

# Dispersion of multi-walled carbon nanotubes and its effects on the properties of cement composites

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In this study, two types of multi-walled carbon nanotubes (pristine, p-CNT and functionalized, f-CNT) were dispersed in water by sonication and then added to cement mortar. The purpose of this study was to characterize the dispersion degree of the CNTs in aqueous suspension and to investigate whether achieving dispersion in water would also result in dispersion inside mortar. Dispersion of the CNTs in water was investigated by means of UV-vis spectroscopy, using different CNT concentrations and sonication durations. Dispersion of the CNTs in cement mortar was investigated by measuring the compressive and flexural strength and fracture toughness as well as the microstructural characterizations of scanning electron microscopy and mercury intrusion porosimetry. The effects of the CNT addition on drying shrinkage and cement hydration were also investigated for cement pastes. The results of UV-vis spectroscopy showed that by increasing the sonication time to 120 min, the dispersion degree of the f-CNT suspension increased progressively, while for p-CNT, a maximum was reached with 60 min of sonication. The compressive and flexural strength and fracture toughness of mortars containing f- and p-CNTs were not significantly improved either by increasing the amount of CNT or imposing sonication in mixing water. High CNT dispersion in cement matrix was not equally obtained by utilizing highly dispersed CNT suspension. Sonication of f- and p-CNT led to a remarkable deceleration of cement hydration in the first hour of hydration and drying shrinkage of the cement composites was found to be reduced by f- and p-CNT addition.

*Keywords:* Carbon nanotube, Fracture toughness, Heat of hydration, Pore analysis, Sonication, UV-vis spectroscopy

## 1. Introduction

Multi-walled carbon nanotubes (CNT) are carbon ordered structure and have unique mechanical properties. Young's modulus is estimated to be as high as 0.45 TPa and their tensile strength may reach 3.6 GPa [1]. Because of these outstanding mechanical properties, addition of CNTs as reinforcement to cementitious materials can potentially improve their properties and has received much interest among researchers.

Pristine CNTs are insoluble in water and are hydrophobic which causes difficulties for dispersion in water. Agglomeration of CNTs originates from several causes. Due to their nano-scale diameter, the surface area of CNTs as well as the surface attraction between CNTs is high. Dispersion difficulties also stem from the CNT

propensity to form bundles that are tightly bound by high van der Waals forces. In addition, the high CNT aspect ratio (length/diameter) combined with their flexibility causes highly entangled agglomerates in liquid phases. Incorporation of CNTs into cement also confronts two main challenges: bonding and dispersion. Strong bonding between CNTs and the cement matrix as well as effective dispersion of CNTs is essential for an effective load-transfer to the CNTs which may act as reinforcement to improve mechanical properties of cement composites. It is also believed that if bonding between CNTs and the cement matrix can be controlled, the CNTs can provide substantial mechanical reinforcement [2] and can thus bridge microcracks and improve the ability of the cement composite to withstand fracture. Conversely, agglomeration of CNT inside cementitious materials could function as a local defect and might be detrimental to the reinforcing role of CNTs. A combination of physical (sonication) and chemical (surfactant usage) dispersion methods is the most recommended way to exfoliate CNT agglomerates in mixing water of cement composites [3]. Surfactants not only aid with exfoliation of CNT bundles, but may also play a role in

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bonding with the cement matrix. Li et al. [4] claim that interfacial interactions between surface-modified CNTs and hydration products will produce high bonding strength, and increase the load-transfer efficiency from the cement matrix to the reinforcement.

Although sonication provides an efficient way to suspend CNTs in aqueous media, it is always related to a certain degree of damage on CNT surfaces [5] and may also cause rupture to shorten CNTs. An optimum sonication duration and, correspondingly, delivered ultrasound power to a unit volume of suspension is introduced as a compromise between the dispersion degree and the level of damage to CNT surfaces. There is still an open question concerning the optimum sonication duration, that leads to the best performance of CNT incorporation into cement composites from the aspect of mechanical properties. CNTs have been dispersed in mixing water by sonication for widely varying durations, from a few minutes [6–9] to a few hours [4,10–12]; investigation of its optimum, however, has received less attention.

To date, many researchers have applied combinations of dispersion with different surfactants followed by sonication to fabricate cement composites containing CNTs, but have obtained conflicting results. Many works, for instance [4,7,10,13–17], reported improvement, while other studies [8,12,18–21] reported a lack of improvement in the mechanical properties of CNT-containing cement composites. The scatter of the results implies that dispersion of CNTs in aqueous suspensions could be reached by usage of surfactant and sonication, but effective dispersion of CNTs in the cement matrix could not necessarily be guaranteed. It is likely that CNTs randomly re-agglomerated after mixing with solid phase (cement and aggregates). A systematic investigation of this CNT re-agglomeration after mixing with cement is presently lacking in the literature. A study is needed to shed light on the re-agglomeration concept by characterizing the degree of dispersion of CNTs in the mixing water and in the cement matrix of cement composites.

Green [22] outlined several methods for characterization of CNT dispersion in suspensions: AFM (most commonly used), Cryo-TEM and UV–vis spectroscopy (as a bulk method). Prior data by Paredes et al. [23] showed that for a sonicated and surfactant-stabilized CNT suspension, as characterized by AFM, dispersion up to very high extent could be reached. Regarding dispersion in cement composites, Yazdanbakhsh et al. [24] suggested that even if nano-objects (e.g. CNTs) are well dispersed in the mixing water, geometry dependent clustering would still prevent their uniform dispersion in cementitious materials. Some researchers [2,3] believe that high dispersion of CNTs inside cement composites mostly influence flexural strength and toughness rather than compressive strength, thus mechanical testing could be an indirect way to characterize CNT dispersion inside cement composites.

In this study, suspensions containing pristine or functionalized CNTs were sonicated for various durations and were used for dispersion characterization via UV–vis spectroscopy. Then, they were used as mixing water for cement composites, where verification of the effective CNT dispersion was performed by mechanical testing. The compressive and flexural strength of mortars containing various CNT contents (of both types) was evaluated and the optimum content, having the highest compressive and flexural strength, was determined. Then, the optimum sonication duration for both CNT types, which resulted in the highest strength, and the optimum CNT content were determined to fabricate specimens for fracture toughness and drying shrinkage tests. In addition, the effects of CNTs on the kinetics of early stage hydration of cement were studied by isothermal calorimetry. Porosity analysis and morphology observation were performed on fragments collected from the specimens to provide further information of the microstructure of cement composites.

## 2. Materials and experimental methods

Ordinary portland cement CEM I 42.5R was used in this study and two types of commercial multi-walled carbon nanotubes were used: pristine (labelled p-CNT) and functionalized (labelled f-CNT). The specifications of p-CNT and f-CNT are presented in Table 1. Standard silica sand with minimum and maximum particle sizes of 0.08 mm and 2 mm and distilled water were used for composite mixtures.

### 2.1. Characterization of CNT dispersion

Individual carbon nanotubes are active in the ultraviolet–visible (UV–vis) region and show characteristic bands in a wavelength range of 200–1200 nm, with a characteristic peak, in this study at 260 nm, while CNT bundles are not active in this range [5,25–27]. It is therefore possible to detect exfoliation of CNT in aqueous media due to the dispersion process by measuring UV–vis absorbance spectra for CNT suspensions in relation to individual CNT concentration by the Beer-Lambert law. According to Beer-Lambert's law, the absorbance  $A$  in a certain wavelength for a suspension is proportional to the concentration of individual CNTs in the suspension:

$$A = -\log(I/I_0) = \epsilon \cdot c \cdot d, \quad (1)$$

where  $\epsilon$  (in  $\text{cm}^2 \text{g}^{-1}$ ) is a material specific extinction coefficient for the specific wavelength,  $c$  is the concentration of individual CNTs,  $d$  is the thickness of the substance exposed to the UV light, and  $I$  and  $I_0$  are the transmitted and incident intensity of radiation (for the specific wavelength), respectively. Accordingly, the observed UV–vis spectra absorbance in the characteristic bands increases with the increasing CNT dispersion degree in aqueous suspension. The characterization of CNT dispersion was performed by comparing the absorbance of each CNT suspension with and without functional groups and with varying sonication duration.

CNTs of both types p and f were added at two contents of 0.22% and 0.45% by mass, into 70 ml of distilled water and manually mixed. The mixture was sonicated by a probe sonicator (Ultrasonic Homogenizer, model JY92-IIN, Ningbo Scientz Biotechnology Co.) with a 6 mm cylindrical tip and the power was set to deliver 1 W for 1 ml of the suspension. A suitable vessel was employed to fulfil requirements given by the sonicator manufacturer regarding the location of the tip between the surface of water and the bottom of the vessel. The sonicator was setup to deliver ultrasonic energy for 3 s followed by 3 s clearance to avoid heating up the suspension. During sonication no agitation or magnetic stirrer was employed and at predefined time intervals (0, 30, 60, and 120 min, corresponding to energy delivery of 0, 1800, 3600 and 7200  $\text{W ml}^{-1}$  (W for each ml of suspension), 1 ml of the suspension was taken and diluted by a factor of 1:40 with distilled water and tested by UV–vis spectroscopy. The tested substances therefore had nominal CNT concentrations of 0.0055% and 0.011% by water mass.

**Table 1**  
Properties of MWCNTs.

| Parameter             | Unit                  | Pristine MWCNT | Functionalized MWCNT |
|-----------------------|-----------------------|----------------|----------------------|
| Outer diameter        | nm                    | 10–20          | 10–20                |
| Length                | $\mu\text{m}$         | 10–30          | 10–30                |
| Purity                | wt%                   | >95            | >95                  |
| Ash                   | wt%                   | <1.5           | <1.5                 |
| Specific surface area | $\text{m}^2/\text{g}$ | >200           | >200                 |
| -COOH content         | wt%                   | 0              | 2                    |
| Designation           | –                     | p-CNT          | f-CNT                |

## 2.2. Specimen casting

Mortar specimens of  $40 \times 40 \times 160$  mm were cast with water/cement ratio 0.45 and sand/cement ratio of 3 for compressive and flexural strength and fracture toughness tests. The compositions of mortar mixtures are presented in Table 2. To study the optimum content of f- and p-CNT, typical CNT concentrations in mortar ranged over 0.1% by mass of cement i.e. 0, 0.044, 0.088, 0.1, 0.2 and 0.3% were added to the whole mixture water and manually stirred together with superplasticizer and then were used for casting. To investigate the effectiveness of the dispersion method on the CNT state inside the mortar, samples containing 0.044% and 0.088% of f- and p-CNT by mass of cement were examined for compressive and flexural strength. CNTs were dispersed inside samples by a similar dispersion method to that of the UV-vis test. These concentrations were chosen to conform to their counterparts used for the UV-vis test with CNT contents of 0.22 and 0.45% by mass of water. The dispersion method was sonication of f- and p-CNT for 30, 60, and 120 min to conform to that of section 3.1. For drying shrinkage,  $25 \times 25 \times 285$  mm paste samples containing 0.1% f-CNT with and without 30 min sonication and containing 0.3% p-CNT were cast.

The samples for which sonication of water containing CNTs was carried out were cast by the same procedure but CNTs were added to a portion of the water (100 g), exposed to ultrasonic waves and added to the rest of the water mixture and superplasticizer.

## 2.3. Test procedures

The compressive and flexural strength tests were performed according to ASTM C 349 and ASTM C 348 standards, respectively.

Fracture toughness testing was performed according to the Two Parameter Fracture Model (TPFM) of Jenq and Shah [28] by a three points bending test of a notched beam, to evaluate the effect of both CNT types and the effect of the dispersed (sonicated) CNT suspension on the capability of the cement composite to withstand fracture. Load versus crack mouth opening displacement (CMOD) data on half-depth notch at mid span were recorded. Young's modulus, ( $E$ ), critical stress intensity factor at the tip of effective crack, ( $K_{Ic}^S$ ), and critical crack tip opening displacement, ( $CTOD_c$ ), were determined utilizing the below formulas for a quasi-brittle material:

$$E = \frac{6Sa V(a/h)}{C_i t h^2} \quad (2)$$

$$K_{Ic}^S = \frac{6P_{max} S}{4t h^2} \sqrt{\pi a_c} F(\alpha) \quad (3)$$

$$CTOD_c = \frac{6P_{max} S a_c V(\alpha)}{t h^2 E} \times \sqrt{(1 - a/a_c)^2 + [1.081 - 1.149(\alpha)] [a/a_c - (a/a_c)^2]} \quad (4)$$

$$\alpha = a_c/h \quad (5)$$

$$a_c = \frac{a C_u V(a/h)}{C_i V(a_c/h)} \quad (6)$$

where  $t$ ,  $h$  and  $S$  are depth, height and span of the sample;  $a$  is the depth of the notch;  $P_{max}$  is maximum load;  $a_c$  is effective elastic critical crack length; and  $C_i$ ,  $C_u$  are initial compliance and secant compliance, respectively, which were calculated with the method adopted from Refs. [29,30]. Geometric factors for the three points

bending of notched beam have been provided by Tada et al. [31]:

$$V(\alpha) = 0.76 - 2.28\alpha + 3.87\alpha^2 - 2.04\alpha^3 + \frac{0.66}{(1 - \alpha)^2} \quad (7)$$

$$F(\alpha) = \left[ \frac{1}{\sqrt{\pi}} \frac{1.99 - \alpha(1 - \alpha)(2.15 - 3.93\alpha + 2.7\alpha^2)}{(1 + 2\alpha)(1 - \alpha)^{1.5}} \right] \quad (8)$$

The machine's crosshead displacement rate of 0.15 mm/min was chosen in order that the maximum load could be reached within 30–60 s, and the data sampling frequency was 200 Hz.

All the samples were demoulded the day after casting and cured in a curing chamber with 95% relative humidity and 23 °C temperature for 28 days. Some fragments were randomly collected from broken samples from the compressive strength test and oven dried for mercury intrusion porosimetry (MIP) tests.

Effects of CNTs on the early hydration reaction of OPC were also investigated using isothermal calorimetry. Water suspensions containing 0.1% of f-CNT, 0.3% of p-CNT and suspensions sonicated for 30 min were added to cement with  $w/c = 0.45$  and the hydration heat was recorded for 48 h.

The drying shrinkage test was carried out according to ASTM C490/C490 M standard on cement pastes, since shrinkage is more pronounced in cement paste than mortar. Having enough strength, the samples were demoulded 18 h after casting and exposed in a climatic chamber to  $50 \pm 4\%$  relative humidity and  $23 \pm 2^\circ$  C temperature.

All the tests were conducted on three replicates except for the compressive strength test (6 replicates) and an average value was reported.

Morphology observations were carried out by environmental scanning electron microscopy on oven dried and gold sputtered fragments of paste with a high CNT content (0.3%) after curing for three days so that the MWCNTs were not completely wrapped by hydration products of cement and thus become clearer for observation.

## 3. Results and discussions

### 3.1. Characterization of CNT dispersion in aqueous suspension

Fig. 1 shows the time evolution of absorbance ( $A$ ) of UV-vis spectra of solutions with concentrations of 0.0055% and 0.011% of functionalized (a,b) and pristine (c,d) CNTs, which were sampled and diluted from reference solutions of 0.22% and 0.45% in water. According to the figure, increasing sonication time corresponds to an increasing degree of dispersion, thus increasing of UV-vis absorbance spectra for CNT-containing solutions. The highest degree of exfoliation was obtained after 120 min of sonication for both concentrations of f-CNT, while for p-CNT it was obtained after 60 min of sonication for both concentrations. The difference in magnitude of absorbance values between f- and p-type CNT is noticeable, and it represents the effect of the surfactant in dispersion. The  $A$  values for p-type are all lower than 0.1 even for 60 min sonication, while those of f-type are above 0.1. The presence of the surfactant alone in f-CNT was effective to disperse CNT to some extent; however, a high degree of dispersion was obtained after combination of surfactant and sonication.

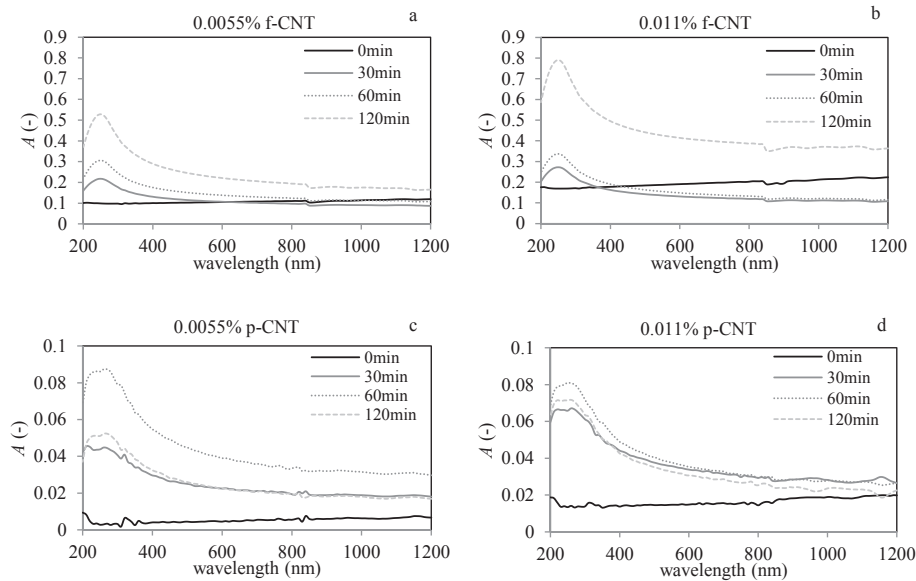
### 3.2. Mechanical properties

Fig. 2 reports compressive and flexural strength of mortars containing f- and p-CNT up to 0.3% without sonication. Shaded areas show the variation of the control sample (CO), i.e., for

**Table 2**

Compositions of the mortar mixtures.

| Designation | w/c  | CNT (%) | CNT type | Composition ( $\text{kg m}^{-3}$ ) |       |      |      |                   | Sonication time (min) |
|-------------|------|---------|----------|------------------------------------|-------|------|------|-------------------|-----------------------|
|             |      |         |          | Cement                             | Water | Sand | CNT  | Super-plasticizer |                       |
| C0          | 0.45 | 0       | —        | 512                                | 230   | 1548 | 0    | 2                 | —                     |
| C04         |      | 0.044   | p,f      |                                    |       |      | 0.23 |                   | 0,30,60,120           |
| C08         |      | 0.088   | p,f      |                                    |       |      | 0.45 |                   | 0,30,60,120           |
| C1          |      | 0.1     | p,f      |                                    |       |      | 0.51 |                   | 0,30                  |
| C2          |      | 0.2     | p,f      |                                    |       |      | 1.02 |                   | —                     |
| C3          |      | 0.3     | p        |                                    |       |      | 1.54 |                   | —                     |

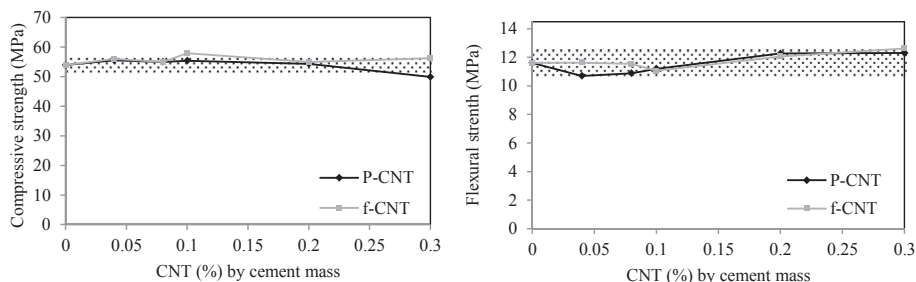


**Fig. 1.** UV absorbance ( $A$ ) versus wavelength for different sonication durations 0, 30, 60, 120 min correspond to different energy delivery of 0, 1800, 3600 and 7200  $\text{W mL}^{-1}$ . Different concentrations of (a,b) f-CNT and (b,d) p-CNT suspension with 0.0055 and 0.011% wt by water, sampled from solution with CNT concentration of 0.22% and 0.45%, respectively, are shown.

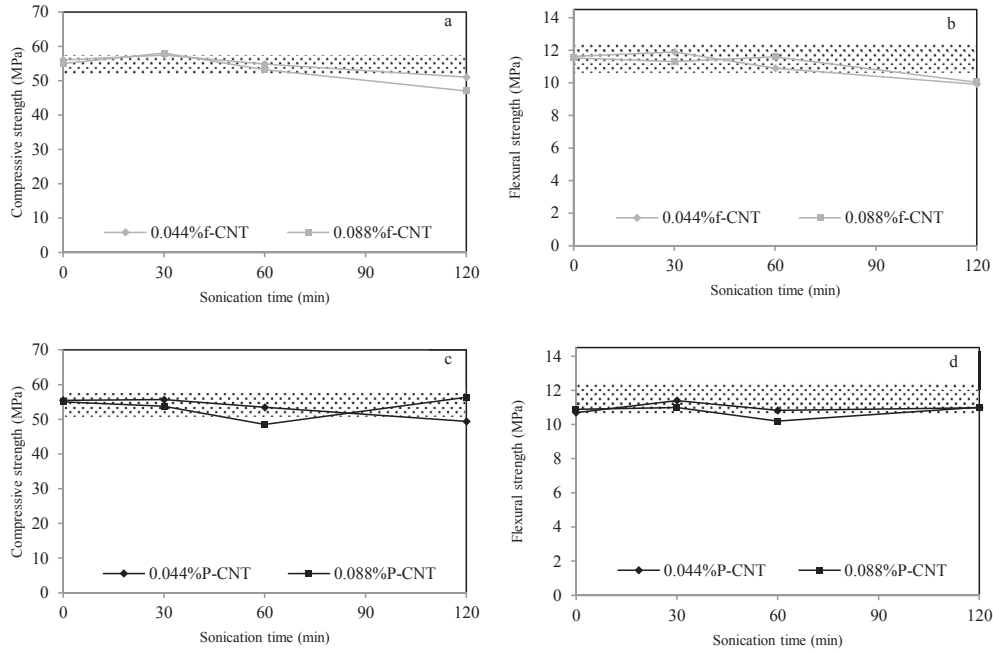
compressive strength  $53.9 \pm 2.6$  MPa and for flexural strength  $11.6 \pm 0.9$  MPa. The optimum flexural strength was reached at 0.3% of p-CNT and compressive strength at 0.1% f-CNT; however, the enhancements were fairly small, i.e., 7.5% and 6% for f- and p-CNT, respectively. These results suggest no appreciable influence of f- and p-CNT on the mechanical strength of mortars.

The compressive and flexural strength of mortar samples in which 0.044% and 0.088% by cement mass of f- and p-CNT was dispersed by the same procedure as their counterparts in section 3.1 are shown in Fig. 3. The shaded region is the control sample variation. For p-CNT, although limited dispersion in aqueous solution was obtained by sonication for 60 min (see section 3.1), the compressive and flexural strength did not considerably change by

increasing the sonication time. In contrast to the p-CNT samples, a slight improvement (6.5% with respect to control) in the compressive strength of mortar containing f-CNTs sonicated for 30 min and a small reduction of compressive and flexural strength for f-CNT after 120 min sonication at both dosages was seen, while the highest degree of dispersion was obtained by 120 min sonication for both dosages according to UV-vis spectroscopy results. Long sonication duration results in a reduction of CNT strength that is more severe in f-CNTs than p-CNTs since, by their nature, f-CNTs contain more structural defects on their surface due to their production method. The reinforcing role of f-CNT, then, may be alleviated by 120 min sonication despite its higher degree of dispersion in aqueous media. After all, the usage of f-CNT sonicated by 30 min



**Fig. 2.** Compressive and flexural strength of mortars containing different amounts of CNT by weight of cement. The shaded area is the variation of control sample (C0).



**Fig. 3.** Compressive and flexural strength of mortars containing 0.044% and 0.088% wt of cement versus sonication duration. (a,b) f-CNTs and (c,d) p-CNTs were used for the mixtures. Shaded area is variation of control specimen's results without CNT.

was considered the most effective CNT dispersion state inside cement composites and was thereafter used in fracture toughness and drying shrinkage tests.

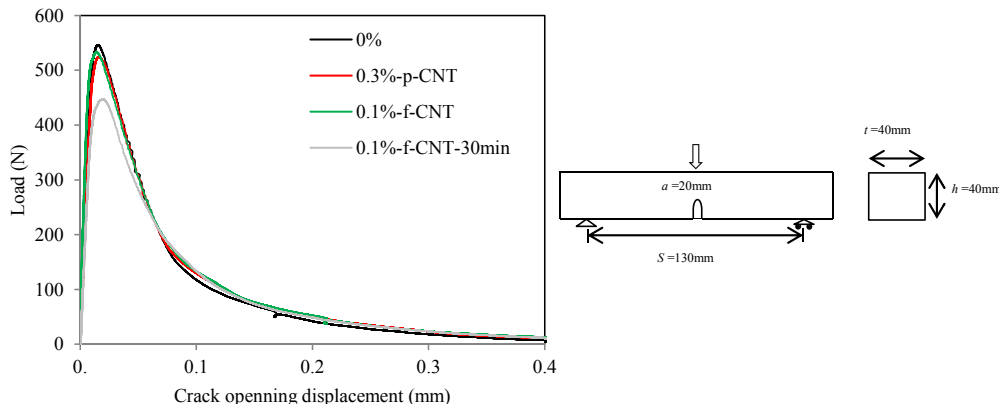
Fracture toughness samples were fabricated by selected contents, i.e., 0.1% and 0.3% for f- and p-CNT, respectively. The f-CNTs were also dispersed by 30 min sonication as the most effective sonication duration inside cement mortar. Typical load-displacement curves are shown in Fig. 4 and the average and standard deviation of  $E$ ,  $K_{IC}^S$  and  $CTOD_C$  parameters were then calculated and tabulated in Table 3. To aid investigation of the effects of CNT and its dispersion on the fracture toughness behaviour of mortars, the effect of adding f- and p-CNT is considered first, and then the effect of sonication will be discussed.

According to Table 3 by adding f- and p-CNT into mortar,  $E$  values increased to some extent compared to reference; however the differences were within standard deviations. Similar results were also obtained by Stynoski et al. [2], who enumerated several possible sources of error for high variance of  $E$ . The elastic modulus was calculated by the linear elastic fracture mechanics method,

which is sensitive to small changes in specimen sizes. Given the high deviation of  $E$  values and low count of the samples, the increase in  $E$ , as a consequence, could not be considered an effect of CNT addition nor an effect of CNT dispersion.

The  $K_{IC}^S$  and  $CTOD_C$  parameters did not exhibit any considerable change with respect to reference after addition of f- and p-CNT, with respect to standard deviations. In contrast, some studies have reported enhancement of fracture toughness of cement paste [9,19] and mortar [12] by CNT addition. Comparing the average  $K_{IC}^S$  and  $CTOD_C$  of C1-30 min with C1, a slight reduction due to sonication of mixing water can be observed. This reduction, however, remained within the standard deviation. The sonication probably caused breakage and shortening of CNTs, thus the crack bridging effect of CNTs might be mitigated. In addition, CNT agglomerates can act as local defects in the matrix and could be responsible for the lack of improvement in compressive strength, flexural strength and fracture toughness of mortar upon their addition.

No improvement of mechanical properties of mortar was observed as a consequence of better dispersion of CNTs in the



**Fig. 4.** Typical load-displacement curve of fracture toughness test of mortars and a schematic of notched samples dimensions.



**Table 3**

Maximum load, elastic modulus,  $E$ , fracture toughness at the tip of effective crack,  $K_{IC}^S$  and critical crack tip opening displacement,  $CTOD_c$ , for different mortars containing CNT. The values are average of three samples with their standard deviation.

| Designation | CNT (%) | CNT type | Sonication time (min) | Maximum load (N)   | $E$ (GPa)       | $K_{IC}^S$ (MPa m <sup>0.5</sup> ) | $CTOD_c$ ( $\mu$ m) |
|-------------|---------|----------|-----------------------|--------------------|-----------------|------------------------------------|---------------------|
| C0          | 0       | —        | —                     | 543.18 $\pm$ 3.96  | 32.5 $\pm$ 2.3  | 0.705 $\pm$ 0.045                  | 4.51 $\pm$ 0.68     |
| C3          | 0.3     | p        | —                     | 548.86 $\pm$ 44.83 | 38.4 $\pm$ 5.5  | 0.715 $\pm$ 0.034                  | 3.83 $\pm$ 0.32     |
| C1          | 0.1     | f        | —                     | 515.01 $\pm$ 33.50 | 44.4 $\pm$ 10.2 | 0.788 $\pm$ 0.098                  | 5.14 $\pm$ 1.25     |
| C1-30min    | 0.1     | f        | 30                    | 462.45 $\pm$ 48.23 | 36.1 $\pm$ 9.4  | 0.703 $\pm$ 0.181                  | 4.99 $\pm$ 0.96     |

mixing water. High CNT dispersion in the cement matrix was not equivalently obtained utilizing highly dispersed CNT suspensions likely because of re-agglomeration after mixing with cement. Yazdanbakhsh et al. [32] have also reported that despite good CNT dispersion in aqueous solution, uniform distribution in cement matrix could not be obtained. The severity of re-agglomeration after mixing with cement with varies many factors such as: CNT specifications, the dispersion technique and casting method and could be the possible explanation for disagreements on the capability of CNTs to improve mechanical properties of cement composites. To clarify re-agglomeration of CNT immediately after mixing with cement, CNT effects on early cement hydration were studied.

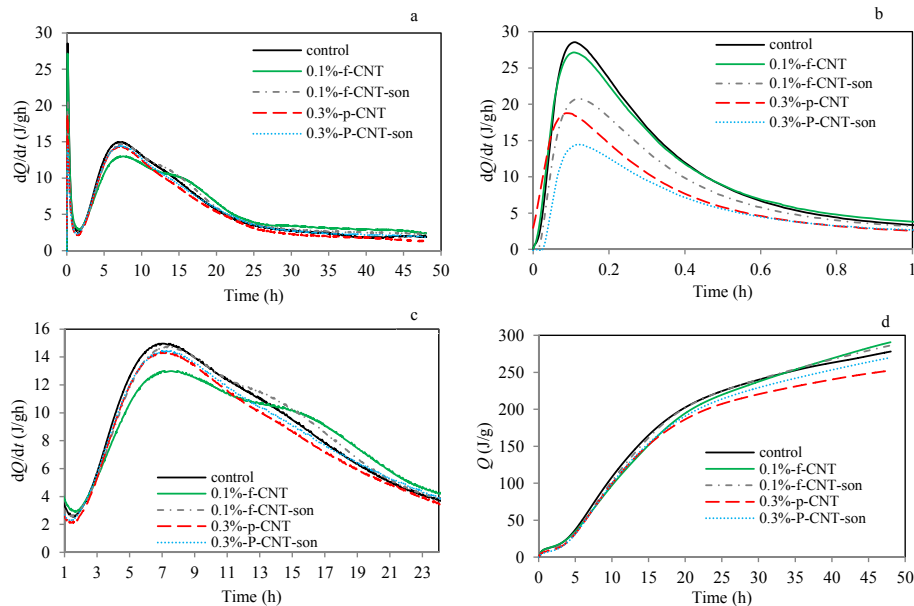
### 3.3. Isothermal calorimetry of cement pastes

It is believed that CNTs have a relevant effect on the early age dissolution and nucleation kinetics of cementitious systems [2,33]. Hence, the amount of heat released in the very early stage of hydration of cement paste containing CNTs was evaluated by isothermal calorimetry. Typical variations of heat flow  $dQ/dt$  per unit weight of cement ( $J (g h)^{-1}$ ) measured with isothermal calorimetry during 48 h of hydration are shown in Fig. 5 from the time when the dry cement came into contact with the aqueous suspension. The curves exhibited typical peaks of cement hydration: the first peak, which is associated with initial hydration at the surface of the cement grains mainly involving tricalcium aluminate ( $C_3A$ ) during the first hour of hydration (Fig. 5b), and the second peak, which is associated with hydration of tricalcium silicate ( $C_3S$ ),

i.e., fairly slowly from 1 to 24 h of hydration (Fig. 5c). Cumulative hydration heat curves up to 48 h are presented in Fig. 5d and the values for each time interval are summarized with their variation in Table 4 for comparison.

From Fig. 5b, 0.3% p-CNT hindered the  $C_3A$  hydration since the associated peak decreased with respect to the control specimens and the addition of f-CNT did not significantly decrease the  $C_3A$  hydration rate. Comparing C1 with C1-30 min and C3 with C3-30 min, sonication of the suspensions containing p- and f-CNT decelerated the hydration of  $C_3A$  and resulted in a reduction of the heat produced with respect to the samples without sonication. The cumulative heat for sample C3 with 30 min sonication decreased remarkably by 43.4% with respect to the control (see Table 4). The most plausible explanation for the reduction of produced heat is that CNT agglomeration around the cement grains hindered  $C_3A$  hydration. CNTs could re-agglomerate around the cement grain, prohibiting dissolution of cement grains and ettringite formation. The re-agglomeration might also restrain the number of extra sites for nucleation of C-S-H in the very early hydration stage. The hindering effect became more pronounced when the suspension was sonicated for 30 min suggesting a more severe re-agglomeration of dispersed CNT around the grains. Similar CNT effects on the first hour of hydration reaction of cement have been obtained by other studies [33,34].

The heat flow curves of Fig. 5c indicate that the peak amplitude decreased with 0.1% f-CNT. The amount of heat released for the time interval from 3 to 24 h (Table 4) decreased by 3% and 6.4% for 0.1% f-CNT and 0.3% p-CNT, respectively, with respect to the reference paste. Eventually, the cumulative hydration heat released up



**Fig. 5.** Heat flow curves of the plain pastes and pastes containing p-CNT, f-CNT and 30 min sonicated samples for: (a) 0–48 h, (b) 0–1 h, (c) 1–24 h, and (d) cumulative heat curves for 48 h hydration.

**Table 4**

Summary of cumulative heat of hydration of the pastes containing p- and f-CNT. The values in parentheses are variations with respect to control.

| Specimen             | CNT (%) | CNT type | Cumulative heat ( $\text{J g}^{-1}$ ) |                  |                  |
|----------------------|---------|----------|---------------------------------------|------------------|------------------|
|                      |         |          | From 0 to 1 (h)                       | From 3 to 24 (h) | From 0 to 48 (h) |
| Control              | 0       | —        | 11.3                                  | 203              | 278.2            |
| C1                   | 0.1     | f        | 11.3                                  | 197 (-3%)        | 290.7 (+4.5%)    |
| C1-30 min sonication | 0.1     | f        | 9 (-20.3%)                            | 205 (+1%)        | 286.4 (+3%)      |
| C3                   | 0.3     | p        | 7.8 (-31%)                            | 190 (-6.4%)      | 252.5 (-9.2%)    |
| C3-30 min sonication | 0.3     | p        | 6.4 (-43.4%)                          | 197 (-3%)        | 269.8 (-3%)      |

to 48 h (see Fig. 5d and Table 4) decreased by 9.2% for 0.3% p-CNT addition with respect to the control sample, while after 30 min sonication decreased only by 3%. It seems that increasing dispersion of p-CNT hindered cement hydration in the first hour but then favoured the hydration up to 48 h with respect to no sonication.

### 3.4. Porosity and pore size distribution

Total porosity volume (%) and median pore size of the mortar mixtures are shown in Table 5. The total porosity decreased from 15.2% for the control to 13.2% for C1 and to 11.1% for C08-120 min. The relationship between pore volume and porosity size is shown in Fig. 6a and c in which  $V$  and  $D$  are pore volume and size. The higher the value of  $dV/d\log D$ , the higher the pore volume fraction related to certain pore sizes with respect to total porosity volume. A distinction should be made between micro- and macro-capillary

porosity, i.e., pores smaller and larger than 50 nm, respectively. The volume of the macropores in the range of 50–100 nm decreased after addition of f- and p-CNT to mortar with respect to the control. Regarding the diameter of the CNTs (theoretically 10–20 nm, see Table 1), the results suggest that bundles of 3–5 NTs reduced the volume of those macropores. The porosity distributions of mixtures are presented in Fig. 6b and d. Comparing C08 with C08-120 min and C04 with C04-120 min, pore sizes lower than 50 nm clearly decreased when a CNT suspension was sonicated for 120 min before casting. This reduction indicates that individual CNTs reduced the micropore volumes suggesting that limited dispersion of CNT in cement composite was obtained by the dispersion method.

Porosity analysis allows discussion of the lack of improvement in mechanical strength in mortars cast with highly dispersed CNT suspensions. Mechanical strength is affected by both micro- and

**Table 5**

Porosity of the mortars.

| Designation      | CNT % | Type | Porosity (%) | Median pore diameter (nm) | Total intrusion volume ( $\text{ml g}^{-1}$ ) |
|------------------|-------|------|--------------|---------------------------|---|
| C0               | 0     | —    | 15.16        | 103.1                     | 0.071   |
| C08              | 0.088 | p    | 12.99        | 94.7                      | 0.060   |
| C08-120 min son. | 0.088 | p    | 11.09        | 84.1                      | 0.051   |
| C3               | 0.3   | p    | 15.66        | 107                       | 0.075   |
| C04              | 0.044 | f    | 14.67        | 131.8                     | 0.069   |
| C04-120 min son. | 0.044 | f    | 13.61        | 120.6                     | 0.063   |
| C1               | 0.1   | f    | 13.22        | 105.8                     | 0.061   |

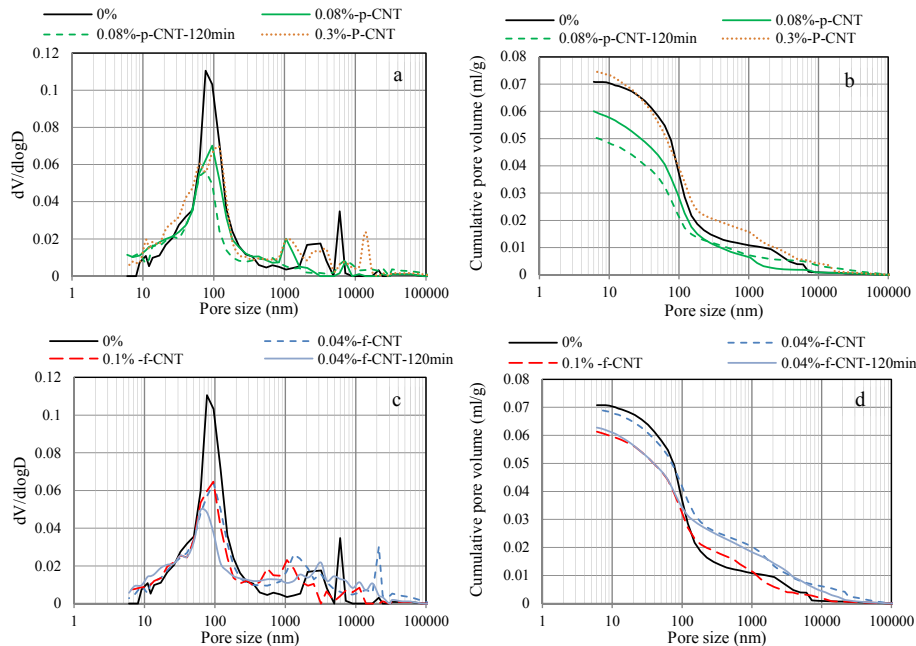
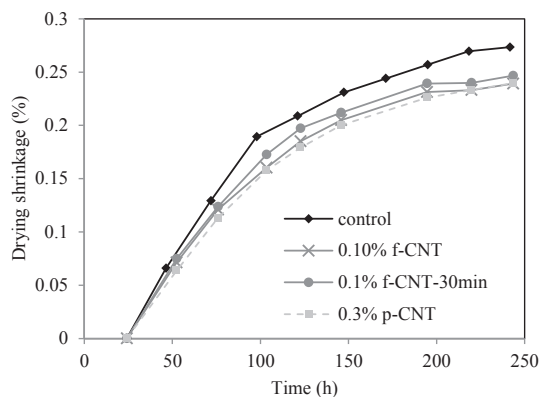


Fig. 6. Relation between pore volume and cumulative pore volume with respect to pore size for samples containing (a,b) p-CNT and (c,d) f-CNT.

macropores, rather than total porosity. On the one hand, a limited degree of dispersion of both f- and p-CNT types in mortar despite preliminary re-agglomeration in the early stage hydration (first hour) mentioned in section 3.3 was obtained by the dispersion method. As a consequence micropores were found to reduce. In addition, macropores smaller than 100 nm were also decreased by f- and p-CNT addition. On the other hand, mechanical strength of the mortar did not show significant improvement by f- and p-CNT addition or by sonication of the CNT suspension. This was likely due to insufficient bonding between exfoliated CNT for f- and p-types with the cement matrix in addition to re-agglomeration of CNTs during the casting process, where the f- and p-CNTs were not able to reinforce the cement composite. It seems that f- and p-CNT only



**Fig. 7.** Drying shrinkage of mortars versus time. Zero time is casting and first data point is demoulding time.

physically filled the pores without sufficient bonding. These findings revealed that the functional carboxyl group used in this study was not able to provide strong covalent bonds in the CNT-cement matrix interface and increase the load-transfer efficiency.

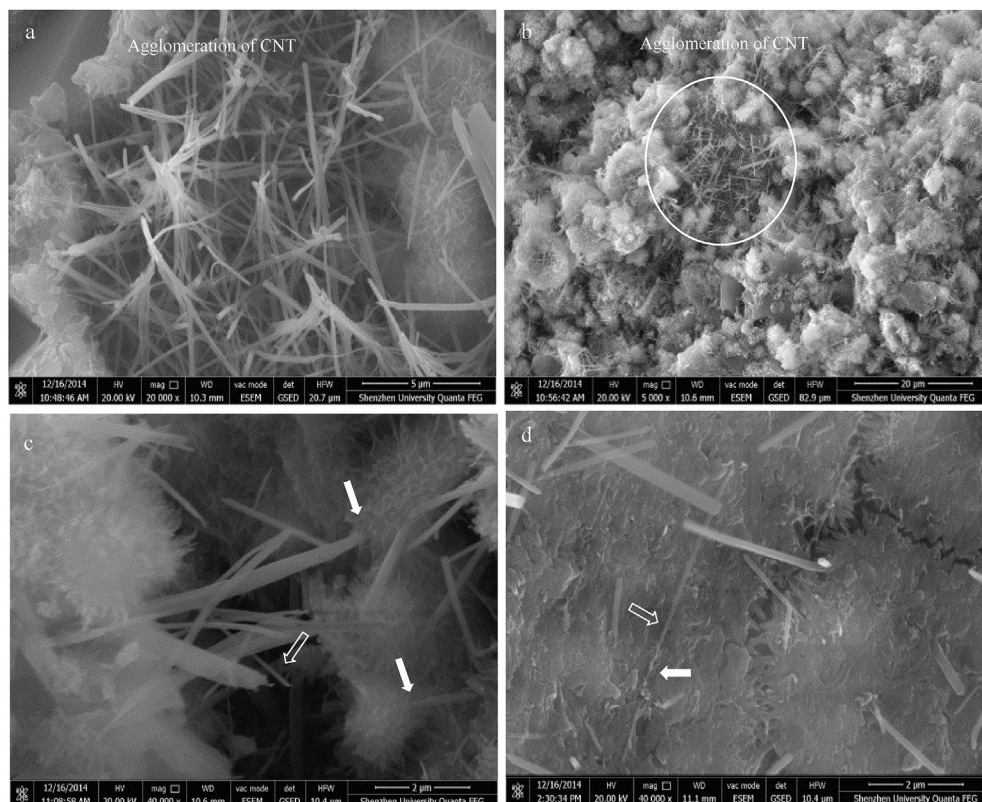
The reduction of micropores can influence shrinkage and creep in cementitious materials [14,19]. In order to reaffirm the influence of CNT on micropores, a drying shrinkage test on pastes using optimum concentrations of f- and p-CNT and the most effective sonication duration inside cement composites was investigated in the following section.

### 3.5. Drying shrinkage

Drying shrinkage of pastes with 0.1% f-CNT and 0.3% p-CNT at times up to 250 h from casting are shown in Fig. 7. The f-CNTs were also dispersed by 30 min sonication as this was found to be the most effective sonication duration inside cement mortar. The drying shrinkage (%) was decreased by the addition of f- and p-CNT to the cement paste, but it was not reduced by the 30 min sonication of the mixing water containing f-CNT. Konsta-Gdoutos et al. [14] also reported that autogenous shrinkage was decreased with addition of CNT to pastes. According to section 3.4, it seems that the reduction of micropores by adding CNT helped decrease shrinkage of cement paste samples.

### 3.6. Microstructure

Fig. 8a and b shows ESEM images of the typical agglomeration of p-CNT inside the cement matrix. Single NTs of both types (pristine and functionalized) after 30 min of sonication inside the cement matrix can be seen (hollow arrows) in Fig. 8c and d. These



**Fig. 8.** Morphology of samples containing: (a,b) p-CNT agglomerates (c) 0.3% p-CNT-30 min sonicated, (d) 0.3% f-CNT-30 min sonicated. Solid arrows show CNTs embedded in hydration products and hallow arrows pointed to individual CNT.



observations support the explanations given in section 3.4 by confirming that a limited degree of dispersion of f- and p-CNT can be obtained by the dispersion process inside the cement matrix despite preliminary re-agglomeration. Thus a portion of the volume of micropores was occupied by single NTs. In addition, f- and p-CNTs evidently were wrapped by the cement hydration products (solid arrows) and interconnected the cement grains (Fig. 8c). Nevertheless a lack of contribution of f- and p-CNTs to the mortar strength as observed with compressive and tensile tests, as well as with fracture toughness tests suggests, that there is insufficient bonding between f- and p-CNTs and hydration products, which makes the CNTs easy to pull out.

#### 4. Conclusions

In this study, the relationship between the degree of dispersion inside water and cement composites with sonication time was determined. The main focus was characterization of dispersion degree of functionalized- and pristine-CNTs in aqueous suspension by UV-vis spectroscopy and comparing with the CNT dispersion state in mortar as verified by its compressive and flexural strength and fracture toughness. Drying shrinkage behaviour of the CNT-containing composites and CNT effects on early cement hydration were also investigated.

The results of UV-vis spectroscopy showed that with increasing sonication time, the degree of dispersion in suspension for f-CNTs increased progressively up to 120 min, while p-CNTs showed a maximum with 60 min sonication. The compressive and flexural strength and the fracture toughness of mortars containing f- and p-CNTs were not significantly improved either by increasing the amount of CNT or imposing dispersion in mixing water. In addition, dispersed f- and p-CNTs decelerated C<sub>3</sub>A hydration in the first hour of hydration. These results suggested that sonication was effective to reach a high degree of dispersion of f- and p-CNT in aqueous media and that the dispersion degree of suspensions containing f-CNTs was higher than p-CNTs. However, utilizing the same dispersion method for mixing water to fabricate CNT-containing cement composites, a corresponding degree of dispersion inside the composite was not obtained. The reason could be re-agglomeration of highly dispersed CNT suspensions after coming into contact with the solid phase. As a consequence, the agglomerates may mitigate the strengthening ability of CNTs. The drying shrinkage and total porosity volume of the cement composites in addition to pore volume related to pore sizes below 100 nm were found to be reduced by f- and p-CNT addition. Porosity analysis and microstructural observations evidenced the presence of individual CNTs inside the cement matrix, thus a limited degree of dispersion inside the cement composite could be reached by using the dispersion method. Insufficient bonding between both types of CNTs and hydration products could also contribute to the lack of mechanical improvement in addition to the negative effects of initial re-agglomeration on mechanical properties.

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