

Concrete and Carbon Nanofibers

[George Turner, Ryder Hendry, Tapsell Gerald]

Abstract— The use of nanotechnology is relatively new in civil engineering industry. Cement and concrete are weak in tension and self-monitoring capability. The modification of the cement matrix with nano particles improves the concrete properties and leads to build a better structure. Mixing of carbon-nanofiber (CNF) to concrete can improve the resistance of water penetration and also improves mechanical and electrical properties such as high Young's modulus, improved fatigue resistance and self-monitoring behavior of concrete. In this paper, the advantages and need of nanotechnology in concrete is discusses.

Keywords—Nanoconcrete, CNF, CNT, carbon fiber, concrete

I. Introduction

Nanotechnology is the science which the material is manipulated with at least one dimension sized from 1 to 100 nanometers. The application of nanotechnology is spanning to different areas including manufacturing, packaging, disinfectants, textiles, and healthcare and in this paper its contribution to the concrete is discussed. Concrete is the most consumed construction material on earth and its production is increasing every year due to increase in construction demand leading from population growth. The carbon nanofibers (CNFs) are proposed to add to concrete due to their superior mechanical and electrical properties [1, 2]. CNFs are cheaper to produce compared to carbon nanotubes (CNTs) which are usually possess better mechanical properties. A good dispersion of CNFs is importance since poor dispersion leads to poor properties of the concrete [3]. The CNFs need to disperse in water using surfactants before dispersion into cement [1,4]. However, most surfactants can interfere with the hydration reaction of cement and refrain cement setting and hardening [5]. Sanchez and Ince proposed to add silica fume to cement to increase the dispersibility of CNFs [6]. The dispersibility of CNFs can be improved using oxidation treatment which create bond between matrix material and carbon nanomaterials [7-11].

The dispersion can also be improved with synthesized cement hybrid material, wherein CNFs are attached to the cement particles which is also reported to increase 2 times the compressive strength and 40 times the electrical conductivity of the hardened cement paste [12- 13]. CNTs/CNFs change their electrical properties while changing the stress level and can be used for nondestructive health monitoring of structure. The details of CNTs and CNFs are discussed in the following sections.

II. Carbon Nanotubes (CNTs)

Carbon nanotubes (CNTs) are allotropes of carbon sheets rolled as hollow tubular cylindrical nanostructure (Fig. 1). Radushkevich and Lukyanovich have first published images of 50 nanometer (nm) diameter carbon tubes in 1952 [14]. CNTs are formed as single walled CNTs (SWCNTs) and multi walled CNTs (MWCNTs). The diameters of SWCNTs range from 1 nm to 20 nm and MWCNTs range from 5 nm to 100 nm. CNTs length can be varied between nanometer to millimeter range as required. Nanotubes have been constructed with an aspect ratio from 1000 up to 100,000,000 [15]. The carbon sheets are rolled with different angle and radius and its combination determines the nanotube properties. At the individual tube level, the tensile strength is about 50 times the strength of the steel, elasticity is about 5 times the strength of the steel, about 300 m²/g surface area and 1000 times the current capacity of copper. CNTs have very good environmental resistance compared to commonly available metals. Its application is increasing day to day due to its performance and greatly accepted in applications of aerospace, defense, energy, consumer, healthcare and infrastructure products.

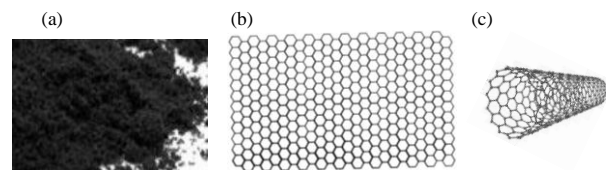


Figure 1. Carbon Nano Tube (a) power form (b) sheet form (c) SWCNT rollup from sheet to tube

The properties of CNTs depend on the synthesis method. The three main approaches to manufacture CNTs are laser ablation (LA), electric arc-discharge and chemical vapor deposition (CVD) [16]. Among the three methods, CVD is the most feasible technique to produce large scale with low-cost but not as pure and uniform compared to other two methods. In this method, high carbon gases like methane, acetylene and ethanol are pumped using high pressure and temperature and they determine the properties and purity of the CNT. The scanning electron microscopy (SEM) of CNT is shown in Fig. 2.

George Turner
University of Auckland
Auckland, New Zealand

Ryder Hendry
University of Auckland
Auckland, New Zealand

Tapsell Gerald
University of Auckland
Auckland, New Zealand

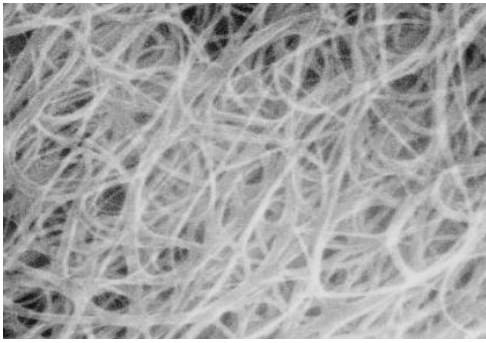


Figure 2. Scanning electron microscopy (SEM) of CNT

The hexagonal structure of the carbon lattice in the CNT provides a strong bond comparing to any other material. The van der Waals forces generated due to large surface area and volume ratio help to align individual nanotubes. The sliding force for an individual MWCNT is weak and therefore will allow the tubes slide with respect to each other.

III. Carbon Nanofibers (CNFs)

CNFs were first patented by Hughes and Chambers in 1889 on synthesis of filamentous carbon [18]. The real usage of the CNFs came to reality in 1950 after their structure was analyzed by electron microscope [19]. CNFs have lower strength and Young's modulus than CNTs but they are very strong and stiff compared to steel.

Carbon nanofibers (CNFs) are larger than carbon nanotubes and are cylindrical in structure with layers arranged as stacked cones or plates (Fig. 3). CNFs have an average diameter of 50 – 200 nm and an average length of 50 - 200 microns. The aspect ratio of CNFs is about 200-2000 and far less than the CNTs. CNF also exhibit superior mechanical and electrical properties like CNTs. CNFs can withstand temperatures up to 3000° C due to which it is also useful to prepare fire resistant materials.



Figure 3. Carbon nanofiber (a) power form (b) nanofiber at nano level

CNFs could also be created similar to CNT by passing carbon feedstock over nanosized particles at high temperature [20-21]. The geometry of CNF is stacked truncated conical or plate shape compared to CNTs which contain hollow cylinder shape [22]. The scanning electron microscopy (SEM) of the CNF is shown in Fig. 4.

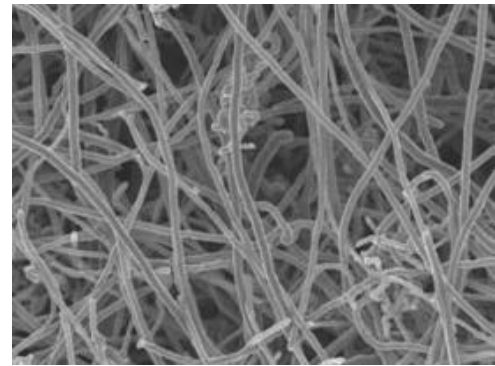


Figure 4. Scanning electron microscopy (SEM) of CNF

The cost of CNTs and CNFs varies depend on the manufacturer but mostly in the range of US \$100 to US \$500. The cost of CNTs depends on purity and process. In general, the cost of CNTs is high compared to CNFs with the inclusion of purification and functionalization.

IV. Carbon Nanofibers and Cement Based Materials

Concrete is the most consumed man made material on earth and any improvement to its composition to better the life of the structure or component is beneficial. Concrete is proved to be good and sustainable with the mix of fly ash, steel fibers, carbon fibers and therefore CNFs/CNTs could be added to cement to create a smart concrete with better electrical and mechanical properties. Nano-concrete can be used as a sensor to measure the health of the structure [2]. CNFs/CNTs can be used to improve the cement coating capability and reduces the required thickness of the cement coating and improves the adhesion. Nano-concrete is also useful to reduce the cracks and to improve the EMI shielding [23]. Self-cleaning façade is possible with the use of titanium nanoparticles to the cement mortar [24]. It is found that the usage of nano-silica improves the permeability and durability [25].

CNTs/CNFs are relatively newly created materials and their use in concrete is still under investigation. The major challenges to use nanofibers in concrete mix are uniform dispersion of CNTs/CNFs within the concrete mix (Fig. 5) and bond strength between the surface of CNTs/CNFs and the cement concrete mix surrounded by them. CNTs/CNFs can be dispersed well using surfactants but they can dissolve in the solution or break CNTs/CNFs into smaller pieces and reduce hydration of cement if an excessive mixing energy is used [17].

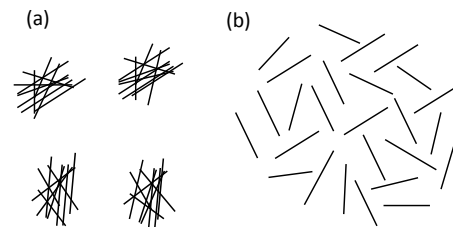


Figure 5. CNTs/CNFs Dispersion (a) bad dispersion and clumping (b) good dispersion and distribution

Mullapudi et al. [1] found that the compressive strength increased upto 21% with the addition of CNFS at 1.0% of volume of binder but reduced the compressive strength with more than 1.0% of CNF concentration in concrete mix due to the discrepancy of the hydration with higher amount of nanofibers. They added few ingredients to the CNF mix and improved the quality of mix. They added a polycarboxylate admixture to decrease the viscosity of the concrete and added an amphiphilic detergent sodium dodecyl sulfate (SDS) to disperse the non-oxidised CNFs in water. They also added silicone-glycol emulsion to CNFs to reduce the amount of foam produced during mixing and after detergent addition. In their research, they pointed that optimum amount of CNF is required to mix with the concrete to reduce clumps of nanofibers and to improve the mechanical and electrical properties.

The flexural strength and Young's modulus of cement matrix are increased up to 40% and 75% respectively with the 0.048% weight of CNFs concentration [26]. The improved mechanical properties of the matrix is attributed to the CNFs to control cracking by bridging nanocracks and pores and the good bond between CNFs and the cement hydration products.

The proper structural modeling and analyses with this new material is also a challenging task. The finite element analyses of structures under different loading conditions were thoroughly studied [27-31] and that knowledge could be used for the analyses of structures made with nanofiber concrete. The CNF used reinforced concrete column load-displacement behavior is analyzed with finite element analyses models developed with the inclusion of effect of axial, shear and bending forces [32-33].

CNTs grow on cement grains after sonicate ethanol for 2 hours and add the solution to the cement powder and then re-sonicate the solution for another 5 hours then evaporate the ethanol. In this process the cement grains will be covered with CNTs [34]. Nano-SiO₂ concrete is stickier than normal concrete due to larger specific surface area and van der Waals forces. Nano-SiO₂ absorbs calcium hydroxide crystals and fills the voids of calcium silicate hydrate (C-S-H) gel which makes the denser binder matrix, and improves long-term mechanical properties, permeability and durability of concrete [35]. The functionalized MWCNTs tend to produce high compressive and flexural strength properties compared to non-functionalized MWCNTs because the functionalized MWCNTs cover with C-S-H gel [36].

The nano-particles with both nano-SiO₂ and with nano-Fe₂O₃ improve the flexural strength of the cement but optimum mixing volume of different nano-particles is not same [37]. The large cement particles prevent a uniform distribution of CNFs/CNTs and need to be careful when mixing the cement with nanofibers [38].

The investigation of nanofiber dispersion effect in measuring the non-destructive and electrical resistivity by Mullapudi et al. [1] is a breakthrough in the usage of CNFs in concrete mix. The steady electrical resistance variation is detected at optimum fiber concentration. The minimum electrical resistance variation is inversely related to CNF concentration. CNFs improve the abrasive resistance and

fatigue strength of concrete [39-40]. The CNFs/CNTs on cement particle surface can grow with the use of acetylene gas as the source of carbon in the CVD technique. The CNTs of long length with smaller quantities (0.025 – 0.048%) and CNTs of short length with large quantities (0.08%) in cement mix achieve good dispersion, high stiffness and less porosity [41]. The alkali-silica reaction (ASR) in concrete occurs over time when alkalis present in the cement paste react with non-crystalline silica present in aggregates and cause volume increase and cracking. The nanosized clay added to cement paste reduces the CH in the matrix due to pozzolanic effect and can potentially reduce the ASR problem.

v. Conclusions

Nanotechnology is still in early stage in concrete industry mainly due to the cost of the material. The continuous research and bulk usage of nanofibers in industrial applications might reduce the price in coming years. The main problem with nanofibers is that due to larger specific surface area and van der Waals forces, it attracts each other to form clumps when mixed with cement, aggregates and water. To overcome, proper dispersion techniques to mix nanofibers to concrete have to be developed. Another problem is the bond between nanofibers and binder mix which it can potentially de-bond during the application of load. Apart from the problems, nanofiber concrete is the future to reduce cracks, to reduce permeability, to improve durability, to improve sensing ability, to improve the EMI shielding, to improve electrical conductivity to reduce the thickness of coatings and to improve strength and ductility. The continuous understanding of cement based materials at nano level will lead to development of a smart concrete which is not only superior in strength and durability but also capable for self-health monitoring of structures. Nanofiber concrete is the future to construct safe, smart and sustainable structures.

References

- [1] T.R.S. Mullapudi, D. Gao, and A. Ayoub, "Non-destructive Evaluation of Carbon Nanofiber Concrete," Magazine of Concrete Research, ICE, vol. 65 (18), 2013, pp. 1081-1091.
- [2] T. Mullapudi, and A. Ayoub, "UPV Method for Detecting Properties of Carbon-Nanofiber Concrete," Structures Congress, 2011, pp. 2963-2970.
- [3] D. D. Chung, "Dispersion of short fibers in cement, Journal of materials in civil engineering," vol. 17(4), 2005, pp. 379-383.
- [4] A. Cwirzen, K. Habermehl-Cwirzen, and V. Penttala, "Surface decoration of carbon nanotubes and mechanical properties of cement/CNT composites," Adv. Cem. Res., 20, 2008, pp. 65-73.
- [5] T. Muhua, and D.M. Roy, "An investigation of the effect of organic solvent on the rheological properties and hydration of cement paste," Cement and Concrete Research, vol. 17(6), 1987, pp. 983-994.
- [6] F. Sanchez and C. Ince, "Microstructure and macroscopic properties of hybrid carbon nanofibers/silica fume cement composites," Composites Science and Technology, 69(7-8), 2009, pp. 1310-1318.
- [7] G.Y. Li, P.M. Wang, and X. Zhao, "Pressure-sensitive properties and microstructure of carbon nanotube reinforced cement composites," Cement and Concrete Composites, vol. 29(5), 2007, pp. 377-382.
- [8] X. Fu, D.D.L. Chung, "Submicron-diameter-carbon-filament cement-matrix composites," Carbon, vol. 36 (4), 1998, pp. 459-462.

- [9] J. Bae, J. Jang, S.H. Yoon, "Cure Behavior of the Liquid-Crystalline Epoxy/Carbon Nanotube System and the Effect of Surface Treatment of Carbon Fillers on Cure Reaction," *Macromolecular Chemistry and Physics*, vol. 203, 2002, pp. 2196.
- [10] A. Eitan, K. Jiang, D. Dukes, R. Andrews, L.S. Schadler, "Surface modification of multiwalled carbon nanotubes: toward the tailoring of the interface in polymer composites," *Chem Mater*, vol. 15, 2003, pp.3198–201.
- [11] G.Y. Li, P.M. Wang, X. Zhao, "Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes," *Carbon*, 43, 2005, pp. 1239–1245.
- [12] Mudimela, P.R., Nasibulina, L., Nasibulin, A., Cwirzen, A., Valkeapaa, M., Cwirzen, K.H., Malm, J.E.M., Karppinen, M.J., Penttala, V., Koltsova, T., Tolochko, O.V., and Kauppinen, E.I. "Synthesis of Carbon Nanotubes and Nanofibers on Silica and Cement Matrix Materials," *Journal of Nanomaterials*, ID. 526128, 4 pages, 2009.
- [13] Nasibulina, L.I., Anoshkin, I.V., Shandakov, S.D., Nasibulin, A.G., Cwirzen, A., Mudimela, P.R., Habermehl-Cwirzen, K., Malm, J.E.M., Koltsova, T.S., Tian, Y., Vasilieva, E.S., Penttala, V., Tolochko, O.V., Karppinen, M.J., and Kauppinen, E.I., "Direct Synthesis of Carbon Nanofibers on Cement Particles," *Transportation Research Record*, No. 2142, 2010, pp. 96-101.
- [14] L. V. Radushkevich, and V. M. Lukyanovich, "About the structure of carbon formed by thermal decomposition of carbon monoxide on iron substrate," *J. Phys. Chem.*, vol. 26, 1952, pp. 88-95.
- [15] Wang, X., Li, Q.; Xie, J., Jin, Z., Wang, J., Li, Y., Jiang, K., Fan, S., "Fabrication of Ultralong and Electrically Uniform Single-Walled Carbon Nanotubes on Clean Substrates," *Nano Letters*, vol. 9 (9), 2009, pp. 3137–3141
- [16] AG, Mamalis, LOG.Vogtländer and A. Markopoulos "Nanotechnology and nanostructured materials: Trends in carbon nanotubes," *Precis Eng.*, vol. 28(1), 2004, pp. 16-30.
- [17] Yazdanbakhsh A., Grasley Z., Tyson B., Abu Al-Rub RK. 2011) Dispersion quantification of inclusions in composites, *Compos Part A: Appl Sci Manuf.*, vol. 42(1), pp. 75-83.
- [18] T. V. Hughes and C. R. Chambers, "Manufacture of Carbon Filaments," *US Patent No. 405*, pp. 480, 1889.
- [19] P. Morgan, "Carbon Fibers and Their Composites," Taylor & Francis Group, CRC Press, Boca Raton, FL, 2005.
- [20] N.M. Rodriguez, "A review of catalytically grown carbon nanofibers," *J. Mater. Res.*, VOL. 8, 1993, pp. 3233–3250.
- [21] G.G. Tibbetts, "Vapor-grown carbon fibers: Status and prospects," *Carbon*, vol. 27, 1989, pp. 745–747
- [22] N.M. Rodriguez, A. Chambers, R.T.K. Baker, "Catalytic engineering of carbon nanostructures," *Langmuir*, vol. 11, 1995, pp. 3862–3866.
- [23] D.D.L. Chung, "Comparison of submicron-diameter carbon filaments and conventional carbon fibers as fillers in composite materials," *Carbon*, vol. 39, 2001, pp. 1119–1125
- [24] Vittoria Diamanti, M., Ormellese, M., Pedferri, M. 2008) Characterization of photocatalytic next term and superhydrophilic properties of mortars containing titanium dioxide, *Cem. Concr. Res.*, vol. 38, pp. 1349–1353.
- [25] M. Collepardi, S. Collepardi, R. Troli, and U. Sarp, "Combination of Silica Fume, Fly Ash and Amorphous Nano-Silica in Superplasticized High-performance Concretes," *Proceeding of First International Conference on Innovative Materials and Technologies for construction and Rehabilitation*, Lecce, Italy, 2004, pp. 459-468.
- [26] Z. S. Metaxa, M. S. Konsta-Gdoutos, and S. P. Shah, "Mechanical Properties and Nanostructure of Cement-Based Materials Reinforced with Carbon Nanofibers and Polyvinyl Alcohol (PVA) Microfibers," *ACI SP 270-10*, 2010, pp. 115-124
- [27] T.R., Mullapudi, and A. Ayoub, "Modeling of the seismic behavior of shear-critical reinforced concrete columns," *Engineering Structures*, vol. 32(11), 2010, pp. 3601–3615.
- [28] T. Mullapudi, and A. Ayoub, "Analysis of Reinforced Concrete Columns Subjected to Combined Axial, Flexure, Shear, and Torsional Loads," *J. Struct. Eng.*, 139(4), 2013, pp. 561–573.
- [29] T. Ravi S. Mullapudi, A. Ayoub "Inelastic Analysis of Semi-Infinite Foundation Elements," *Mechanics Research Communications*, vol. 37, Issue 1, 2010, pp. 72-77.
- [30] T.R.S. Mullapudi, and A. Ashraf , "Nonlinear Analysis of Reinforced Concrete Walls under Three-Dimensional Loading," *Magazine of Concrete Research*, vol. 65, Issue 3, 2012, pp. 172-184.
- [31] T.R.S. Mullapudi, P. Charkhchi, and A. Ayoub, "Behavior of Shear-Dominant Thin-Walled RC Structures," *Thin-Walled Structures*, vol. 63, 2013, pp. 134-146.
- [32] R. Mullapudi, A. Ayoub, "Analysis of Concrete Structures Reinforced with Carbon Nano-Fibers," *IABSE Symposium, Sharm El Sheikh, Global Thinking In Structural Engineering: Recent Achievements*, 2012, pp. 42-49.
- [33] T. Mullapudi, and A. Ayoub, "Analysis of RC Structures with Carbon-Nanofiber Concrete," *Structures Congress*, ASCE, 2011, pp. 1169-1178.
- [34] JM. Makar, JJ. Beaudoin, "Carbon nanotubes and their application in the construction industry," *1st International Symposium on Nanotechnology in Construction*, Paisley, Scotland; 2003, pp. 331-41.
- [35] T. Ji, "Preliminary study on the water permeability and microstructure of concrete incorporating nano-SiO₂," *Cement and Concrete Research*, vol. 35(10), 2005, pp. 1943–1947
- [36] GY. Li, PM. Wang, XH. Zhao, "Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes," *Carbon*, vol. 43(6), 2005, pp.1239-45.
- [37] Li, H., Xiao, H., Yuan, J., Ou, J. 2004) Microstructure of cement mortar with nano-particles, *Composites: Part B*, vol. 35, pp. 185–189.
- [38] Yazdanbakhsh, A., Grasley, Z., Tyson, B., Rashid, K. Al-Rub, A. 2010) Distribution of Carbon Nanofibers and Nanotubes in Cementitious Composites, *Journal of the Transportation Research Board*, vol. 2142, pp. 89-95
- [39] H. Li, M. H. Zhang, and J. P. Ou, "Abrasion resistance of concrete containing nano-particles for pavement," *Wear*, VOL. 260(11), 2006, pp. 1262-1266.
- [40] H. Li, M. H. Zhang, and J. P. Ou, "Flexural fatigue performance of concrete containing nano-particles for pavement," *International Journal of Fatigue*, vol. 29(7), 2007, pp. 1292-1301.
- [41] Z. S. Metaxa, M. S. Konsta-Gdoutos, and S. P. Shah, "Carbon nanotubes reinforced concrete," *Nanotechnology of Concrete: The Next Big Thing is Small*, ACI SP 267, 2009, pp. 11-20.