Nanoscale Modification of Cementitious Materials

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Abstract. This research investigates changes in the nanostructure and the nanoscale local mechanical properties of cement paste with micro- and nano-modifiers. Silica fume and multiwall carbon nanotubes (MWCNTs) were used as micro- and nano-modifiers. An effective method of dispersing CNTs in cement matrix was developed. A detailed study on the effects of CNTs concentration and aspect ratio on the fracture properties, nanoscale properties and microstructure of nanocomposite materials, was conducted. Significant improvements on the macro and nanomechanical properties of cement paste were observed with the incorporation of CNTs. Results suggest that CNTs can strongly modify and reinforce the cement paste matrix at the nanoscale.

1 Introduction

The fundamental properties of cementitious materials, such as concrete, are affected by the material properties at the nanoscale [1]. The ultimate goal of this research is to modify the properties at the nanoscale and develop nano-engineered materials with improved macroscopic properties.

In general, cement based materials are typically characterized as quasi-brittle materials that exhibit low tensile strength. Typical reinforcement of cementitious materials is usually done at the millimeter scale and/or at the micro scale using macrofibers and microfibers, respectively. However, cement matrix exhibits flaws which are at the nanoscale. The development of new nanosized fibers, such as carbon nanotubes (CNTs), has opened a new field for nanosized reinforcement within concrete [2-8]. The remarkable mechanical properties of CNTs [9-10] suggest that are ideal candidates for high performance cementitious composites.

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The major drawback however, associated with the incorporation of CNTs in cement based materials is poor dispersion [11]. To achieve good reinforcement in a composite, it is critical to have uniform dispersion of CNTs within the matrix [12]. Few attempts have been made to add CNTs in cementitious matrices at an amount ranging from 0.5 to 2.0% by weight of cement. Previous studies have focused on the dispersion of CNTs in liquids by pre-treatment of the nanotube's surface via chemical modification [2-8]. Preliminary research has shown that small amounts of CNTs can be effectively dispersed in cementitious matrix [13].

In this study, the effect of multiwall carbon nanotubes (MWCNTs) on the macro and nanoscale mechanical properties of cement paste was investigated. An effective method of dispersing carbon nanotubes in cement paste matrix, by applying ultrasonic energy and using a surfactant, was developed. A detailed study on the effects of CNTs concentration and aspect ratio, was conducted. The nano-mechanical properties of CNTs nanocomposites were compared to cement paste with silica fume, which is commonly used as an additive for high strength concrete.

2 Experimental Details

For the preparation of the CNTs nanocomposites ordinary Portland cement and multiwall carbon nanotubes (MWCNTs) were used. Prior to their addition to cement MWCNTs were dispersed in water using a surfactant and by applying ultrasonic energy. A 500 W cup-horn high intensity ultrasonic processor was used to apply constant energy (1900-2100 J/min) to the CNT dispersions. After the sonication, cement was added into the CNT dispersions at a water to cement ratio of 0.5. To make the samples with the silica fume ordinary Portland cement and silica slurry (1000D from W.R. Grace) was used. 15wt% silica fume was used to replace cement. The percentage of water present in the slurry was considered so as to maintain water to binder ratio of 0.5. All materials were mixed according to ASTM C 305. Following mixing, the paste was cast in plastic molds. After demolding the specimens were cured in water saturated with lime until testing.

The morphology and the microstructure of the fracture surface of CNTs nanocomposites were investigated using an ultra-high resolution field emission SEM (Hitachi S5500). Specimens were tested after 18 hours of curing. Prior to their observation, the fracture surface of the specimens was sputter-coated at a 20nm thick layer of gold-palladium (Au/Pd).

The mechanical performance of the CNTs nanocomposites was evaluated by fracture mechanics tests. Notched specimens of 20×20×80 mm were tested at the age of 3, 7 and 28 days, by three-point bending. The tests were performed with a closed-loop testing machine with a 89 kN capacity. The feedback control signal for running the test was the crack mouth opening displacement (CMOD) at the notch, which was advanced at a rate of 0.12 mm/min. The load and the CMOD were recorded during the test. The Young's modulus was calculated from the load versus CMOD results using the two-parameter fracture model by Jenq and Shah [14].

The nanomechanical properties of the CNTs nanocomposites were investigated using a Hysitron Triboindenter following the method described in Ref. 15. Before testing, thin slides of approximately 5 mm were cut out of the specimens. The surfaces were polished with silicon carbide paper discs and diamond lapping films in order to obtain a very smooth and flat surface. Nanoindentation was performed in a 12×12 grid (10 μm between adjacent grid points). This procedure was repeated in at least two different areas on each sample.

3 Results and Discussion

In order to investigate the effectiveness of the dispersing method nanoimaging of the fracture surfaces of samples reinforced with 0.08% by weight of cement CNTs, were performed. Results from SEM images of cement paste samples reinforced with CNTs that were added to cement as received (without dispersion) and CNTs that were dispersed following the method described previously are presented in Fig. 1. As expected, in the samples where no dispersing technique was used [Fig. 1 (a)] CNTs appear poorly dispersed, forming large agglomerates and bundles. On the other hand, in the samples where dispersion was achieved by applying ultrasonic energy and using a surfactant [Fig. 1 (b)] only individual CNTs were identified on the fracture surface. The results indicate that the application of ultrasonic energy and the use of surfactant can be employed to effectively disperse CNTs in cementitious matrix.

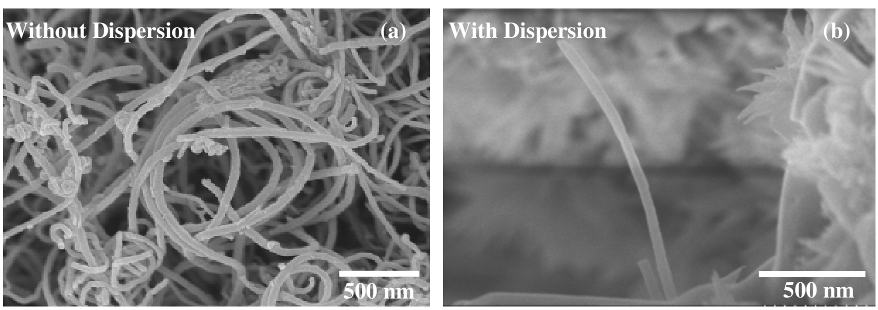

Fig. 1 SEM images of cement paste reinforced with CNTs dispersed with (FIG. 1(b)) and without (FIG. 1(a)) the application of ultrasonic energy and the use of surfactant

To evaluate the reinforcing effect of CNTs fracture mechanics tests were performed using MWCNTs with aspect ratios of 700 and 1600 for short and long CNTs, respectively. Additionally, to investigate the effect of CNTs concentration cement paste samples reinforced with lower and higher amounts of CNTs (0.048wt% and 0.08wt%, respectively) were tested. The fracture mechanics test results of the average Young's modulus of the nanocomposites which demonstrated the best mechanical performance are illustrated in Fig. 2. In all cases, the samples reinforced with CNTs exhibit much higher Young's modulus than plain cement paste. More specifically, it is observed that the specimens reinforced with either short CNTs at an amount of 0.08wt% or long CNTs at an amount of 0.048wt% provide the same level of mechanical performance. Generally, it can be concluded that the optimum amount of CNTs depends on the aspect ratio of

CNTs. When CNTs with low aspect ratio are used a higher amount close to 0.08wt% by weight of cement is needed to achieve effective reinforcement. However, when CNTs with high aspect ratio are used less amount of CNTs close to 0.048 wt% is needed to achieve the same level of mechanical performance.

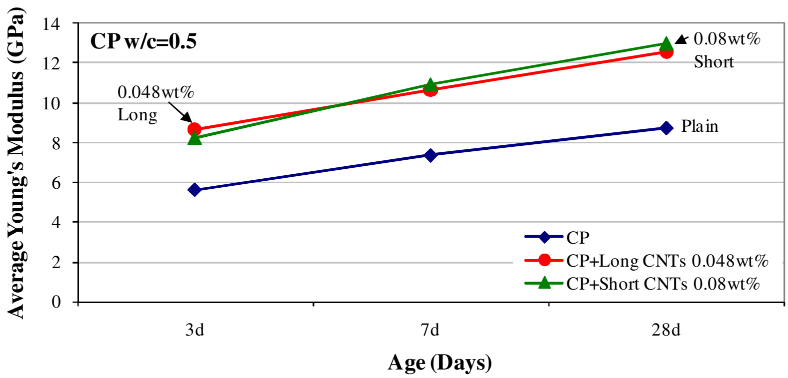

Fig. 2 Fracture mechanics test results of the Young's modulus of CNTs nanocomposites which exhibit the best mechanical performance among the different mixes tested

Comparing the 28 days Young's modulus of the nanocomposites with that of the plain cement paste, a 50% increase is observed. Based on the parallel model [16] the predicted Young's modulus of cement paste nanocomposites reinforced with either 0.048wt% or 0.08 wt%CNTs at the age of 28 days (~9.1 GPa) is much lower than the experimental values obtained (~13 GPa). To further investigate the increase of the Young's modulus, nanoindentation tests on 28 days cement paste samples reinforced with CNTs were performed. The results were compared with cement paste samples with silica fume.

Fig. 3 illustrates the probability plot of the Young's modulus of plain cement paste (w/c=0.5), cement paste reinforced with 0.08wt% short CNTs, cement paste reinforced with 0.048wt% long CNTs and cement paste with silica fume. A peak analyzing protocol was used to fit four normal distributions to the probability plot of the Young's modulus corresponding to the porous phase, low stiffness C-S-H, high stiffness C-S-H and calcium hydroxide [1, 17]. It is observed that the peak of the distribution of the nanoindentation modulus of the plain cement paste and cement paste with silica fume falls in the area of 15 to 20 GPa which corresponds to the low stiffness C-S-H. However, the peaks of the probability plot of the Young's modulus of the CNTs nanocomposites were found to be in the area of 20 to 25 GPa which corresponds to the high stiffness C-S-H gel. These results indicate that the incorporation of CNTs increased the amount of high stiffness C-S-H gel resulting in a stronger material. Additionally, it is observed that the probability of the Young's modulus below 10 GPa, which represents the porous phase, is reduced for the samples with silica fume and CNTs. These results suggest that CNTs similarly with silica fume reduce the nanoporosity of cement paste by filling the gaps between the C-S-H gel. Furthermore, comparing the probability plots of the

Young's modulus of the CNTs nanocomposites it is observed that the probability of high-stiffness C-S-H is higher for the samples with short CNTs and lower for the samples with long CNTs. This indicates that the samples reinforced with 0.08wt% short CNTs exhibit more improved properties at the nanoscale than the samples reinforced with 0.048wt% long CNTs. This response comes into agreement with the macromechanical properties of the samples where the samples with 0.08wt% short CNTs exhibit slightly higher Young's modulus than the samples reinforced with 0.048wt% long CNTs.

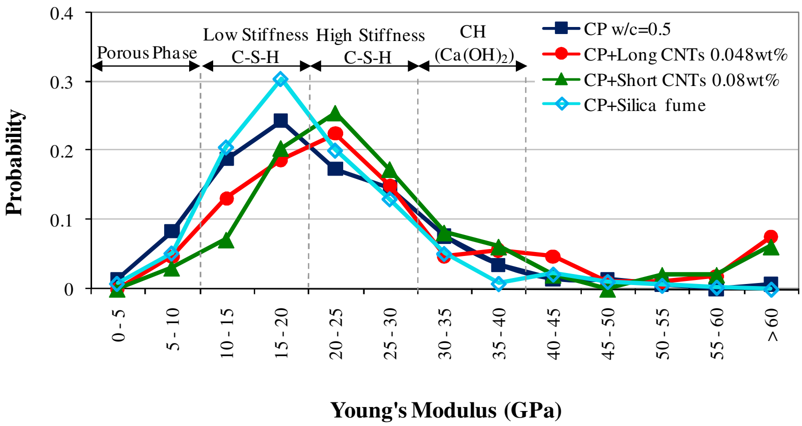

Fig. 3 Probability plot of the calculated Young's modulus of 28 days cement paste (w/c=0.5), cement paste reinforced with 0.048wt% long CNTs, cement paste reinforced with 0.08wt% short CNTs and cement paste with silica fume

4 Conclusions

The effect of multiwall carbon nanotubes (MWCNTs) on the nanostructure as well as the macro and nanoscale mechanical properties of cement paste has been investigated. An effective method of dispersing carbon nanotubes in cement paste matrix by applying ultrasonic energy and with the use of a surfactant has been developed. The fracture mechanics test results indicate that the fracture properties of cement matrix are increased through proper dispersion of small amounts of CNTs (0.048wt% and 0.08wt%). In particular, when short CNTs are used, higher amounts of CNTs (0.08wt%) are required to achieve effective reinforcement, while when longer CNTs are incorporated, lower amounts of CNTs (0.048wt%) are needed to achieve the same level of mechanical performance. The nanoindentation results suggest that CNTs can strongly modify and reinforce the cement paste matrix at the nanoscale by increasing the amount of high stiffness C-S-H and decreasing the porosity. A comparison of the nano-mechanical properties of bulk paste, cement paste reinforced with CNTs and cement paste with silica fume has shown that CNTs substantially enhance the Young's modulus of the C-S-H phase.

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