Huge opportunities for industry of nanofibrous concrete technology

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Abstract

In spite of the fact that cementitious and concrete materials are mainly used on a large scale and in huge quantities for roads, dams, bridges and building constructions, the mechanical behavior of these materials depends to a great extend on structural elements and phenomena which are effective on a micro and nanoscale. Although this is well known by researchers, material producers and engineers for many years, the aspect of nanoscience and nanotechnology has hardly found any special attention, so far. New efforts and possibilities of material engineering on nanoscale in other fields may well lead to a new leap forward to improve mechanical and physical properties as well as durability of this important group of composite construction materials. This paper intends to stimulate the application and development of nanoscientific and nanotechnological concepts of nanofiber materials and their applications in concrete. Due to the wide range of possibilities, however, it does not claim to present a complete overview of the whole field. This would clearly go beyond the scope of this paper. It rather gives a short outline on the related cementitious and concrete material problems and research topics where nanoscience and nanotechnology could produce a major contribution to improve the nanofibrous materials where research needs to be done. Capability to accurately predict failure in joints offers significant potential for developing higher performance structural designs that are safer at the same time since these nanotubes can be used to accurately assess the behavior of joints, members and structures. Nanofibrous cement based materials can monitor regions of partial damages, localized changes in strains, stresses and temperatures of any joints and members.

Keywords: *Nanotechnology, Cement, Concrete, Nanofibrous, Carbon Nanotubes, Multy-wall nanotubes, Single-wall nanotubes, Strength*

1. INTRODUCTION

Nanotechnology is defined as the control and manipulation of material at the nano scale (nm or 10^{-9} m) in the range from 0.1 to 100 nm. The diagram opposite depicts a progression of images from 10 cm to 1 nanometer, with the dimension of each side of each square reducing by a factor of 100 between each image. Rather than a specific area of science or engineering, nanotechnology is a general technology. Nanotechnology may have far-reaching effects across many sectors of the economy over the next two or three decades. It refers to a cluster of techniques and processes concerned with new ways of making things by designing and engineering them at the atomic level [CRISP, 2004]. This has already created many new products and processes, such as the lab-on-a-chip, surface coatings, nanostructur materials, nano-instruments and tools, and nanosensors. Nanotechnology applications 'promise more for less: smaller, cheaper, lighter and faster devices with greater functionality, using less raw material and consuming less energy' [Smith et. al., 2000].

Study the feasibility of embedding wireless Micro Electro Mechanical Systems (MEMS) and Nano Electro mechanical Systems (NEMS) devices into concrete to measure concrete density and viscosity, temperature, moisture content, shrinkage stresses, pH, chloride concentration and carbon dioxide are the potential application of nanotechnology in concrete material which are carried out by many researchers in the world [Saafi, 2006]. The objective of these studies is to analyze the behavior of concrete material during mixing and curing as well as when the concrete structure is put in service. For example, with wireless MEMS and NEMS sensors the density and viscosity of unset concrete in mixing and pumping equipment can be measured. The use of these devices in concrete material would also increase the understanding of the cement hydration process and damage evolution, and detect crack initiation under loading. Also, another research potential is studied to analyze the applicability of environmental responsive hydrogels as sensing elements that can actuate in response to an environmental condition, such as pH or temperature [Peppas and Wolfgang, 2006]. The actuation is powered by water up-take and expulsion from a network system, which makes this an attractive sensing/actuating element for micro devices to be used in aqueous systems. A micro cantilever will be utilized as the transduction mechanism due to its ability to detect surface stress changes with ultra sensitivity.

Nanotechnology is usually associated with high profile telecommunications, biomedical and military applications. But for most nations and citizens, one of the main ways of this science at nanometer level which is revolutionizing our daily lives is right under our feet concrete [NRC-IRC, 2005]. At the civil and material engineering research institutes for research in construction materials, researchers are helping lead the way in understanding the nano scale properties of concrete and using this knowledge to create stronger more durable concrete in a more sustainable manner [Cientifica 2004, U.S. Army 2005, Keyvani 2005].

2. SIGNIFICANCE OF NANOFIBERS AND NANOTUBES COMPONENTS

Nano tubes are the subject of one of the most important areas of research in nanotechnology. Their unique properties and potential for valuable commercial applications ranging from electronics to chemical process control have meant that an enormous amount of effort has been undertaken on the investigation of nanotubes in the last six years [Cientifica 2004, Makar et.al. 2003]. Despite this high level of research activity, very little attention has been paid to potential applications in the construction industry. This paper seeks to bridge the gap between nanofibrous concrete and construction materials research. It describes carbon nanotubes, including their structure, and their properties. Potential applications, both generally and specifically for the construction industry, are also presented.

Nanotechnology offers construction professional opportunities for designing, engineering and building in new ways. It can change the rules of designing and engineering, through the auspices of specifying the properties and performance of materials and components in advance. This will challenge existing engineering, designing practice, unlocking the potential for architecture, civil, structural, environmental, and electrical and mechanical engineering, as well as other professions to break away from their traditional design parameters. A dialogue is needed across the professions to assess and explore how they can become fully involved in future developments, translating technological promise into new benefits for customers and users of the built environment, (Table 1).

3. CARBON NANO FIBERS PRODUCTION PROCESSES

Term of nanofibers refer to hollow and solid carbon fibers with lengths and widths varying from some tens of nanometers. These materials are often referred to as nanotubes but they do not have the cylindrical chicken wire structure of Single-Walled-Nano-Tubes (SWNTs) and Multi-Walled-Nano-Tubes (MWNTs), where the walls of the tube are parallel to the central axis, Figures 1 and 2 [Cientifica 2004, Makar et.al. 2003]. Production processes for carbon nanotubes vary from blasting carbon with an electrical arc or a laser to growing them from a vapor, either en masse (usually in tangled bundles)

Table 1: Nanotehnology applications lead to new products in construction

Market Availability	General Applications	Functions
Already available	Nano measurement techniques	Nanoindentation, nanoscratch and nanofabrication methods – used to evaluate weak links in the structure of materials and to test materials for their fracture and bond properties.
	Nanostructured materials, nanoparticles and nanofibres	Used to strengthen and improve the performance of construction materials. Certain types of concrete and cement incorporate superplasticers and stabilizers that are already produced by using nano techniques. Nanoparticles provide new improved methods to manufacture high-quality glass.
	Surface layers and coatings	Used to protect and strengthen materials, as well as provide new functions. Examples include: ultra-thin energy-saving reflecting layers composed of ultra-fine particles that allow only light of a certain wavelength to pass through; adhesion techniques and adhesion processes used as coatings on surfaces; surfaces with catalytic activities; and corrosion-resisting layers.
	Sensors	Such as biosensors, chemo sensors, mm-wave sensors, NEM-sensors that are embedded in materials that are used to monitor and control the performance of materials.
Close to market	Cement and plaster (hydraulic binders)	Cheaper, more durable, less cement hydration, self-repairing, etc.
	Surface coatings	On glass (various oxides) - e.g. self-cleaning, water repellent glass, depolluting catalyzers under solar energy, photosensitive applied to other materials (e.g. paints) - improved scratch resistance, UV protection.
	Nano-composite materials	Fire protection materials, i.e. increased flame resistance.
	Responsive materials	Adapt to the environment and change their appearance: for example, cladding systems that respond to change heat or light to maximize comfort and minimize use of energy in buildings.
	General sensors	For environmental, safety or security purposes.

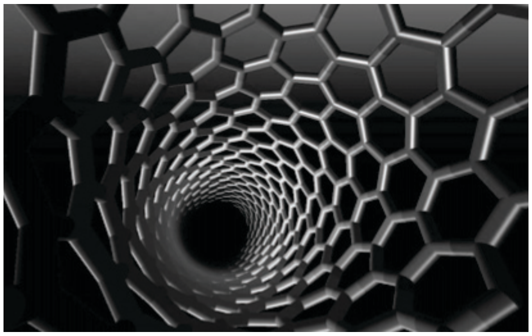

Figure 1: A single-walled carbon nanofibers

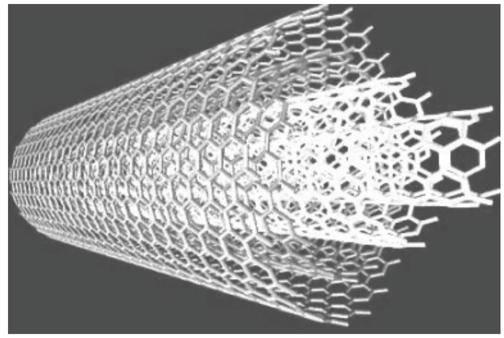

Figure 2: A multi-walled carbon nanofibers

or on nanoparticles, sometimes in predetermined positions. These processes vary considerably with respect to the type of produced nanotube, quality, purity and scalability. Carbon nanotubes are usually created with the aid of a metal catalyst and this ends up as a contaminant with respect to many potential applications. IBM has very recently, however, grown nanotubes on silicon structures without a metal catalyst [Cientifica 2004].

Current estimated global production of carbon nanofibers is more than 40 tons per a year, and is expected to reach more than 58 tons by 2006. Total global production capacity of multi-walled nanotubes is higher than 99 tons a year and expected to increase to at least 268 tons annually by 2007. Current global production of single walled nanofibers can be estimated to be at least 9000 kg/year [Cientifica 2004]. The production is expected to increase up to more than 27 tons by 2005 and to reach 100 tons by 2008.

In nanofibers the angle between the graphite planes and the tube axis is non-zero, and the resulting structures are sometimes referred to as stacked-cone structures. When they exhibit only small angular deviations from the axis and are not solid cylinders but hollow, they are often called multi-walled carbon nanofibers (MWNFs).

Nanofibers mostly consist of a mixture of forms of carbon, from layers of graphite stacked at various angles to amorphous carbon (lacking any large-scale regular structure). Because of this variable structure they do not exhibit the strength of pure nanofibers but can still be quite strong (e.g. around 7 gigapascals tensile strength for the heat-treated, which compares with under 5 gigapacals for the best traditional carbon fibers) and possess other useful properties, such as good electrical and thermal conductivity.

This is an appropriate point at which to introduce a note of caution, and an area of research worth keeping an eye on. Just because the perfect nanotube is 100 times stronger than steel at a sixth of the weight doesn't mean you are going to be able to achieve those properties in a bulk material containing them. To remember that the chicken wire arrangement makes up the layers in graphite does not stick at all well to other materials, which is why graphite is used in lubricants and pencils. The same holds true of nanotubes-they are quite insular in nature, preferring not to interact with other materials. To capitalize on their strength in a composite they need to latch on to the surrounding polymer, which they are not inclined to do (blending a filler in a polymer is difficult even without these issues-it took a decade to perfect this for the new nanoclay polymers now hitting the markets).

One way of making a nanotube interact with something else, such as a surrounding polymer, is to modify it chemically. This is called functionalization and is being explored not just for composite applications but also for a variety of others, such as biosensors. For structural applications, the problem is that functionalization can reduce the valuable qualities of the nanotubes that you are trying to capitalize on. This is an issue that should not be underestimated. Of course, in theory you don't need to mix the nanotubes with another material. If you want to make super-strong cables, for example, the

Figure 3: Nanoparticles of three calcium aluminate (3CaO, Al_2O_3)

best solution would be to use bundles of sufficiently long nanotubes with no other material added. For this reason, one of the dreams of nanotube production is to be able to spin them, like thread, to indefinite lengths.

Mechanically, carbon nanotubes appear to be the strongest materials yet to be discovered. Experimental results have shown that they have modulated of elasticity that exceed 1 TPa in value [Salvetat et al., 1999] Measurements of ultimate strength and strain have been more difficult to make, but measurements of the yield strength of SWNTs of 63 GPa have been reported as well as yield strains are on the order of 6%, [Yu et.al 2000, Walters et.al 1999]. Carbon nanotubes are also highly flexible, being capable of bending in circles or forming knots. Like macroscopic tubes, they can buckle or flatten under appropriate loadings [Lourie et.al 1998]. Yakobson and Avouris have summarized carbon nanotubes mechanical behavior [Yakobson and Avouris, 2001].

4. STRUCTURE OF CEMENT AND BEHAVIOR OF CARBON NANOFIBERS REINFORCED CONCRETE

Nanoscience has played a central role to produce innovative concretes for the 21st century [Keyvani 2005]. Nanoscience enables scientists to work at the molecular level- atom by atom- to develop new materials with fundamentally new physical and chemical properties. Nanotechnology is already used in a variety of ways to produce innovative construction materials. Nanoparticulate additives are now widely used as fillers in protective paints, coatings, and superplasticizers for producing high performance concrete and monuments exposed to radioactive materials.

Concrete has the largest production of all man-made materials with an annual global production of about one cubic meter for every person on Earth. Asian, American, European, Canadian, Japanese and … industry account for about more than $100 billions for concrete construction annually [Keyvani, 2005]. Concrete is the single most important construction material. Composed of fine and coarse aggregates held together by a hydrated cement binder, it forms a part of most construction projects, ranging from house foundations through high-rise tower components to dams and highway bridges. Ordinary portland cement is the most common form of cement binder used in concrete, although there are a large number of specialty forms of cement. Ordinary portland cement is typically formed by grinding amorphous masses of cement clinker and gypsum into powder. The primary constituents of the clinker are a series of oxides, including tricalcium silicate (C_3S in cement chemistry notation), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF). C_3S and C_2S are the most important constituents in ordinary portland cement. These oxides, when were mixed with water, undergo hydration reactions to form the solid cement binder. Direct observations of cement grains show that many of them have dimensions on the order of 5 to 30 μm. However, smaller particles are also present in ordinary portland cement (Figure 3). The impact of these finer particles, if any, on the

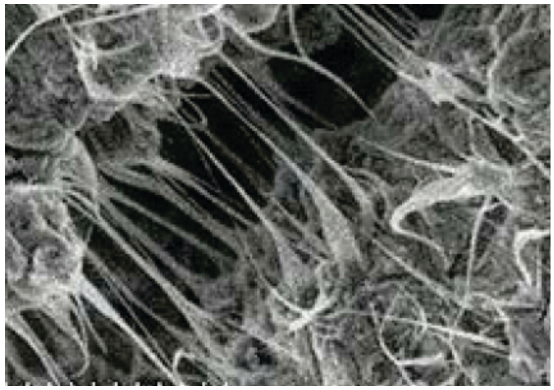

Figure 4: Carbon nanofibers interaction in cement matrix to hinder crack propagation

cement hydration process is not yet understood.

The strength of concrete is depend on the number of factors, which include, among others, the ratio of water to cement in the original mix of materials, degree and size of porosities present in the cement, the presence of micro-cracking in the binder and the quality of binding of the aggregate to the cement. Hydrated cement is porous with a pore size distribution that ranges from the nanometers to millimetres. However, the pores are also a core weakness: they are a pathway for chloride salts and other chemicals to seep into concrete causing cracking and deterioration that costs countries economy billions of dollars annually [Keyvani, et.al., 2000].

High value added materials with carbon nanotubes are suitable for reinforcement of infrastructure materials such as cement and concrete. Nanofiber reinforced cement offers unique capabilities. Because of the high strength and nanoscopic scale of the reinforcement, high strength cementitious composites can be anticipated with uniform structure. As a result, a high strength, machinable ceramic-like material can be produced. Carbon nanofibers were found to provide significant improvements in compression strength, tensile strength and flexural strength when are used in macro-defect free cement (MDF). Table 2 shows the compressive strength improvements were observed in macro-defect free cement with only 3% by weight of carbon nanofibers [Ohio CDO and Ohio Uni., 2004].

One of the important characteristics of the carbon nanofiber reinforced cement is highly resistant to microcracking. The level of microcracking prevention is the ability to machine carbon nanofiber reinforced macro defect free cement on conventional lathes. While the market for machined cement parts is almost non-existent, the machinability of carbon nanofiber reinforced cement demonstrated the ability to produce machinable ceramic composite parts and the ability to reduce the failure of cement and concrete products due to the "freeze-thaw"

Table 2: Carbon nanotubes mechanical properties improvements in macro-defect free cement

Strength	MDF cement (kg/cm^2)	Carbon nanofiberous MDF cement (kg/cm^2)	Change Percent
Compression	256.2	1113.1	+334%

cycles that are so prevalent in icy and snowy regions of the world. Thus the cost of carbon nanofibers will need to be dramatically reduced in order for carbon nanofibers to find use in infrastructure applications.

A quick overview of the scope of the global concrete industry and its environmental impact makes it clear why nanotechnology R&D advances will have enormous economic, social and environmental impacts. Concrete has the largest production of all man-made materials with an annual global production of about one cubic meter for every person on Earth [Keyvani, 2006]. Thus, a better understanding of the nanoscience of cement hydrates and cementitious materials will reveal new routes for tackling this problem. For example, the addition of nanoparticulates to concrete can improve its durability through physical and chemical interactions such as pore filling. The addition of nanoscale particles to concrete is expected to improve control of concrete porosity beyond what is presently possible with silica fume. The performance of concrete can also be improved by adding nanofibres. Carbon nanotubes have the potential to enhance the strength, to effectively hinder crack propagation in cement composites, and to act as nucleating agents. Reinforcing concrete with nanofibres will produce tougher concretes by interrupting crack formation as soon as it is initiated (Figure 4).

Development of efficient nucleating agents and low energy cements will contribute to increase usage of supplementary cementing materials, such as fly ash and slag while making concrete production more environmentally sustainable. While the exploration of various applications of nanotechnology to develop innovative construction materials continues, it is already clear that the science of the very small particles is making big changes, with numerous economic benefits for the construction industry.

Numerical methods and experimental techniques are providing useful descriptions of the processes responsible for the emergence of micro-cracks and other sources of degradation at the nanoscale. The challenge is to move back from nanoscale to the macroscopic level to see how the whole system works together as part of a building. This can be achieved, for example, by creating more reliable and longer lasting components and structures-such as high specific strength and fatigue resistant materials. While some engineers have worked on micro structures, greater effort is now required to push the technological frontier below the micro to the nanoscale.

5. APPLICATIONS OF CARBON NANOFIBROUS FOR CONCRETE CONSTRUCTION

Failures in many construction materials at the macro or micro-scale are typically the result of tiny micro-cracks. Traditionally, new materials have been developed to overcome such failures by improving macro-engineering properties. But the real source of the problems caused by micro-cracks often occurs much earlier and can only be observed at the nanoscale.

When thinking about structural applications such as concrete construction, it should be remembered that, in general, as the fibers get smaller so the number of defects decreases, in a progression towards the perfection of the single-walled nanotube. Recent advances in high-performance computing now make it possible to predict the bulk mechanical properties of engineered carbon nanotube composite materials based on molecular dynamics [U.S. Army, 2005]. Improved mechanical performance is one of the benefits expected to be obtained through the application of nanofibrous and nanotechnology to concrete structures. Just because the perfect carbon nanofiber is 100 times stronger than steel at a sixth of the weight [Makar and Beaudoin, 2003]. These materials are expected to have several distinct advantages as a reinforced material for cements as compared to more traditional fibers [Makar and Beaudoin, 2003, Salvetat et.al. 1999]. First, they have significantly greater strengths than other fibers, which should improve overall mechanical behavior. Second, carbon nanofibers have much higher aspect ratios, requiring significantly higher energies for crack propagation around a tube as compared to across it than would be the case for a lower aspect ratio fiber. Third, the smaller diameters of these fibers mean both that they can be more widely distributed in the cement matrix with reduced fiber spacing and that their interaction with the matrix may be different from that of the larger fibers. Fourth, carbon nanofibers have ultra electronic behavior and high thermal conductivity. Nonaofibers, with their diameters being close in size to the thickness of the calcium silicate hydrate (C-S-H) layers hydrated cement, could show very different behavior, including different bonding mechanisms. Finally, carbon nanotubes can be functionalized to react chemically with cement components, providing routes for other forms of interaction and cement system property control.

The capability to predict accurately failure in materials offers significant potential to develope higher performance structural designs that are at the same time safer since these nanotubes can be used to accurately assess the behavior of joints, members and structures. These nanofibrous cement based materials can monitor regions of partial damages, localized changes in strains, stresses and temperatures of any joints and members. Additionally, prediction capability also can result in lower development cost due to less reliance on experimental testing to determine optimal design details. Specifically, the use of modeling can increase likelihood that the joints and members will meet strength requirements when structural validation tests are conducted, thereby avoiding costly redesign and retesting activities. This challenge is being conducted along three areas: (i) thermal gradient measurement; (ii) fracture prediction; and (iii) failure characterization by strain-stress zone laws. In all three areas, experimental investigation was being used in conjunction with finite element analysis (FEA) to define the aforementioned methodologies for joints and members' failure prediction. However, applying a thin film of nanofibrous concrete as a sensitive electronic circuit over any joints and members with suitable tools will be possible not only to strengthening target but also can monitor all necessary safety data in the mentioned three areas at any time and with any accurate level.

6. CONCLUSION

Nanofibers are one of the most important materials under investigation for nanotechnology applications. Their unique properties, ranging from ultra high strength through unusual electronic behavior and high thermal conductivity to an ability to store nanoparticles inside the tubes themselves has suggested potential applications in many different fields of scientific and engineering endeavor. Reinforcing concrete with nanofibers will produce tougher concretes by interrupting crack formation as soon as it is initiated. Carbon nanotubes have the potential to enhance the strength, to effectively hinder crack propagation in cement composites, and to act as nucleating agents. Current technology has shown that it is possible to distribute carbon nanofibers bundles across cement grains. Capability to accurately predict failure in joints offers significant potential to develope higher performance structural designs that are at the same time safer since these nanotubes can be used to accurately assess the behavior of joints, members and structures. Embedding wireless nano electro mechanical systems devices into concrete to measure concrete density and viscosity, temperature, moisture content, shrinkage stresses, pH, chloride concentration and carbon dioxide are the potential application of nanotechnology in concrete material.

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