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ScienceDirect

Procedia Engineering 149 (2016) 94 – 99

Procedia Engineering

www.elsevier.com/locate/procedia

International Conference on Manufacturing Engineering and Materials, ICMEM 2016,
6-10 June 2016, Nový Smokovec, Slovakia

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

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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doi:10.1016/j.proeng.2016.06.643

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].

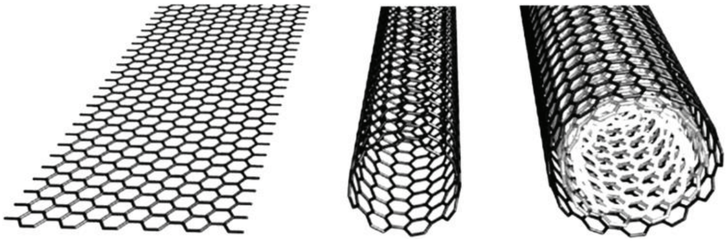

Figure 1: From left - graphene, SWCNT, MWCNT [9].

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