Available online at www.sciencedirect.com

ScienceDirect

Procedia Structural Integrity 3 (2017) 11–17

Structural Integrity Procedia

www.elsevier.com/locate/procedia

XXIV Italian Group of Fracture Conference, 1-3 March 2017, Urbino, Italy

Improving the mechanical performance of cement composites by carbon nanotubes addition

Syed Shujat-ul-Hussan Gillani[a], Anwar Khitab[a], Sajjad Ahmad[a]*, Rao Arsalan Khushnood[b], Giuseppe Andrea Ferro[c], Syed Minhaj Saleem Kazmi[a], Liaqat Ali Qureshi[d], Luciana Restuccia[c]

[a]*Mirpur University of Science and Technology (MUST), Mirpur-10250 (AJK), Pakistan*
[b]*National University of Sciences and Technology (NUST), Islamabad-54000, Pakistan*
[c]*Politecnico di Torino (PoliTo), Corso Duca degli Abruzzi 24, Turin-10129, Italy*
[d]*University of Engineering and Technology (UET), Taxila-47080, Pakistan*

Abstract

The addition of high performance nano materials like carbon fibers, carbon nanotubes, graphene etc. in the cement and concrete is gaining attention for achieving multifunctional composite materials with enhanced mechanical, physical and electrical properties. The nano-metric size range and the exceptionally high mechanical properties of carbon nanotubes possess very great potential for their utilization in cementitious composites for obtaining remarkable properties. Billions of ton of concrete is used every year in construction industry and its quantity may be reduced to a large extent only by improving the mechanical and durability properties. One way of achieving the enhanced mechanical properties of cement composite is the utilization of thoroughly dispersed carbon nanotubes in the composite matrix. In the present research, small fractions of multiwall carbon nanotube (MWCNTs) i.e. 0.05 and 0.10 wt.% of cement have been incorporated into the cement concrete and their influence on the mechanical properties of the resulting composites have been studied. It is a well-known fact that the uniform dispersion of the MWCNTs in the composite matrix holds the key for the performance improvement. Therefore, special attention was paid to this aspect and uniform dispersion of MWCNTs was achieved through the use of high energy sonication in the presence of modified acrylic based polymer (acting as a surfactant). The concrete specimens were tested in splitting tensile, flexure and compressive strength after 3, 7, 28 and 56 days of immersed water curing. It was observed that the addition of 0.05wt.% MWCNTs increased the splitting tensile strength by 20.58%, flexural strength by 26.29% and compressive strength by 15.60% as compared to the control mix at 28 days of curing. The strength enhancements for the concrete mixes containing MWCNTs may be regarded to the phenomenon of bridging, pinning and branching of the cracks at nano/micro level due to the presence of MWCNTs. Beside strength enhancements, it was also

* Corresponding author. Tel.: +92-336-626-3798; fax: +0-000-000-0000 .
E-mail address: Sajjad.ce@must.edu.pk

Peer-review under responsibility of the Scientific Committee of IGF Ex-Co.
10.1016/j.prostr.2017.04.003

observed that the MWCNTs had tremendously enhanced the fracture energy and breaking strains of the concrete mixes as observed in three-point bending tests. The research concludes that very low amounts of MWCNTs incorporated in the cement concrete mixes improve their mechanical strengths and fracture behavior remarkably but the thorough dispersion of MWCNTs in the matrix have to be insured.

Peer-review under responsibility of the Scientific Committee of IGF Ex-Co.

Keywords: Fracture energy; MWCNTs; Concrete; Nanaotechnology; Toughness; Crack pinning; Micro cracking

1. Introduction

Cement and concrete composites are the basic construction materials which are extensively used around the globe. The production of cement involves generation of enormous amounts of anthropogenic carbon dioxide (CO_2) in the atmosphere, contributing approximately 5.0% CO_2 generation around the globe. Beside this, other environmental concerns are also associated with the use of cement and concrete composites such as depletion of virgin aggregates and its impact on the ecosystem. Ordinary cement and concrete composites offer much flexibility and cost effectiveness in their utilization but they are vulnerable to physical and chemical attacks affecting their performance in service life span; therefore, requiring costly repair and maintenance works. Construction of super-paves, tunneling, long span structural members and pre-stress technology demands the concretes of ultra-high strength and performance. For effective service life in different situations and under different loading conditions, ordinary concrete is not much beneficial. Therefore, the production of modified concrete with exceptional properties in terms of mechanical strength and with minimum amount of cement is highly desired so that economical and sustainable construction may be achieved along with reduction in CO_2 emissions in the atmosphere.

The idea of nanotechnology for the modifications of composite properties at nano scale is not new in relation to the construction materials. Nanotechnology deals with the synthesis, characterization, utilization and analysis of materials at nano scale. Several researchers have explained that the properties of cement and concrete composites may greatly be modified by using nano and micro sized particle inclusions in the matrix Raki et al. (2010); Lopez et al. (2013); Ferro et al. (2015); Ahmad et al. (2015); Khushnood et al. (2014); Khushnood et al. (2016); Ferro et al. (2014). The nano level inclusions in concrete have shown improved durability, mechanical strength, porosity reduction and economical construction Lothenbach et al. (2011); Lothenbach et al. (2008); Wu et al. (2016); Khushnood, Ahmad, Savi, et al. (2015); Barbhuiya et al. (2015); Abd Elrahman & Hillemeier (2014); Khushnood, Ahmad, Ferro, et al. (2015). The nano metric inclusions includes nano silica, graphene, multi walled carbon nano tubes (MWCNTs), nano $CaCO_3$, nano TiO_2 etc. Li et al. (2015); Li et al. (2005); Siddique & Mehta (2014); Wang et al. (2013); Chithra et al. (2016); Chuah et al. (2014); Vulic et al. (2013). The studies show that the inclusions improve the packing of particles and produce crack bridging phenomena by densifying the nanostructures. Nano particles control the C-S-H reaction and improves the concrete durability Singh et al. (2016); Kong et al. (2012); Hou et al. (2013); Fan et al. (2015); Hu et al. (2014).

Among above mentioned nano materials, MWCNTs possess unique and exceptional characteristics in terms of physical and mechanical properties. MWCNTs have tubular structure composed of folded layers of graphene with exceptionally high aspect ratios Mubarak et al. (2014); Broza (2010); Mamalis et al. (2004); Popov (2004). Several researchers have been reported the utilization of MWCNTs in preparing cement and mortar composites and studied the behavior but limited work is available describing the full scale utilization of the MWCNTs in the concrete matrix. Therefore, in the present research MWCNTs were utilized in the preparation of concrete matrix and their influence on the mechanical behavior of concrete is discussed in detail.

Nomenclature

C-S-H	Calcium silicate hydrate	CMOD	Crack mouth opening displacement
MWCNTs	Multi walled carbon nano tubes	w/c	Water to cement ratio

2. Experimental program

2.1. Materials

The concrete mixes were prepared from ordinary Portland cement (ASTM Type 1 grade 52.5), having specific gravity of 3.10. Locally available sand having fineness modulus of 2.13 and water absorption of 2.87% was utilized. Crushed lime stone aggregates confirming to the ASTM C33 were incorporated in the concrete mix. The characteristics of MWCNTs used for the preparation of concrete samples are presented in Table 1.

Table 1. Characteristics of MWCNTs.

Diameter (*nm*)	Length (μm)	Purity (*%*)	Surface area (m^2/g)	Density (g/cm^3)
6-25	10-50	>90%	250-300	2.35

2.2. Dispersion of MWCNTs

The dispersion of MWCNTs was achieved by the help of bath sonication in the presence of modified acrylic based surfactant. For attaining good dispersion of MWCNTs in water a solution of surfactant and water was prepared and then the measured amount of MWCNTs was added to the solution. The solution was sonicated for 20 min at 25±5ºC. The dispersion was assessed qualitatively by filling test tubes with dispersed MWCNTs solution and observing the color of solution for next 48 h. The observations revealed that the MWCNTs did not settled down in the test tube and remained in the solution indicating effective dispersion of MWCNTs. The composition details of solution containing dispersed MWCNTs are presented in Table 2.

Table 2. Composition of solution containing dispersed MWCNTs

Designation	Water (*g*)	Surfactant (*g*)	MWCNTs (*g*)	Comments
C	100	2.0	0.000	Control mix Mix containing 0.00% MWCNTs by mass of cement
C0p05	100	2.0	0.125	Mix containing 0.05% MWCNTs by mass of cement
C0p10	100	2.0	0.250	Mix containing 0.10% MWCNTs by mass of cement

2.3. Mixture proportioning and sample preparation

The sand, aggregate and cement were mixed in dry condition as per the required quantities mentioned in Table 3. After dry mixing half of the water containing MWCNTs was added into the mixing machine and mixing was continued for 2 minutes at slow speed. After slow mixing, the machine was stopped for 30 seconds and walls of the machine were cleaned by trowel to separate any material attached to them. Then remaining water was added into the mix and the mixing was continued for 2 more minutes at high speed to achieve workable concrete mixture Rizwan et al. (2012). The mix proportions of concrete containing MWCNTs are reported in Table 3.

Table 3. Mix proportions of concretes containing MWCNTs

Designation	Cement (kg/m^3)	Sand (kg/m^3)	Aggregate (kg/m^3)	Water (kg/m^3)	Surfactant (kg/m^3)	MWCNTs(g/m^3)
C	476	690	1047	190.40	3.81	-
C0p05	476	690	1047	190.40	3.81	238
C0p10	476	690	1047	190.40	3.81	476

After complete mixing, the concrete was poured into standard cylinders having 150 mm diameter and 300 mm height and beam molds of 100 mm x 100 mm x 400 mm. The molds were then kept in closed containers having 90% humidity for 24 h. The dried samples were then removed from the molds, labelled, weighed and cured in water at 25±2°C until the day of testing. The beam samples were notched with water cooled diamond saw blade and tested in three-point bending in CMOD controlled mode. The rate of CMOD was kept at 0.50 mm/min. The schematic diagram of test setup and sample geometry are shown in Figure 1.

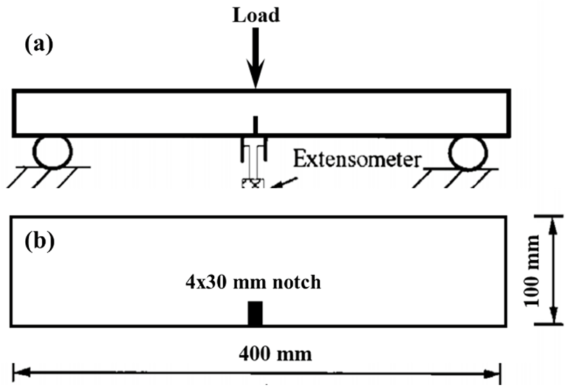

Fig. 1. Schematic diagram of (a) Test setup; (b) Specimen geometry.

3. Results and discussion

3.1. Performance evaluation of samples in tension and flexure

The splitting cylinder tensile strength of concrete specimen was studied at 3, 7, 28 and 56 days of curing. The cylindrical specimens were tested according to ASTM C496 under constant rate of loading of 0.8 MPa/min to determine the splitting tensile strength of control mix and the MWCNTs reinforced mixes. The test results are presented in Figure 2 (a) below. The results revealed that the mixes containing MWCNTs exhibit higher tensile strength as compared to the plane concrete samples. Maximum enhancement around 26% was observed for C0p05 at 56 days of age whereas, it was around 18% for C0p10. The overall trend shows that the addition of small amounts of MWCNTs produce better results. This behavior may be regarded to the effective dispersion of MWCNTs at lower percentage addition. Whereas, in case of enhancement of compressive strength of modified samples the direct relation between the amount of MWCNTs inclusion and modification of strength was observed. It reveals that the reduction of effective water content which ultimately results into the improvement in compressive strength. Dispersion concerns and agglomeration sometimes cause the reduction in strength in case of inclusion of more quantity of MWCNTs as compared to that of small fraction of MWCNTs.

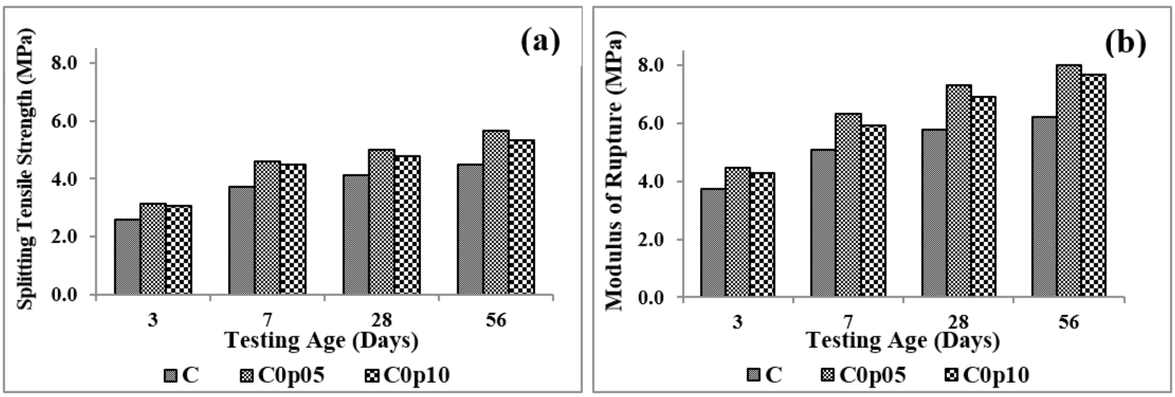

Fig. 2. (a) Splitting cylinder tensile strength of concrete mixes; (b) Modulus of rupture of concrete mixes.

The three-point bending tests showed similar trend as produced by the splitting cylinder tensile tests. Overall better performance was achieved at 0.05wt.% addition of MWCNTs. A typical stress vs crack mouth opening displacement (CMOD) curve is presented in Figure 3 where it can be seen that the MWCNTs not only enhanced the modulus of rupture but also substantially prolonged the post peak response of the specimens under investigation. The extended post peak behavior of concrete reinforced with MWCNTs is due to the crack bridging phenomena of MWCNTs thus imparting ductility and toughness.

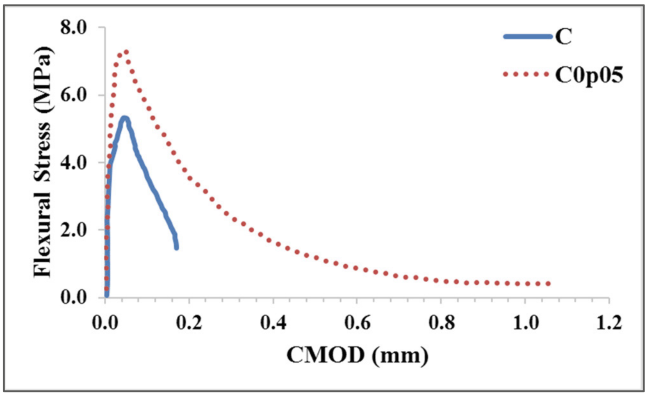

Fig. 3. Typical stress vs CMOD curves of concrete specimen with and without MWCNTs

3.2. Performance evaluation of samples in compression

The concrete samples were also investigated for their compressive strength at 3, 7, 28 and 56 days of curing to assess the influence of MWCNTs addition on compressive behavior of concrete. The results of the compressive strength tests are presented in figure 4. The results indicate that the mix containing higher amount of MWCNTs exhibited higher compressive strength as compared to others. At 56 days of curing the mix C0p10 gives 24.66% higher compressive strength than the control mix whereas, the enhancement was 19.11% for the mix C0p05. Similar pattern can be observed for strength at other ages.

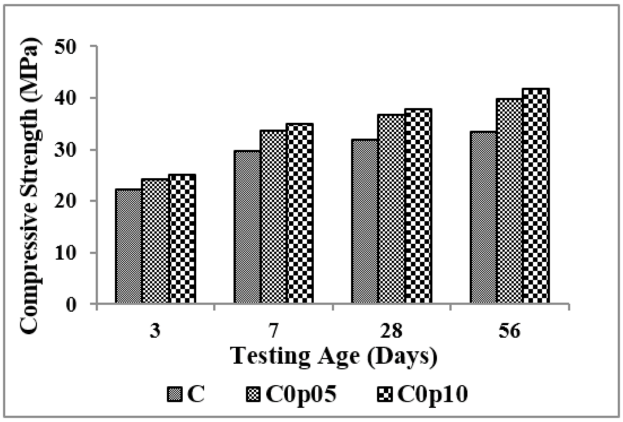

Fig. 4. Compressive strength of concrete mixes with and without MWCNTs

Unlike flexural and tensile behavior, where better performance was observed at 0.05wt.% addition of MWCNTs; here in compression the performance improves with the increase in the MWCNTs addition. This behavior may be regarded to the reduction in water content (i.e. effective w/c ratio) in the concrete mix due to the presence of large number of MWCNTs.

3.3. Strength activity indices of concrete mixes

For relative comparison of the influence of MWCNTs addition on the concrete mixes strength activity indices were evaluated and reported in Figure 5 (a, b & c) below. The observations reveal that the concrete mixes containing 0.05wt.% MWCNTs performed better in splitting tensile strength and modulus of rupture whereas, concrete containing 0.10wt.% addition of MWCNTs performed better in compression as explained earlier.

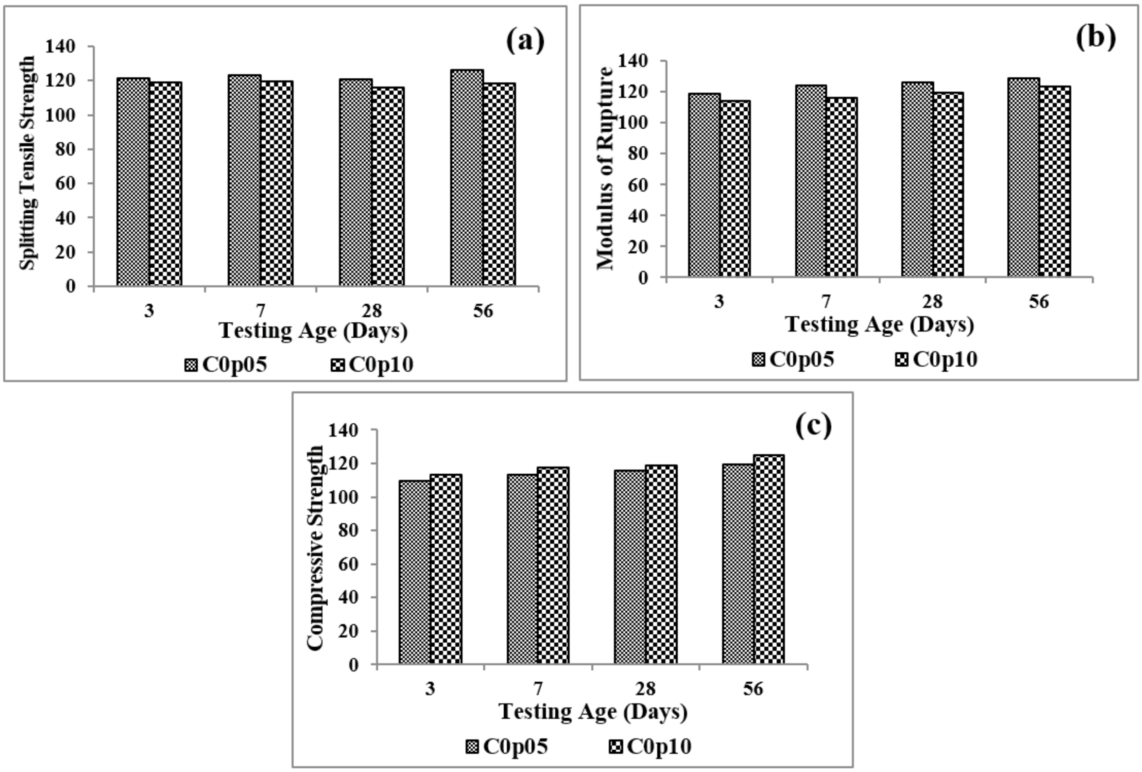

Fig. 5. Strength activity indices for concrete mixes containing MWCNTs (a) Splitting tensile strength, (b) Flexural strength, (c) Compressive strength

Conclusions

The remarkable improvement in the mechanical properties of concrete was observed on the inclusion of small fractions of MWCNTs in concrete matrix. The effect and behavior of MWCNTs addition is purely dependent upon the dispersion of MWCNTs in the mix. Many other factors other than dispersion, are also associated with effective outcomes of the inclusion of MWCNTs in concrete i.e., size, aspect ratio, purity etc. of MWCNTs being utilized in the mix. From the present study it may be concluded that the same amount of MWCNTs may exhibit different behavior in certain mechanical properties of concrete mix i.e. the lower amount of MWCNTs are fruitful in case of enhancement of tensile and flexural strength but in case of compressive strength the larger fraction was more effective.

Acknowledgements

The authors acknowledge the partial financial support of Higher Education Commission, Pakistan for this research.

References

Abd Elrahman, M. & Hillemeier, B., 2014. Combined Effect of Fine Fly Ash and Packing Density on the Properties of High Performance Concrete: an Experimental Approach. Construction and Building Materials, 58, 225–233.

Ahmad, S. et al., 2015. High Performance Self-Consolidating Cementitious Composites by Using Micro Carbonized Bamboo Particles. Materials & Design, 76, 223–229.

Barbhuiya, S., Chow, P. & Memon, S., 2015. Microstructure, Hydration and Nanomechanical Properties of Concrete Containing Metakaolin. Construction and Building Materials, 95, 696–702.

Broza, G., 2010. Synthesis, Properties, Functionalisation and Applications of Carbon Nanotubes: A State of the Art Review. Chemistry & Chemical Technology, 4(1), 35–45.

Chithra, S., Senthil Kumar, S.R.R. & Chinnaraju, K., 2016. The Effect of Colloidal Nano-Silica on Workability, Mechanical and Durability Properties of High Performance Concrete with Copper Slag as Partial Fine Aggregate. Construction and Building Materials, 113, 794–804.

Chuah, S. et al., 2014. Nano Reinforced Cement and Concrete Composites and New Perspective from Graphene Oxide. Construction and Building Materials, 73, 113–124.

Fan, Y. et al., 2015. Effects of Nano-Kaolinite Clay on the Freeze–Thaw Resistance of Concrete. Cement and Concrete Composites, 62, 1–12.

Ferro, G.A. et al., 2014. Improvements in Self-Consolidating Cementitious Composites by Using Micro Carbonized Aggregates. Frattura Ed Integrita Strutturale, 30, 75–83.

Ferro, G.A. et al., 2015. New Cementitious Composite Building Material with Enhanced Toughness. Theoretical and Applied Fracture Mechanics, 76, 67–74.

Hou, P. et al., 2013. Modification Effects of Colloidal Nanosio2 on Cement Hydration and its Gel Property. Composites Part B: Engineering, 45(1), 440–448.

Hu, C. et al., 2014. Property Investigation of Calcium–Silicate–Hydrate (C–S–H) Gel in Cementitious Composites. Materials Characterization, 95, 129–139.

Khushnood, R.A. et al., 2016. Carbonized Nano/Microparticles for Enhanced Mechanical Properties and Electromagnetic Interference Shielding of Cementitious Materials. Frontiers of Structural and Civil Engineering, 10(2), 209–213.

Khushnood, R.A. et al., 2014. Experimental Investigation on Use of Wheat Straw Ash and Bentonite in Self-Compacting Cementitious System. Advances in Materials Science and Engineering, 2014, 1–11.

Khushnood, R.A., Ahmad, S., Savi, P., et al., 2015. Improvement in Electromagnetic Interference Shielding Effectiveness of Cement Composites using Carbonaceous Nano/Micro Inerts. Construction and Building Materials, 85, 208–216.

Khushnood, R.A., Ahmad, S., Ferro, G.A., et al., 2015. Modified Fracture Properties of Cement Composites with Nano/Micro Carbonized Bagasse Fibers. Frattura Ed Integrita Strutturale, 9(34), 534–542.

Kong, D. et al., 2012. Influence of Nano-Silica Agglomeration on Microstructure and Properties of the Hardened Cement-Based Materials. Construction and Building Materials, 37, 707–715.

Li, G.Y., Wang, P.M. & Zhao, X., 2005. Mechanical Behavior and Microstructure of Cement Composites Incorporating Surface-Treated Multi-Walled Carbon Nanotubes. Carbon, 43(6), 1239–1245.

Li, Q., Liu, J. & Xu, S., 2015. Progress in Research on Carbon Nanotubes Reinforced Cementitious Composites. Advances in Materials Science and Engineering, 2015.

Lopez, A. et al., 2013. Influence of Carbon Nanotubes Addition onto the Mechanical Properties of Restoration Mortars. In Convegno Nazionale IGF XXII. Rome, Italy, 278–286.

Lothenbach, B. et al., 2008. Influence of Limestone on the Hydration of Portland Cements. Cement and Concrete Research, 38(6), 848–860.

Lothenbach, B., Scrivener, K. & Hooton, R.D., 2011. Supplementary Cementitious Materials. Cement and Concrete Research, 41(12), 1244–1256.

Mamalis, A., Vogtländer, L.O.. & Markopoulos, A., 2004. Nanotechnology and Nanostructured Materials: Trends in Carbon Nanotubes. Precision Engineering, 28(1), 16–30.

Mubarak, N.M. et al., 2014. An Overview on Methods for the Production of Carbon Nanotubes. Journal of Industrial and Engineering Chemistry, 20(4), 1186–1197.

Popov, V., 2004. Carbon Nanotubes: Properties and Application. Materials Science and Engineering: R: Reports, 43(3), 61–102.

Raki, L. et al., 2010. Cement and Concrete Nanoscience and Nanotechnology. Materials, 3(2), 918–942.

Rizwan, S.A., Ahmad, S. & Bier, T.A., 2012. Application of Packing Concepts to High Performance Self-Consolidating Mortar (SCM) Systems. In American Concrete Institute, ACI Special Publication. 299–315.

Siddique, R. & Mehta, A., 2014. Effect of Carbon Nanotubes on Properties of Cement Mortars. Construction and Building Materials, 50, 116–129.

Singh, L.P. et al., 2016. Studies on Early Stage Hydration of Tricalcium Silicate Incorporating Silica Nanoparticles: Part II. Construction and Building Materials, 102, 943–949.

Vulic, T. Et Al., 2013. Improvement of Cement-Based Mortars by Application of Photocatalytic Active Ti–Zn–Al Nanocomposites. Cement and Concrete Composites, 36, 121–127.

Wang, B., Han, Y. & Liu, S., 2013. Effect of Highly Dispersed Carbon Nanotubes on the Flexural Toughness of Cement-Based Composites. Construction and Building Materials, 46, 8–12.

Wu, Z. Et Al., 2016. Effects of Different Nanomaterials on Hardening and Performance of Ultra-High Strength Concrete (UHSC). Cement and Concrete Composites, 70, 24–34.