

Nanotechnology: The Emerging Field of Civil Engineering Particularly in Developing Countries

Tanvir Manzur^a, MA Bashir Emon^b, and Kabirul Islam^c

Department of Civil Engineering, Bangladesh University of Engineering and Technology, Dhaka, Bangladesh

^atmanzur.buet@gmail.com; ^ba.001.bashar@gmail.com; ^crajabd4bd@yahoo.com

Keywords: Nanotechnology, Cement, Concrete, Carbon Nanotubes, Nano-Particles

Abstract Nanotechnology has taken the world of science by a storm and construction industry is no exception. The most important aspect of construction industry that can be influenced by nanotechnology is cement and concrete. Recent research on application of carbon nano tubes (CNT), both single-walled and multi-walled, shows significant increase in mechanical properties of concrete. Other properties of concrete e.g. durability, permeability, cement hydration etc. can be conveniently influenced with the help of Alkali-Silicate Reaction (ASR) studies, Nano-Scale Silica Fume, integration of Nano-Particles in cement-synthesis and a lot other methods. And as a matter of fact, the future of cement based construction industry seems to be shaped by nanotechnology as even developing countries like Bangladesh are coming forward now-a-days to harness the potential of this rapid growing field.

Introduction

Nanotechnology or Nano-science, considered to be the forth industrial revolution, has received considerable attention in the past decade. Nanotechnology is based on manipulation of material at the nano-scale, where at least one dimension of the material should be sized between 1 and 100 nanometers. Therefore, through nanotechnology it is possible to enhance and control the physical properties of materials to a great extent. Composites such as concrete materials have very high compressive strength and Young's modulus but relatively low toughness and ductility due to their covalent bonding between atoms and lacking of slip systems in the crystal structures. However, the strength and life of concrete structures are determined by the microstructure and mass transfer at nano scale. Cementitious composites are amenable to manipulation through nanotechnology due to the physical behavior and size of hydration products.

One of the most profound effects of nanotechnology is expansion of surface area by sizing down the material. Eventually, it creates more space to perform novel modification at a scale which was not possible before. Therefore, sizing down of a material provides scientists the opportunity to incorporate more functional entities on the newly exposed planes.

Now the question is would it be possible for a developing country like Bangladesh to take the advantage of this cutting edge technology. Definitely nanotechnology is an advanced technology and in most cases it will require expensive nano-fabrication facilities to conduct research and development. Therefore, to pursue nanotechnology based research and application in Bangladesh, the most important task would be to point out the fields (if any) that require relatively less expensive equipment and relevant to the needs of the country. Nano-electronic sector requires highly expensive instruments and ultra-clean facilities and a country like Bangladesh should not focus on such fields of nanotechnology. Rather the spotlight should be on those kinds of nano-materials which can easily be synthesized by following relatively simple process (wet-chemical process) and can be carried out anywhere. The prime focus of the nanotechnology based research and development in Bangladesh may be on garment sector, pharmaceuticals, construction material like cement, and agriculture. This article focuses on the application of nanotechnology in construction industry.

Scope of nanotechnology in construction industry

The construction industry, compared to other major industrial sectors such as medicine, electronics, biomaterials etc., has suffered a lag in exploitation of nanotechnology. But fortunately, an increase in awareness and actual exploitation in construction is being noticed of late. Quite a few aspects of construction can be influenced by the potentials of nanotechnology. The most vital part of construction that can be positively boosted by nanotechnology is concrete. Some unique properties of Portland cement e.g. room temperature processing, low shrinkage, temperature resistance up to 600 °C (1,115 °F), compatibility with a number of fiber types including carbon fibers, reaction capability with currently available nano-materials such as nano-silica and non-toxic characteristics can be effectively used to create unique products. One major area of application of nano-cement can be coatings. Nano-cement can make crack-free decks, which is a dream with OPC, a reality.

Nanotechnology in Concrete Concrete can be a very interesting subject to nanotechnology as it already contains nano-particles as ingredients including nano-water particles and nano-air voids. However, with the aid of nanotechnology, the quantity and the locations of these nano-ingredients inside the final products can be controlled. If we can create chemical or mechanical tools to control nano-scale pores and the placement of calcium-silicate hydration products then concrete becomes a product of nanotechnology. Current research activities of nanotechnology in concrete include: cement hydration characterization, impact of the addition of nano-size silica to concrete, synthesis of cement using nano-particles and coatings (that contain nano-size particles) applied to protect concrete. These activities are briefly described in the following sections.

Application of Carbon Nanotubes (CNT) Carbon nanotube (CNT) is one of the most important areas of research in the field of nanotechnology. CNTs have already proven their reinforcing performance in polymer based materials [1, 2, and 3]. The size and exceptional mechanical properties of CNT show their high potential to be used to produce high performance next generation cementitious composites. The physical structure of cement hydration products is such that flaws within cementitious composite exist at nanoscale. Therefore, research at nano scale has a huge potential to contribute to resolve these flaws. Application of fibers at nanoscale can significantly control cracks of cement matrix at nanoscale and eventually result in stronger and tougher composites. Carbon nanotubes can be considered as an exceptional reinforcing material due to their extremely high aspect ratios [4], ultra high strength [5], modulus [6] and elasticity [7]. The dimensions of nanotubes are at nanoscale which means that they can be distributed within the cement matrix at much more finer scale as compared to traditional reinforcing fibers since reinforcement of cement is typically done at millimeter scale. The application of carbon nanotubes to reinforce cementitious composites is therefore intended to enhance the reinforcing behavior at nano level instead of micro level. Cracks can be interrupted much more quickly and eventually hinder growth of crack at early stage and prevent propagation of cracks to micro scale. In addition, nanotubes have the potential to act as filler within the cement grains, thus producing denser composites. Therefore, CNT reinforcements have the ability to produce significantly stronger and tougher composites as compared to traditional reinforcing fibers.

A study by Makar et al. [8] shows that addition of single-walled nanotubes (SWNT) accelerates the hydration process at early age. The effect of CNT addition on cement hydration process is explained in details in another study by Makar et al. [9]. It was found that the presence of nanotubes affected the morphology of cement hydration products, both the initial C₃A and the C₃S hydration products. It was observed that CNT accelerated the rate of hydration process by acting as a matrix for the development of C-S-H and Ca(OH)₂ produced during the hydration. CNT act as nucleating agent during cement hydration by providing more sites for the reaction to occur and encourage the formation of reaction products. Li et al. [10] found that an addition of 0.5% multiwalled nanotubes (MWNT) increased both the 28-day cement mortar compressive and flexural strength as compared to Portland cement composite. Cwirzen et al. [11] obtained an increase of 10% in flexural strength of MWNT reinforced composites in comparison with plain cement mortar. A comprehensive study [12] conducted by one of the authors also found improved mechanical properties of MWNT reinforced cement composites. Seven different sizes of treated and untreated MWNT have been

utilized. Statistical analysis in the form of hypothesis testing has been conducted. Based on the parametric study and statistical analysis, a tentative optimum mix proportion has been proposed. The mix proportion consists of plasticizer proportion of 0.008 in terms of the weight of the cementitious material. Tentative optimum dosage rates of treated MWNT, ranging from 0.1-0.3% of the weight of cementitious material, have been proposed to be used as reinforcement. MWNT with OD smaller than 30 nm has been suggested as the effective size to produce cementitious composites. Figures 1 and 2 show the effect of MWNT addition on compressive and flexural strengths of cementitious composites at different ages to provide a tentative idea to the readers.

Performance Enhancement with Nano-Scale Silica Fume Certain performance criteria for concrete such as permeability, durability etc. was found to improve much more efficiently with the use of Ultra-fine amorphous colloidal silica compared to micron sized silica [13]. A very interesting finding is that, reduced amount of about 15 to 20 kg of nano-silica was found to provide same strength as 60 kg of regular or micro silica.

Alkali-Silicate Reaction (ASR) Studies The product of ASR is alkali/silica gel, which is detrimental to the material due to its expansion. The gel is formed due to the reaction between cement alkalis and is active form of silica from aggregates or supplementary additions. Using neutron scattering and positron annihilation spectroscopy, Federal Highway Administration (FHWA) researchers have succeeded in measuring nano-scale changes in gel microstructure as a function of gel chemistry, temperature and relative humidity [14].

Cement Reactivity University of Connecticut is running a collaborative research supported by FHWA and NSF to study cement hydration at a nano-scale level [14]. Nuclear resonance reaction analysis (NRA) is being used in this study to investigate what takes place on the surface of the cement particle as hydration takes place. A beam of nitrogen atoms is used to probe a reacting cement grain to locate hydrogen atoms, a necessary component of water, or reaction by-products. To create hydrogen depth profile locating these hydrogen atoms is necessary. The rate of water penetration and the arrangement of various surface layers formed during the reaction can be understood with hydrogen depth profile. The 20- nanometer-thick (7.87×10^{-7} in.) semi-permeable surface layer allows water to enter the cement grain and leaches out calcium ions. Behind this layer the larger silicate ions are trapped. With the continuation of reaction, silica gel forms causing swelling within the cement grain which eventually leads to breakdown of the outermost shell. The surface disintegration then releases accumulated silicate into the surrounding solution. The silicate reacts with calcium ions to form a calcium-silicate hydrate gel, which binds cement grains together and sets the concrete. The timing of the surface layer's breakdown can be shown in the hydrogen profile.

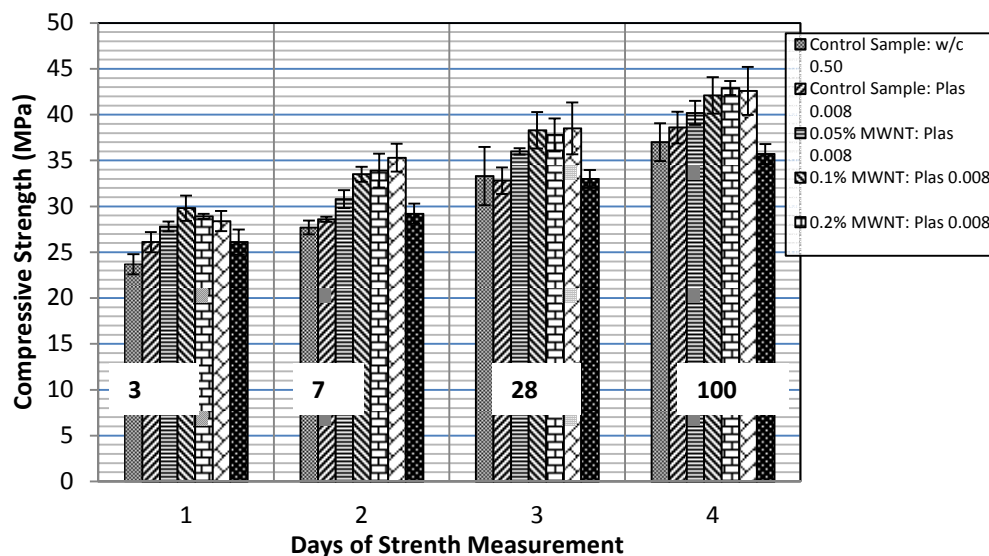


Fig1: Compressive strengths of control samples and composite samples with different dosage rate of MWNT at different ages

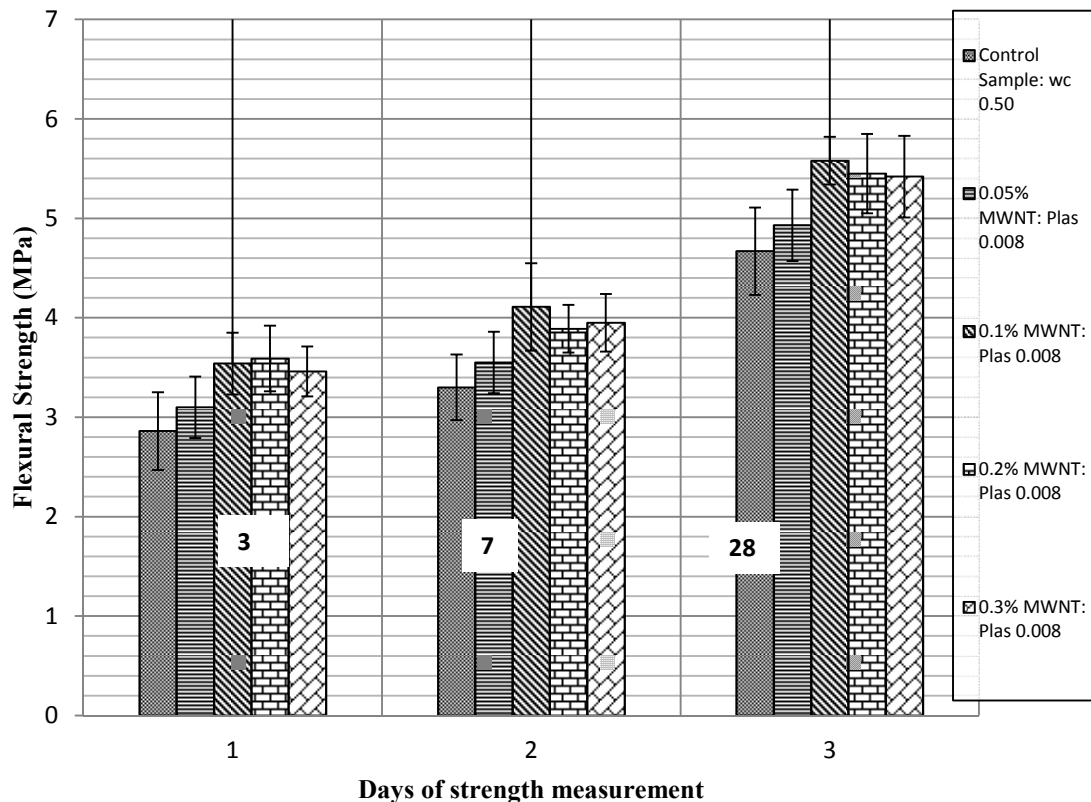


Fig 2: Flexural strengths of control samples and composite samples with different dosage rate of MWNT at different ages

This information can be used to study the concrete setting process as a function of time, temperature, cement chemistry, and other factors. For example, researchers used NRR to determine that in cement hydrating at 30°C (86°F); the breakdown occurs at 1.5 hours.

Kinetics of Cement Hydration Since the reactions occur in the nano-scale pores of the cement gel, conventional analytical methods are unable to provide an accurate model for the rate of cement's reaction with water as a function of temperature, water/cement ratio, and grain size. Therefore, scientists from National Institute for Standards & Technology's (NIST) Center for Cold Neutron Research and FHWA are using neutron scattering methods to measure motions and reactions of water at a nano-scale.

Integration of Nano-Particles in cement-synthesis Cement type-I has been synthesized using nano-particles in a project supported by National Science Foundation (NSF) and its property has been compared with that of commercial cement [14]. To evaluate the morphology and structure of synthesized tri-calcium silicate (C_3S) components, scanning electron microscopy (SEM) and X-ray diffraction (XRD) equipment were used. The synthesized cement is found to contain conglomerated nano-particles with crystalline structures containing quantities of tri- and di- calcium silicate compounds as well as copper oxide. Hydration rate is more rapid in nano-cement than Portland cement Types I and III. But compressive strength of the cement synthesized using nano-particles was found to be less than that of ordinary Portland cement. A number of factors such as particle aggregation, rapid hydration, a high water to cement ratio, and the lack of gypsum can be hold responsible for this phenomenon.

From the perspectives of Bangladesh

It is obvious from the above discussion that there are numerous avenues to pursue research on application of nanotechnology in concrete industry. Now, the decision has to be taken by the concerned researchers and government officials to select the fields to emphasize for research. The

existing imaging facilities at the Dhaka center of the Atomic Energy Commission, the center of excellence at University of Dhaka and Department of MME of BUET are capable of identification and characterization of nano-materials which is an essential part of wet chemistry. A project is undertaken in joint collaboration of Department of Civil Engineering, BUET and Department of Chemistry, BUET to investigate the application of nano-silica within cement matrix. Currently, research is going on to develop a low-cost production process to generate nano-silica using the sol-gel process. The initial result of the research is very promising. Rice husk based nano material could be another potential field of research to be pursued since Bangladesh is one of the leading rice producing countries of the world. It is imperative that the industrial wing should pursue collaboration with researchers to manufacture products related to the construction industry.

Conclusions

A number of developing countries have already launched nanotechnology initiatives to strengthen their capacity and sustain economic growth. These countries are directing their nanotechnology based initiatives towards their imperative needs. Countries like India, Thailand have significant research schemes for nano-material science and nanotechnology. As already mentioned, relatively less expensive and simple synthesis process should be adopted initially in a developing country like Bangladesh. India and Philippines followed and implemented such techniques successfully and showed exemplary path to be followed by Bangladesh. The research efforts in the field of nanotechnology in Bangladesh should focus on utilization of the existing infrastructure and strength that the country possesses. These research initiatives should be well coordinated and well planned for proper utilization of resources.

References

- [1] B. Marrs, R. Andrews, and D. Pienkowski: Multiwall Carbon Nanotubes Enhance the Fatigue Performance of Physiologically Maintained Methyl Methacrylate-Styrene Copolymer. *Carbon*, 45(10), 2098-2104. (2007).
- [2] J.N. Coleman, U. Khan, W.J. Blau, and Y.K. Gum'ko: Small but Strong: A Review of the Mechanical Properties of Carbon Nanotube-Polymer Composites. *Carbon* 44(9), 1624-1652. (2006).
- [3] J.G. Wang, Z.P. Fang, A.J. Gu, L.H. Xu, and F. Liu: Effect of Amino-Functionalization of Multi-Walled Carbon Nanotubes on the DIspersion with Epoxy Resin Matrix. *Journal of Applied Polymer Science*, 100(1), 97-104. (2006).
- [4] L.X. Zheng, M.J. O'Connell, S.K. Doorn, X.Z. Liao, Y.H. Zhao et al.: Ultralong single-wall carbon nanotubes. *Nature Materials*, 3: 673-676. (2004)
- [5] M.F. Yu, O. Lourie, M.J. Dyer, K. Moloni, T.F. Kelly, and R.S. Ruoff: Strength and Breaking Mechanism of Multiwalled Carbon Nanotubes under Tensile Load. *Science*, 287 (5453), 637-640. (2000).
- [6] J.P. Salvetat, J.M. Bonard, N.H. Thomson, A.J. Kulik, L. Forró, W. Benoit, and L. Zuppiroli: *Applied Physics A*, 69, 255. (1999).
- [7] D.A. Walters, L.M. Ericson, M.J. Casavant et al.: Elastic strain of freely suspended single-wall carbon nanotube ropes. *App. Phys. Let.*, 74, 3803-3805. (1999).
- [8] J. Makar, J. Margeson, and J. Luh: Carbon nanotube/cement composites-early results and potential application, 3rd International Conference on Construction Materials: Performance, Innovations and Structural Implications, Vancouver, B.C., Aug. 22-24, pp. 1-10. (2005).

-
- [9] J.M. Makar, G.W. Chan: Growth of Cement Hydration Products on Single Walled Carbon Nanotubes. Institute for Research in Construction, NRC-CNRC. (2009).
- [10] G.Y. Li, P.M. Wang and X. Zhao: Mechanical Behavior and Microstructure of Cement Composites Incorporating Surface-Treated Multi-walled Carbon Nanotubes. Journal of Cement & Concrete Composites, Elsevier Ltd. (2004).
- [11] A. Cwirzen, K. Habermehl-Cwirzen, and V. Penttala: Surface Decoration of Carbon Nanotubes and Mechanical Properties of Cement/Carbon Nanotube Composites. Adv. Cem. Res., 20, 65-73. (2008).
- [12] T. Manzur: *Nano-Modified Cement Composites and its Applicability as Concrete Repair Material*. PhD diss., University of Texas at Arlington, 2011. e-thesis. ProQuest Dissertations and Theses (database). (2011)
- [13] M. Collepardi, S. Collepardi, R. Troli and U. Skarp: Combination of Silica Fume, Fly Ash and Amorphous Nano-Silica in Superplasticized High-performance Concrete. Proceeding of First International Conference on Innovative Materials and Technologies for Construction and Rehabilitation, Lecce, Italy, 459-468. (2004).
- [14] P. Balaguru and K. Chong: Nanotechnology and Concrete: Research Opportunities. The ACI Special Publication, "Nanotechnology of Concrete: Recent Developments and Future Perspectives", SP-254-2, 15-28. (2008).