as the ratio of the area covered by CNF agglomerates to the total area of the cement paste section analyzed. The spatial distribution of the CNF agglomerates in a given cement paste cross-section was generated from the distance to the five closest neighboring CNF agglomerates. A total surface area of *ca.* 6.45 cm^2 was investigated for each cement paste. Only CNF agglomerates of size area greater than 0.007 mm^2 were considered in the analysis due to limitations in the imaging resolution of the optical mapping tool.

2.4.3. Microstructural analysis of CNF/cement pastes

The dispersion and arrangement of the CNFs in the cement pastes was evaluated using a Hitachi S4200 high resolution, scanning electron microscope (SEM) equipped with a cold field emission electron gun, digital imaging, and a thin-window energy dispersive spectrometer (EDS). Fracture surfaces of the 7-day-cured cement pastes were soaked in acetone for at least 7 days to stop further hydration prior to being sputter coated with gold using a deposition time of 100 seconds

and mounted on an aluminum stub using copper tape. For imaging, an accelerating voltage of 20 kV and a working distance of 15 mm were employed.

2.4.4. Mechanical testing

Early age (7 days) flexural properties of the cement pastes were determined by three-point bending using a Tinius Olsen Super L 60K (300 kN) universal testing machine (Tinius Olsen, Inc., Horsham, PA, USA) following modification of ASTM C293 [32]. Per ASTM C293, each beam was turned “on its side with respect to its position as molded” and centered on the support blocks in preparation for testing [32]. The beams were tested in displacement-controlled mode with a displacement rate of 0.1 mm/min. Due to the sensitivity of flexural strength to testing variation [33, 34], particular attention was given to specimen preparation and handling to maintain similar experimental conditions for all cement pastes and allow for internal dataset comparisons. A minimum of five specimens of each cement paste was tested. The load and displacement data were recorded during testing and used to determine the flexural strength, modulus, strain capacity at failure, and flexural toughness. The ultimate strength was determined according to the procedures outlined in ASTM C293, and the strain capacity at failure was determined from the peak load and corresponding strain. The modulus was determined as the slope of the linear portion of the stress-strain curve (R^2 value of 0.995 for a linear fit). The toughness was estimated using the trapezoidal method for estimating the area under the stress-strain curve. The effect of CNF addition on the flexural properties was evaluated relative to controls containing the respective DAs and no CNFs so that any change in mechanical properties could only be attributed to the presence of the CNFs. The Welch’s t-test (unequal variance t-test) was used to test for statistical difference between the means of two data sets of different variances.

3. Results and discussion

3.1. Disaggregation and relative agglomeration state of CNFs in *mix water* solutions

Visual inspection of the aqueous CNF suspensions made with the *mix water* solutions (Fig. 1) indicated a greater ability of the DAs (i.e., N-HRWR, P-HRWR, and AE) to disaggregate the CNFs compared to surface treatment with HNO_3 alone. Though the suspension of HNO_3 treated CNFs showed an improved dispersion over that of as received CNFs with more CNFs in the

solution instead of at the liquid-air interface, it clearly showed a poor dispersion quality with large size agglomerates and poor content uniformity. In contrast, the DAs presented a good overall macroscopic dispersion (i.e., no visibly identifiable agglomerates in solution). The N-HRWR, P-HRWR, and AE assisted suspensions had, however, a dispersion quality that could not be distinguished from each other from sole visual inspection, except for the presence of a thin film of CNF agglomerates observed at the surface of the N-HRWR assisted suspension and a layer of foam with CNF agglomerates at the surface of the AE assisted suspension.

Fig. 1. Dispersion state of CNFs in *mix water* with different dispersing agents (DAs) and as received or surface treated CNFs: (a) Polycarboxylate-based HRWR and as received CNFs, (b) polycarboxylate-based HRWR and HNO_3 treated CNFs, (c) naphthalene-based HRWR and as received CNFs, (d) air entraining admixture and as received CNFs, (e) no dispersing agent and as received CNFs, and (f) no dispersing agent and HNO_3 treated CNFs. Suspensions prepared with a DA to CNF mass ratio of 5:1 and a CNF concentration of 7.2 g/L.

Differences in CNF relative agglomeration state when the DAs were used were revealed from optical microscopy investigations (Fig. 2). The largest number of CNF particles per mm^2 in the smallest size area class ($< 100 \mu\text{m}^2$) was seen for the P-HRWR assisted CNF suspension, indicating a greater ability of the P-HRWR to prevent large particles from forming and/or break up a larger number of bigger particles into smaller particles than the N-HRWR and AE. The dual effect of electrostatic repulsion and steric hindrance of the P-HRWR with the non-covalent wrapping of macromolecules around the CNFs provided a greater reduction of CNF aggregation

and yielded an overall better dispersion compared to the single mechanisms of electrostatic repulsion (i.e., N-HRWR) and lowering of surface tension (i.e., AE). Surface treatment with HNO_3 further improved the CNF dispersion in the P-HRWR assisted CNF *mix water* suspension as evidenced by the greater number of particles per mm^2 in the smallest size area class ($< 100 \mu\text{m}^2$) compared to that with the as received CNFs. A similar result for surface-treated CNTs was reported in [17]. The HNO_3 surface treatment was thought to further reduce CNF agglomeration by enhancing interfacial wettability with P-HRWR through the presence of hydroxyl and carboxylic groups. The N-HRWR assisted CNF suspension showed the highest frequency of relatively large size agglomerates ($> 500 \mu\text{m}^2$) and the lowest number of particles per mm^2 in the smallest size area class ($< 100 \mu\text{m}^2$), indicating that N-HRWR was not as effective in the disaggregation of large agglomerates as the other DAs. The AE decreased CNF aggregative tendency in water but not as well as the P-HRWR. For all CNF suspensions, the number of particles in the smallest size area class ($< 100 \mu\text{m}^2$) was at least one order of magnitude greater compared to the other size area classes. The largest agglomerate size was seen for the AE and N-HRWR assisted CNF suspensions ($\sim 25,000 \mu\text{m}^2$) and was twice the maximum size seen for the P-HRWR assisted CNF suspensions. All DA assisted CNF *mix water* suspensions remained stable over a two (2) week period.

a W/P-HRWR/T-CNF

b W/P-HRWR/CNF

c W/N-HRWR/CNF

Fig. 2. Optical micrographs (400X) and histograms of the number of CNF particles per mm² areal coverage versus the area of the projected CNF particles of each area class showing the agglomeration state of CNFs in *mix water* suspensions. (a) Polycarboxylate-based HRWR assisted suspension of HNO₃ treated CNFs, (b) polycarboxylate-based HRWR assisted suspension of as received CNFs, (c) naphthalene-based HRWR assisted suspension of as received CNFs, and (d) air entraining admixture assisted suspension of as received CNFs (greyscale threshold values used for segmentation are found in Table S3).

3.2. Disaggregation and relative agglomeration state of CNFs in *pore water* solutions

Effect of DA type. Visual inspection immediately after ultrasonication showed all *pore water* CNF suspensions prepared with the various DAs to be uniformly dispersed at the macroscopic level (Fig. 3). The *pore water* suspensions prepared with no DA showed, in contrast, a separated layer of unwetted CNFs at the liquid-air interface immediately after sonication that persisted for the entire monitoring time period with no significant change seen in the amount of settling during the first thirty (30) minutes (as seen in Fig. 3d from little change in the solution color from 0 to 30 minutes). Thirty (30) minutes after ultrasonication, separation of the CNFs from the solution was, however, seen in all suspensions containing DAs. The separation was less in the suspension that contained P-HRWR with a large number of CNFs still suspended in the solution. This was no longer the case after three (3) hours as most CNFs had separated from the solutions, even for the P-HRWR assisted suspension.

Fig. 3. Dispersion state and stability of CNF suspensions in *pore water* with different dispersing agents (DAs): (a) Polycarboxylate-based HRWR, (b) naphthalene-based HRWR, (c) air entraining admixture, and (d) no DA. Suspensions prepared with a DA to CNF mass ratio of 5:1 and as received CNFs at a concentration of 7.2 g/L. [From left to right: immediately, 30 minutes, and 3 hours after ultrasonication].

Further investigations of the P-HRWR assisted *pore water* CNF suspension immediately after ultrasonication using optical microscopy revealed a clear decrease in CNF dispersion when compared to the P-HRWR assisted *mix water* CNF suspension (Fig. 5). The presence of larger agglomerates and overall less CNFs were seen in the micrographs of the *pore water* CNF suspension due to separation of the CNFs from the solution. For the P-HRWR assisted *pore water* CNF suspension, a greater percentage of the cumulative area of CNFs were made up of particles with a larger Feret's diameter compared to that of the P-HRWR assisted *mix water* CNF suspension (Fig. 5). The instability of the *pore water* CNF suspensions was thought to be the result of the combined effect of the highly alkaline conditions, high ionic strength, and ionic composition of the simulated cement *pore water* environment [35-37] that can aggregate the

otherwise stabilized CNFs. A schematic representation of the mechanisms of destabilization of the CNF dispersion in the cement pore water environment is shown in Fig. 4 for the P-HRWR DA. The presence of cationic ions with high concentration and high valence, as in the case of the simulated *pore water* solution, has been shown in the literature to destabilize CNT suspensions [37]. Changes in electrostatic interaction (P-HRWR and N-HRWR) and surface tension (AE) can in part account for the differences seen in the stability of the CNF suspensions in the *pore water* solution environment. The presence of cationic ions in the *pore water* solution altered the electrostatic layer surrounding the CNFs in the P-HRWR and N-HRWR assisted suspensions, allowing the CNFs to come into contact or within the distance in which the van der Waals forces are dominant, thus leading to the re-formation of microscale CNF agglomerates. Divalent cations may also cause bridging between P-HRWR molecules, further disrupting the P-HRWR availability for dispersion. During the first 30 minutes, the steric hindrance provided by the P-HRWR dispersing agent was minimally affected by the presence of electrolytes [38], allowing some of the CNFs to remain suspended in solution. The effect of the steric hindrance, however, dissipated after 3 hours. The long-term stability of sterically stabilized suspensions has been shown in the literature to be affected in the presence of electrolytes and calcium-containing media [39, 40]. For the AE assisted dispersion, the ions present in the simulated cement *pore water* were thought to increase the surface tension of the solution [41], thus negating the effect of the AE.

Fig. 4. Schematic representation of the mechanisms of destabilization of the CNF dispersion in the cement pore water environment for the P-HRWR DA.

Fig. 5. (a) and (b) Optical micrographs (400X) of the polycarboxylate-based HRWR assisted *mix water* and *pore water* CNF suspensions, immediately after ultrasonication. (c) Comparison of the cumulative area of CNFs as a function of the maximum Feret's diameter of the CNF agglomerates found in the polycarboxylate-based HRWR assisted *mix water* and *pore water* CNF suspensions (greyscale threshold values used for segmentation are found in Table S3).

Effect of DA to CNF mass ratio. Separation of the CNFs from the *pore water* solution was seen at all DA to CNF mass ratios investigated. Increasing the DA concentration did not improve the stability of the *pore water* suspensions for any of the three CNF concentrations examined (Figure S1). CNF agglomerates of sufficient size for the Brownian forces to be overcome by gravitational forces were formed, resulting in agglomerates that fell to the bottom of the suspension (i.e., agglomerates denser than the suspending solution). In all cases, sedimentation of the CNFs towards the bottom of the suspension was observed within the first 30 mins after sonication. This fact indicated that the DA to CNF mass ratio was not a critical parameter with regards to the stability of the *pore water* suspensions. This, furthermore, inferred that the DA to

CNF mass ratio cannot be used as the only parameter of the quality of CNF dispersion in cement composites.

Effect of bath sonication time and sonication technique. The stability of the *pore water* suspension was assessed by visual inspection of agglomerate formation. Increasing bath sonication time did not prevent the separation of the CNFs from the *pore water* solution. In all cases, the suspension settled down during or immediately after sonication, resulting in an inhomogeneous solution with considerable sedimentation towards the bottom of the container (Figure S2). Instability of the suspensions was observed at all three bath sonication times evaluated. The use of probe sonication did not improve the stability of the *pore water* suspensions. All probe sonicated suspensions exhibited separation of the CNFs from the solution. A bath sonication time of 30 mins was thus chosen for subsequent preparation of the CNF cement composites since longer sonication times and use of probe sonication did not result in further improvement of the suspension stability.

3.3. Effect of cement addition on the stability of CNF dispersion in *mix water*

A decrease in dispersion quality of the CNF *mix water* suspensions was observed with increasing cement addition. Formation of CNF agglomerates and separation of the CNFs from the solution were seen when the suspension pH reached a value of *ca.* 11 and above (Fig. 6). This result agreed with the literature, where a decrease in dispersion as a function of increasing pH has been reported for CNTs [11, 42]. The settling rate of the CNF suspensions was fast and independent of the DA to CNF mass ratio used (see Figure S3 for time lapse video showing the destabilization of a CNF suspension as a function of pH), indicating that any benefit of the DA was severely compromised at high pH. Similar results for CNTs in $\text{Ca}(\text{OH})_2$ solutions with and without superplasticizer as DA have been reported in the literature [11] at pH above 11. These results clearly demonstrated the negative effect of the alkaline environment of hydrating cement on the homogeneity and stability of the CNF dispersion. Furthermore, these results inferred that homogeneous dispersion in the mix water is not a guarantee of subsequent effective dispersion in the cement matrix (i.e. individually embedded CNFs that have a uniform spatial distribution) as formation of CNF agglomerates and sedimentation occurred almost immediately in dynamic conditions close to the ones obtained during cement mixing.

3.4. Selection of dispersion conditions for CNF/cement paste fabrication

While the *mix water* study indicated that the P-HRWR was the most effective in disaggregating CNFs and maintaining the stability of the CNF dispersion, the *pore water* and cement addition studies revealed instability of the CNF suspensions in the chemical environment generated during cement hydration where there was formation of large agglomerates and sedimentation regardless of the DA type, DA to CNF mass ratio, or sonication time and technique used. Based on these results, the impact of the DA on CNF agglomeration in cement paste was still unknown. Cement pastes were thus prepared using all DAs and the same CNF loading (0.2%) to investigate the effect of the suspension instability on the relative agglomeration state of the CNFs within the cement pastes. Cement pastes were also prepared for the P-HRWR at different CNF loadings (0.02%, 0.08%, 0.2%, 0.5%, and 1.0%) to study the effect of the distribution of the CNF agglomerates on the mechanical properties of the material. To allow for appropriate controls (i.e., same amount of DA) and comparisons across all cement pastes and CNF loadings, the amounts of DA, *mix water*, and cement were kept constant so that the CNF loading was the only independent variable. Therefore, a fixed DA to *mix water* mass ratio of 0.036 that accommodated incorporation of a wide range of CNF loading was used, resulting in DA to CNF mass ratios of 50.4, 12.6, 5.0, 2.0, and 1.0 for CNF loadings of 0.02%, 0.08%, 0.2%, 0.5% and 1.0%, respectively.

Fig. 6. Effect of cement addition on the stability of CNF dispersion in *mix water* solution. Suspensions prepared with various DA to CNF mass ratios (1:1, 3:1, 5:1, 7:1, and 10:1) and as received CNFs at a concentration of 7.2 g/L (see Figure S3 for time lapse video showing destabilization of a CNF suspension as a function of pH).

3.5. Relative agglomeration state and distribution of CNFs in cement pastes

The dispersion state of CNFs in the cement paste depended upon the scale of evaluation and included the disaggregation of CNF agglomerates at the individual CNF level (nanoscopic dispersion) and the uniform distribution of individual CNFs and their agglomerates throughout the cement matrix (micro- and macroscopic dispersion). Both CNF agglomerates and individual fiber level CNFs were found in all cement pastes. The CNF agglomerates could be clearly identified visually or with the aid of an optical microscope over each cement paste cross-section as shown in Fig. 7 and confirmed by SEM/EDS analysis (see Figure S4 for additional SEM images). The agglomerates were of varied size and shape and were randomly distributed within the cement matrix. SEM investigations further revealed that the spatial distribution of the individual CNFs was not uniform within the cement pastes with the presence of CNF rich and CNF poor regions (Fig. 8). The non-uniform spatial distribution of the individual CNFs was seen for all dispersion methods and CNF loadings used. The large size and clumping of cement grains have been reported in the literature [5] to be responsible for the non-uniform dispersion of the CNFs by creating zones absent of CNFs even after hydration has progressed.

Fig. 7. CNF agglomerates in a representative cement paste cross section. (a) optical microscope image (b) SEM backscatter electron image, and (c) EDS map for carbon.

Fig. 8. Scanning electron micrographs showing a non-uniform distribution of CNFs within the cement matrix with CNF rich and CNF poor regions representative to all CNF loadings. Cement pastes prepared with the P-HRWR assisted *mix water* CNF suspension (shown for 1.0% CNFs per mass of cement).

Secondary agglomeration and density gradients. The microscale CNF agglomerates were seen regardless of the initial degree of CNF dispersion in the *mix water* suspensions (Fig. 9) and became more prominent with increasing CNF loading (Fig. 10). Larger size agglomerates (as much as an order of magnitude greater) than what was observed in the CNF *mix water* suspensions were seen in all cement pastes as a result of the growth of non-dispersed primary agglomerates and secondary agglomeration of formerly dispersed CNFs after cement mixing. For the cement pastes prepared with the P-HRWR, N-HRWR, and AE assisted *mix water* suspensions, more than 40% of the CNF agglomerates observed at the surface of representative cement paste cross-sections had a size area greater than the maximum size observed in the *mix water* suspensions. Agglomerate growth and secondary agglomeration occurred regardless of the dispersion method and CNF loading.

a Cement paste prepared with W/P-HRWR/T-CNF

b Cement paste prepared with W/P-HRWR/CNF

c Cement paste prepared with W/N-HRWR/CNF

Fig. 9. Binary images of the 2-D distribution of CNF agglomerates and corresponding relative frequency histograms of size area of CNF agglomerates for cement pastes prepared with 0.2% (per mass) CNFs added as (a) polycarboxylate-based HRWR assisted *mix water* suspension of as received CNFs, (b) polycarboxylate-based HRWR assisted *mix water* suspension of HNO₃ treated CNFs, (c) naphthalene-based HRWR assisted *mix water* suspension of as received CNFs, and (d) air entraining admixture assisted *mix water* suspension of as received CNFs.

Fig. 10. Binary images of the 2-D distribution of CNF agglomerates for cement pastes prepared with the P-HRWR assisted *mix water* suspension of as received CNFs showing the distribution of CNF agglomerates of size area greater than 0.007 mm² and average area fraction of CNF agglomerates. Density gradient of CNF agglomerates seen for 0.2 % and 0.5 % CNFs.

Furthermore, the cement pastes prepared with the P-HRWR assisted *mix water* suspension showed a density gradient of CNF agglomerates at low CNF loadings (less than 0.5% per mass of cement), with a greater number of agglomerates at the specimen top surface (as poured) (Fig.

10). Migration of the CNFs within the cement paste has been previously reported by the authors for higher w/c ratios [18] and occurred with the bleed water during the initial stage of curing before hardening. The CNF agglomerates tended to locate themselves to minimize their surface tension, concentrating during curing at the top surface of the specimens (i.e., liquid-air interface). The density gradient was predominant at CNF additions less than 0.5% but not present for a CNF addition of 1.0%, most likely as a result of changes in the paste rheological properties. A lower paste workability was observed upon addition of 1.0% CNFs per mass of cement. While the lower workability did not affect casting, it resulted in lower water movement during curing. Migration of the CNFs was not observed for the other cement pastes, including the cement pastes prepared with the N-HRWR and AE assisted *mix water* suspensions and that prepared with CNFs in water. Since similar workability (not measured) was observed in all cases with 0.2% CNF loading, it was thought that, in the case of the P-HRWR, the CNFs remained as individual fibers and in smaller size agglomerates for longer periods of time, allowing easier movement through the developing pore network at low CNF loadings.

The instability of the CNF suspensions in the highly alkaline environment of hydrating cement pastes and the migration of the CNFs with the bleed water during the initial stage of curing increased the probability of CNF re-agglomeration within the cement matrix. The combined effect of the high pH (13.5-13.8 [43]), ionic strength (0.3-0.7 mol/L [43]), and ionic composition (Ca^{2+} , OH^- , Na^+ , K^+) of the hydrating cement paste affected the mechanisms of action of the different DAs. The electrostatic stabilization of the N-HRWR assisted *mixed water* suspension was altered by the ions present in the hydrating cement environment [35-37], leading to re-agglomeration of the CNFs within the cement paste – similar to what was observed in the *pore water* suspensions. Though electrosteric stabilized suspensions are less sensitive to electrolytes than electrostatically stabilized suspensions [38], the re-agglomeration observed in the cement pastes prepared with the P-HRWR assisted *mix water* suspension was believed to be the result of the complex interplay between electrostatic and steric effects and a potential decrease in the thickness of the sterically-stabilizing “hairy” layer on exposure to the alkaline environment and mechanical mixing [44]. Consequently, the steric hindrance imposed by the P-HRWR on the CNFs became practically nonexistent, resulting in CNF re-agglomeration. Surface treatment of the CNFs with HNO_3 did not prevent secondary agglomeration. The presence of

ions in the hydrating cement paste most likely increased the surface tension of the AE assisted *mix water* suspension, resulting in re-agglomeration of the CNFs within the cement paste.

Agglomerate size and spatial distribution. While agglomeration was observed in all cement pastes, the cement pastes prepared with the AE and N-HRWR assisted *mix water* suspensions exhibited a greater relative frequency of large size agglomerates than that prepared with the P-HRWR assisted *mix water* suspension, as evidenced from the frequency distribution of maximum Feret's diameters (Fig. 11). For the cement pastes prepared with the AE and N-HRWR assisted *mix water* suspensions, as much as 78% and 64%, respectively, of the CNF agglomerates observed at the surface of representative cement paste cross-sections had a maximum Feret's diameter greater than 200 μm vs. 58% and 57% for the cement pastes prepared with the P-HRWR assisted *mix water* suspensions of as received and HNO_3 treated CNFs, respectively. In comparison, the cement pastes prepared with the *mix water* suspensions with no DA and as received CNFs or CNFs surface treated with HNO_3 showed 62% and 76%, respectively, of the CNF agglomerates with a maximum Feret's diameter greater than 200 μm . The use of HNO_3 surface treatment alone (i.e., with no dispersing agent) favored larger scale agglomeration of the CNFs in the cement paste compared to the as-received CNFs. The alkaline medium of the cement environment (i.e. high pH) led to deprotonation of the carboxylic groups (i.e. formation of COO^-), which provided electrostatic interactions favorable for adsorbing cationic species, destabilizing the CNF dispersion and leading to the formation of larger agglomerates in the cement paste. This result was consistent with that reported in the literature for functionalized CNTs in the presence of $\text{Ca}(\text{OH})_2$ [7]. However, when HNO_3 surface treatment was used in combination with the P-HRWR dispersing agent, the relative frequency of large size agglomerates present in the cement paste cross-section was not affected because of the increased interfacial wettability of the CNFs with P-HRWR.

Fig. 11. Relative frequency histograms of maximum Feret's diameter of CNF agglomerates of representative cement paste sections prepared with CNFs added as (a) polycarboxylate-based HRWR assisted *mix water* suspension of as received CNFs, (b) polycarboxylate-based HRWR assisted *mix water* suspension of HNO₃ treated CNFs, (c) naphthalene-based HRWR assisted *mix water* suspension of as received CNFs, (d) air entraining admixture assisted *mix water* suspension of as received CNFs, (e) as received CNFs in water, and (f) HNO₃ treated CNFs in water.

As with a greater relative frequency of smaller size agglomerates (100-200 μm), the cement pastes prepared with the P-HRWR assisted *mix water* suspensions presented a smaller agglomerate-to-agglomerate average distance and a more homogeneous (i.e., narrower) spatial distribution of the CNF agglomerates (Fig. 12). The cement pastes prepared with the AE assisted *mix water* suspension and CNFs in water with no DA showed, in contrast, the greatest agglomerate-to-agglomerate average distance and the widest spatial distribution of the CNF agglomerates. Increased CNF loading resulted in an increase in the area fraction and size of the

CNF agglomerates (Fig. 10 and Fig. 11), a decrease in agglomerate-to-agglomerate average distance, and a more homogeneous (i.e., narrower) spatial distribution of the CNF agglomerates (Fig. 13).

Fig. 12. Effect of the dispersion method on the 2-D spatial distribution of CNF agglomerates for cement pastes prepared with 0.2% (per mass) CNFs added as (a) polycarboxylate-based HRWR assisted *mix water* suspension of as received CNFs, (b) polycarboxylate-based HRWR assisted *mix water* suspension of HNO₃ treated CNFs, (c) naphthalene-based HRWR assisted *mix water* suspension of as received CNFs, and (d) air entraining admixture assisted *mix water* suspension of as received CNFs.

Fig. 13. Effect of CNF loading on the 2-D spatial distribution of CNF agglomerates for cement pastes prepared with the P-HRWR assisted *mix water* suspension of as received CNFs. (a) 0.2%, (b) 0.5%, and (c) 1.0% CNFs per mass of cement.

These results clearly demonstrated that the dispersion state of CNFs in solution was not indicative of the final dispersion state in the hydrated cement paste and provided evidence of secondary agglomeration of formerly dispersed CNFs and growth of non-dispersed primary agglomerates within the cement matrix. The final state of dispersion of the CNFs within the cement paste was the complex result of a competition between (i) the tendency of CNFs to migrate towards each other or existing agglomerates due to Brownian motion and van der Waals interactions during cement mixing and the initial stage of curing, (ii) the influence of the high ionic strength, pH, and ionic composition of the cement paste medium on altering the surface properties of the CNFs, resulting in greater propensity for loss of individual CNFs and rebundling/agglomeration, and (iii) the effect of mechanical mixing, further increasing the probability of CNF agglomerates or individual CNFs to come in contact with each other. The size of the CNF agglomerates was a balance of agglomerate growth and destruction.

3.6. Early age flexural response of CNF/cement pastes and agglomeration state relationship

A close relationship existed between the relative agglomeration state of the CNFs within the cement matrix and the flexural response of the CNF/cement pastes. The presence of CNF agglomerates resulting from non-dispersed primary agglomerates and secondary agglomerates formed during cement mixing and curing limited the ability of the CNFs to act as nano-reinforcements. The paste reinforcement was mostly dominated by the collective behavior of the CNF agglomerates rather than the strength of the individual CNFs. The size and spatial distributions of the CNF agglomerates and the nanoscale reinforcing behavior of the agglomerates (i.e. collective behavior) were found to influence the flexural performance of the CNF/cement pastes. The reinforcing behavior of the agglomerated CNFs was a mix of the common reinforcing behavior seen for macroscale non-continuous fibers (i.e. pull-out and crack bridging) and that seen for aggregates (i.e. crack deflection). This behavior was consistent with that reported in the literature for bundled CNTs [45]. Reduction in aspect ratio, presence of voids, and presence of non-wetted surface of CNFs as a result of agglomeration were thought to be important factors in the failure mechanisms of the CNF/cement pastes.

Fig. 14 presents the 7-day flexural strength results of cement pastes prepared with 0.2% CNFs as affected by the dispersion methods. Only the cement pastes prepared with the P-HRWR assisted *mix water* CNF suspension showed improvement in the 7-day flexural strength (Welch's t-test, Table 3) with an increase in the median value of *ca.* 11% for the P-HRWR/as received CNFs and *ca.* 22% for the P-HRWR/HNO₃ treated CNFs. However, there was no statistical difference (p-value of 0.644, Welch's t-test) in the 7-day flexural strength of these two cement pastes, indicating that surface treatment with HNO₃ did not provide additional mechanical benefit. The cement pastes prepared with the other DA assisted *mix water* suspensions showed no statistically significant changes at the 95% confidence level in the 7-day flexural strength with respect to their control (Table 3). The gain in flexural strength seen for the pastes prepared with the P-HRWR assisted *mix water* CNF suspension was attributed to having the smallest percentage of large micrometer scale agglomerates (i.e., less than 30% with a size greater than 300 μm) and the greatest percentage of small micrometer scale agglomerates (i.e., more than 40% with a size ranging 100-200 μm) along with a smaller agglomerate-to-agglomerate average distance and a more homogeneous (i.e., narrower) spatial distribution of the CNF agglomerates. The presence of a greater percentage of small size agglomerates was thought to result in more

interfacing with the cement matrix, potentially allowing a more efficient stress transfer mechanism than the larger agglomerates. In contrast, the larger agglomerates acted as flaws within the cement matrix, causing non-uniform stress distributions and high stresses near the agglomerates, which weakened the cement paste. This behavior was exacerbated when a significant number of large size agglomerates (i.e., more than 30% with a size greater than 300 μm) was present, as in the cement pastes prepared with the CNF suspensions with no DA and that prepared with the N-HRWR and AE assisted *mix water* CNF suspensions, causing the mechanical behavior of the agglomerates to outweigh the potential benefit of the individual CNFs.

Fig. 14. Effect of the dispersion method on the 7-day flexural strength of cement pastes prepared with (a) polycarboxylate-based HRWR assisted *mix water* suspension of as received and HNO₃ treated CNFs, (b) naphthalene-based HRWR assisted *mix water* suspension of as received CNFs, (c) air entraining admixture assisted *mix water* suspension of as received CNFs, and (d) as received and HNO₃ treated CNFs in *mix water* with no dispersing agent (DA). Cement pastes with each DA and no CNFs were used as controls.

Table 3. Analysis of the 7-day flexural strength results for the cement pastes prepared with 0.2% (per mass) CNFs using different dispersing agents (DAs) with respect to the control cement pastes.

Nanofiber dispersion method	P-value (Welch's t-test)	Min increase ^a (%)	Max increase ^b (%)	% increase ^c (median value)
W/P-HRWR/CNF	0.039	---	63.0 ^d	11.0 ^d
W/P-HRWR/T-CNF	2.6×10 ⁻⁴	10.5 ^d	44.5 ^d	22.0 ^d
W/N-HRWR/CNF	0.910	n.s. ^e	n.s. ^e	n.s. ^e
W/AE/CNF	0.077	n.s. ^e	n.s. ^e	n.s. ^e
W/CNF	0.083	n.s. ^e	n.s. ^e	n.s. ^e
W/T-CNF	0.312	n.s. ^e	n.s. ^e	n.s. ^e

^a (min value - max value for control)/max value for control

^b (max value - min value for control)/min value for control

^c (median value - median value for control)/median value for control

^d significant at 95% confidence (Welch's t-test; P-value ≤ 0.050)

^e non-significant at 95% confidence (Welch's t-test)

The 7-day flexural strength of the cement pastes prepared with the P-HRWR assisted *mix water* CNF suspension increased with increasing CNF loading above 0.2% (Fig. 15). In contrast, the low percent of CNFs (i.e., 0.02% and 0.08%) were not high enough to generate a statistically significant effect on the flexural strength. The addition of 0.5% and 1.0% CNFs resulted in *ca.* 35% and *ca.* 65% increase, respectively, in the median peak stress at the 95% confidence level (Welch's t-test, Table 4). While increasing the CNF loading from 0.5 to 1.0% did not affect significantly the area fraction of CNF agglomerates (i.e., 3.2% vs. 3.9%) and number of large size agglomerates (i.e., *ca.* 42% vs. *ca.* 39% with size greater than 300 μm) present in the cement pastes, it did, however, result in a significant gain in the flexural strength (i.e., *ca.* 85% gain). The smaller agglomerate-to-agglomerate average distance and more homogeneous (i.e., narrower) spatial distribution of the CNF agglomerates observed with the 1.0% CNF loading (Fig. 13) along with the presence of a greater effective fraction of individual CNFs in the paste with increased CNF addition were thought to have positively impacted the paste's flexural behavior. However, the analysis of the relative agglomeration state of the CNFs did not provide information about the fraction of individual CNFs that was effectively dispersed.

Fig. 15. Effect of CNF loading on the 7-day flexural properties of the cement pastes prepared with the P-HRWR assisted *mix water* CNF suspension. (a) Strength, (b) toughness, (c) modulus, and (d) strain capacity.

Table 4. Analysis of 7-day flexural strength results for the cement pastes prepared with the P-HRWR assisted *mix water* suspension and different CNF loadings with respect to the control cement paste.

CNF (%)	Strength		Toughness		Modulus		Strain capacity	
	P-value	% increase ^a	P-value	% increase ^a	P-value	% increase ^a	P-value	% increase ^a
0.02	0.057	n.s. ^b	0.589	n.s. ^b	0.034	30.4	0.531	n.s. ^b
0.08	0.061	n.s. ^b	0.084	n.s. ^b	0.406	n.s. ^b	0.336	n.s. ^b
0.20	0.039	11.1 ^c	0.657	n.s. ^b	0.038	24.6 ^c	0.277	n.s. ^b
0.50	3.7×10^{-6}	35.4 ^c	0.009	41.3 ^c	0.019	29.5 ^c	0.912	n.s. ^b
1.00	5.2×10^{-8}	65.9 ^c	1.2×10^{-4}	124 ^c	0.079	n.s. ^b	0.079	n.s. ^b

^a (median value – median value for control)/median value for control

^b non-significant at 95% confidence (Welch's t-test)

^c significant at 95% confidence (Welch's t-test; P-value ≤ 0.050)

As with the strength, an improvement in the flexural toughness represented by the area under the stress-strain curve was observed upon addition of 0.5% and 1.0% CNFs with an increase in the median value of *ca.* 42% and *ca.* 125% beyond that of the control, respectively (Table 4). In contrast, the addition of CNFs had limited and inconsistent effect on the flexural modulus, which was in agreement with the flexural properties being in part dominated by the agglomerate behavior rather than the individual CNFs, thus limiting the stiffening effect of the CNFs. Additionally, no statistically significant changes at the 95% confidence level were observed in the cement paste strain capacity at any CNF loading, suggesting a weak interaction between the CNFs and the cement matrix. A closer inspection of the fracture surface of the cement pastes revealed that, upon failure, most of the individual CNFs were pulled out from the other wall of the cement matrix rather than broken apart with no evidence of cement phases covering the surface of the protruding CNFs. Holes and grooves left by fiber pull out and CNFs pulled out from a microcrack can be seen in Fig. 16. The tensile stresses created during the mechanical testing simply slid the CNFs from the cement matrix. As a result, the full strength of the individual CNFs could not be used, and the efficiency of the load transfer from the cement matrix to the fibers was reduced. The problem of bond strength between CNFs and the cement matrix has been reported by others [5].

Fig. 16. Scanning electron micrographs showing evidence of fiber pull out in cement pastes prepared with the P-HRWR assisted *mix water* CNF suspension (shown for 0.5% CNFs per mass of cement). Representative to all CNF loadings. (a) Holes left by CNF pull out (white circles), (b) grooves from CNF pull-out, and (c) CNF pulled out at microcrack. Cement paste prepared with the P-HRWR assisted *mix water* suspension

4. Conclusions

For the first time, the effects of the chemical environment reflective of cement composites on the quality and stability of CNF dispersion in aqueous solutions have been investigated and changes in relative agglomeration state of CNFs from the aqueous solution to the hydrated cement paste were studied and quantified. The results clearly demonstrated that the dispersion state of the CNFs in solution was not indicative of the final dispersion state in the hydrated cement paste and that the current strategy commonly employed for dispersing CNFs in cement composites cannot ensure uniform dispersion of the CNFs in the cement matrix and typically results in the formation of large agglomerates. The results furthermore provided evidence that mechanical testing is not a good indicator of the dispersion state of the CNFs in the cement pastes as increases in flexural strength were seen even with the presence of large agglomerates. While the P-HRWR DA provided the most improvement in the disaggregation of the CNFs in the *mix*

water suspensions, instability of the CNF suspensions in the hydrating cement paste environment was seen regardless of the DA type, DA to CNF mass ratio, or sonication time and technique used. For all CNF/cement pastes, evidence of secondary agglomeration of formerly dispersed CNFs and growth of non-dispersed primary agglomerates was shown irrespective of the dispersion method and CNF loading. The size and spatial distributions of the CNF agglomerates were, however, affected by the DA type and CNF loading. The P-HRWR DA resulted overall in a smaller number of large agglomerates (greater than 200 μm) and a smaller agglomerate-to-agglomerate average distance when compared to the other DAs. For the P-HRWR DA, increased CNF loading resulted in a more homogeneous spatial distribution and a decrease in the agglomerate-to-agglomerate average distance. The size and spatial distributions of the CNF agglomerates, including the agglomerate-to-agglomerate average distance, influenced the early age flexural response of the CNF/cement pastes, and the ability to homogeneously disperse the CNF agglomerates within the cement matrix appeared to be a key factor in the optimization of the paste flexural properties.

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