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Microstructure and mechanical properties of carbon nanotube reinforced cementitious composites developed using a novel dispersion technique

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ABSTRACT

The present paper reports the first attempt of developing carbon nanotube (CNT) reinforced cement composites through a short dispersion route using Pluronic F-127 as a novel dispersing agent. Optimum concentrations of Pluronic for various types of CNT were determined, and the influences of Pluronic and CNT on the microstructure and mechanical properties of cementitious composites were thoroughly investigated. Pluronic with optimized defoamer concentration significantly improved the bulk density and mechanical properties of cement mortar. Further, dispersion of 0.1% single walled nanotube (SWNT) improved flexural modulus of mortar by 72% and flexural and compressive strengths by 7% and 19%, respectively after 28 days of hydration. Flexural and compressive strengths with functionalized SWNT increased with the hydration period up to 17% and 23% after 56 days, respectively. All CNT reinforced samples exhibited significantly higher stiffness, fracture energy and ductility as compared to plain mortar and composite samples prepared using a common surfactant.

1. Introduction

Concrete is the most frequently used construction material all over the world. However, its major drawback is the brittleness and susceptibility to crack formation and growth that reduces its performance and durability. The concept of dispersing nanomaterials within concrete in order to develop crack free and durable construction materials has been realized in recent times [1–4]. Carbon nanotubes (CNTs) are getting tremendous attention for this purpose in order to develop high performance and piezoresistive cementitious composites [5–10]. Although CNTs possess exceptional physical and chemical properties, the successful transfer of these properties into composite materials is strongly dependant on the state of CNT dispersion within the matrix. Due to their strong agglomeration tendency, it is extremely challenging to obtain a homogeneous CNT dispersion, which is, however, a prerequisite for successful utilization of CNT in most of the applications including composite materials. The approach of dispersing CNTs directly within cement paste during mixing is not feasible, as the thickening of cement paste begins within a short period after addition of water. The mixing process using a Hobart mixer, commonly used to prepare mortar paste cannot ensure proper dispersion of CNT within cementitious matrix [11]. To overcome this problem, the strategy commonly employed for mixing CNTs with cementitious matrices is to disperse these nanomaterials first in water, followed by mixing of nanomaterial/water suspensions with cement using a conventional mixer. Various physical and chemical techniques have been tried to prepare homogeneous aqueous dispersion of CNT such as ultrasonication, mechanical stirring, using surfactants, polymers, CNT functionalization, etc. [12–22]. CNT suspensions prepared using these various techniques can be subsequently mixed with the cement mixtures to prepare cementitious composites [23–29]. However, these dispersion routes should be carefully selected so that they do not interfere with the processing of cementitious composites. Many surfactants that are successfully used to disperse carbon nanomaterials in polymeric matrices have been reported to create problems in cement hydration, entrap air in the cement paste or react with the water reducing admixtures [5]. Alternative ways to improve dispersion of CNT within cementitious matrices are to use of chemical admixtures during mixing process [30,31] or through fabricating cementitious composites by directly growing CNTs on the cement particles [32].

Among the various carbon nanotubes, single walled nanotubes (SWNTs) are considered as the best reinforcement for different matrices due to their huge surface area and exceptional mechanical properties [5]. However, these nanotubes are expensive and obtaining homogeneous dispersion is a highly challenging task due to their strong agglomeration tendency. More often, they are dispersed using a very long dispersion route involving physical and chemical treatments, which either leads to nanotube's damage or make the process unsuitable for industrial application. Due to these reasons, only a few research studies have been conducted till date on utilizing SWNTs within cementitious matrices, most of which are for developing piezoresistive composites [33]. However, research studies by Makar et al. demonstrated that SWNTs can accelerate the hydration reaction

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of tricalcium silicate (C_3S) in the OPC and show strong effect on the morphology of the hydration products [34,35]. Evidence of classical reinforcing behaviour such as crack bridging and fibre pullouts as well as strong adherence between C–S-H and SWNTs, as observed in their study, indicated high potential of SWNT for developing high strength cementitious composites. Nevertheless, development of a short and efficient route for SWNT dispersion is highly essential for developing such composites.

As compared to other routes for preparing aqueous CNT suspensions, the non-covalent functionalization technique is better in the sense that it does not alter the inherent electrical, optical or mechanical properties of CNT. In this route, CNTs are commonly dispersed using various surfactants, such as ethyltrimethylammonium bromide, Triton X-100, sodium dodecylbenzene sulfonate (SDBS), Pluronic F127, etc. [12–22], with the help of ultrasonication process, which breaks down or de-bundles the CNT aggregates. The treatment time or energy of the ultrasonication process has strong influence on CNT dispersion and within limits, the longer is the treatment time (and higher is the ultrasonication energy), the better is the CNT dispersion [15]. However, a longer ultrasonication treatment or higher ultrasonication energy may also reduce the aspect ratio and lead to CNT damage. From this point of view, a short and mild dispersion process is always favourable. On the other hand, among the various surfactants, currently Pluronic block copolymers are finding a special attention due to its biocompatibility and lower toxicity as compared to other surfactants [13–15]. A few research studies have been carried out on the aqueous dispersion of CNT at very low concentrations using Pluronic for biomedical applications [13–15]. However, according to author's knowledge, no attempt has been made to use Pluronic F-127 to disperse CNT for cementitious matrices. The chemical structure of Pluronic F-127 contains polyethylene oxide side (PEO) chains, similar to the polycarboxylates used as superplasticizer in cementitious composites [36]. Although the use of polycarboxylates was not much effective for SWNTs [36], MWNTs were successfully dispersed using this surfactant for developing cementitious composites and the main factors contributing towards good CNT dispersion were the electrostatic (due to carboxylate groups) and steric repulsions (due to long lateral ether chains) [30]. However, in case of Pluronic F-127, only steric stabilization is possible due to the absence of ionic groups and the dispersion behaviour of CNT (any type) and cement particles in such system is completely unknown. Therefore, an in-depth investigation is necessary to apply this new dispersant for cementitious composites, in which the challenge is to disperse relatively higher CNT concentrations without affecting the hydration behaviour of cement. So, in the present study, CNT reinforced cementitious composites were developed using Pluronic F-127 as the dispersing agent. Optimum concentrations of Pluronic to achieve homogeneous and stable dispersions of various types of CNT (SWNT and MWNT, both pristine and carboxyl functionalized) at high concentrations were determined, and the influence of Pluronic and CNT on the microstructure and mechanical properties of cementitious composites were thoroughly investigated. In addition, the results obtained in case of optimum samples have been compared with those obtained using a common surfactant (sodium dodecylbenzene sulfonate or SDBS).

2. Materials and methods

2.1. Raw materials

Different types of CNTs (SWNT, MWNT, functionalized SWNT or f-SWNT and functionalized MWCNT or f-MWNT) were purchased from Nanostructured & Amorphous Materials, Inc. (Houston, USA). The morphology of these CNTs, as characterized by Scanning Electron Microscope (SEM) is shown in Fig. 1 and their properties are listed in Table 1. Impurity (wt.%) was determined using Energy Dispersive X-ray (EDX) analysis (using Si(Li) detector and an acceleration voltage of 5 kV). Except pristine SWNTs, other CNTs contained negligible quantity of impurities and the impurities present in the pristine SWNTs were mainly metal catalyst particles (Ni, Fe, etc.) and a small amount of other types of CNT. The metal particles were embedded within the structure of SWNTs. Aqueous suspension of these CNTs was prepared using two different types of surfactant, namely Pluronic F-127 and SDBS, both purchased from Sigma Aldrich. Chemical structure of these surfactants is shown in Fig. 2. To reduce the generation of foam during dispersion process, tributyl phosphate (mol. wt. 266.31), purchased from Sigma Aldrich, was used as the defoaming agent.

2.2. Preparation of CNT aqueous suspensions

To prepare CNT suspensions, defoaming agent (1/3 or 1/2 of the surfactant weight) was first added to water, followed by addition of surfactant and magnetic stirring for 10 min for proper mixing. To disperse both 0.1% and 0.2 wt.% of CNT in water, 3% and 5% of Pluronic F-127 was used, in order to study the influence of surfactant concentration. On the other hand, a fixed surfactant to CNT weight ratio of 4:1 was used in case of SDBS, based on previous literature [23]. The CNT suspensions were then subjected to ultrasonication for 1 h in a bath sonicator (CREST Ultrasonicator, CP 230T) operated at 45 kHz frequency and 80 W power.

2.3. Characterization of CNT suspensions

2.3.1. Microscopic and visual observation

The freshly prepared CNT suspensions were observed visually for any noticeable sedimentation. Further, CNT suspensions were subjected to ultracentrifugation at 3000 rpm for 20 min and noticed for any settling down of CNT at the bottom of centrifuge tubes. Also, freshly prepared CNT suspensions were characterized by optical microscopy to investigate the dispersion homogeneity and the presence of CNT clusters or agglomerates. Further, area % of CNT agglomerates (the ratio of CNT cluster's area to the total area scanned, expressed in %) was calculated from the microscopy pictures using an image analysis software (Image J). Long term stability of CNT suspensions was also studied through visual observation of sedimentation after standing for more than 2 years.

2.3.2. Measurement of extractability

The extractability% of prepared CNT suspensions indicates the concentration of individually dispersed nanotubes expressed in percentage with respect to total CNT concentration (Eq. (1)) Concentration of individually dispersed CNTs was calculated using UV–Vis spectroscopy (UV 2401 PC, Shimadzu) from their characteristic absorption peak near 253 nm [37]. For this purpose, calibration curves between absorption and concentration for both SWNT and MWNT were determined and concentrations were calculated using these calibration curves.

$$\text{Extractability} = 100 * \left(\frac{\text{Conc. of individully dispersed CNT}}{\text{Original conc. of CNT}}\right). \quad (1)$$

2.4. Preparation of plain mortar and CNT/mortar composites

Plain mortar and CNT/mortar samples were prepared through mixing of prepared CNT suspensions with Ordinary Portland Cement (OPC) and standardized sand in a Hobart mixer. A cement to water ratio of 0.5 was used in all samples. Samples were prepared in rectangular moulds with dimensions of 160 mm × 40 mm × 40 mm. The moulds were kept in a moist atmosphere for 24 h and then the samples were de-moulded and kept under water for 28 days to carry out hydration or setting. The samples containing SDBS were kept in the moulds for 48 h, since it was not possible to de-mould them without breakage after 24 h. This was probably attributed to the delayed hydration in the presence of SDBS and the resulting specimens were not strong