Fracture Mechanics of Concrete and Concrete Structures -
Recent Advances in Fracture Mechanics of Concrete - B. H. Oh, et al.(eds)

Exploration of fracture characteristics, nanoscale properties and nanostructure of cementitious matrices with carbon nanotubes and carbon nanofibers

S.P. Shah
Center for Advanced Cement Based Materials, Department of Civil and Environmental Engineering, Northwestern University, Evanston, IL 60208, USA

M.S. Konsta-Gdoutos & Z.S. Metaxa
Department of Civil Engineering, School of Engineering, Democritus University of Thrace,

Xanthi, Greece

ABSTRACT: This research investigates changes in the fracture mechanics characteristics and nanoscale properties of cement paste materials reinforced with nanofibers, such as multiwall carbon nanotubes (MWCNTs) and carbon nanofibers (CNFs). The effect of the nanofibers on the microstructure of cement paste was also investigated. It was found that MWCNTs and CNFs reinforce cementitious materials by controlling cracks at the nanoscale level and improving the Young's modulus and the flexural strength of the matrix. The use of MWCNTs was also found to improve the nanomechanical properties of cement matrix. In particular, nanoindentation results have shown that the incorporation of MWCNTs led to the reduction of the nanoporosity of the matrix and significantly increased the amount of high stiffness C-S-H gel. Additionally, the nanocomposites reinforced with CNFs showed improved fracture behavior when compared to the samples with MWCNTs.

1 INTRODUCTION

It is well known that cementitious materials are susceptible to cracking. Under loading, initially, short and discontinuous microcracks are created in a distributed manner (Jia & Shah 1994). These microcracks coalesce to form large macroscopic cracks that propagate and lead to ultimate failure of the material. Traditionally, fibers, which control cracking by bridging the cracks and retarding their propagation, are used as reinforcement in cementitious matrices. The mechanical performance as well as the crack formation in cementitious matrices is affected by the size, type and volume of fiber reinforcement (Balaguru & Shah 1992). Fine microfibers are utilized to bridge the microcracks which delay the process by which the microcracks coalesce to form macrocracks. Macrofibers on the other hand, can be used only to bridge macrocracks.

However, crack formation in cement based materials initiates from the nanoscale where microfibers can not be effective. With the introduction of nanofibers a new field for reinforcement within concrete was developed (Konsta-Gdoutos et al. 2008, Konsta-Gdoutos et al. 2009, Metaxa et al. 2009, Shah et al. 2009). This research investigates the changes in the fracture properties, nanostructure and nanoscale mechanical properties of cement paste reinforced with highly dispersed multiwall carbon nanotubes (MWCNTs) and carbon nanofibers (CNFs). The results suggest that nanofibers substantially improve the nanoscale properties and fracture characteristics of cementitious matrices, by controlling the matrix cracks at the nano level. Comparing the response of the nanocomposites reinforced with MWCNTs to the ones with CNFs it was found that CNFs provide the nanocomposite with the capacity to carry higher loads at lower strains.

2 EXPERIMENTAL PROGRAM

2.1 *Nanocomposites Preparation*

The nanocomposites were prepared using Type I ordinary Portland cement (OPC) and commercially available, as received, nanofibers, such as multiwall carbon nanotubes (MWCNTs) and carbon nanofibers (CNFs). The geometry of the nanofibers is shown in Table 1. It is observed that both nanofibers exhibit similar length range but different diameter, with MWCNTs to demonstrate almost 3 times higher aspect ratio.

Table 1. Geometry of nanofibers

	Diameter, nm	Length, μm	Aspect Ratio
MWCNTs	20-40	30-100	1600
CNFs	60-150	30-100	650

In general, MWCNTs and CNFs are described as ultra-high strength materials, characterized by a high tensile modulus, tensile strength, electrical and thermal conductivity and corrosion resistance. To develop high performance nanofiber/cement nanocomposites homogeneous dispersion of nanofibers in the cementitious matrix must be accomplished (Xie et al. 2005).

In this study, the dispersion method described in Konsta-Gdoutos et al. (2008) was used. Based on this method, MWCNTs and CNFs were dispersed in an aqueous surfactant solution by applying ultrasonic energy using a 500 W cup-horn high intensity ultrasonic processor. After dispersion, OPC was added to the nanofiber suspensions at a water to cement ratio of 0.5 (w/c=0.5). The materials were mixed using a standard Hobart mixer, following the procedure outlined by ASTM 305. After mixing, the material was cast in 20 × 20 × 80 mm molds.

2.2 *Fracture mechanics tests*

The mechanical properties of the mixes were measured by three-point bending tests of beams with a 6 mm notch cut at the midspan. The beams were tested at the age of 3, 7 and 28 days. An average value of three specimens was used for each curing age, based on ASTM C 348. The tests were performed with a closed-loop MTS servo-hydraulic testing machine with an 89 kN capacity. Crack mouth opening displacement was used to control the test and was advanced at a rate of 0.012 mm/min. 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 & Shah (Shah et al. 1995). Strength was calculated using the net specimen depth.

2.3 *Nanoindentation tests*

The nanomechanical properties of CNTs nanocomposites were investigated using a Hysitron Triboindenter. Prismatic specimens of 25.4 × 6.35 × 6.35 mm were prepared and cured in water saturated with lime for 28 days. 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. A Berkovich tip with a total included angle of 142.3 degrees was used for indentation. Multiple cycles of partial loading and unloading were used to make each indention, eliminating creep and size effects (Nemecek 2009). 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. The Oliver & Pharr (1992) method was used to determine the mechanical properties, where the indentation modulus is calculated from the final unloading curve.

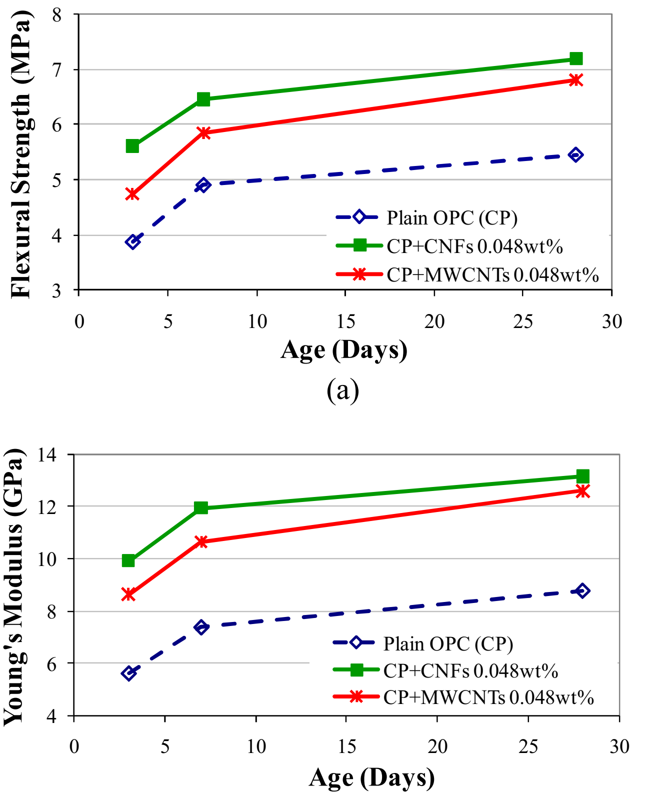
2.4 *Scanning electron microscopy*

An ultra-high resolution field emission scanning electron microscope (LEO Gemini 1525) was used to examine the morphology and microstructure of the fracture surfaces of the nanocomposites. Specimens of 25.4 × 6.35 × 6.35mm were prepared for each mix. Prior to their observation, the fracture surface of the specimens was sputter-coated using the Denton Desk III system. Due to the roughness of the surface, a 20 to 25 nm thick layer of gold-palladium (Au/Pd) was used to eliminate charging effects caused by insufficient coating. The SEM machine was operated at 3 to 5 kV. Secondary electron (SE) imaging was employed to obtain clear images at medium to high magnifications (10,000× to 150,000×).

3 RESULTS AND DISCUSSION

The flexural strength rate of the nanocomposites incorporating either MWCNTs or CNFs up to the age of 28 days of hydration is shown in Figure 1(a). The samples reinforced with nanofibers at all ages exhibit higher flexural strength than plain cement paste. In particular, an increase up to 25% is achieved when MWCNTs are utilized. The use of CNFs results in an increase of the flexural strength up to 45%. Comparing the two nanocomposites it is observed that despite the fact that MWCNTs exhibit a higher aspect ratio due to their smaller diameter and larger amounts of nanotubes is reinforcing the cement matrix since the concentration of the fibers is constant, CNFs provide the matrix with the ability to carry higher flexural loads at lower strains. A possible explanation could be that the bonding between the CNFs and the matrix is enhanced due to the unusual outer surface texture of the carbon nanofibers. The CNFs used in this study exhibit graphite planes which extend beyond the diameter of the nanofiber and are present along the circumference of the fiber. These edges probably help anchor the fiber in the matrix, preventing interfacial slip and enable more sufficient load transfer across nanocracks and pores.

The Young's modulus of the samples reinforced with either MWCNTs or CNFs at the age of 3, 7 and 28 days is illustrated in Figure 1(b). Similar to the flexural strength results, samples reinforced with nanofibers clearly exhibit improved Young's modulus over OPC specimens. Specifically, an increase of the Young's modulus of 44% to 50% over plain cement specimens is achieved with the use of MWCNTs. In the case of the samples with CNFs, an increase of at least 50% is observed.



(b)

Figure 1. Flexural strength (a) and Young's modulus (b) of plain cement paste (w/c=0.5) and cement paste reinforced with either 0.048% by weight of cement MWCNTs or CNFs.

In order to investigate the increase in Young's modulus, the 28 day predicted Young's modulus of the nanocomposites with MWCNTs was calculated, using the upper bound parallel model. The Young's modulus of the MWCNTs was taken as 1 TPa. According to the model, the modulus of the nanocomposites should be about 9.1 GPa, which is lower than the experimental value (~13 GPa) obtained in this and previous studies (Konsta-Gdoutos et al. 2009, Metaxa et al. 2009, Shah et al. 2009). This suggests that, to increase the stiffness of the cementitious composites small amounts of effectively dispersed MWCNTs in the cementitious matrix are needed. Additionally, an evaluation study of the Young's modulus of concrete nanocomposites reinforced with 1% CNTs, predicts a 33% increase in Young's modulus (Rouainia & Djeghaba 2008), which is lower than the increase obtained in this study. 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 MWCNTs.

The probability plots of the Young's modulus of 28 days plain cement paste and cement paste reinforced with MWCNTs are shown on Figure 2. Values of the Young's modulus less than 50 GPa represent four different phases of cement paste corresponding to the porous phase, low stiffness C-S-H, high stiffness C-S-H and calcium hydroxide phase (Constantinides & Ulm 2007, Mondal et al. 2008, Mondal 2008). As expected, the peak of the probability plot of plain cement paste falls in the area of the low stiffness C-S-H, which is the dominant phase of cement nanostructure. On the other hand, the peak of the probability plot of the nanocomposite is in the area of 20 to 25 GP, which corresponds to the high stiffness C-S-H, suggesting that the addition of MWCNTs results in a stiffer material with increased amount of high stiffness C-S-H. Additionally, the nanoindentation results provide an indirect method of estimating the volume fraction of the capillary pores (Constantinides & Ulm 2007). It is observed that the probability of Young's modulus below 10 GPa is significantly reduced for the samples with MWCNTs. This indicates that the MWCNTs reduce the amount of fine pores by filling the area between the C-S-H gel.

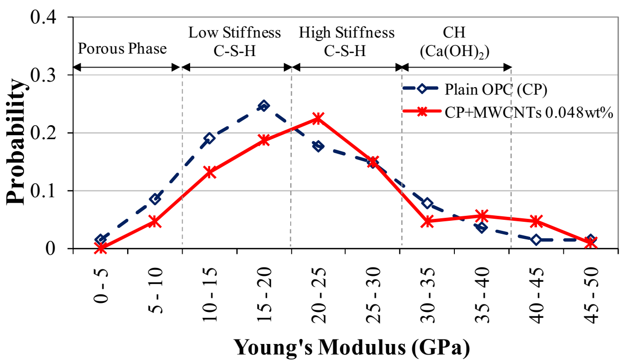


Figure 2. Probability plots of the Young's modulus of 28 days plain cement paste (w/c=0.5) and cement paste reinforced with 0.048 wt% MWCNTs.

To better understand the effect of nanofibers on the nanostructure of cement paste SEM was employed. Figure 3 shows SEM images of the fracture surface of the nanocomposites reinforced with MWCNTs (Fig. 3(a)) and CNFs (Fig. 3(b)) at a scale of 500 nm. It is observed that mostly individual nanofibers can be identified on the fracture surface. This indicates that good dispersion was achieved. It can also be seen that nanofibers appear to be embedded into the hydration products, showing that good bonding between the nanofibers and the matrix was also achieved. Good bonding enables the load transfer between the matrix and the nanofibers, which results in the improvement of the overall strength of the nanocomposite. Additionally, in both images, MWCNTs and CNFs are observed bridging nanocracks and pores, indicating that well dispersed nanofibers at low concentrations can enable the control of the cracks at the nanoscale level and effectively reinforce the cement paste matrix.

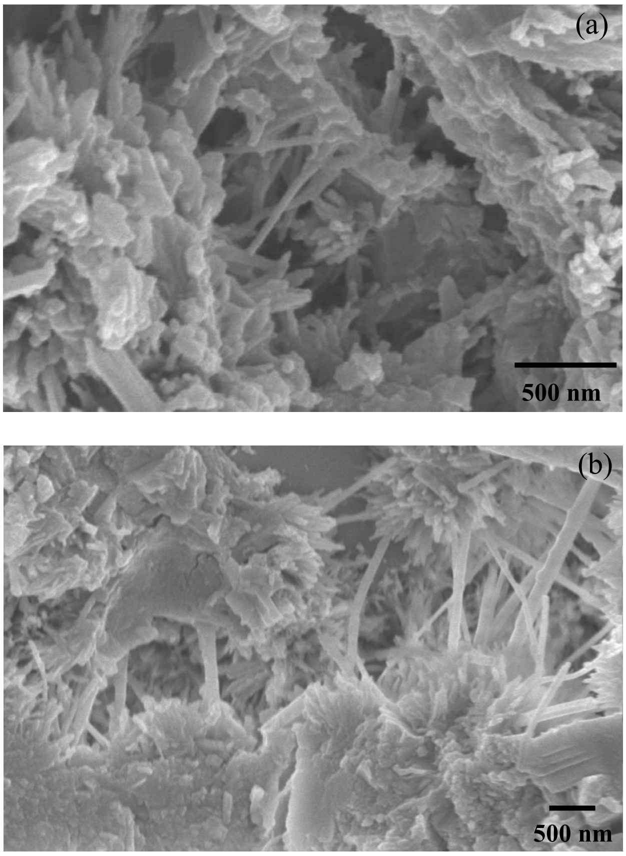


Figure 3. Scanning electron microscopy images of the fracture surface of cement paste reinforced with 0.048wt% (a) MWCNTs and (b) CNFs.

4 CONCLUSIONS

Fracture mechanics and nanoindentation tests were employed to investigate the effect of MWCNTs and CNFs on the mechanical and fracture characteristics of cementitious matrix. SEM was also utilized to investigate the nanostructure of the cement nanocomposites. It was shown that MWCNTs as well as CNFs can be used to improve the flexural strength and the Young's modulus of cementitious matrices. In particular, nanocomposites with CNFs outperformed compared to the samples with MWCNTs. Also, it was found that the incorporation of MWCNTs led to the reduction of nanoporosity in the matrix and significantly increased the amount of high stiffness C-S-H gel. SEM results show that nanofibers reinforce cementitious matrices by bridging nanopores and nanocracks.

5 REFERENCES

Balaguru, P.N. & Shah, S.P. 1992. *Fiber reinforced cement composites*. New York: McGraw-Hill Inc.

Constantinides, G. & Ulm, F.J. 2007. The nanogranular nature of C-S-H. *Journal of the Mechanics and Physics of Solids* 55(1): 64–90.

Jia, Z. & Shah, S.P. 1994. Two-dimensional electronic-speckle-pattern interferometry and concrete fracture process. *Experimental Mechanics* 34: 262-270.

Konsta-Gdoutos, M.S., Metaxa, Z.S. & Shah, S.P. 2008. Nano-imaging of highly dispersed carbon nanotube reinforced cement based materials. Proceedings of the Seventh International RILEM Symposium on Fiber Reinforced Concrete: Design and Applications. Gettu R. (ed.), *RILEM Publications S.A.R.L.*: 125–131.

Konsta-Gdoutos, M.S., Metaxa, Z.S. & Shah, S.P. 2009. Multi-Scale Mechanical and Fracture Characteristics and Early-Age Strain Capacity of High Performance Carbon Nanotube/Cement Nanocomposites. *Cement and Concrete Composites*, 10.1016/j.cemconcomp.2009.10.007.

Metaxa, Z.S., Konsta-Gdoutos, M.S. & Shah S.P. 2009 Carbon nanotubes reinforced concrete. *ACI Special Publications 267: Nanotechnology of Concrete: The Next Big Thing is Small*. SP-267-2 2009:11-20.

Mondal, P., Shah, S.P. & Marks, L.D. 2008. Nanoscale characterization of cementitious materials. *ACI Materials Journal* 105(2): 174–179.

Mondal, P. 2008. *Nanomechanical Properties of Cementitious Materials*. PhD Thesis, Northwestern University: Evanston.

Nemecek J. 2009. Creep effects in nanoindentation of hydrated phases of cement pastes. Materials Characterization 60(9): 1028-1034.

Oliver, W.C. & Pharr, G.M. 1992. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *Journal of Material Research* 7(6): 1564-1583.

Rouainia, G. & Djeghaba, K. 2008. Evaluation of Young's modulus of single walled carbon nanotube (SWCNT) reinforced concrete composite. *Journal of Engineering and Applied Sciences* 3(6): 504-515.

Shah, S.P., Swartz, S.E. & Ouyang, C. 1995. *Fracture mechanics of concrete: application of fracture mechanics to concrete, rock and other quasi-brittle materials*. New York: John Willey and Sons.

Shah, S.P., Konsta-Gdoutos, M.S., Metaxa, Z.S. & Mondal P. 2009. Nanoscale modification of cementitious materials. In: Bittnar Z, Bartos PJM, Nemecek J, Smilauer V, Zeman J, (eds), *Nanotechnology in construction 3. Proceedings of the Third International Symposium on Nanotechnology in construction*. Springer: 125-130.

Xie, X.L., Mai, Y.W. & Zhou, X.P. 2005. Dispersion and alignment of carbon nanotubes in polymer matrix: A review. *Materials Science and Engineering: Reports* 49(4): 89-112.