Powder Technology 307 (2017) 1–9

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Characterizing dispersion and long term stability of concentrated carbon nanotube aqueous suspensions for fabricating ductile cementitious composites

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ARTICLE INFO

Article history:
Received 5 July 2016
Received in revised form 31 October 2016
Accepted 9 November 2016
Available online 14 November 2016

Keywords:
Carbon nanotube
Pluronic F-127
Extractability
Zeta potential
Long-term stability

ABSTRACT

This paper reports a systematic attempt of preparing concentrated aqueous suspensions (up to 0.3 wt.%) of different types of carbon nanotubes (CNTs) using Pluronic F-127 for developing ductile cementitious composites. Single-walled and multi-walled nanotubes, both pristine and functionalized, were dispersed in water using a short (1 h) and medium energy (80 W) ultrasonication process using pluronic at high concentrations (above critical micelle concentration, 1–5 wt.%) and also using sodium dodecylbenzene sulphonate (SDBS) for comparison purpose. The CNT suspensions were characterized for agglomerate area, particle size, zeta potential, extractability and long-term storage stability for a period over 4 years. The optimum suspensions were used to fabricate cementitious composites and their fracture behavior was characterized. Experimental results suggested that the optimum pluronic concentrations (1% for 0.1% CNT, 5% for 0.2% and 0.3% CNT, all in weight percent) provided highly homogeneous CNT dispersion with very low area of agglomerates. The best dispersion quality was obtained with f-SWCNT/pluronic system, which provided very low agglomerate area (<0.5%), lower CNT bundle size, good quantity of well dispersed nanotubes (up to 50%) and excellent long term storage stability. Cementitious composites fabricated using SWCNT and f-SWCNT suspensions showed ductile fracture behavior and improvement in fracture energy up to 164%.

1. Introduction

Carbon nanotubes (CNTs) are finding widespread applications in various fields including catalyst supports, optical devices, quantum computers, biomedical sensors and composite reinforcement due to their unique electronic, thermal, optical, and mechanical properties [1–4]. Most of these applications require stable suspensions of high concentration of CNTs. De-agglomeration and homogeneous dispersion of CNTs in different media is one of the key challenges for successful utilization of their properties and therefore, various physical, chemical and biological techniques such as ultrasonication, high shear mixing, ball milling, calendering, plasma and irradiation techniques, covalent and non-covalent functionalization, etc. have been extensively studied to improve CNT dispersion in different matrices [5–24]. The non-covalent functionalization technique of producing CNT suspensions does not alter the inherent electrical, optical or mechanical properties of CNT. In this route, CNTs are commonly dispersed using various aromatic small molecules, surfactants, polymers, biomacromolecules and through endohedral method [5–24]. Currently, among various surfactants, Pluronic F-127 is finding a special attention due to its biocompatibility and lower toxicity as compared to other surfactants [25–29]. Pluronic F-127 is a non-ionic triblock copolymer composed of a central hydrophobic chain of polyoxypropylene (PPO) flanked by two hydrophilic chains of polyoxyethylene (PEO). As Pluronic F-127 possesses an amphiphilic structure, it has been proved to be an effective surfactant for CNT dispersion [26]. It has high solubility in water at room temperature (up to 10 wt.% at 20 °C), allowing to prepare CNT suspensions at high surfactant concentration. The dispersion of CNT in Pluronic solution is attributed to the steric stabilization induced by the PEO chains which extend in to the water. Recently, MWCNTs suspensions with up to 0.016 wt.% were obtained in water using 0.1% Pluronic F-127 and 8 h magnetic stirring at 70 °C followed by 16 h of ultrasonication [25]. Good dispersion of 0.1 wt.% SWCNT in water using Pluronic was also achieved applying ultrasonication for 1 h, followed by ultracentrifugation for another 1 h [26]. The prepared SWCNT suspensions exhibited stability up to 3 months. Pluronic surfactants were also found to disperse MWCNTs better in highly acidic or basic aqueous media, as compared to ionic surfactants [14]. MWCNTs were also effectively dispersed in the mixture of ethoxy-modified trisiloxane (a silicone surfactant) and Pluronic F-127 [28].

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http://dx.doi.org/10.1016/j.powtec.2016.11.010
0032-5910/

In general, reports on the preparation of concentrated CNT aqueous suspensions are very few. The process requires either intensive ultrasonication (longer time/higher energy), which is detrimental for CNT's inherent properties, or needs high surfactant concentrations (above the critical micelle concentration or CMC), which may result in CNT flocculation due to micelle formation. Therefore, extensive research studies have been reported on the study of water dispersions of CNT mainly at low concentration using different surfactants [9–12,30,31]. Recently, good dispersion of high concentration of SWCNTs up to 2 wt.% has been achieved using ionic surfactants such as SDBS at long ultrasonication treatment (24 h) and high surfactant concentrations [17]. However, studies of CNT/pluronic aqueous suspensions at high CNT concentrations are rarely reported and the influence of different factors such as CNT type and functionalization, as well as CNT and surfactant concentrations in such systems has not, to our knowledge, been reported in the literature. To bridge the knowledge gap of existing literature, the present research investigates systematically the various factors influencing CNT dispersion in pluronic solution and characterizes, for the first time, the long term stability of prepared suspensions for several years. The influence of different factors on the dispersion quality has been discussed and the suspensions prepared using pluronic were compared to that obtained with sodium dodecylbenzene sulphonate (SDBS).

Reinforcement of concrete to improve its mechanical performance is one of the emerging applications of CNT in civil engineering sector. Cementitious materials are characterized by high strength and modulus, however they present brittle fracture. In the past, it was observed that the addition of flexible fibers to cement mortar increased its strain capacity significantly [3]. Recently, the authors reported the beneficial effect of the addition of concentrated CNT suspensions prepared using pluronic to cement, to improve the composite micro-structure and mechanical performance [32]. In order to further address this application, in the present research, optimum CNT/pluronic suspensions were added to cement and the fracture energy of resulting cementitious composites was characterized.

2. Materials and methods

2.1. Raw materials and characterization

Four different types of nanotubes have been used in the present study, namely SWCNT, MWCNT, f-SWCNT and f-MWCNT (the morphology is provided in Fig. 1S of Supplementary information). Nanotubes were purchased from Nanostructured & Amorphous Materials, Inc. (Houston, USA). Length, diameter and the amount of metal catalyst in these CNTs are listed in Table 1. For EDX analysis, thin films of nanotube powder were prepared on conductive carbon tape and analysis was performed using Si(Li) detector (SEM ultra-thin window type) and an acceleration voltage of 5 kV. f-SWCNTs and f-MWCNTs were functionalized with carboxyl groups. Two types of surfactants were used in this study: Pluronic F-127, which was the primary surfactant and sodium dodecylbenzene sulfonate (SDBS), which was used only for the comparison purpose at CNT: surfactant ratio of 1:4 (according to Ref [3].).

Table 1
Properties of different types of CNT.

Type of CNT	Diameter (nm)[a]		Length (μm)[a]	Elements (wt.%)[b]		Impurity (%)[b]
				C	O	
SWCNT	1–2		5–30	91.1	5.0	3.9
f-SWCNT	1–2		5–30	88.4	11.6	0
MWCNT	2–5 nm (inner)	<8 nm (outer)	10–30	92.1	7.9	0
f-MWCNT	2–5 (inner)	<8 nm (outer)	10–30	88.2	11.8	0

[a] Source: Manufacturer's data.
[b] Elements and metal impurities estimated by EDX.

The surfactants were purchased from Sigma Aldrich (Portugal). Their properties and concentrations are listed in Table 2. Fig. 1 shows the chemical structure of the surfactants. Pluronic F-127 is a non-ionic surfactant containing hydrophobic PPO and hydrophilic PPO segments. The PPO segments interact with the hydrophobic surface of CNTs, while PEO groups extend into the water. The separation of individual CNTs (or small bundles) and the stabilization of separated CNTs occur due to the steric hindrance induced by the long chain of PEO groups. Therefore, CNT dispersion is highly dependent on PEO molecular weight [27]. According to recently performed molecular dynamics (MD) simulation, once adsorbed on to CNT surface, Pluronic F-127 molecules could only stay on the CNT surface without wrapping [29]. On the other hand, SDBS is an anionic surfactant with strong hydrophobic/hydrophilic interaction, and its hydrophobic tails and benzene rings interact with CNT surface, whereas the hydrophilic sulphonate head groups go to the aqueous phase and stabilize the dispersion due to long range Coulombic repulsion between the anionic groups. According to the MD simulation, SDBS molecules form disordered self-assembled aggregates on nanotube surface and tend to orient parallel to the nanotube's axis [33]. Moreover, Pluronic F-127 contains PEO side chains similar to polycarboxylate superplasticizers commonly used in cementitious composites. Due to the presence of PEO chains, Pluronic F-127 was found compatible with the cement mortar and could improve its dry bulk density and mechanical performance probably because of improved cement particle dispersion and mortar's fluidity [32].

For each type of nanotube, 0.1% CNT was dispersed using 1% and 3% pluronic, 0.2% CNT was dispersed using 3% and 5% pluronic and 0.3% CNT was dispersed using 5% pluronic. On the other hand, 0.1%, 0.2% and 0.3% nanotubes were dispersed using 0.4, 0.8 and 1.2% SDBS, respectively. For fabricating cementitious composites, Ordinary Portland Cement (OPC) and standardized sand were used along with a defoaming agent (tributyl phosphate) to reduce foam formation during mixing.

2.2. Carbon nanotube dispersion

A fast and medium energy ultrasonication process was used to disperse the nanotubes. The CNT powder was mixed in water along with the required amount of surfactant and subjected to magnetic stirring for 5–10 min. Then ultrasonication was carried out at room temperature using a bath sonicator (CREST Ultrasonicator, CP 230T) for 1 h at 45 kHz frequency and 80 W power. Under these mild mixing conditions negligible structural damage is expected for the CNT. The concentrations of CNT and surfactants tested are listed in Table 2.

2.3. Characterization of carbon nanotube dispersion

Different techniques were used for characterizing various parameters of prepared CNT suspensions. The main characteristics of the suspensions which have been studied are: (a) total area of agglomerates, (b) CNT bundle size, (c) zeta potential, (d) extractability or concentration of well dispersed CNTs, and (e) long term storage stability over a period of 4 years.

2.3.1. Optical microscopy and image analysis

Optical microscopy was used to monitor the presence of CNT agglomerates in suspension, and to quantify the agglomerated area. For this purpose, a small drop of suspension was deposited on a glass slide and covered with a cover slip and analyzed. Pictures were obtained at different locations of each suspension prepared repeated times and at different magnifications for a broad quantification of the agglomerates. The optical micrographs of the samples prepared from the CNT suspensions were analyzed by image processing, using ImageJ software, and the total area of agglomerates observed within the analyzed sample area was determined.