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Multi-scale mechanical and fracture characteristics and early-age strain capacity of high performance carbon nanotube/cement nanocomposites

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ABSTRACT

Due to their exceptional mechanical properties, carbon nanotubes (CNTs) are considered to be one of the most promising reinforcing materials for the next generation of high-performance nanocomposites. In this study, the reinforcing effect of highly dispersed multiwall carbon nanotubes (MWCNTs) in cement paste matrix has been investigated. The MWCNTs were effectively dispersed in the mixing water by using a simple, one step method utilizing ultrasonic energy and a commercially available surfactant. A detailed study on the effects of MWCNTs concentration and aspect ratio was conducted. The excellent reinforcing capabilities of the MWCNTs are demonstrated by the enhanced fracture resistance properties of the cementitious matrix. Additionally, nanoindentation results suggest that the use of MWCNTs can increase the amount of high stiffness C–S–H and decrease the porosity. Besides the benefits of the reinforcing effect, autogenous shrinkage test results indicate that MWCNTs can also have a beneficial effect on the early strain capacity of the cementitious matrix, improving this way the early age and long term durability of the cementitious nanocomposites.

1. Introduction

Advanced technological aspects of cement based materials have recently focused on developing high-performance cementitious composites, which exhibit high compressive strengths. Such composites however, exhibit also extremely brittle failure, low tensile capacity and appear sensitive to early age microcracking as a result of volumetric changes due to high autogenous shrinkage stresses. These characteristics of cement based materials are serious shortcomings that not only impose constrains in structural design, but also affect the long term durability of structures. To overcome the aforementioned disadvantages reinforcement of cementitious materials is typically provided at the millimeter and/or the micro scale using macrofibers and microfibers, respectively. Cementitious matrices however, exhibit flaws at the nanoscale, where traditional reinforcement is not effective.

Carbon nanotubes (CNTs) present several distinct advantages as a reinforcing material for high strength/performance cementitious composites as compared to more traditional fibers. First, they exhibit significant greater strength and stiffness [1,2] than conventional fibers, which should improve overall mechanical behavior. Second, their higher aspect ratio is expected to effectively arrest the nanocracks and demand significantly higher energy for crack propagation. Thirdly, provided that CNTs are uniformly dispersed, and due to their nanoscale diameter, fiber spacing is reduced.

Few attempts have been made to add CNTs as reinforcement in cementitious matrices. Makar et al. [3,4] investigated the reinforcing effect of 2.0 wt.% CNTs in cement using SEM and Vickers hardness measurements. The results obtained indicated that CNTs may affect the early hydration progress, producing higher hydration rates. Li et al. [5,6] employed a carboxylation procedure to improve the bonding between 0.5 wt.% MWCNTs and cement matrix and obtained a 25% increase in flexural strength and a 19% increase in compressive strength. Saez de Ibarra et al. [7] measured the stiffness of cement samples reinforced with MWCNTs and SWCNTs using an AFM nanoindentation technique and reported modest gains in the Young's modulus. More recently, Cwirzen et al. [8,9] investigated the mechanical properties of cement matrices reinforced with different concentrations of MWCNTs. The results showed no increase in the flexural strength and a slight increase in compressive strength of the cement paste with the addition of CNTs. More recently, research on the reinforcing effect of MWCNTs in cement matrix ($w/c = 0.5$) indicated that CNTs can strongly reinforce the cement paste matrix by increasing the flexural strength and the Young's modulus of plain cement paste by 25% and 50%, respectively [10,11].

In this study, the development of high-performance nanocomposites reinforced with multiwall carbon nanotubes was investigated. The two major drawbacks associated with the incorporation

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Table 1
Properties of multiwall carbon nanotubes (MWCNTs).

	Aspect ratio	Diameter (nm)	Length (μm)	Purity (%)	Surface area (m^2/g)
Short	700	20–40	10–30	>95	110
Long	1600	20–40	10–100	>97	250–300

of CNTs in cement based materials are poor dispersion and cost. To achieve good reinforcement, it is critical to have uniform dispersion of CNTs within the matrix [12]. However, since CNTs tend to adhere together due to Van der Waals forces, are particularly difficult to separate [13]. In this experimental work, effective dispersion of MWCNTs in the mixing water was achieved by using a simple, one step technique involving the application of ultrasonic energy and the use of a commercially available surfactant, commonly used in the development of advanced high performance cement based materials [10,11,14]. Fracture mechanics tests were performed to investigate the effect of MWCNTs aspect ratio in conjunction with the effect of the concentration of MWCNTs on the fracture characteristics of the nanocomposites. A determination of the nanomechanical properties and the porosity of the composites was carried out through nanoindentation experiments. Finally, since nanoindentation results implied significant changes in the nanostructure of the composites, autogenous shrinkage experiments were conducted to determine the effect of the MWCNTs on the early strain capacity of the cementitious matrix.

2. Experimental study

2.1. Preparation of the MWCNTs nanocomposites

Two types of commercially available purified multiwall carbon nanotubes (MWCNTs), designated as short and long, were used. The MWCNTs were produced by catalytic chemical vapor deposition (CCVD) of carbon and were used untreated as received. The MWCNTs had the same diameter, but different aspect ratios, close to 700 for the short and 1600 for the long MWCNTs. The characteristic properties of the MWCNTs used are shown in Table 1. The cementitious material used was Type I ordinary Portland cement (OPC).

To disperse the MWCNTs homogeneously in the mixing water, MWCNT suspensions were prepared by adding the MWCNTs in an aqueous surfactant solution. The resulting dispersions were sonicated at room temperature following the method described in [10,11,14]. Mix proportions of sonicated suspensions with short MWCNTs at amounts of 0.048 wt.%, 0.08 wt.% and 0.10 wt.%, and long MWCNTs at amounts of 0.025 wt.%, 0.048 wt.% and 0.08 wt.% by weight of cement were investigated. Based on the authors' previous research [10,14], a constant surfactant to MWCNTs weight ratio of 4.0 was found to achieve effective dispersion. After sonication, OPC was added to the MWCNT dispersions at a water to cement ratio (w/c) of 0.3. Mixing of the materials was performed according to the procedure outlined by ASTM 305 using a standard Hobart mixer. After mixing, the paste was cast in 20 × 20 × 80 mm molds. After demolding, the samples were cured in water saturated with lime until testing.

Initial evaluation of the dispersion of MWCNTs in the cementitious matrix was performed by scanning electron microscopy (SEM). Images of cement paste reinforced with MWCNTs that were added to cement as received (without dispersion) and MWCNTs that were dispersed following the method described previously are illustrated in Fig. 1a and b, respectively. As expected, in the samples were no dispersion was employed (Fig. 1a), large agglomerates and bundles of MWCNTs were observed. However, when MWCNTs were dispersed in the mixing water following the aforementioned procedure (Fig. 1b) only individual MWCNTs could be identified on the fracture surface.

2.2. Testing procedures

2.2.1. Fracture mechanics testing

Fracture tests were conducted to assess the mechanical performance of the nanocomposites. A 6 mm notch was placed into the specimens using a water-cooled diamond saw. The specimens were then tested at the age of 3, 7 and 28 days, by three-point bending, with a closed-loop MTS servo-hydraulic testing machine with a 89 kN capacity. To ensure stable crack propagation, a clip gauge was used to measure the crack mouth opening displacement (CMOD) and provide feedback to the loading machine. The rate of CMOD was set at 0.009 mm/min. The load versus CMOD graphs were created from the test results. Young's modulus was then calculated from these graphs using the two-parameter fracture model by Jenq and Shah [15]. An average value of three specimens was used for each curing age. A typical load-CMOD curve of the plain cement paste and cement paste reinforced with MWCNTs is shown in Fig. 2.

2.2.2. Nanoindentation

The nanomechanical properties of the MWCNT composites were investigated using a commercially available triboindenter. The triboindenter is a special type of nanoindenter that combines nanoindentation to determine the local properties of the material at the nanoscale, with high-resolution in situ scanning probe microscopy (SPM) imaging that allows pre- and post-test observation of the sample. A Berkovich tip with a total included angle of 142.3° was used for indentation and SPM imaging. Multiple cycles of partial loading and unloading were used to make each indentation, to help minimize creep and size effects [16]. The nanoindentation depth, as a function of the imposed load, was recorded during the test. The Oliver and Pharr method was used to determine the mechanical properties, where the indentation modulus

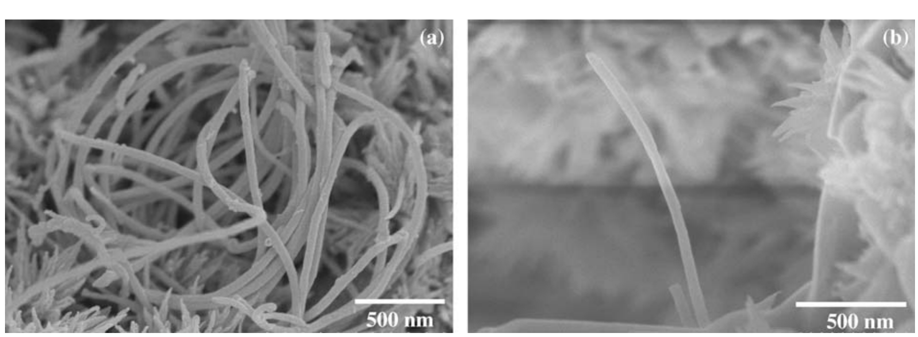

Fig. 1. SEM images of cement paste fracture surfaces reinforced with undispersed and dispersed MWCNTs (a) and (b), respectively.

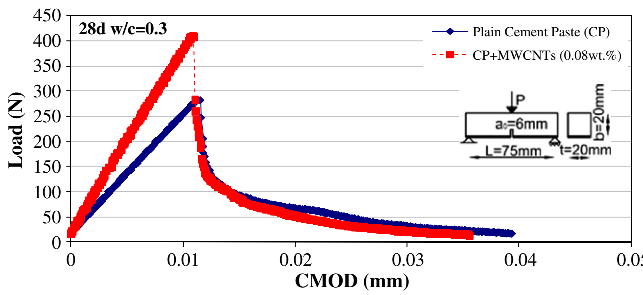

Fig. 2. Mechanical behavior of 28 day plain cement paste and cement paste reinforced with 0.08 wt.% MWCNTs ($w/c = 0.3$).

is calculated from the final unloading curve [17]. Prior to nanoindentation, the machine was calibrated by indenting a material (quartz) of known mechanical properties.

Prismatic specimens of 25.4 × 6.35 × 6.35 mm were prepared and cured in water saturated with lime for 28 days. After curing, specimens were kept in acetone to stop the hydration and ensure that all samples were tested at the same age. Before testing, thin sections of approximately 5 mm were cut out of the specimens, using a water lubricated diamond saw, and mounted using an adhesive (softening temperature 71 °C) on a metal sample holder for polishing. Sample preparation is very important for nanoindentation, an extremely smooth surface is necessary for the reliable determination of the local mechanical properties [18]. The surface of the samples were polished using silicon carbide papers of gradation 22 μm, 14 μm, 8 μm and 5 μm, diamond lapping films of gradation 6 μm and 3 μm and diamond water suspension of gradation 0.1 μm. Water was used in the first two and last three gradations. At every step, an optical microscope was used to check the effectiveness of the polishing. In the final step, the polished samples were ultrasonically cleaned in water for 1 min using a bath sonicator to remove polishing debris. At the end of polishing, an environmental scanning electron microscope (ESEM), in low vacuum mode, was used to investigate the effectiveness of the polishing procedure and find representative areas of the samples.

Before nanoindentation, the area was imaged using the Berkovich tip of the triboindenter to provide surface information and to ensure that the location of the nanoindentation is sufficiently smooth. Due to the highly heterogeneous nature of cement based materials, a large array of nanoindentations needed to be carried out [19]. Each test consisted of 144 indents performed in a 12 × 12 grid (10 μm between adjacent grid points) with depths varying from 50 to 300 nm. This procedure was repeated in at least three different areas on each sample, providing a total of at least 432 indentation tests for each sample. Fig. 3a shows a typical nanoindentation curve. Irregular nanoindentation curves may occur due to the presence of large voids or cracking in the material [18] and can not be included in the analysis (Fig. 3b). The nanoindentation curves were examined in order to determine the validity of each indentation.

2.2.3. Autogenous shrinkage testing

The autogenous shrinkage of cement nanocomposites was studied using a modified version of ASTM C 341 and ASTM C 490. Cement paste specimens of 20 × 20 × 80 mm were cast following the procedure described above. Immediately after setting (~6 h after casting) specimens were demolded and sealed using plastic wrap. Stainless steel gage studs were glued directly to the surface of the specimens maintaining a 50.8 mm gage length, using a five minutes epoxy resin. A length comparator was used to measure the distance between the stubs from the time of final setting up to 96 h after casting. From these measurements, the autogenous shrinkage was calculated.

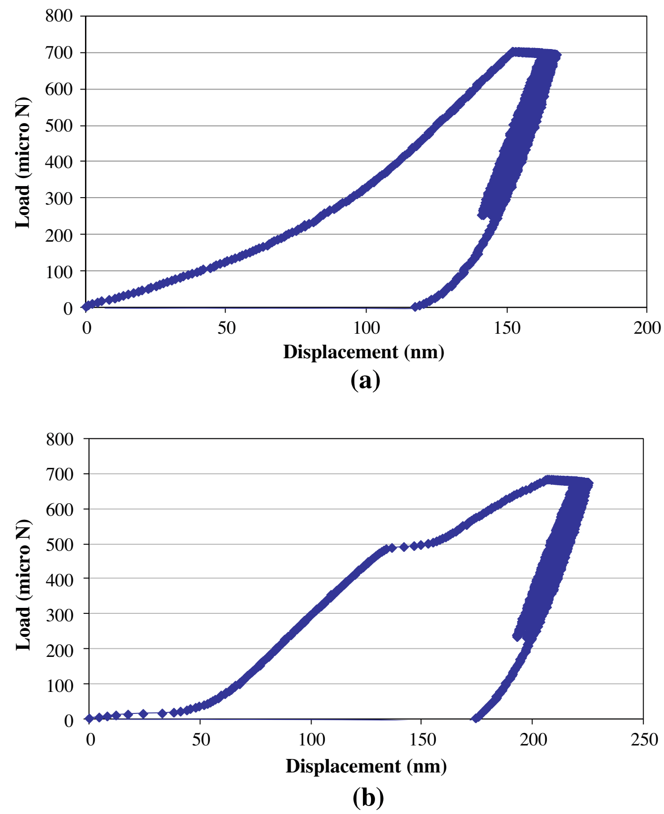

Fig. 3. Load–indentation depth curves: (a) acceptable and (b) not acceptable.

3. Results and discussion

3.1. Mechanical performance

The fracture mechanics test results of the average flexural strength of cement paste samples reinforced with short MWCNTs at amounts of 0.048 wt.%, 0.08 wt.% and 0.10 wt.% by weight of cement at the age of 3, 7 and 28 days are presented in Fig. 4. In all cases, the samples reinforced with MWCNTs exhibit higher flexural strength than plain cement paste. Samples reinforced with 0.08 wt.% short MWCNTs outperformed all other mixes, exhibiting the largest increase in flexural strength. Generally, the reinforcing effect of the MWCNTs mainly depends on their dispersion within the matrix [12], which leads to the reduction of the fiber spacing in the nanocomposite. It is observed that samples containing 0.10 wt.% MWCNTs exhibit consistently lower strength than the 0.08 wt.% mixes at all ages. It is possible that effective dispersion of short MWCNTs at a concentration higher than 0.08 wt.% cannot be achieved. At concentrations lower than 0.08 wt.% the amount of the MWCNTs in the matrix is too low to arrest the nanocracks. The results indicate that a concentration of short MWCNTs, close to 0.08 wt.%, is optimal to achieve effective reinforcement under the test conditions employed in the research reported here. These findings compare well with previous studies [10,11].

Fig. 5 shows the flexural strength results of specimens reinforced with 0.025 wt.%, 0.048 wt.% and 0.08 wt.% long MWCNTs. Similar to the specimens with short MWCNTs, it was observed that in all cases, the samples reinforced with long MWCNTs show improved mechanical performance compared to the plain cement

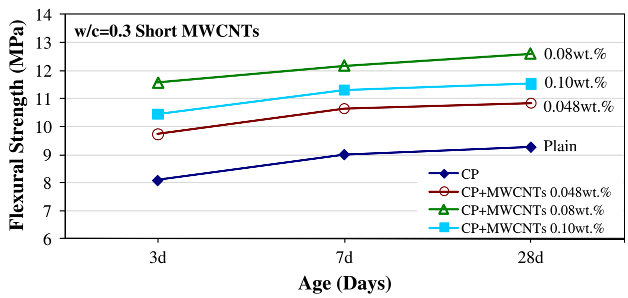

Fig. 4. Effect of short MWCNTs concentration on the flexural strength of cement paste ($w/c = 0.3$).

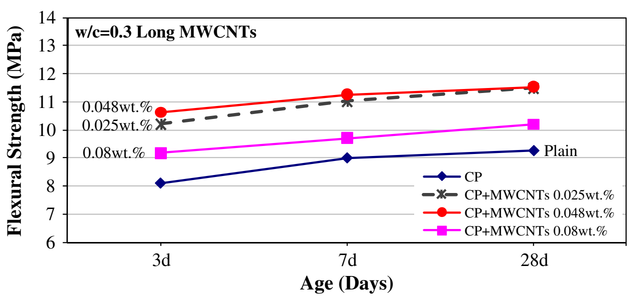

Fig. 5. Effect of long MWCNTs concentration on the flexural strength of cement paste ($w/c = 0.3$).

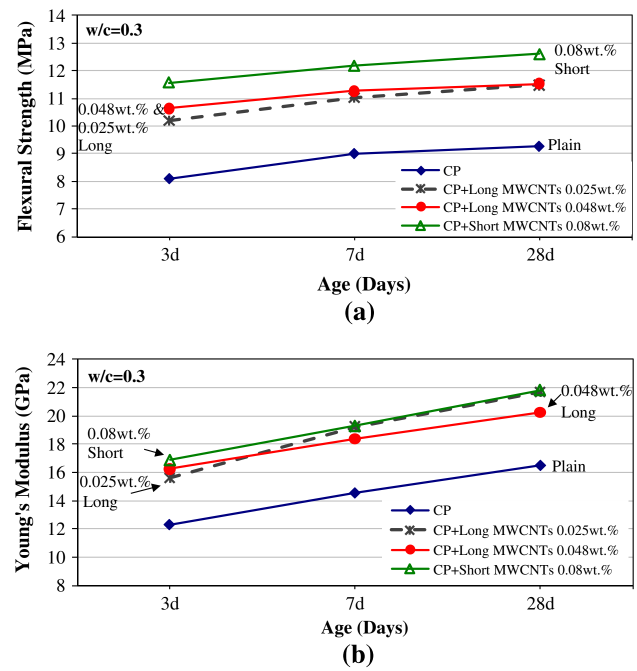

Fig. 6. Fracture mechanics test results of the flexural strength (a) and Young's modulus (b) of nanocomposites that exhibit the best mechanical performance among the different mixes tested.

paste. However, contrary to the results obtained with the short MWCNTs, it is observed that samples reinforced with smaller amount of MWCNTs demonstrate higher flexural strength. These results are in good agreement with previous findings [10,11].

The results of the average flexural strength and Young's modulus of the nanocomposites, which illustrated the best mechanical performance, are compared in Fig. 6a and b, respectively. Generally, it can be concluded that the optimum concentration of MWCNTs depends on the aspect ratio of MWCNTs. When MWCNTs with a low aspect ratio are used (short MWCNTs), a higher amount close to 0.08 wt.% by weight of cement is needed to achieve effective reinforcement. When MWCNTs with higher aspect ratio (long MWCNTs) are used, amounts less than 0.048 wt.% are needed to achieve a similar level of mechanical performance. These differences are attributed to the degree of dispersion of the MWCNTs. Comparing similar amounts of MWCNTs in the mixes, long MWCNTs exhibit a lower degree of dispersion due to their higher aspect ratio. Consequently, adequate dispersion can be achieved at lower amounts. Short MWCNTs exhibit a higher degree of dispersion however, because they are shorter, a higher concentration in cement paste matrix is needed to reduce the fiber free area and arrest the nanocracks.

The flexural strength of the specimens reinforced with MWCNTs shows an increase of 30–40% over plain cement specimens. This increase in the flexural strength seems to be the highest published so far with the lowest concentration of MWCNTs. Until now, the addition of the MWCNTs in cementitious matrices has resulted in either a decrease or smaller increase, up to 25%, of the flexural strength [5,8–11]. Furthermore, the nanocomposites show an increase in Young's modulus, close to 35%, over the plain specimens. The 28 day predicted Young's modulus of the nanocomposites was calculated using the upper bound parallel model [20]. The Young's modulus of the MWCNTs was taken as 1 TPa. According to the model the modulus of the nanocomposites should be about 17 GPa, which is lower than the experimental values (~21.9 GPa) obtained in this and previous studies [10,11]. This suggests that to increase the stiffness of the cementitious composites small amounts of effectively dispersed MWCNTs in the cementitious matrix are needed. To further investigate the increase of the Young's modulus and study the reinforcing mechanism of the MWCNTs, nanoindentation tests were performed on 28 days cement paste samples reinforced with short MWCNTs at an amount of 0.08 wt.% and long MWCNTs at concentrations of 0.025 wt.% and 0.048 wt.%.

3.2. Nanomechanical properties

The structure of cement paste at the nanoscale is dominated by the calcium–silicate–hydrate (C–S–H) phase. Fundamental properties such as strength, fracture behavior, shrinkage and durability are basically controlled by the properties of the C–S–H and the porosity. Fig. 7 illustrates the probability plot of the 28 days Young's modulus of plain cement paste ($w/c = 0.3$) and cement paste reinforced with 0.025 wt.% long MWCNTs, 0.048 wt.% long MWCNTs and 0.08 wt.% short MWCNTs. Based on the literature on a typical nanoindentation plot nanoindentation values of the Young's modulus less than 50 GPa represent 4 phases: the porous phase, low stiffness C–S–H, high stiffness C–S–H and calcium hydroxide [19,21]. Values greater than 50 GPa are attributed to nanoindentation on unhydrated particles (clinker phases) presented in the material [18,19,21]. These properties of cement based materials have been found to be independent of the mix proportions and can be considered as intrinsic material properties [19,21]. The probability plot of plain cement paste is in good agreement with results from the literature [19,21]. It is observed that the peak of the probability plot of plain cement paste falls between 15 and 20 GPa, corresponding to low stiffness C–S–H, which is the dominant phase of the cement nanostructure. However, the peak of the probability plot of Young's modulus for the samples reinforced with MWCNTs, is in the area of 20–25 GPa, which is attributed to high stiffness C–S–H. This suggests that the amount of high stiffness C–S–H was increased by the incorporation of the MWCNTs.

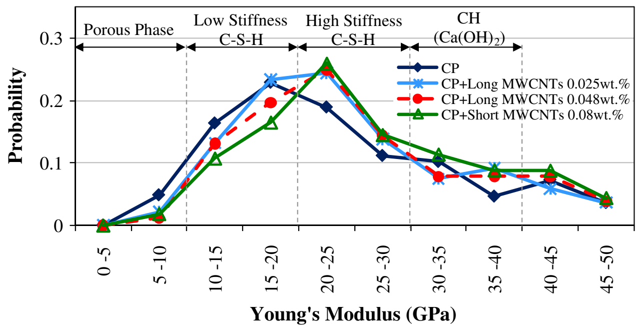

Fig. 7. Probability pots of the Young's modulus of 28 days cement paste ($w/c = 0.3$) and cement paste reinforced with 0.025 wt.% long, 0.048 wt.% long and 0.08 wt.% short MWCNTs.

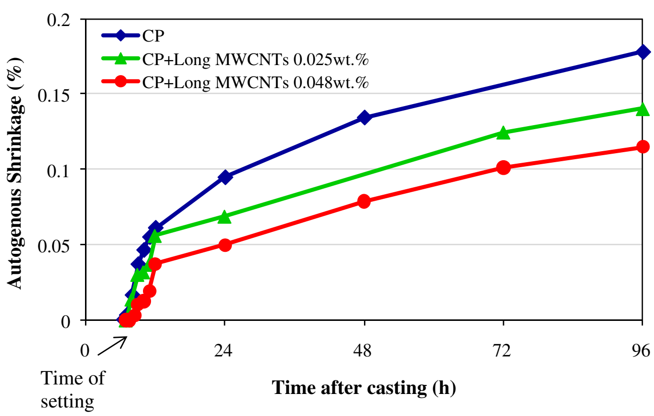

Fig. 8. Autogenous shrinkage of cement paste ($w/c = 0.3$) and cement paste reinforced with 0.025 wt.% and 0.048 wt.% long MWCNTs.

The nanoindentation results also provide an indirect method of estimating the volume fraction of the capillary pores [19]. It is observed that the probability of Young's modulus below 10 GPa, which corresponds to the porous phase, is significantly reduced for the samples with MWCNTs indicating that the MWCNTs reduce the amount of fine pores by filling the area between the C–S–H gel. All the above results compare well with previous findings of the authors in mixes with $w/c = 0.5$ [10,11].

3.3. Autogenous shrinkage

Typically, changes in the nanostructure affect the transport properties (properties that are related with the movement of the water in the pores). Recently, it has been increasingly recognized that high strength and high performance concrete is sensitive to the microcracking that occurs at early ages, as a result of the volumetric changes due to the development of high autogenous shrinkage stresses [22]. A possible solution to this problem is to provide embedded source of water by the addition of saturated lightweight fine aggregates or polymers [23,24]. Fig. 8 shows the autogenous shrinkage results of plain cement paste and cement paste reinforced with 0.025 wt.% and 0.048 wt.% long MWCNTs. It is observed that the samples reinforced with MWCNTs exhibit lower shrinkage than the plain cement paste. Furthermore, it is observed that the samples reinforced with a higher amount of MWCNTs demonstrate lower autogenous shrinkage. The shrinkage development is known to be proportional to the amount of the fine pores (pores with diameter < 20 nm) in the binder at early ages [25,26]. Higher percentage of the volume fraction of small pores in a cementitious system at early ages leads to the increase of autogenous shrinkage. Due to their small diameters (20–40 nm) CNTs appear to reduce the amount of fine pores. This leads to the reduction of the capillary stresses, resulting in lower autogenous strains. The results suggest that the incorporation of MWCNTs has lead to a substantial reduction of the autogenous shrinkage, at least 30% and near 40%.

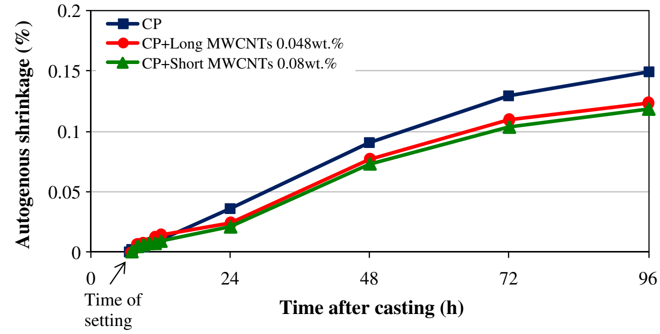

Fig. 9. Autogenous shrinkage of cement paste ($w/c = 0.3$, Type II cement) and cement paste reinforced with 0.048 wt.% long and 0.08 wt.% short MWCNTs. The suspensions of MWCNTs used were 4 months old.

Additional autogenous shrinkage experiments, illustrated in Fig. 9, were conducted using type II cement and MWCNT suspensions that were prepared following the aforementioned procedure and were kept for 4 months. The suspensions were mixed with the cement in concentrations of 0.048 wt.% for long and 0.08 wt.% for short CNTs, respectively. The additions of the MWCNTs in a different cementitious matrix gave analogous results; shrinkage strains were reduced of about 25%. It should be noted that besides the observation of the development of similar shrinkage strains in mixes with different cement types, these results are very important since they can also serve as an indication of the stability of the sonicated MWCNT dispersions over a period of 4 months after sonication. This could be visually observed as no agglomeration or sedimentation of the MWCNTs was seen in the sonicated suspensions.

4. Conclusions

The development of high-performance cementitious nanocomposites reinforced with multiwall carbon nanotubes was studied. It was found that small amounts of effectively dispersed MWCNTs (0.025–0.08 wt.% of cement) can significantly increase the strength and the stiffness of the cementitious matrix. In particular, lower amounts of long MWCNTs (0.025–0.048 wt.%) provide effective reinforcement, while higher amounts (close to 0.08 wt.%) of short MWCNTs are required to achieve the same level of reinforcement. It was also found that effectively dispersed MWCNTs provide a unique role in cement based materials. The nanoindentation results suggest that MWCNTs can strongly modify and reinforce the nanostructure of the cementitious matrix. Compared to plain cement matrix, the nanocomposites appear to have a higher amount of high stiffness C–S–H and reduced nanoporosity. Due to their small diameters (20–40 nm) MWCNTs appear to specifically reduce the amount of fine pores. This phenomenon leads to the reduction of the capillary stresses, resulting in a beneficial effect on the early strain capacity of the nanocomposites.

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