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Dispersion of carbon nanotubes for application in cement composites

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Abstract

Advanced technological aspects of cement based composites have been recently focused on developing new materials, which are high performance and exhibit high compressive strength. Using of carbon nanotubes improve microstructure and properties of cement matrix and make them promising fillers into many engineering materials. In this paper, experiments oriented at the study of dispersion of CNTs in water with respect to their use in cement compositions are described and a novel method of CNTs dispersion in water using pulsating water jets is proposed.

Keywords: carbon nanotubes, dispersion, sonication, pulsating water jet, impact pressure

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1. Introduction

Portland cement is widely used and the most common construction material worldwide. The main advantages are the availability of raw materials for production all over the world, ease of construction, room temperature setting, low cost and the ready availability of properties and performance data for design and construction [1, 2]. Advanced technological aspects of cement based composites have been recently focused on developing new materials, which are high performance and exhibit high compressive strength. However, these composites exhibit also low tensile capacity and extremely brittle failure. They are sensitive to early age microcracking as a result of volumetric changes due to high autogenous shrinkage stresses. Hence, there is a big effort to tailor the flexural and tensile mechanical properties of the cement paste in order to improve the damage and fracture resistance of concrete. To deal with previous mentioned disadvantages reinforcement of cementitious material is typically provided at the micro and milliscale using microfibers and macrofibers [3, 4]. Cementitious matrices however exhibit flaws at the nanoscale, where traditional fillers are not effective.

Nanomaterials provide unique multifunction properties due to its nanoscale. Using of nanoparticles such as TiO_2, Fe_2O_3 SiO_2 and especially carbon nanotubes (CNTs) improve microstructure and properties of cement matrix and make them promising fillers into many engineering materials [5].

Beneficial effects of nanomaterials on the microstructure and properties of cement nanocomposites:

- Properly dispersed nanoparticles form crystallic centers and speeds up cement hydration process
- Nanoparticles fill up free space between cement grains and prevent flow of water
- Nanoparticles contribute to creation of small crystals such as $Ca(OH)_2$ and uniform agglomeration of C-S-H products
- Nanoparticles accelerate pozzolanic reactions, which consume $Ca(OH)_2$ and produce additional C-S-H gel
- Nanoparticles also enhance contact zone, which increase bonding strength between cement compound and aggregates

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Probably the most promising material to use as filler is CNTs to improve concrete nanocomposite properties. Carbon nanotubes are cylindrical nanostructures formed from rolled up graphene hexagonal nets into nanometer diameter tubes. CNTs are divided into two groups: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). SWCNTs are composed of single graphene sheet and MWCNTs are nested arrays of SWCNTs (see Fig. 1). In general, MWCNTs are more widely used than SWCNTs because they are cheaper to manufacture and offer better reinforcement in cement composites. They are getting increasing scientific and industrial interest due to their exceptional chemical and physical properties that render them suitable for numerous applications such as electronic materials, medicine, energy, chemistry, and high-functional composites on the basis of advantages such as outstanding mechanical properties, thermal conductivity, electrical conductivity, low specific weight, and high resistance to corrosion. [6-8].

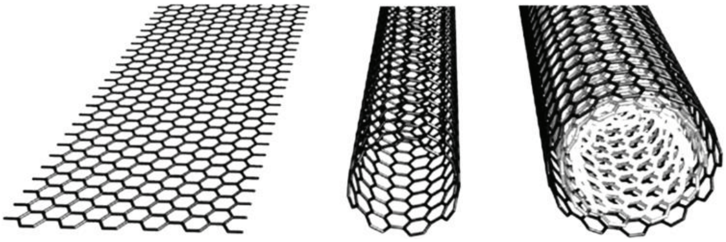

Figure 1: From left - graphene, SWCNT, MWCNT [9].

The average diameter of an individual SWCNT is in the order of nanometers and the average diameter of an individual MWCNT is in tens of nanometers. Theoretical and experimental investigations have demonstrated Young´s modulus as high as 1 TPa and tensile strength of approximately 100 GPa and an ultimate strain of 12%. Common characteristics of fiber (e.g. glass fibers or carbon fibers) introduced to enhance mechanical properties of cement composites include high tensile strength, large aspect ratio (length-to-diameter ratio), and adhesion. Considering these points, carbon nanotubes are outstanding candidates for filler and are expected to greatly enhance mechanical properties. Due to their size and aspect ratios (ranging from 30 to more than many thousands), CNTs can be distributed in much finer scale than common fibers. This results in more efficient crack bridging at very preliminary stage of crack propagation within composites. [10, 11]

In recent years, the influence of CNTs in cement based composites has been investigated. The research shows that the use of MWCNTs as filler improves both compressive and tensile strengths from 10 to 25% [6]. Al-Rub et al. showed that low concentration (0.04 wt.%) of long MWCNTs give comparable mechanical performance to the nanocomposites with higher concentration of short MWCNTs. The short MWCNT at 0.2 wt.% concentration had better results than other specimens at age of 28 days [12]. However, the reinforcement effect is not as prominent when we consider the great mechanical properties and geometrical shape of CNTs. Also disadvantages of using CNTs as reinforcement for cementitious composites have been widely reported. Firstly, the strong van der Waals force between CNTs makes it difficult to disperse them homogenously. This force is strong due to large surface-area-to-volume (SA/V) ratio. CNTs tend to attract agglomerate and sediment. Secondly, the hydrophobicity of CNTs leads to weak bonding of CNTs to the cement matrix [6].

There are two major problems need to be solved to create successful CNTs/cement nanocomposite:

- Homogenous dispersion of the CNTs within the cement paste matrix
- Bonding and cohesive properties between the cement paste and surface of CNTs

Following methods are suitable to improve dispersion:

- Ultrasonication of solution to facilitate dispersion
- Using a surfactant to improve affinity between carbon nanotubes and matrix
- Chemical modification of CNTs

Good dispersion can be achieved by using of ultrasonic mixer with surfactants in aqueous solution, with specific time and amount of energy. Zou et al. obtained the best mechanical performance of CNTs/cement pastes with ultrasonication energy of 20 J/mL per unit CNTs to cement (C/c) with 84% of maximum dispersion [13]. However, CNTs might dissolve into solution or tear into small pieces if excessive force is used. Compatibility of surfactant with cement is also very important. The hydration, chemical reactions and hardening process of cement paste could be delayed or even stopped [14].

Chemical activation places functional groups on the surfaces of CNTs and facilitating dispersion as well as improving the bonding between CNTs and the matrix. Methods include surface modification with exposure to ozone gas at high temperatures and the formation of carboxyl groups through acid treatment. The formation of carboxyl groups on the surface improves the bonding by inducing chemical reactions with hydraulic cementitious materials. Kang et al. used acid treatment to improve tensile and compressive strength by more than 30% without any surfactant [6].

There are still a lot of open questions:

- How to test compatibility of surfactants with CNTs or particular nanoparticles?
- How intense, long sonication use and how does it affect dispersion of CNTs?
- How to avoid tearing of CNTs during ultrasonication?
- Does strength and stiffness of CNTs directly improve the mechanical properties of hardened cement paste?
- What are other effects of CNTs on e.g. formation of high density C-S-H phases?

There is lack of systematic investigations of these issues yet. There is only little of the knowledge about shape and length of CNTs in hardened cement composite. What are their positions to voids and hydration products?

In this paper, experiments oriented at the study of dispersion of CNTs in water with respect to their use in cement compositions are described and a novel method of CNTs dispersion in water using pulsating water jets is proposed.

2. Testing of standard methods of dispersing CNTs

Three basic ways of dispersing carbon nanotubes are commonly used: (1) mechanical mixing (high speed mixing in water environment, hydro-cavitation, mixing by means of ball mill), (2) ultrasonic method and (3) use of surface active substances, or alternatively suitable combination of these methods [15, 16]. Based on the result of experiments oriented at the verification of the above mentioned methods, the method combining ultrasonic cavitation and suitable surface active substance was selected. Energy supplied from outside was determined with respect to the amount of dispersed suspension, i.e. ultrasonic energy was expressed in $J \cdot ml^{-1}$. Energies used were from 200 to 2000 $J \cdot ml^{-1}$. Influence of so-called intermittent dispersing was also examined using various setting of pulses (30 seconds standstill, 30 seconds dispersing). However, this cycling had no observable influence on the quality of dispersing.

Another crucial step for dispersing CNTs in water environment is represented by selection of suitable surface active substances (surfactants). Collins et al. stated that suitable surface active substances for dispersing and also partly for limiting re-agglomeration of nanoparticles are polycarboxylates and lignosulphates; to the contrary, naphthalene-sulphates and styrene-butadiene rubber are not suitable [15].

Based on results of previous tests of number of various surfactants to improve dispersing CNTs in water, superplasticizer Ethacryl HF made by Coatex Arkema group was used as surfactant. The mixture of MWCNTs with Ethacryl HF in the water solution exhibited long term stability of the suspension, proven by both long term observation and UV-Vis spectroscopy measurement.

Quality of dispersing of CNTs was studied using optical microscopy and UV-Vis spectroscopy. Combination of the two optical methods helped to determine optimal dose of ultrasonic energy to obtain the best possible quality of the CNTs dispersion (see Figure).

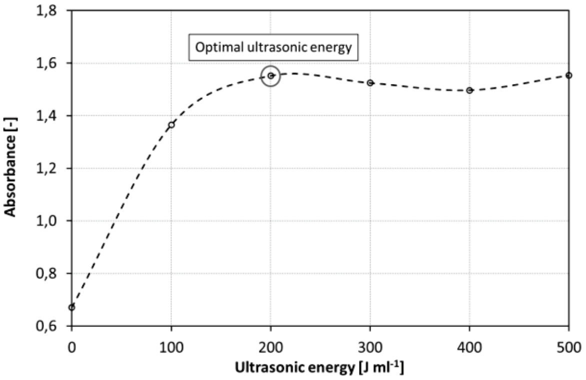

Figure 2. Influence of delivered ultrasonic energy on the absorbance of the CNTs suspension determined by UV-Vis spectroscopy.

Extent of possible damage of individual graphene leafs of nanotubes was checked as a part of monitoring quality of dispersing. Observation of possible damage of nanoparticles is very important for optimization of ultrasonic energy necessary for defibering of pellets of CNTs. Changes of the structure of individual carbon nanotubes at various doses of ultrasonic energies were studied by means of transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) analyses – see Figures 3-5. The analyses show obvious influence of the amount of sonication energy on the structure of the CNTs. Sonication by ultrasonic energies 5 and 20 kJ caused recasting of carbon bonds in a way that bending and twisting can be observed in surface layers. Newly created structures resembles onion-like particles. At the same time, bending of whole parts of CNTs can be observed. On the contrary, sonication at ultrasonic energy of 40 kJ led to the breakage of MWCNTs walls and creation of multilayer graphene. The results proved the assumption that ultrasonic energy is capable of damaging or even breaking the structure of CNTs if certain level of ultrasonic energy is exceeded and as a consequence the behaviour of CNTs changes (ζ - potential, surface tension and other parameters with influence on aggregation of nanotubes) [17].

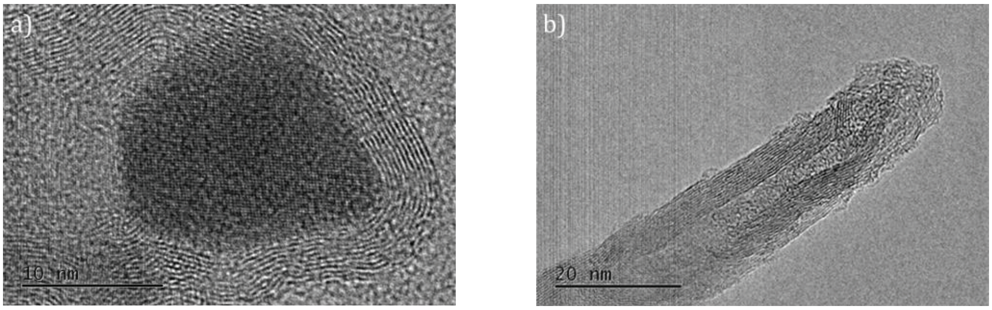

Figure 3. Sonication of MWCNTs at 5 kJ/ml. a) Image of catalytic particle with created carbon envelope, b) end of the nanotube damaged due to sonication.

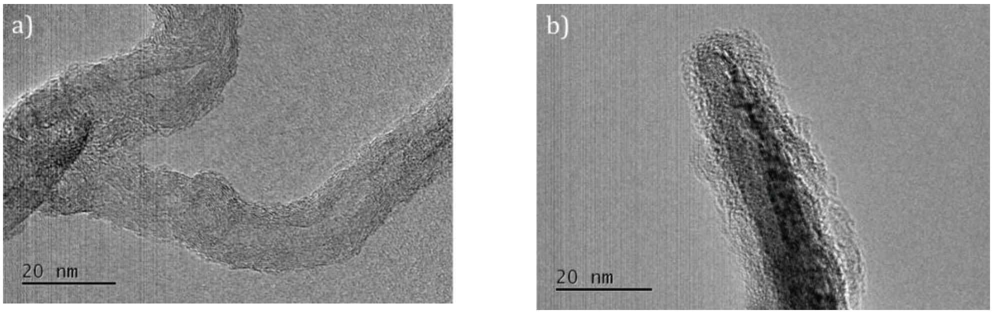

Figure 4. Sonication of MWCNTs at 20 kJ/ml. a) Image of damaged and twisted nanotubes, b) nanotube with damaged surface layers.

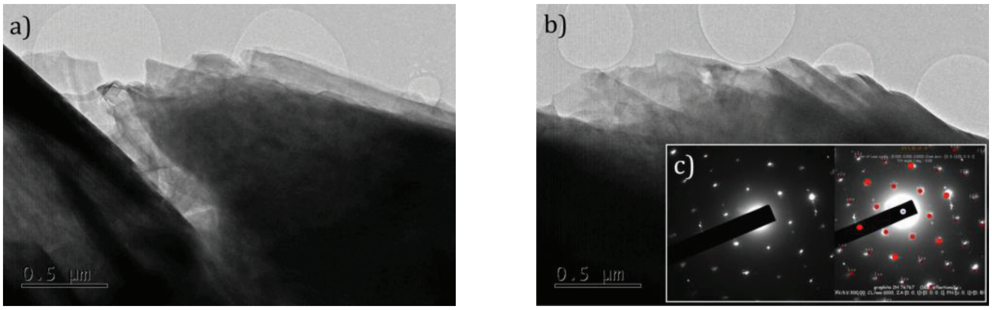

Figure 5. Sonication of MWCNTs at 40 kJ/ml. a, b) Images show unfolded graphene layers, possible remains of original nanotubes are surrounded by unfolded graphene layers which created graphene structure, c) SAED of unfolded layers.

3. Proposal of novel technique of dispersing CNTs

The novel technique of dispersing of CNTs in aqueous environment is based on the proprietary method of generation of pressure pulsation in high-pressure system [18]. The method is based on generation of acoustic waves by the action of acoustic actuator on pressure liquid and their transmission via high-pressure system to the nozzle (see Fig. 6 for schematic drawing). The use of acoustic generator of pulsating jet to disperse CNTs in aqueous environment can provide some additional effects to the standard method of sonication that can be beneficial for the CNTs dispersion without their undesirable destruction.

If CNTs (or CNTs with suitable surfactant) are added into the water which is pressurized and supplied to the acoustic generator of pulsating jet, then CNTs can be exposed to high-frequency pressure pulsations, cavitation and impact pressure. High-frequency pressure pulsations are generated by the action of the acoustic actuator on the pressure liquid in the acoustic chamber of the acoustic generator of pulsating jet. The pulsations are amplified by properly designed liquid waveguide and their level can be adjusted by the amplitude of vibrations of the acoustic actuator, tuning of the generator and by liquid pressure. This allow to adjust the pressure pulsations quite precisely to disperse CNTs without damaging them.

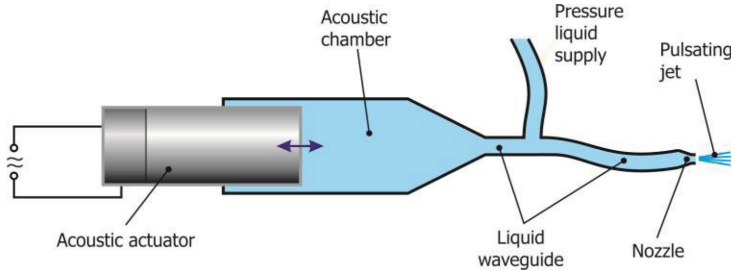

Figure 6. Schematic drawing of the acoustic generator of pulsating jet.

The proposed technique will also allow to study the influence of cavitation on the process of CNTs dispersion because the acoustic generator of pulsating jet can be operated with or without cavitation inside the liquid waveguide. The mode of operation is controlled by the level of operating pressure – the cavitation disappears at pressures higher than about 8 MPa.

Impact pressure generated at the point of impact of water slug on solid surface can be also used to enhance the dispersion of CNTs in water. It is well known that the collision of a high-velocity liquid mass with a solid generates short high-pressure transients at the very beginning of the impact. The liquid behaves in a compressible manner generating the so-called ‘‘water-hammer’’ pressures. The situation shortly after the initial impact of the liquid on the solid surface is illustrated in Fig. 7. The level of these high pressures corresponds to the velocity of impacting liquid and its proper adjusting can enhance dispersion of CNTs contained in the pulsating water jet without their undesirable destruction.

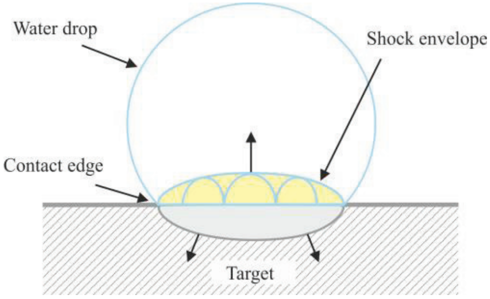

Figure 7. Initial stage of impact between a water drop and a solid target with the contact edge moving faster than the shock velocity in the liquid. The liquid behind the shock envelope is compressed and the target beneath this area subjected to high pressure [19].

4. Conclusion

The paper presents introduction to the problem of addition of carbon nanotubes to enhance properties of cement composite. One of the crucial aspects of successful use of CNTs in preparation cement composites is proper dispersion of CNTs in water and subsequently in cement paste. The tests performed so far show that standard methods commonly used for CNTs dispersion (such as sonication) can cause destruction of CNTs and, as a result, the addition of CNTs to concrete composites can have adverse influence on their properties.

Therefore, a novel technique of CNTs dispersing using acoustic generator of pulsating jets was proposed. The technique should allow controllable action of high-frequency pressure pulsations, cavitation and impact pressure on CNTs dispersion without CNTs damage or disintegration.

The next research will be oriented at the determination of optimum parameters of amplitude and frequency of vibrations of the acoustic actuator and operating pressure to obtain required dispersion of CNTs without their damage.

5. Acknowledgement

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