AN INNOVATIVE HYBRID NANO-FIBERED CONCRETE

Yu Bao*, PhD, PE, Department of Civil Engineering Technology, Environmental Management and Safety, Rochester of Institute of Technology, Rochester, NY
Chad Stevens, Department of Civil Engineering Technology, Environmental Management and Safety, Rochester of Institute of Technology, Rochester, NY
Miao Yu, PhD, Department of Chemical and Biological Engineering, University of Colorado at Boulder, Boulder, CO
Todd Dunn, PE, Department of Civil Engineering Technology, Environmental Management and Safety, Rochester of Institute of Technology, Rochester, NY
*: Corresponding author, 78 Lomb Memorial Drive, CST-3151, Rochester, NY 14623, Email: axbite@rit.edu

ABSTRACT:
In this paper, the experimental work on an innovative hybrid nano-fibered cement/concrete is presented. The hybrid nano-fibered cement/concrete consists of multi-walled carbon nanotubes (MWNT) and micro-synthetic fibers. Four groups of mortar mixtures are prepared, and tests are performed on cured cube samples. Group 1 samples are made with ordinary Type I Portland cement, Group 2 samples are made by adding MWNT, 0.5% by weight, to the mortar mixture, Group 3 samples are made by adding micro-synthetic fibers, 0.05% by weight, to the mortar mixture, and Group 4 samples feature both MWNT (0.5%) and micro-synthetic fibers (0.05%) in the mortar mixture. The water-cement ratio used in all samples is 0.485. The compressive stress-strain curves for the samples are obtained by an automatic data collection system. The samples with hybrid nano-fibers (Group 4) show significant increase in compressive strength as well as high performance of cracking control. Scanning Electron Microscope (SEM) images are obtained to investigate the micro-structures of the mortar mixtures. The SEM images verify that MWNT form strong braces in the pores and micro- cracks of the mortar mixture, which contributes to higher strengths. The proposed innovative hybrid nano-fibered concrete is proved to be a successful combination of nanotechnology and traditional construction materials and has very promising applications in bridge and roadway construction and precast/prestressed concrete industry due to its high strength and cracking control behavior.

Keywords: Cement, Concrete, Carbon Nanotubes, Micro-Synthetic Fibers, Compressive Strength

INTRODUCTION

Concrete has been the most widely used material in the modern construction industry ranging from buildings, water pipes and dams to roads and bridges. According to national bridge inventory data, more than 70 percent of the bridges built today are made of concrete. Due to its durability, versatility and economy, concrete has many advantages over other materials and concrete is the material of choice for superior structures. However, concrete tends to crack due to shrinkage and loads. Synthetic fibers (polypropylene multifilament fibers) have been used in concrete to reduce cracking, but such formulations do not enhance the compressive strength of concrete. Carbon nanotubes (CNTs) are proven as the strongest fibers of all known materials and are a promising candidate for the next generation of high performance structural composite materials[1]. CNTs have been reported to enhance the strength and ductility of plastic and rubbers[5]. Theoretically, CNTs are ideal reinforcing fibers in concrete. First, CNTs have much higher strength than other fibers, which should contribute to overall strength of concrete. Second, the aspect ratio of CNTs is much higher than other fibers, which requires higher energy for cracking propagation. Third, the nano size of CNTs is similar to the thickness of calcium silicate hydrate layers of hydrated cement, allowing CNTs to be widely distributed into the cement matrix with much smaller spacing than traditional fibers. The mechanical behavior of CNTs has generated great interests in their use as a structural material and substantial progress is expected in construction and construction material fields[5, 6]. Incorporating CNTs into conventional cement-based concrete remains in its pre-exploration and fundamental research stage. Nevertheless, the potential of CNTs to improve the mechanical properties of conventional concrete is promising.

There are three areas of research that are specially related to the construction industry. These include CNTs composites made with existing construction materials such as concrete, CNTs ropes for use as structural components and CNTs ropes for use as heat transfer systems[2]. Most recent research of CNTs in cement-based concrete has focused on the structure and fracture mechanisms of the composite materials[6]. Advances in imaging technique make it possible to observe the microscopic structure at its nano-scale. Scanning Electron Microscope (SEM) has recently been used to investigate the nanoscopic structure of CNTs reinforced concrete[1, 2, 7]. The SEM can produce very high resolution images of a sample surface, revealing details as small as 1 nanometer in size.

Ordinary Portland cement (OPC) is the most commonly used cement binder in concrete. Cement powders, when mixed with water, undergo hydration reactions to form the solid cement binder. Cement is a porous material and the porosities formed by the cement grains have dimensions on the order of 5 to 30 micrometers. Unreinforced concrete is a brittle material, and is much stronger in compression than in tension, and therefore is susceptible to cracking. Synthetic fibers are added into concrete for the purpose of cracking control. The strength of concrete is affected by many factors including water to cement ratio, pore sizes in cement and the presence of micro-cracking in the cement binder. The nanoscale structure of cement itself is complex[2]. Some of the properties that affect concrete strength are in nanoscale, and the nanostructure of cement opens possibilities to use nanotechnology to enhance cement and concrete behavior. One approach to improving the strength of the concrete is the addition of CNTs into the cement matrix[2].

Cement based concrete CNTs composites have great potential, and current research is in progress to investigate the mechanical performance of cement CNTs composites. Yakovlev et al. (2006) reported that cement based foam concrete reinforced by single walled CNTs shows its compressive strength increasing by up to 70%[7]. Lab research observed crack bridging in cement CNTs composites[3]. Rouainia et al. (2008) employed finite element modeling to evaluate the Young's modulus of the single walled CNTs reinforced concrete composites[3]. Li et al. (2007) investigated the pressure-sensitive properties and microstructure of CNTs reinforced cement composites[1]. Raki et al. (2010) reviewed recent innovative achievements in cement and concrete nanoscience and nanotechnology[4].

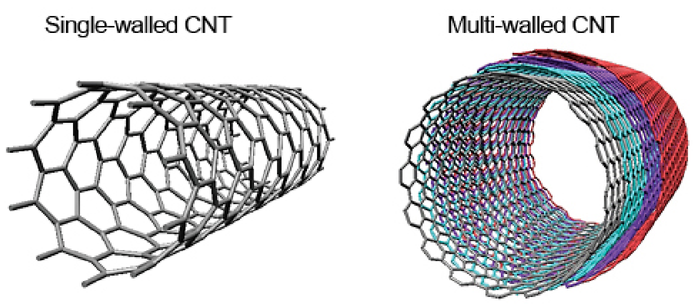

Fig. 1 SWNT and MWNT

Most published research results have focused on single walled CNTs (SWNT) reinforced cement composites. The synthetic process of SWNT is much more complex than multi-walled CNTs (MWNT), and therefore, the cost of SWNT is much higher than that of MWNT. Also, dispersion of SWNT is more difficult to achieve than that of MWNT. The mechanical properties of MWNT, such as compressive strength and tensile strength, however, are almost identical to those of SWNT. Thus, MWNT have more potential than SWNT in the construction industry due to its lower cost and simpler preparation process. The structures of SWNT and MWNT are shown in Fig. 1. So far, no published records have shown research work on combined use of CNTs and synthetic fibers in cement and concrete composites. In this paper, the research on studying the mechanical performance of cement composites reinforced by MWNT/synthetic hybrid fibers is presented. The nanoscopic microstructure of the MWNT/synthetic hybrid fibered cement composites is investigated by SEM. We have discovered that the innovative MWNT/synthetic hybrid fibered cement composites show significant enhancement in both compressive strength and cracking control behavior. The new concrete shows promise for applications in precast/prestressed concrete members for bridges, buildings, oil pipes and nuclear facilities, where both strength and cracking control are critical. The strength increase of the new concrete will make possible the design of slimmer structural members, which in turn leads to savings in materials, labor, and energy.

EXPERIMENT

The cement composites cube specimens were prepared according to ASTM C109 "Standard Test Method for Compressive Strength of Hydraulic Cement Mortars." The size of the cube specimens was 50mm×50mm×50mm. In order to investigate the effect of different types of fibers on compressive strength of cement composites, four groups of cement mortar specimens were prepared. The first group of samples was made with ordinary Type I Portland cement, the second group differed from the first by adding multi-walled carbon nanotubes (MWNT), 0.5% by weight, to the mortar mixture. The third group of samples was made by adding micro-synthetic fibers, 0.05% by weight, to the cement mortar mixture, and the fourth group featured both MWNT (0.5%) and micro-synthetic fibers (0.05%) in the mortar mixture. The water-cement ratio used in all samples was 0.485. The physical properties of the MWNT used in this paper are listed in Table 1, and the chemical and physical properties of the micro-synthetic fibers are listed in Table 2.

Table 1: Physical Properties of MWNT

Description	Purity	Inside Diameter (ID)	Outside Diameter (OD)	Length	Specific Surface Area	Bulk Density	True Density	Color
Industrial Grade, 10-30 nm OD	85%	5-10 nm	10-30 nm	10-30 μm	> 200 m^2/g	0.14 g/cm^3	2.1 g/cm^3	Black

Table 2: Chemical and Physical Properties of Micro-Synthetic Fibers

Description	Specific Gravity	Fiber Length	Fiber Diameter	Acid & Salt Resistance	Melt Point	Ignition Point	Thermal Conductivity
Polypropylene Multifilament Fibers	0.91	10-20 mm	1-10 μm	High	162 ºC	593 ºC	Low

MWNT need to be homogenously dispersed in water before mixing with cement[8]. Due to the poor compatibility of CNTs and water, it is difficult to disperse CNTs in water without any treatment. In this paper, MWNT were dispersed in 2% Sodium Dodecyl Sulfate (SDS) solution and soaked into ultrasonic bath for 25 minutes as shown in Fig. 2. No other treatment for MWNT was needed. As there are no definitive data on carbon nanotube on toxicity yet, we took precautionary approach to use certain type of mask to prevent hazards from breathing in CNTs when we prepared the specimens.

Fig. 2 MWNT Dispersion Using Ultrasonic Bath

The cement mortar cube compressive strength tests were conducted on a MTS 45/G Material Testing System and the compressive stress-strain curves were automatically captured by the computer connected to the test machine, as shown in Fig. 3. The peak compressive strength was also automatically recorded by the computer.

Fig. 3 Cube Compression Test on 45/G Test Machine

The digital pictures of the failure samples were taken right after the compression tests in order to investigate the macroscopic failure modes of different samples. Scanning Electron Microscope (SEM) images were taken for each sample as shown in Fig. 4 to explore the microstructures of

MWNT and micro-synthetic fibers in cement mortar specimens and to investigate how MWNT and micro-synthetic fibers might affect the compressive strength of the cement composites.

Fig. 4 SEM Imaging System

RESULTS

Four groups of cement mortar cubes were tested. Group 1 samples were made with ordinary Type I Portland cement, Group 2 samples were made by adding MWNT, 0.5% by weight, to the mortar mixture. Group 3 samples were made by adding micro-synthetic fibers, 0.05% by weight, to the mortar mixture, and Group 4 samples featured both carbon nanotubes (0.5%) and micro-synthetic fibers (0.05%) in the mortar mixture. The description of the samples is listed in Table 3. For each group of the cement composites, three cube specimens were selected and the compressive strength of each group was obtained by averaging the ultimate strength of the three samples. The cube compression tests were conducted at 1-day, 7-day and 28-day after the cement mortar cubes were poured. The compressive strengths of the four groups are listed in Table 4 and the plots of compressive strength vs. time are shown in Fig. 5.

Table 3: Cube Specimens Description

Group No.	Cube Size	Components	Water/Cement Ratio
1	50 mm × 50 mm × 50 mm	Ordinary Portland Cement, Type I	0.485
2	50 mm × 50 mm × 50 mm	Cement + Micro-synthetic Fiber	0.485
3	50 mm × 50 mm × 50 mm	Cement + MWNT	0.485
4	50 mm × 50 mm × 50 mm	Cement + MWNT + Micro-synthetic Fiber	0.485

Table 4: Compressive Strength

Time	Compressive Strength Group 1		Compressive Strength Group 2			Compressive Strength Group 3			Compressive Strength Group 4		
(day)	(psi)	(Mpa)	(psi)	(Mpa)	% change to Group 1	(psi)	(Mpa)	% change to Group 1	(psi)	(Mpa)	% change to Group 1
1	1350	9.3	1200	8.3	-11.1	1300	9.0	-3.7	1620	11.2	20.0
7	3200	22.1	2900	20.0	-9.4	3100	21.4	-3.1	3800	26.2	18.8
28	3900	26.9	3550	24.5	-9.0	4000	27.6	2.6	4700	32.4	20.5

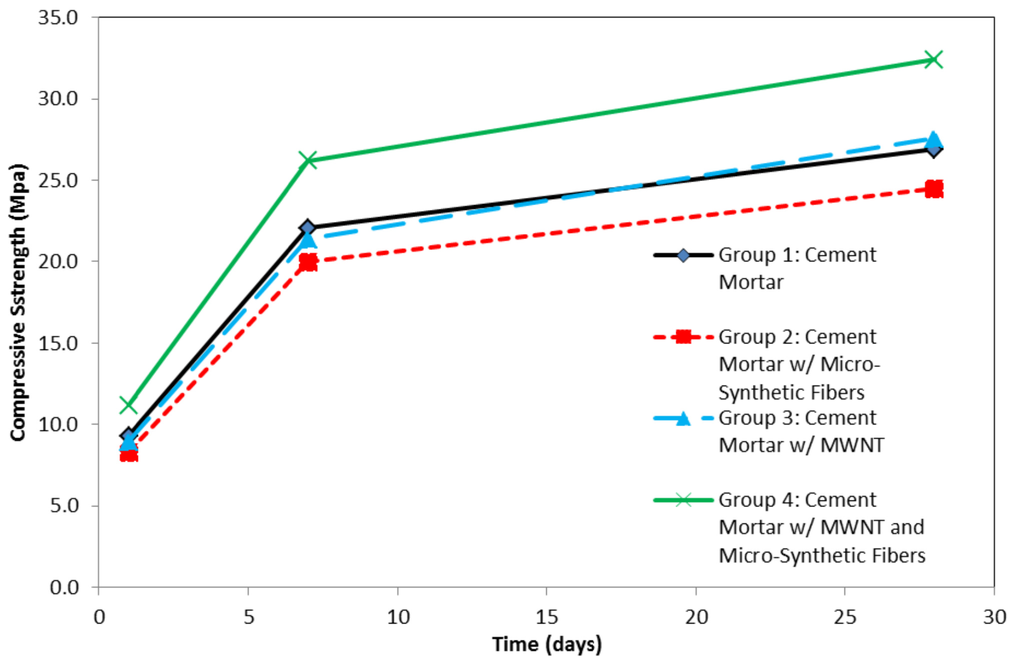

Fig. 5 Compressive Strength vs. Time

Group 1 samples were traditional cement mortar cubes and the compressive strength of Group 1 samples was used as a reference value for the other groups. The 28-day compressive strength of Group 1 samples was 26.9 Mpa (3900 psi). From the experimental data, we found that:

1) For 1-day and 7-day compressive strengths, Group 4 > Group 1 > Group 3 > Group 2.
2) For 28-day compressive strengths, Group 4 > Group 3 > Group 1 > Group 2.
3) Group 2 consistently had the lowest compressive strength of the four groups for 1-day, 7-day and 28-day compression tests. The 28-day compressive strength of Group 2 samples was 24.5 Mpa (3550 psi), which was 9% lower than that of Group 1.
4) Group 4 consistently had the highest compressive strength of the four groups for 1-day, 7-day and 28-day compression tests. The 28-day compressive strength of Group 4 samples was 32.4 Mpa (4700 psi), which was 20.5% higher than that of Group 1.
5) The compressive strength of Group 3 was very close to that of Group 1. The 28-day compressive strength of Group 3 samples was 27.6 Mpa (4000 psi), which was only 2.6% higher than that of Group 1. Using MWNT alone as fibers in cement mortar shows no obvious increase in compressive strength.

Cracking control behavior and ductility are important factors in concrete design. Brittle failure modes should be avoided in concrete structures. In order to reveal the failure modes of the cement mortar cube specimens, digital pictures were taken for the four different groups of samples at failure as shown in Fig. 6 through 9.

Fig. 6: Group 1 Sample at Failure

Fig. 7: Group 2 Sample at Failure

Fig. 8: Group 3 Sample at Failure

Fig. 9: Group 4 Sample at Failure

The pictures tell us:

1) The failure modes of Group 1 and Group 3 samples were brittle. The samples experienced serious spalling and were crushed at failure. We can clearly see the hour-glass shape cores.
2) The failure modes of Group 2 and Group 4 samples were ductile. The samples still held their cubical shapes. No spalling and crushing occurred at failure.

The microstructures of cement composites are complex and understanding the microstructures is critical to explain the macroscopic mechanical properties of the samples. Since the dimensions of MWNT and calcium silicate hydrate layers of hydrated cement are in nano-scale, SEM was used to obtain the nanoscopic images of the samples. The SEM images with scales are shown in Fig. 10 through Fig. 13 for the four groups of samples, respectively.

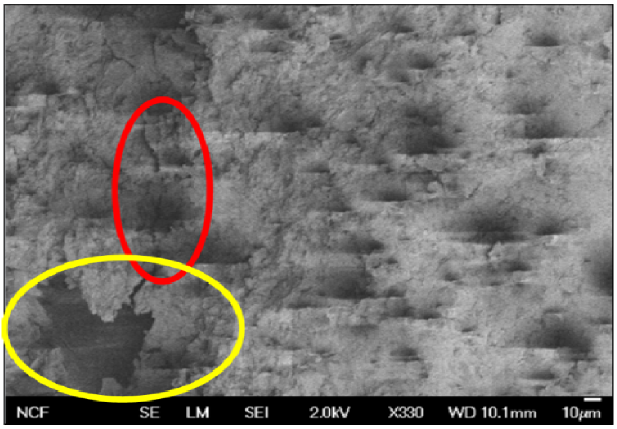

Fig. 10 SEM Image for Group 1 Sample
(Showing micro defects in cement composites)

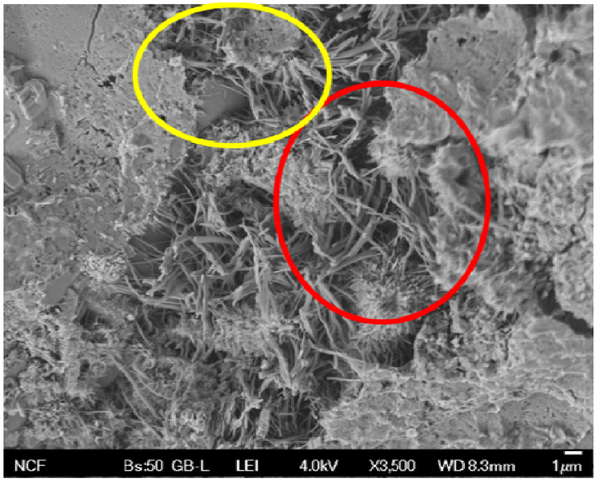

Fig.11 SEM Image for Group 2 Sample
(Showing micro-crack bridging)

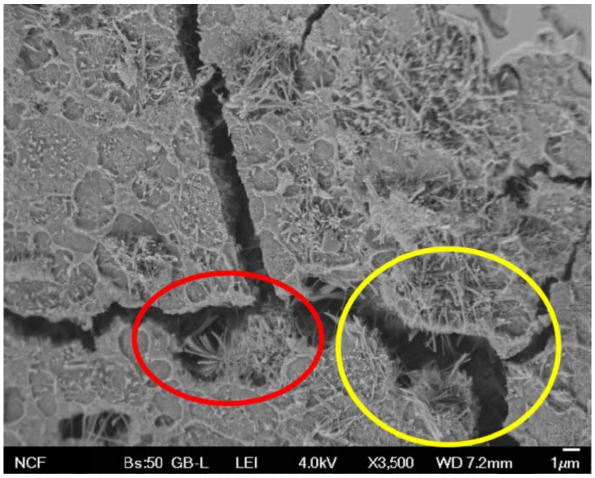

Fig.12 SEM Image for Group 3 Sample
(Showing MWNT pull-out and MWNT being too short to span over the micro deflects)

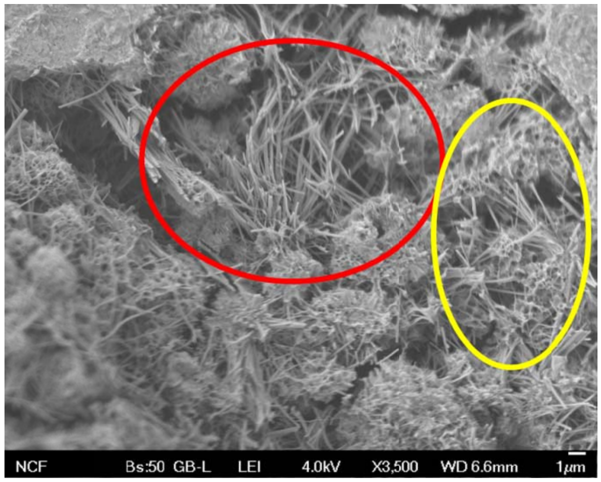

Fig.13 SEM Image for Group 4 Sample
(Showing MWNT bridging the micro-cracks and micro-voids)

The SEM images make it possible to explore the microstructures of the cement composites. We observed the following phenomena through the SEM images:

1) The SEM image of Group 1 sample clearly shows there are microscopic defects, such as voids and cracks in the sample. The existence of these defects directly affects the sample's compressive strength.
2) Fig. 11 shows that the micro-synthetic fibers are uniformly distributed in the cement composites and bridge the micro-cracks, and therefore control the cracking propagation. However, micro-synthetic fibers provide little compressive resistance, and their presence reduces the compressive strength of the cement composites.
3) The SEM image of Group 3 sample shows that the MWNT are uniformly distributed in the cement composites and bridge the micro-voids. Since the length of MWNT is ranging from a few microns to a few tens microns, there is not enough embedment length for the MWNT to tie the cracks. The MWNT can easily pull out. As the cracks widen, the MWNT become too short to bridge the voids and cracks, despite MWNT's high compressive strength, there is no continuous load path to transfer the compression to the MWNT.
4) The SEM image of Group 4 sample shows that the sizes of micro-voids and micro-cracks are smaller than that of Group 3. The micro-synthetic fibers control the crack propagation and the MWNT effectively bridge the voids and cracks and form continuous load paths to transfer the loads. The high strength of MWNT, coupled with the presence of the fibers significantly increases the compressive strength of the cement composites.

DISCUSSION

Four groups of cement mortar cube specimens as listed in Table 3 were tested to investigate the effects of combined use of MWNT and micro-synthetic fibers on the compressive strength of cement composites. From the experimental results, we discovered that the compressive strength is dramatically enhanced by the use of the hybrid fibers consisting of MWNT and micro-synthetic fibers. The use of the hybrid fibers also significantly improves the cracking control behavior of the cement composites. SEM imaging makes it possible to explore the nanoscale microstructures of the cement mortar samples reinforced by MWNT and micro-synthetic fibers. The microstructures reveal the reasons of the significant enhancement of the mechanical properties of the hybrid fibered cement composites.

1) MWNT are the strongest and stiffest material yet discovered. Labs have measured the tensile strength of 63 Gpa for MWNT. The compressive strength of MWNT can reach as high as 60 Gpa if no compression buckling occurs. MWNT are ideal reinforcing material due to their unique mechanical properties.
2) The micro defects, such as micro-voids and micro-cracks in the cement composites, affect the strength of the cement composites. Effectively bridging the micro-voids and micro-cracks with high strength material will increase the strength of the cement composites.
3) Using micro-synthetic fibers alone improves the cracking control behavior, but sacrifices the compressive strength of the cement composites. This is because micro-synthetic fibers have high tensile strength but can resist little compression. The experimental data verify that while micro-synthetic fibers control cracking, they reduce the compressive strength of cement composites.
4) Using MWNT alone shows no obvious improvement in both compressive strength and cracking control behavior. From the SEM images, we find that many MWNT pull out and MWNT are too short to span over the entire cracks and/or voids due to crack widening, and the load transfer paths are impossible to pass through the MWNT, and therefore using MWNT alone do not contribute to strength increase.
5) Using MWNT and micro-synthetic fibers together shows significant enhancement in both compressive strength and cracking control. The interaction between MWNT and micro-synthetic fibers contributes to the improvement of mechanical properties of cement composites. Micro-synthetic fibers control the cracking propagation and restrain the width of the cracks. MWNT effectively bridge the cracks and voids and generate continuous load paths through the MWNT in the cracks and voids to transfer loads. These additional load paths through the strong MWNT directly contribute the compressive strength increase in the cement composites.

CONCLUSIONS

In this paper, an innovative hybrid nano-fibered cement/concrete is proposed. The hybrid nano-fibers consist of 0.5% by weight MWNT and 0.05% by weight micro-synthetic fibers. The interaction mechanism of among MWNT, micro-synthetic fibers and hydrated cement is investigated. Four groups of cement mortal cube compression tests are conducted and compared. The microstructures of the cement composites are revealed by SEM images. According to the experimental data and analysis, we can conclude that:

1) MWNT are ideal reinforcing material in cement/concrete composites due to their high strength and stiffness, and the application of MWNT in construction material has great potential.
2) MWNT have many advantages over SWNT in construction material applications, such as easier fabrication, lower cost, simpler dispersion technique and higher buckling resistance under compression.
3) The MWNT dispersion procedure proposed in this paper is simple and practical, and no additional chemicals such as acids are involved.
4) Neither compressive strength nor cracking control behavior improves if MWNT alone are used as the reinforcing fibers in cement composites. This is because that the length of MWNT is only a few microns to a few tens of microns. When the cracks widen, the MWNT are either too short to span over the cracks or do not have enough embedment length and pull out, and the MWNT do not play an effective role in load transfer and do not contribute to compressive strength.
5) The combined use of MWNT and micro-synthetic fibers in cement composites both dramatically increases compressive strength and controls cracking propagation. MWNT and micro-synthetic fibers work interactively to contribute to the enhancement of mechanical properties. Micro-synthetic fibers control cracks and restrain the cracking width while MWNT effectively brace the cracks and voids and transfer the loads.
6) The proposed innovative hybrid nano-fibered cement/concrete has promising applications in bridges, roadways, pipes and precast/prestressed concrete structural members, where both strength and cracking control are critical.

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References

1. Li, G. Y., Wang, P. M., and Zhao, X., “Pressure-Sensitive Properties and Microstructure of Carbon Nanotube Reinforced Cement Composites”, *Cement & Concrete Composites*, No. 29, 2007, pp. 377-382.
2. Makar, J. M. and Beaudoin, J. J., “Carbon Nanotubes and Their Application in Construction Industry”, *Proceedings of 1st International Symposium on Nanotechnology in Construction*, June 23-25, 2003, Paisley, Scotland, pp. 331-341.
3. Rouainia, G. and Djeghaba, K. “Evaluation of Young’s Modulus of Single Walled Carbon Nanotube (SWNT) Reinforced Concrete Composite”, Journal of Engineering and Applied Sciences, V. 3, No. 6, 2008, pp. 504-515.
4. Raki, L., Beaudoin, J., Alizadeh, R., Makar, J. and Sato, T., “Cement and Concrete Nanoscience and Nanotechnology”, *Materials* 2010, No. 3, 2010, pp. 918-942.
5. Sobolev, K. and Gutierrez, M. F., “How Nanotechnology Can Change Concrete World, Part One of a Two-Part Series”, *American Ceramic Society Bulletin*, V. 84, No. 10, October, 2005, pp. 14-17.
6. Sobolev, K. and Gutierrez, M. F., “How Nanotechnology Can Change Concrete World, Part Two of a Two-Part Series”, *American Ceramic Society Bulletin*, V. 84, No. 11, November, 2005, pp. 16-19.
7. Yakovlev, G., Keriene, J., Gailius, A., and Girniene, I., “Cement Based Form Concrete Reinforced by Carbon Nanotubes”, *Material Science*, V. 12, No, 2, 2006, pp. 147-151.
8. Zhou, X., Wu, T., Ding, K., Hu, B., Hou, M. and Han, B., “The Dispersion of Carbon Nanotubes in Water with the Aid of Very Small Amounts of Ionic Liquid”, *Chemical Communications*, 2009, pp. 1897-1899.