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Carbon nanofiber cementitious composites: Effect of debulking procedure on dispersion and reinforcing efficiency

Zoi S. Metaxa [a], Maria S. Konsta-Gdoutos [a,*], Surendra P. Shah [b]

[a] *Department of Civil Engineering, Democritus University of Thrace, Xanthi, Greece*
[b] *Center for Advanced Cement-Based Materials, Northwestern University, Evanston, IL, USA*

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The use of new reinforcing materials like carbon nanofibers (CNFs) makes it possible to produce cement based nanocomposites with revolutionary properties. However, in order to take advantage of the CNF's excellent reinforcing efficiency it is necessary to achieve a uniform distribution in the matrix. In this work, nanofiber cementitious composites were produced containing CNFs at an amount of 0.048 wt.% of cement. To achieve good dispersion of the CNFs, a method utilizing a surfactant and ultrasonic processing, was employed. The method was optimized using two parameters: the effect of ultrasonic energy and the effect of surfactant to CNF (SFC/CNF) ratio. Initially, the SFC/CNF ratio on the dispersion of two types of CNFs, one subjected to a new special debulking method and one with minimal debulking process, was investigated. An ultrasonic energy of 2800 kJ/l and a SFC/CNF ratio close to 4.0 was found to be optimal for effective dispersion. Following these values, cement based nanocomposites reinforced with four types of CNFs, subjected to different debulking processes and having different morphology, were produced. Their nanostructure was studied using scanning electron microscopy (SEM). Their mechanical performance was evaluated using fracture mechanics tests. All four CNFs were found to control nanoscale cracking. As a result, both the flexural strength and the stiffness of the nanocomposites were significantly improved. Furthermore, the reinforcing efficiency of the CNFs in the cementitious matrix was shown to depend on the debulking procedure: at later ages, the use of the CNF subjected to the special debulking process was found to be more efficient in improving the mechanical performance of the nanocomposites.

1. Introduction

Cementitious materials suffer from low tensile strength and limited strain capacity, which gives rise to the formation of nanocracks under relatively low tensile loads. Cracking at the nanoscale has a high impact on the durability of the matrix. The presence of very fine cracks at the nanoscale accelerates the matrix deterioration process by increasing the permeability of the cement based materials, which can cause degradation through leeching, freezing-and-thawing damage, corrosion, chloride penetration, alkali silica reaction and other mechanisms. Previous research has shown that nanoscale cracking in cementitious materials can be controlled by incorporating nanoscale fibers. Most of research has focused on using carbon nanotubes (CNTs) as the reinforcing material. The incorporation of highly dispersed multiwalled carbon nanotubes (MWCNTs) at low amounts has been shown to effectively arrest the cracks at the nanoscale [1], imposing significant improvements in the mechanical properties of the nanocomposites [1–3]. Moreover, CNTs were found to reduce the capillary stresses, improving the early age and long term durability of the cementitious nanocomposites [2].

Carbon nanofibers (CNFs) exhibit a similar potential in their role as the reinforcement component in cementitious composites. They possess excellent properties, similar to the properties of MWCNTs, including high stiffness, tensile strength, electrical and thermal conductivity and corrosion resistance. Nanoscale three-point bending tests have shown that the Young's modulus of an individual nanofiber ranges from 25 to 200 GPa, depending on the nanofiber's wall thickness [4]. Other studies have reported higher values for the tensile strength and Young's modulus of 12 GPa and 600 GPa, respectively [5]. Recently, Ozkan et al. [6] used microelectromechanical systems (MEMS) to perform nanoscale tensile experiments on individual CNFs and obtained values of 3.34 and 180 GPa for the tensile strength and the Young's modulus, respectively. Another advantage of CNFs is that they can be produced in larger quantities at a similar or lower cost than CNTs.

The most important advantage of CNFs is that they possess a very complex nanostructure. Their outer surface usually consists of conically shaped graphite planes canted with respect to the longitudinal fiber axis [7,8]. These edges, which are present along the

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* Corresponding author. Tel.: +30 25410 79658; fax: +30 25410 79652.
E-mail address: mkonsta@civil.duth.gr (M.S. Konsta-Gdoutos).

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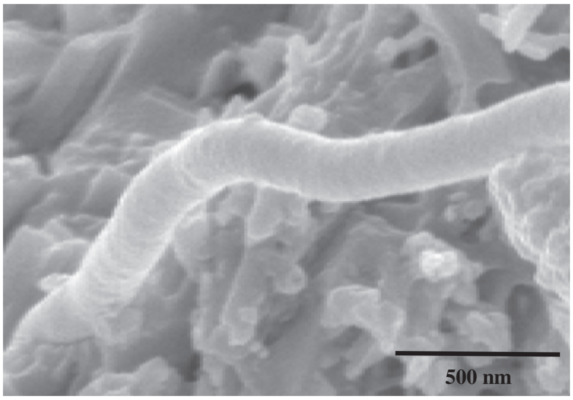

Fig. 1. SEM image of the fracture surface of a cementitious nanocomposite reinforced with CNFs showing the morphology of the nanofibers.

circumference of the fiber, can be used to help anchor the fiber in the matrix and prevent interfacial slip. The morphology of the fibers can be seen in Fig.1. The sidewalls are the thin lines on the surface of the nanofiber.

In light of these exceptional properties, CNFs are expected to be ideal for the development of advanced cementitious nanocomposites. However, as with the case of CNTs, the reinforcing capabilities of CNFs in cementitious materials have not been realized heretofore, possibly due to the challenge of achieving proper fiber to matrix interaction. Dispersing CNFs uniformly in cementitious materials is probably the most critical issue for a successful production of a carbon nanofiber composite. Furthermore, in order to achieve optimal load transfer, the ends of individual CNFs must be sufficiently bonded to the matrix.

Few methods to overcome the dispersion issue have been proposed. Sanchez and Ince [9] used 10% silica fume to facilitate CNF dispersion and improve the interfacial interaction between the CNFs and the cement matrix. They investigated the effect of 0.005%, 0.02%, 0.05%, 0.5% and 2% CNFs by weight of cement on the microstructure and mechanical properties of cement matrix. Sanchez et al. [10] also studied the effect of 0.5% CNFs surface treated with nitric acid. It was found that silica fume and the surface treatment facilitated CNF dispersion and improved the interfacial interaction between CNFs and cement paste, though areas of agglomerated CNFs still remained. Furthermore, no increase in the compressive and splitting tensile strength was observed. More recently, Yazdanbakhsh et al. [11,12] used a polycarboxylate based water-reducing agent and a nonionic surfactant in combination with sonication in order to obtain uniform dispersions of CNFs in water. SEM images of the fractured surface of the nanocomposites reinforced with 0.4 wt.% CNFs revealed a non-uniform dispersion including the absence of CNFs in a large portion of the surface and the presence of closely spaced and packed CNFs in some other areas.

In the present work, carbon nanofiber cementitious composites were fabricated containing CNFs at an amount of 0.048 wt.% of cement. For the effective dispersion of the CNFs in the mixing water a method by Konsta-Gdoutos et al. [1], previously shown to successfully disperse MWCNTs in the cement based matrix, was followed. This method involves the dispersion of the nanomaterials in the mixing water utilizing a surfactant and ultrasonic processing. The applicability of this method for the dispersion of CNFs in the cementitious matrix was investigated by examining the morphology and the nanostructure of the nanocomposites using SEM and accessing their mechanical performance using fracture mechanics tests. As the surfactant concentration influences the dispersion of the nanomaterials, the effect of surfactant to CNF (SFC/CNFs) ratio on the dispersion of two different types of CNFs: a new generation nanofiber that has been subjected to a special debulking method and a nanofiber with minimal debulking process was investigated at first. To optimize the dispersion method the effect of different ultrasonic energy values on the CNFs dispersion was examined. Moreover, the effect of four different CNF types, subjected to different debulking processes and having different morphology, on the mechanical properties and the nanostructure of cementitious nanocomposites was experimentally determined.

2. Experimental procedure

2.1. Materials

Four types of highly graphitic, Pyrograf-III, carbon nanofibers with the following commercial names: PR-24-LD, PR-24-PS, PR-19-XT-PS and PR-24-XT-PS, provided by Applied Sciences Inc., were used (Table 1). Hereafter, these nanofibers will be designated as type A, type B, type C and type D, respectively. All CNFs were synthesized using chemical decomposition of primarily natural gas over iron-sulfide catalyst in a reactor maintained near 1100 °C [8]. After fabrication the as-grown vapor grown carbon nanofibers (VGCNFs) were subjected to pyrolytic stripping (PS) by the manufacturer to remove polyaromatic hydrocarbon residues from the nanofiber surface. This procedure takes place by rapid heating at around 600 °C and does not alter the nanofiber's microstructure [6]. Furthermore, it helps the nanofibers to become more hydrophilic facilitating their solubilization in water [7]. Characteristic properties of CNFs used can be seen in Table 1. All fibers exhibit a tensile strength of 7 GPa, tensile modulus of 600 GPa and the same length range of 30–100 μm. Types A, B and D fibers have an average diameter of 100 nm while type C fibers are thicker with an average diameter of 150 nm because they exhibit a thin chemically vapor deposited (CVD) carbon layer on the surface of the fiber. Types A, B and D nanofibers are designed such as to have minimal or no CVD layers [7]. CNFs were subjected by the manufacture to different debulking processes. Debulking creates loose structures of the carbon nanofiber bundles and helps with its dispersion. Type A CNF was treated with a minimal debulking process. Type B nanofiber has been subjected to a typical debulking process while type C and D nanofibers, are new generation nanofibers having a special debulking method. The cementitious material used was Type I ordinary Portland cement (OPC).

2.2. CNF/cement nanocomposites preparation

CNFs were initially dispersed in the mixing water utilizing a surfactant and ultrasonic processing. In a typical procedure, CNFs were added to a water/surfactant solution. The resulting suspensions were subjected to intensive sonication using a 500 W cuphorn ultrasonic processor. The processor was set to operate at an amplitude of 50% to deliver constant energy of 1900–2100 J/min to the CNF suspensions at 20 s intervals to prevent overheating of the suspensions. This dispersion method developed by Konsta-Gdoutos et al. [1] was successfully applied in the preparation of carbon nanotube/cement nanocomposites [1–3]. One objective of this study was to examine whether this method can be applied for the dispersion of CNFs and to optimize the method for use with CNFs.

After dispersion, OPC was added to the dispersions to prepare cementitious nanocomposites with a water to cement ratio of 0.5. The materials were mixed following the ASTM 305 using a standard Hobart planetary mixer. After mixing, the paste was cast in $20 \times 20 \times 80$ mm molds. Following demolding, the samples were cured in lime-saturated water until testing. All CNF/cement nanocomposites were prepared at an amount of 0.048 wt.% of

Table 1
Properties of carbon nanofibers (CNFs).

No.	Commercial name	Aspect ratio	Diameter (nm)	Purity (%)	Surface area (m^2/g)	Density (g/cm^3)
Type A	PR-24-LD	650	60–150	>98	45	1.6
Type B	PR-24-PS	650	60–150	>98	45	1.6
Type C	PR-19-XT-PS	430	70–200	>98	20–30	1.9
Type D	PR-24-XT-PS	650	60–150	>98	40–50	1.6

cement CNFs. This dosage has been shown to be optimal for the dispersion of long CNTs which exhibit similar length range (10–100 μm) to the CNFs (length: 30–100 μm) used in this study [1,2].

2.3. Experimental characterization

The dispersion of the CNFs and the morphology of the CNF/cement nanocomposites' fracture surfaces were investigated using an ultra-high-resolution scanning electron microscope (SEM, LEO Gemini 1525). For the SEM study, small size specimens of 25.4 × 6.35 × 6.35 mm were prepared for each mix following the procedure described previously. Specimens were demolded after 18 h of curing and placed in acetone to stop the hydration. This ensures that all samples were tested at the same age. To eliminate charging effects, the fracture surfaces of the nanocomposites, prior to their observation, were coated with a 20–25 nm thick layer of gold/palladium (Au/Pd) using the Denton Desk III TSC Sputter Coater. The SEM was operated at 3–5 kV using secondary electron imaging. This mode provides high-resolution imaging of the surface morphology at medium to high magnifications (10,000×).

The mechanical performance of the CNF/cement nanocomposites was assessed using fracture mechanics tests. Prior to testing, a 6 mm notch was placed into the specimens using a water-cooled diamond saw. The length of the notch was calculated based on the RILEM standard, which requires a notch to depth ratio of close to 1/3. A closed-loop MTS servo-hydraulic testing machine with a 20 kip (89 kN) capacity was used to perform the test. The specimens were tested at the age of 3, 7 and 28 days, by three-point bending, according to the procedure described in [1,2]. The load versus crack mouth opening displacement (CMOD) data values were recorded during experimental testing. The Young's modulus was calculated from the load–CMOD graphs using the two-parameter fracture model by Shah et al. [13].

3. Results and discussion

3.1. Effect of surfactant to nanofiber ratio

The surfactant concentration has been shown to have a significant effect on the nanofiber dispersion. Several studies have indicated that, depending on the surfactant type, there exists an optimum surfactant to nanofibers ratio, for which the dispersion of the nanofibers is uniform [14,15]. Suspensions with surfactant concentrations above or below the optimum ratio typically demonstrate less dispersibility [15]. Previous research using the same type of surfactant for the dispersion of MWCNTs has shown that the optimum surfactant to MWCNTs ratio is close to 4.0 [1]. To investigate whether this also applies to CNFs, the effect of surfactant/CNFs ratio (SFC/CNF) on the dispersion of two different types of CNFs, type A and type D, was investigated.

Initially, the effect of surfactant concentration on the dispersion of type D CNF was studied. The type D nanofiber was selected as a new generation nanofiber subjected to a special debulking method. This method creates loose structures of the carbon nanofiber bundles and helps with its dispersion. According to the manufacturer, nanofibers subjected to this debulking procedure can be dispersed in the matrix without the aid of a dispersing agent. Samples were prepared with CNFs that were dispersed at a constant ultrasonic energy without using a surfactant. Fig. 2 depicts the mechanical performance of the nanocomposites compared to the reference cement paste. An improvement in the mechanical properties can be correlated to an effective dispersion of the CNFs. The flexural strength of the nanocomposites shows a slight increase, nearly 8%, at all ages. An SEM observation of the samples' fracture surface revealed that the CNFs are poorly dispersed, and they appear entangled into the hydration products, forming bundles in the matrix (Fig. 3). Though some increase in mechanical performance was observed, it appears that the CNFs cannot be sufficiently dispersed by simply the application of ultrasonic energy. Thus, under the test conditions employed in the research reported here, the use of a dispersing agent is absolutely required.

In order to determine the effect of surfactant concentration on the dispersion of CNFs, nanocomposites with surfactant to type D CNF weight ratios of 2.0, 4.0, and 6.0 were prepared, the amount of CNFs was kept constant at 0.048 wt.%. Fig. 4 shows the mechanical performance of the nanocomposites compared to the plain cement paste. All samples exhibit up to 32% higher flexural strength than the plain cement paste specimens. The samples dispersed with a SFC/CNF ratio of 6.0 demonstrate a slightly lower strength increase than the other specimens, which could be attributed to the excessive amount of surfactant. According to previous research

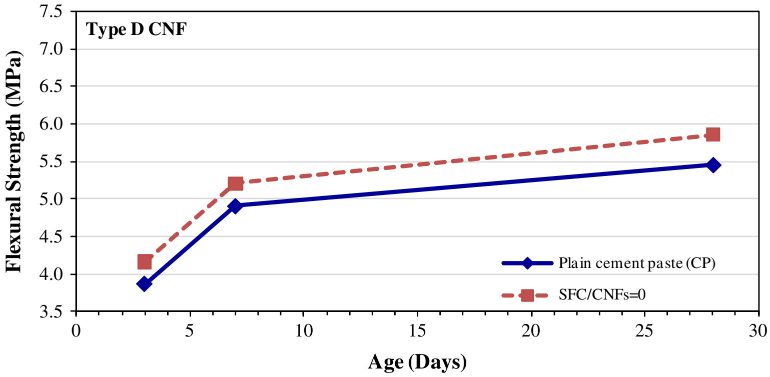

Fig. 2. Flexural strength of cement paste (w/c = 0.5) and cement paste nanocomposites reinforced with 0.048 wt.% type D CNFs dispersed without the use of surfactant (SFC).

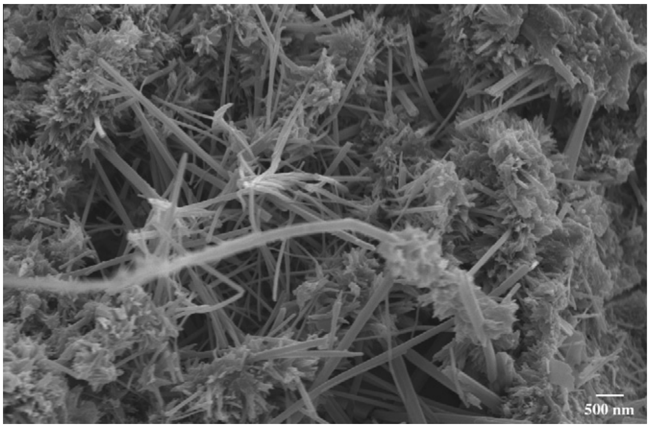

Fig. 3. Typical SEM image of cement nanocomposites reinforced with type D CNFs dispersed without the use of surfactant.

on MWCNTs, at high amounts the surfactant molecules form multilayers on the nanofiber surface. As a result, portions of surfactant molecules that extend into the liquid phase start interacting. This interaction causes flocculation of the nanofibers which decreases their dispersion [14,15]. At lower surfactant to CNF ratios the nanocomposites demonstrated a similar strength increase. To further explore the dispersion of those samples SEM was conducted (Fig. 5). In both cases with ratios of 2.0 and 4.0, individual nanofibers bridging nanocracks and pores were observed. The combination of SEM and mechanical tests indicates that for SFC/CNF ratios of 2.0 and 4.0 the amount of surfactant is sufficient to evenly cover the CNF surface and achieve adequate dispersion of the CNFs.

To investigate the effect of surfactant to CNFs ratio on the dispersion of CNFs, samples reinforced with 0.048 wt.% type A CNFs dispersed using SFC/CNF ratios of 3.0, 4.0, and 5.0 were also prepared. Compared to type D CNFs, type A CNFs exhibit lower bulk density and have not been subjected to an extensive debulking process. Preliminary experiments have indicated that they are more sensitive to the SFC/CNF ratio used thus, compared to type D CNFs, a narrower range for the SFC/CNF ratios was used to investigate the effect of surfactant concentration. Strength tests on samples dispersed using a SFC/CNF ratio of 4.0 demonstrate slightly higher strength increase than other SFC/CNF ratios (Fig. 6). Fig. 7 depicts the nanostructure of all samples. In the case of SFC/CNF ratios of 3.0 and 5.0 some areas with individual CNFs were observed. However, the CNFs appeared to form bundles of two or more in a few areas, indicating that a small amount of CNFs was not well dispersed. Nevertheless, only well dispersed CNFs were observed on the fracture surface of the nanocomposites of a SFC/CNF ratio of 4.0 without any sign of entanglement of CNFs, regardless of the debulking procedure used. Similar results were obtained for MWCNT with different aspect ratios [1–3] indicating that the optimum SFC/CNFs ratio is possibly independent of the nanoscale fiber type and mainly depends on the type of surfactant.

3.2. Effect of ultrasonic energy

The effect of ultrasonic energy on the dispersion of CNFs was investigated to further optimize the dispersion method. Type A CNFs were used for this investigation since nanocomposites reinforced with those nanofibers were found to exhibit higher increase in strength when compared with the nanocomposites reinforced with type D CNFs. The CNF suspensions were dispersed at a SFC/CNF ratio of 4 and sonicated at room temperature at energies of 2100, 2800 and 3500 kJ/l following the procedure described previously. Fracture mechanics test results of the flexural strength of nanocomposites dispersed using different dispersing energies, at the age of 3, 7 and 28 days, are plotted in Fig. 8. Nanocomposites fabricated using CNF suspensions dispersed at an ultrasonic energy of 2800 kJ/l illustrate the best mechanical performance at all ages, while nanocomposites prepared using suspensions dispersed with energies either lower or higher than 2800 kJ/l yield a smaller flexural strength increase. Generally, sonication energy results in two effects on the nanofiber dispersion: it mechanically disentangles the nanofiber agglomerates and simultaneously breaks the individual nanofibers so that their aspect ratio is reduced [16]. Usually, lower ultrasonic energies cannot effectively disperse the CNFs. On the other hand, higher ultrasonic energies may reduce the aspect ratio of the nanofibers, which ultimately results in a reduced embedding fiber length. The fibers become less effective in transferring load, and their reinforcing efficiency is diminished. For complete dispersion, under the conditions employed in the research reported here, the application of an ultrasonic energy close to 2800 kJ/l was found to be most effective.

3.3. Effect of CNF type

To access the reinforcing effect of the different CNF types cementitious nanocomposites were produced, each reinforced with a different CNF type. All CNFs were dispersed following the optimum dispersion method described previously, using a constant SFC/CNF ratio of 4.0 and a constant ultrasonic energy of 2800 kJ/l.

Fig. 9 shows SEM images of fracture surfaces of the samples reinforced with the four different types of CNF, at a scale of 500 nm. It is observed that, in all cases, mostly individual CNFs can be identified on the fracture surface. Furthermore, CNFs appear

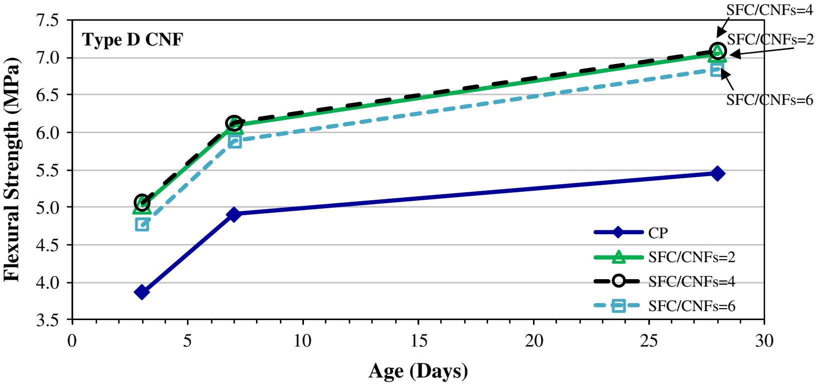

Fig. 4. Effect of SFC/CNF weight ratio on the flexural strength of cement paste (w/c = 0.5) nanocomposites reinforced with 0.048 wt.% type D CNFs.

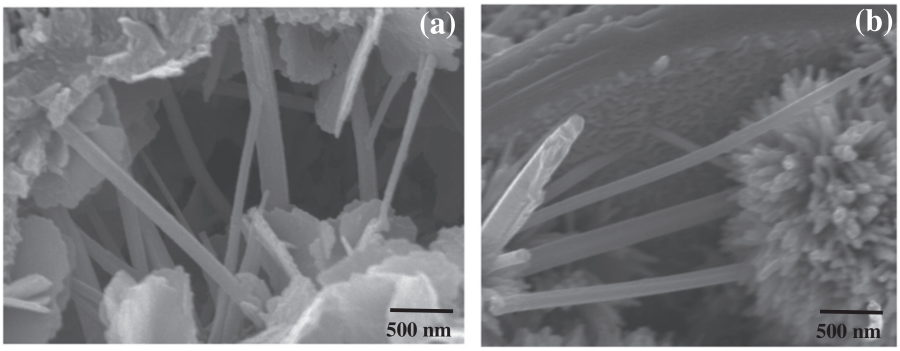

Fig. 5. Effect of surfactant to CNF weight ratio of (a) 2.0 and (b) 4.0 on the dispersion of type D CNFs.

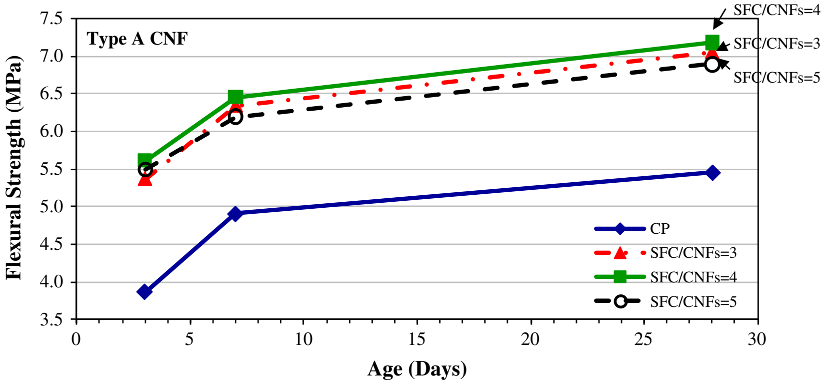

Fig. 6. Effect of SFC/CNF weight ratio on the flexural strength of cement paste (w/c = 0.5) nanocomposites reinforced with 0.048 wt.% type A CNFs.

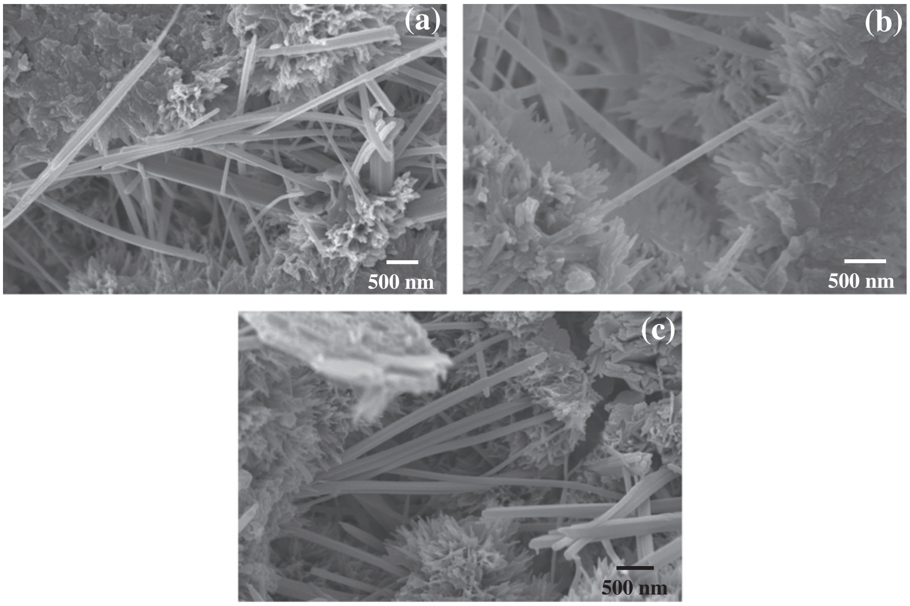

Fig. 7. Effect of surfactant to CNF weight ratio of (a) 3.0, (b) 4.0, and (c) 5.0 on the dispersion of type A CNFs.

to be embedded into the hydration products and arresting nanocracks. This indicates that adequate dispersion was achieved and suggests that the aforementioned dispersion method can be used to effectively disperse all types of CNFs. This finding is in good agreement with previous studies on carbon nanotube/cement nanocomposites [1,2], demonstrating that this method can be successfully applied for the dispersion of nanoscale fibers. Interestingly in the case of type A CNFs composites it is observed that part of the surface of the CNFs is covered with cement hydration products. This suggests that not only effective dispersion was achieved; also good bonding exists between the nanofibers and the matrix, which enables the load transfer between the matrix and the nanofibers that bridge the nanocracks, resulting in the improvement of the overall strength of the nanocomposite.

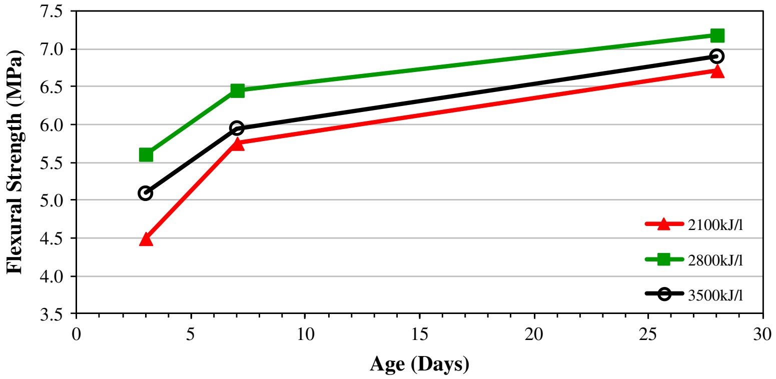

Fig. 8. Effect of ultrasonic energy on the flexural strength of cement paste (w/c = 0.5) nanocomposites reinforced with 0.048 wt.% CNFs.

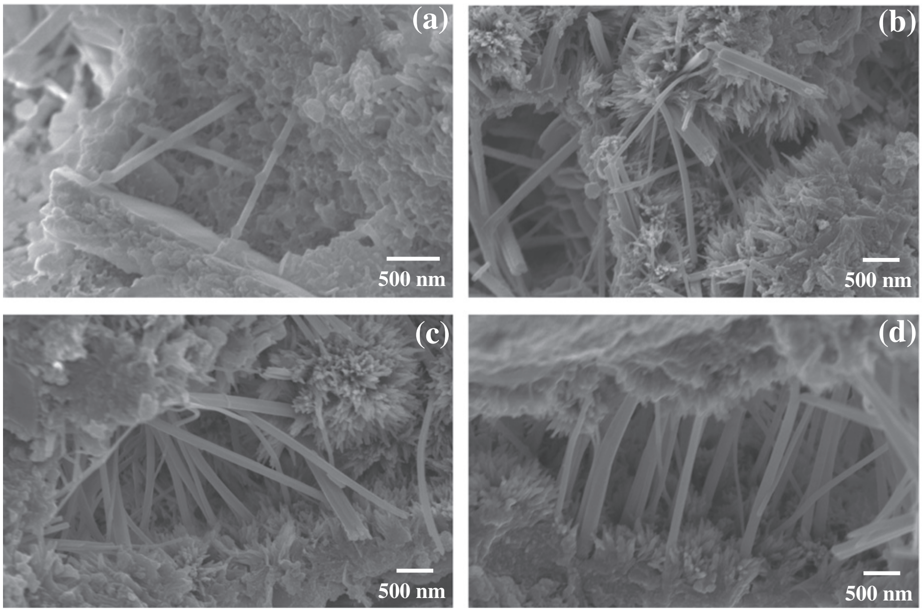

Fig. 9. SEM images of the fracture surface of cement nanocomposites reinforced with (a) type A, (b) type B, (c) type C and (d) type D CNFs, respectively.

The results of the flexural strength and the Young's modulus of the nanocomposites are illustrated in Fig. 10a and b, respectively. Samples reinforced with type A CNF appear to outperform for both properties. Compared to plain cement paste they exhibit a 50% and 75% increase in flexural strength and Young's modulus, respectively. This improved reinforcing effect of type A CNF can be possibly attributed to its lower bulk density. The nanocomposites reinforced with Type A CNF incorporate a slightly larger amount of CNFs since CNFs were incorporated in the matrix according to a constant (0.048 wt.%) weight percentage by weight of cement. A larger volume of well dispersed CNFs enables the ability of the matrix for a higher load transfer efficiency, which is the key element that determines the mechanical response of the fiber nanocomposites.

The type B CNFs nanocomposites demonstrate the lowest strength and Young's modulus increase. The debulking process that the type B nanofibers have been subjected to is possibly the main reason for their reduced reinforcing effect. Typical debulking processes have been shown to shorten the nanofibers' length, downgrading this way their role as the reinforcing component [8]. Nanofibers types C and D were treated to an improved debulking process developed by the manufacturer, which cause less damage to the nanofiber length. Comparing the nanocomposites reinforced with type C and type D CNFs it is observed that the rate of flexural strength development is higher for the type D. At 3 and 7 days of hydration, samples reinforced with type C CNFs depict slightly higher strength and Young's modulus increase than the type D CNFs samples. However, at the age of 28 days, the nanocomposites reinforced with type D CNFs demonstrate better mechanical performance. The two factors that need to be considered when explaining this is the different aspect ratio fibers type C and type D exhibit, as well as their morphology. Type C CNF is thicker, characterized by a lower aspect ratio. A thin CVD carbon layer is also deposited on the surface of the fiber. This CVD layer consists of nested graphene tubes resembling multi wall carbon nanotubes that coat some of the rough outer surface of the CNF [17]. There is a possibility that the presence of this outer layer of multiwall graphene tubes favors the debonding and the interfacial slip between the nanofibers and the matrix at later ages. The slightly higher increase in the strength and stiffness observed at the age of 3 and 7 days could be attributed to the fact that at these ages type C nanofibers act more like high stiffness fillers, rather than fibers. Compared to type C CNF, type D CNF has a minimal or no CVD layer and exhibits a rougher surface consisting of conically shaped graphite planes, which could help anchor the fiber in the matrix and thus, prevent interfacial slip. It is due to these graphite planes

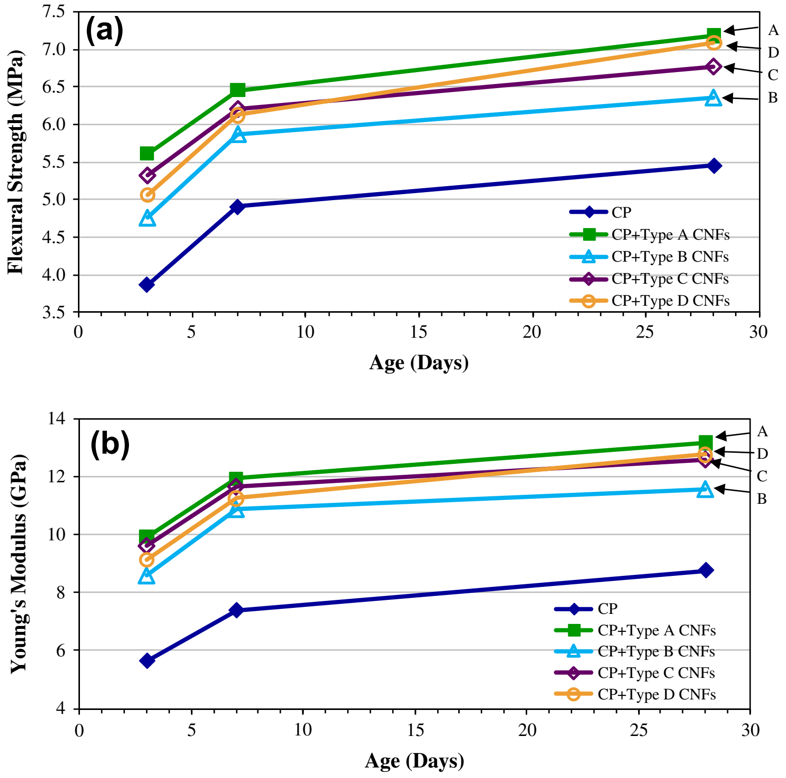

Fig. 10. Effect of CNF type on the (a) flexural strength and (b) Young's modulus of cementitious nanocomposites (w/c = 0.5) reinforced with 0.048 wt.% CNFs.

that at the age of 28 days the bonding of type D CNF with the cement hydration products is stronger and the load transfer between the fibers and the matrix is more efficient, resulting to the observed enhanced mechanical performance of these nanocomposites. It is apparent that when compared to the improved debulking method type D CNF, type B CNF nanocomposites exhibit lower strength and Young's modulus, indicating that the new improved debulking procedure increases the reinforcing efficiency of the CNFs in the cementitious matrix.

4. Conclusions

The effect of the debulking procedure on the dispersion and the reinforcing efficiency of carbon nanoscale fibers was studied. CNFs were dispersed following a method previously shown to successfully disperse MWCNTs in the cementitious matrix. It was proven that this method can be also successfully applied for dispersing CNFs. Independent of the debulking method used and similar to the results obtained with MWCNTs, a surfactant to CNF ratio close to 4.0 was found to be optimal. For complete dispersion, the application of an ultrasonic energy close to 2800 kJ/l was found to be most effective. Lower ultrasonic energies cannot effectively disperse the CNFs, while higher ultrasonic energies possibly reduce the aspect ratio of the nanofibers, which in turn diminishes their reinforcing efficiency in the cementitious matrix.

The addition of CNF to cement paste was found to offer a significant property enhancement to the cementitious nanocomposites, mainly increased flexural strength and stiffness, and crack control at the nanoscale. SEM analysis also confirmed the results of the mechanical testing; nanoimaging showed that good bonding exists between all types of carbon nanofibers and the matrix. Overall, the reinforcing efficiency of the CNFs in the cementitious matrix was shown to depend on the debulking procedure. At early ages of hydration, CNFs with an outer layer of multiwall graphene tubes (CVD layer) improve the mechanical performance of the matrix, possibly acting like high stiffness fillers. At later ages, the use of a CNF with a rougher surface consisting of conically shaped graphite planes was found to be more efficient for improving the mechanical performance of the matrix. These graphite planes improve the bonding of the CNFs with the cement hydration products, resulting to a higher load transfer efficiency between the fibers and the matrix, the key element that determines the mechanical response of the nanofiber nanocomposites.

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