CONCRETE REINFORCEMENT ON SUBMICRONIC LEVEL

P. Bílý [1]

Abstract

The paper reviews state of the art in the area of reinforcing concrete on submicronic level, i.e. by fibers less than 1 micrometer in diameter. Materials suitable for utilization, methods of their incorporation into concrete matrix and contributions to concrete properties are discussed. Attention is devoted to the fact that compared to classic dispersed reinforcement, low-scale fibers not only prevent propagation of cracks, but also act as nucleation centers, thus increasing the level of cement paste hydration and improving its mechanical properties and chemical resistance. In order to be objective, technical and other difficulties that are so far encountered and potential drawbacks of the new materials are considered. Regard is given to the questions of submicronic fibers impact on health of workers that would get into everyday contact with these materials and also to the environmental issues.

Keywords: Carbon, cement paste, hydration, nanofibers, nanotubes, reinforcement.

1. Introduction

Concrete reinforced by steel, polypropylene or glass macrofibers is well-established material that is used in various applications round the world. Microfibers are employed in practice to prevent propagation of cracks. Although there are still a lot of aspects to examine with respect to dispersed reinforcement on macro- and micro- levels, the research goes forward, scientists are trying to find even more progressive ways of concrete improvement. As American physicist Richard Feynman said in his famous lecture in 1959, "There is plenty of room at the bottom". The next step from microfibers logically leads to submicronic grade.

To have an idea of the scale we are talking about, it is necessary to quote several numbers. Microfibers are fibers less than 300 μm in diameter. Their thickness is therefore comparable to human hair that is typically some 50 – 80 μm across. The objects this paper is dealing with, so called nanofibers, are limited by maximum dimension of 300 nm. Therefore, they are at least 150 times thinner than such a tiny thing as the hair is.

[1] Petr Bílý, Department of Concrete and Masonry Structures, Faculty of Civil Engineering, Czech Technical University in Prague, Thákurova 7, 166 29 Praha 6, Czech Republic, petr.bily@fsv.cvut.cz

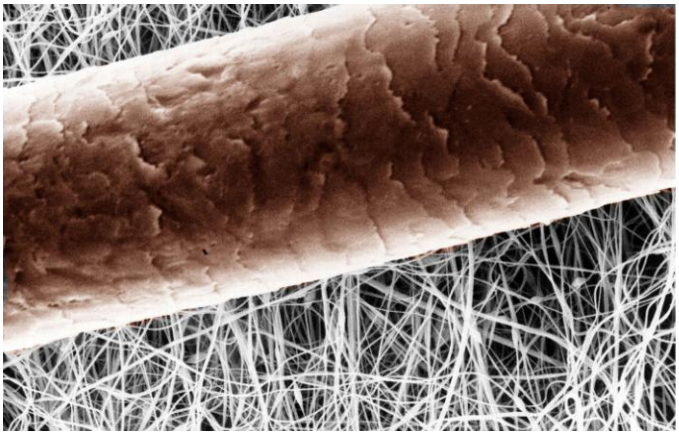

Fig. 1: Comparison between size of human hair (at the front) and nanofibers (in the background)[2].

What materials are the best for application in concrete? How can they improve concrete properties? Are there any drawbacks of this technology? There are many questions waiting to be answered. Exploration of this problem is in its early phase and we are definitely at least several years from first practical exploitation at present. However, the expectations are very high. Following text is trying to provide the reader with a brief overview of current state of the art and outlook to early future.

2. Types of fibers

So far all the researchers have focused on carbon based materials, specifically carbon nanofibers (CNFs) and carbon nanotubes (CNTs).

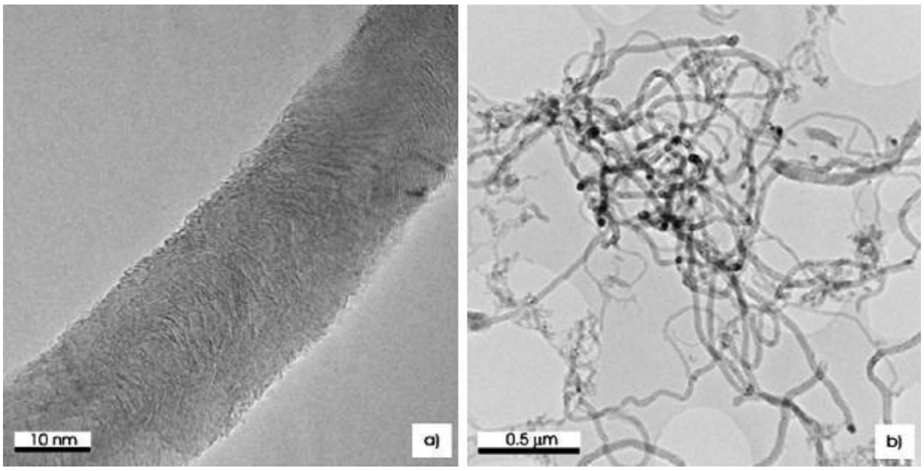

Fig. 2: Transmisson electron microscopy (TEM) images of single carbon nanofibre (left) and a bundle of CNFs (right), reprinted from [1].

CNFs are one-dimensional objects, usually produced by a method called chemical vapor deposition (CVD). Gas-phase molecules of hydrocarbon (e.g. methane) are decomposed

[2] Photo by eSpin Technologies, Inc., Chattanooga, Tennessee, USA

at high temperatures and carbon is deposited on a substrate. The presence of metal catalyst is necessary for the reaction to take place with iron, cobalt and nickel being the most often used catalysts. The nanofiber diameter, length and other characteristics depend on catalyst size, state quantites like temperature, pressure or concentration and other variables. For example, Kvande et al. [1] defined that use of Ni-Al catalyst sieved to a size of 100 – 145 µm, temperature of 580 °C and a total pressure of 380 kPa was optimal for synthesizing the maximum amount of CNFs from methane-nitrogen mix while the average diameter of received fibres was 35 nm. As the length of CNFs can be nudging several hundreds micrometers, their aspect ratio is very high.

So far, CNFs with tensile strength of 12 GPa and Young's modulus of 600 GPa were prepared [2]. Nevertheless, even higher values are theoretically possible.

CNTs are produced in a way similar to CNFs, just the values of individual parameters are different, for example temperature is typically some 1100 °C. One can imagine singlewall carbon nanotube (SWCNT) as graphene sheet rolled into a cylinder with the tips of the tube sealed by two hemi-fullerene caps. Graphene is a monoatomic layer consisting of carbon atoms arranged in hexagons, fullerene is a hollow spherical or ellipsoidal molecule of carbon (the most famous buckminsterfullerene C_{60} resembles soccer ball by its shape). The most frequent diameter encountered in SWCNTs is 1,4 nm regardless the synthesis technique due to energetical reasons [3], while the length can be in the micrometer or even milimeter range implying huge aspect ratios. Multiwall carbon nanotube (MWCNT) is characterized by the Russian doll-like arrangement – it consists of several concentric SWCNTs. Their aspect ratios are significantly lower.

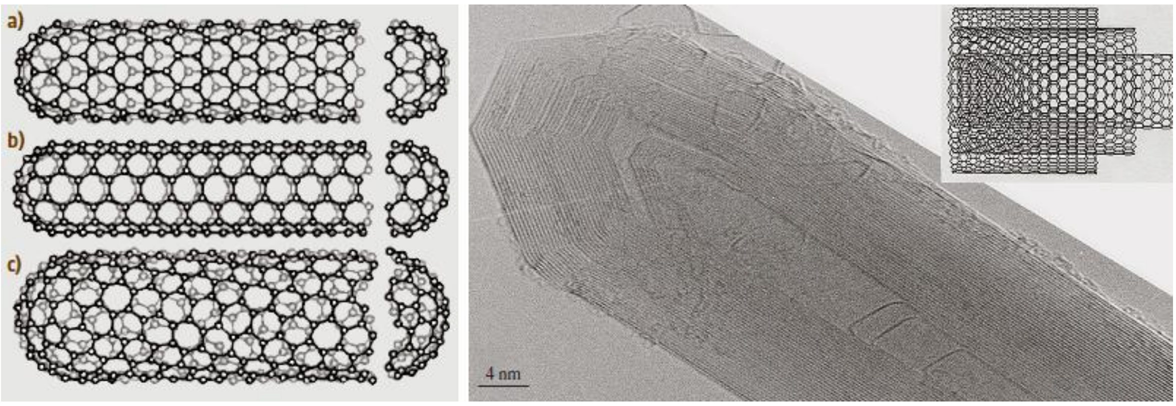

Fig. 3: Sketches of different SWCNT structures (left), TEM image of MWCNT (right), sketch of Russian-doll like arrangement of graphene sheets (upper right corner insert), reprinted from [2].

Mechanical properties of CNTs are exceptional. Tensile strength of 150 GPa was measured [4], elastic modulus higher than 5 TPa was reported by various authors [5]. This is because of fine character of the tubes – as there are only several layers of atoms in a wall, crystal lattice failures that would weaken the structure are much less likely to occur than in bulk materials.

Polymers used for concrete reinforcement on macroscopic level (polypropylene, polyvinyl alcohol) are available in the shape of nanofibers as well thanks to the electrostatic spinning methods. They could have similar impact on concrete properties as carbon materials in some cases, as will be discussed later. However, author of this paper is not aware of any experiments that have been done on the effect of polymer nanofibers on concrete up to the present time.

3. Incorporation of fibers into cement

The method of adding CNTs/CNFs into cement that might look quite straightforward is based on mixing nanomaterial with cement grains. However, it is not so simple as fibers or tubes tend to create bundles due to their high self-attraction caused by van der Waals interactions. To ensure good distribution in the matrix, they are usually first dispersed in some sort of surfactant (acetone, isopropanol [6], nitric acid [7]) and then subjected to ultrasonic vibrations (so called sonification) that further increases homogeneity. After that, cement is blended with the solution. Either the preparation of specimens follows immediately or surfactant is evaporated, material is ground and cement particles coated with CNTs/CNFs are received. In any case, addition of polycarboxylated-based superplasticizer or viscosity modifying agent during mixing with water is required to improve workability.

While the question of dispersion can be somehow solved using the technique described above, another problem is caused by very low surface friction of CNTs/CNFs. Their smoothness makes it difficult to bind them with the matrix. Under loading, they can be pulled out of the matrix before their outstanding mechanical properties can be fully exploited. Very promising material that could eliminate the drawback is called carbon hedgehog cement (CHH).

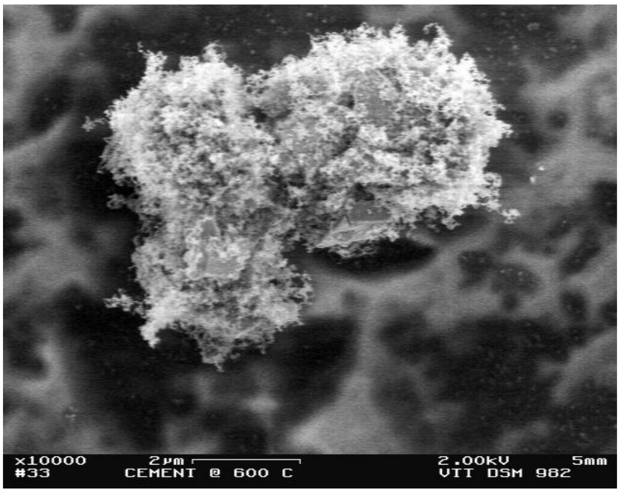

Fig. 4: Scanning electron microscopy (SEM) image of CHH particle, reprinted from [9].

CHH cement prepared by Nasibulin, Cwirzen et al. [8], [9] is a novel cement-based material. Instead of mixing with cement, CNFs and CNTs are grown directly on the surface of cement grains by modified CVD method. This is possible thanks to Fe catalyst particles naturally occurring in the cement. Carbon nanomaterials are uniformly dispersed in the cement powder and as they are chemically bonded with cement grains, solid linking with the matrix is secured.

4. Principles of concrete properties improvements

The question is how do these tiny carbon particles improve the properties of concrete. Three main principles can be defined.

The first thing is that the fibers act as a nanosized reinforcement of cement paste. By bridging the cracks during loading and load transferring, CNTs/CNFs prevent crack propagation on the most fundamental level of material structure where traditional reinforcement is not effective, thus creating very compact substance with increased mechanical properties and resistance to chemical agents penetration.

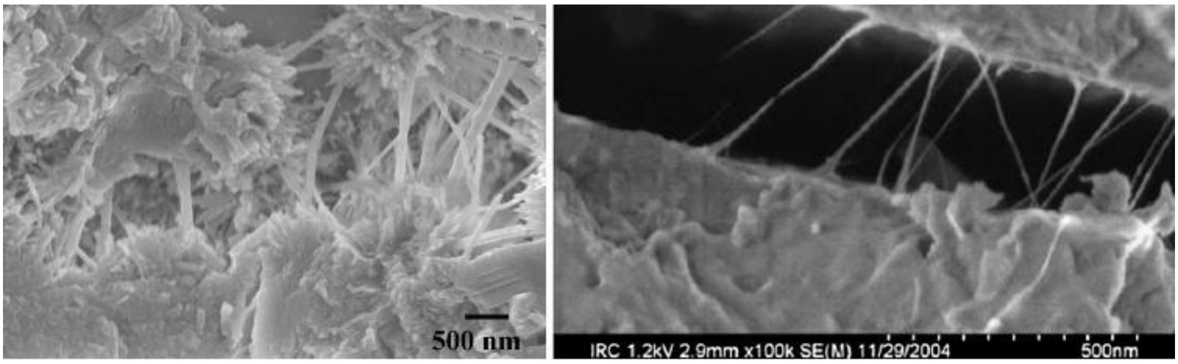

Fig. 5: Left: SEM image of fracture surface of cement nanocomposite reinforced with CNFs [11]. Right: Crack bridging observed in cement-CNT composite, reprinted from [6].

Previous way of acting is analogical to the effect of macroscopic fibres. What is completely new with nanomaterials is their influence on cement hydration. Generally, each crystallization is conditioned by presence of nucleation centers (so called homogeneous crystallization that occurs without nuclei is very rarely encountered in practice). Usually some impurities in the main material play the role of nucleation centers. If a phase change of the main material is about to happen, it usually begins on the surface of these impurities, because they are places of slightly different conditions (chemical composition, pressure, temperature etc.) that induce the change. Subsequently the crystallization proceeds it the whole volume. Properties of emerging crystals are defined by properties of the nuclei to a large degree.

In case of cement hydration, calcium-silicate-hydrate (CSH) gel crystals are created with fine aggregates, microsilica or non-hydrated cement grains normally being the nuclei. The finer the nuclei, the finer the CSH gel crystals. If the nucleation centers are submicronic, resulting cement paste is denser, contains significantly lower number of non-hydrated cement grains, inhomogeneities, pores and cracks, which again leads to a material that is more resistant both mechanically and chemically.

Finally, nanoobjects can serve also as filling material lowering porosity of cement paste, leading to higher modulus of elasticity, lower bleeding and lower autogenous shrinkage. The latter is known to be proportional to the amount of fine pores in the binder at early ages. Due to their small diameters, nanoobjects are able to reduce the amount of fine pores which results in reduction of capillary stresses, ending in lower autogenous strains [10].

From the above mentioned, it is obvious that polymer nanofibers could be able to fulfill the same functions as carbon ones theoretically. They could be utilized as nucleation centers, fillers and also reinforcement, although their mechanical properties are worse than these of carbon fibers. Nevertheless, these are only considerations that should be proved by experiments and evaluated with respect to economical feasibility.

5. Examples of concrete properties improvements

In this chapter, several examples of experimental results obtained by various authors will be presented to demonstrate improvements of concrete properties by nanomaterials.

Metaxa et al. [10] added MWCNTs in cement. On 20x20x80 mm notched cement paste specimens, mechanical performance was tested by three point bending and autogenous shrinkage was measured. The dose of nanotubes was only 0,08 % of cement weight for mechanical tests and 0,048 % for shrinkage test. Specimens exhibited much higher modulus of elasticity and fracture load than reference plain cement samples. Autogenous shrinkage was significantly lower. See figures 6 and 7, respectively.

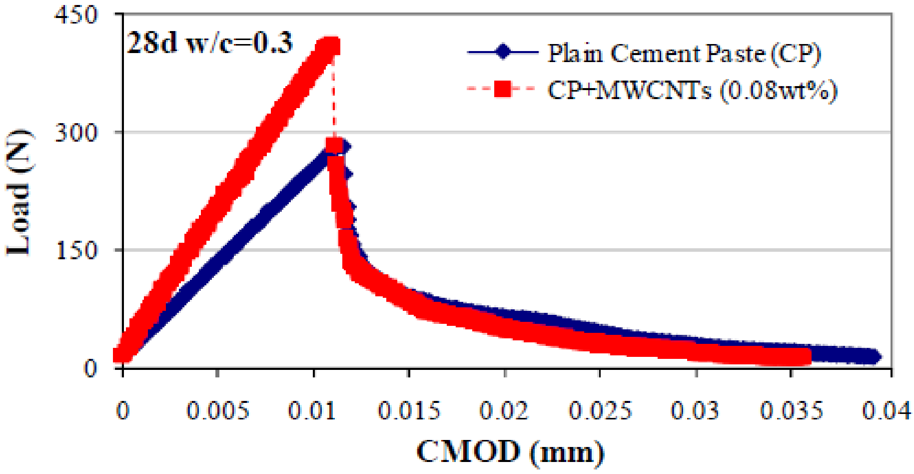

Fig. 6: Mechanical behavior of 28-day plain cement paste and MWCNTs reinforced paste, reprinted from [10].

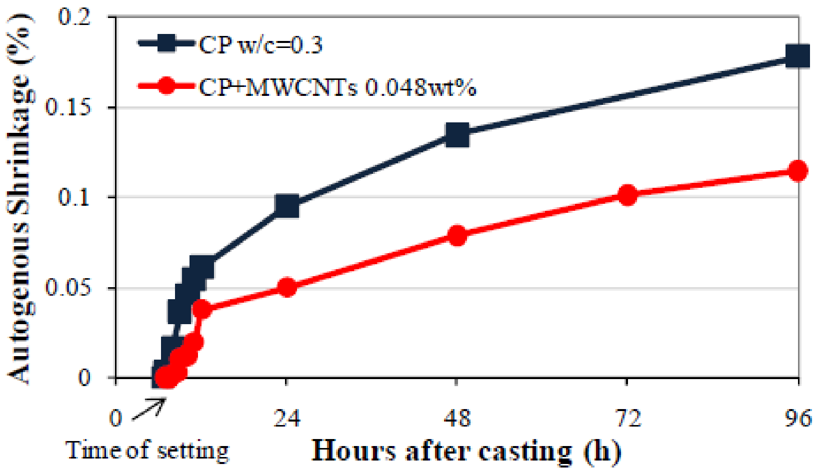

Fig. 7: Autogenous shrinkage of plain cement paste and MWCNTs reinforced paste, reprinted from [10].

CNF/cement composite tested later by the same authors led to similar results [11], see figure 8. Testing setup was identical to previous case, dose of CNFs was 0,048 % of cement weight.

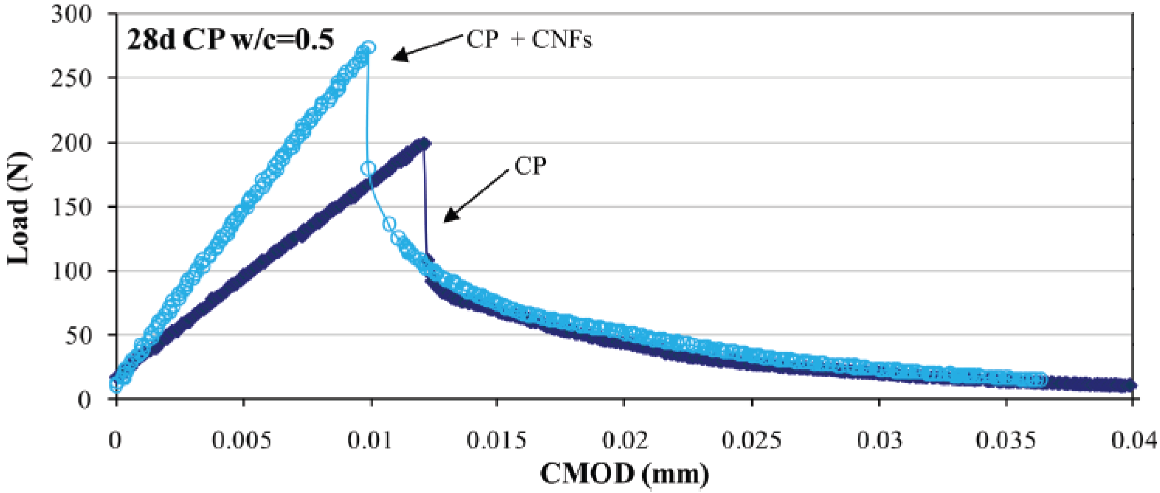

Fig. 8: Mechanical behavior of 28-day plain cement paste and CNFs reinforced paste, reprinted from [10].

Cwirzen et al. [12] reported compressive strength improvement of nearly 50 % with 0,045 – 0,15 % of cement weight MWCNTs in cement paste.

CHH cement [9], [10] is the most promising material in area of nanoreinforced concrete according to the opinion of author of this paper. Theoretically, compressive strength of CHH cement paste could be up to 5 times higher than that of plain cement paste. So far, twofold increase was experimentally verified, but in some cases decrease was also recorded. Seven mixes are compared in figure 9. Each mix contained CHH cement produced under different conditions, which resulted in different amounts of grown CNTs/CNFs varying from 2 to 20 % by weight of produced binder. Carbon content in CHH is much higher than in case of simple mixing, where 1,5 % is considered to be a maximum.

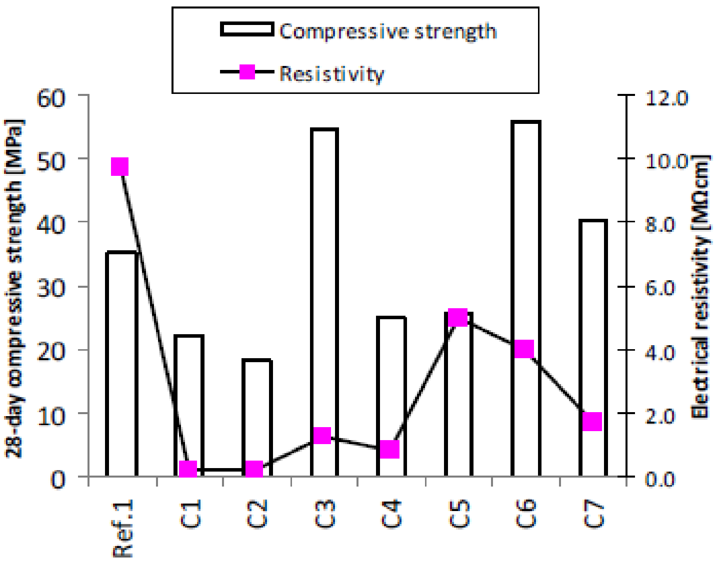

Fig. 9: 28-day compressive strength and electrical resistivity of plain cement paste (Ref.1) and CHH cement pastes with different CNTs/CNFs contents (C1 – C7), reprinted from [9].

Decalcification of cement paste can be used as a good indicator of chemical deterioration of concrete. Sanchez et al. [13] compared ductility of plain cement paste and 0,5 % of cement weight CNFs paste exposed to decalcificating ammonium nitrate solution for 95 days. Significantly higher ductility was observed in reinforced paste.

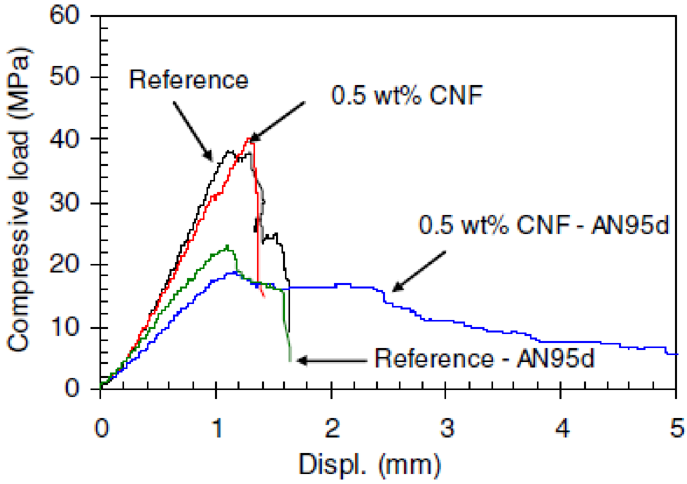

Fig. 10: Comparison of compressive load displacement curves of reference plain cement paste and CNF/cement composite before and after decalcification for 95 days (AN95d), reprinted from [13].

Utilization of nanomaterials could also lead to decrease in the amount of cement necessary for obtaining the required concrete strength, thus reducing environmental impact of cement production and construction process.

6. What's the catch?

Having read previous chapter, one might wonder why CNTs/CNFs have not been used in practice till now. Unfortunately, there are still many questions that have to be solved before nanocement composites will be prepared for field applications.

Firstly, there are technical problems related to CNTs/CNFs distribution and bonding with the cement matrix that were mentioned in chapter 3. Some prospective paths were showed, but final solution have not been found yet. The same is with dosing – if the cement composite is overdosed by nanoadmixture, properties might get worse compared to plain cement paste, but it is difficult to define what amount to use as CNTs/CNFs can have very wide range of characteristics (diameter, aspect ratio, production conditions, surface treatment etc.), making preliminary estimation of final state almost impossible. For instance, Musso et al. [14] prepared three identical cement pastes that differed only by surface treatment of CNTs used. Whilst two of them showed ca 15 % upgrade in compression resistance, the third one was six times weaker compared to reference plain cement paste specimen. It also should be emphasized that almost all experiments have been conducted on cement pastes, not concrete mixes, so that the effect of aggregate is another factor that remains to be examined.

Secondly, developing of more effective production techniques and price reduction of carbon nanomaterials will be necessary for mass utilization in construction industry. Current prices of CNTs start at some $100 per kilogram and go up to $750 per gram, depending on exact type and purity. CNFs' price is usually between $100 and $500 per kilogram.

Thirdly, health and environmental aspects mustn't be ignored. Extensive research activities in this area were summarized by Lee et al. [15]. Experiments carried out on E. coli bacteria showed that SWCNTs or fullerenes can cause disruption of cell wall integrity. Mice subjected to MWCNTs influence encountered respiratory problems, pulmonary toxicity was detected. With at least one quarter of a population in developed countries suffering from some kind of allergy, it is not a surprise that certain nanomaterials were proven to bring on skin inflammation.

Further investigation will be necessary to define safety limits for nanomaterials exposure and their life cycle in the nature. Anyway, it is appropriate to gain maximum possible control of nanomaterials flow through the construction process from the beginning to the end. Workers that will get into everyday contact with them should use protective measures (respirators, coveralls). Users should not be affected as CNFs/CNTs will be embedded in concrete matrix tightly. What seems to be the biggest problem is demolition. Removal of structure is usually accomplished by means like explosives, bulldozers and others that do not allow to fully control release of dust to the environment, where it could negatively impact on organisms or water quality. The same concern is applicable to disposal of construction waste.

7. Conclusions

Many people believe that next industrial revolution will be nanotechnology. Plenty of abovementioned facts strongly support this idea. Although serious issues keep nanofibers and nanotubes from practical application in civil engineering nowadays, researchers worldwide struggle to break through the obstacles and considerable progress is to be expected in the near future. In the meantime, it is important to create civil engineering public awareness of the basics of nanotechnology. This paper is trying to contribute to meet this target.

Acknowledgements

The author is indebted to the support of Studentská grantová soutěž ČVUT 2011 (SGS 2011) under grant SGS11/106/OHK1/2T/11 „Engineered Concretes and Cement Composites“.

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