Evaluation of the Potential of Single-Wall Carbon Nanotubes in Improving the Properties of Cement-Composites

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Abstract. The experimental investigation described in this paper deals with the characterization, functionalization, dispersion and use of single-wall carbon nanotubes (SWCNT) in cement-composites. The dispersion of SWCNT was achieved using sonication and modification with a surfactant. The rheological modelling of the SWCNT-surfactant system was carried out, which is shown to reduce the viscosity of the system. In order to better understand the effect of SWCNT in cementitious systems, detailed characterization of the SWCNT and sedimentation tests in water were carried out. To assess the effect on mechanical properties, different loading percentages of the SWCNT were added to the cement mortar, which lead to significant improvement in compressive strength compared to the reference mortar. A threshold dosage range of SWCNT was identified for the optimum mechanical performance of the cement mortar. These results demonstrate the potential of using SWCNT to produce better performing cement-composites.

Keywords: Low clinker cement concrete · Single-wall carbon nanotubes · Nano-modification

1 Introduction

The cement industry is responsible for a significant part of the atmospheric carbon dioxide (CO_2) emission. To reduce this carbon footprint, reduction of clinker content from the cement-concrete mixtures and carbon capture, utilization and storage (CCUS) are two main strategies adopted by the cement-concrete industry [1]. The CCUS is still largely under research and needs to solve several other technical challenges before its large-scale implementation. Other measures like improving the energy efficiency of cement plants, reducing the clinker content from cement and reducing cement content from the concrete mix designs are currently being adopted [2]. Use of alternate binders like geopolymer concrete and use of supplementary cementitious materials (SCM) like silica fume, fly ash and slags in the concrete mixes, as a partial replacement to cement are also being practiced [3, 4]. However, these SCM and alternate binders alone cannot

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achieve the clinker reduction goals. Moreover, achieving sufficient early-age strength for the low-clinker concrete products and identification of suitable alternative binders instead of clinker are remaining as a challenge for the concrete industry. The application of nano materials in cement-concrete is hence interesting for the researchers, as there is a growing need of identifying materials that can contribute to the clinker reduction objective.

Materials in nano metric size were of interest because their material properties differ from the same bulk material. Higher surface area and small particle size of nano materials are the main reasons for this peculiar behavior. Different nano materials exhibit different properties depending upon their morphological features and chemical composition. Selection of suitable nano material based on the target application and their uniform dispersion are the two key factors that govern the success in nano modification of materials.

1.1 Nanomaterials in Cement Concrete

The use of nano materials as an additive in the concrete mix designs modifies the properties of cement concrete in several ways. They increase the viscosity of the liquid phase and thereby improve segregation resistance and workability. They fill the voids between cement grains, act as centers of crystallization of the cement hydrates, which also accelerates the rate of hydration [5]. The interfacial transition zone between the aggregates and cement paste also gets improved in presence of nano materials.

The benefits of nano modification vary with the type and dosage of nanomaterial used. Nano SiO_2 participates in the pozzolanic reactions, resulting in the consumption of $Ca(OH)_2$ and the formation of an additional calcium silicate hydrate which would contribute to the strength development [6, 7]. Nano Al_2O_3 and nano TiO_2 improve the compressive strength, latter also enhances the Photocatalytic properties [8, 9]. Other materials like nano $CaCO_3$, nano Carbon black, and graphite nano particles are all found to be improving the hydration kinetics and compressive strength [10]. Other benefits like crack arrest, improvement in the toughness were also observed with nano modification. Thus, proper application of nano materials improves the fresh, hardened and durability properties of the cementitious materials.

CNTs are the type nano particles, which increase both compressive and tensile properties of the cement composites at their optimum dosage [11]. Due to the special morphology of the CNT, proper dosing and uniform mixing of them in cement concrete is important to observe the beneficial effects. Improper dosing and insufficient mixing could lead to adverse effects in the strength development of the composite. Extensive studies on the surface modification of SWCNT and their modeling were performed to identify the optimum usage of surfactants [12].

Challenges and Way forward. Despite all this laboratory-scale research, the transfer of technology from the laboratory to industrial-scale production was not smooth due to several reasons. Firstly, the uniform dispersion of nanomaterials in the cementitious matrix was difficult to achieve during the mass production of concrete. Secondly, the high cost and energy required for the production of nano-materials made this economically not viable for commercial cement concrete producers.

To address some of the challenges mentioned above, the following specific objectives were identified for the experimental investigation described in this paper.

- Development of a specific dispersion protocol for the SWCNT in the cementitious matrix, which can also be used in industrial-scale cement concrete production.
- Quantification of the effect of SWCNT modification in the mechanical properties of cementitious matrix.

2 Experimental Investigation

2.1 Materials and Methods

Characterization. The SWCNT used in all the tests were supplied by InnTeG and the surfactant Sodium dodecylsulfate (SDS) supplied by Sigma Aldrich. TEM analysis was performed to observe the morphology of the nanoparticles. The powder samples were dispersed in an aqueous medium, making serial dilutions until the optimum concentration of particles was achieved. A drop was placed on a copper grid and observed in a JEOL equipment (model JEM 1230 microscope), with a resolution of 0.4 nm and an acceleration voltage of 100 kV.

The Z potential measurements were performed using a Delsa Nano C Particle Analyzer (Beckman Coulter). In order to monitor the behavior of the different nanomaterials for Z potential tests, the pH was varied from 3 to 11. The carbon nanotubes were analyzed in a range of 800–4000 cm^{-1}, using a diamond ATR device for solid samples.

Dispersion of carbon nanotubes and sedimentation tests. First, tests were carried out to monitor the sedimentation of carbon nanotubes in an aqueous medium. This is to ensure that proper dispersion of SWCNT will be achieved when it is incorporated into the cementitious matrix. For the dispersion of the carbon nanotubes, SDS was used to improve the colloidal behavior. 30 g of deionized water was added to 0.6% by weight of SWCNT (0.18g) with two SWCNT: SDS ratios (1:0, 1:1) (labeled as T).

The carbon nanotube suspensions were subjected to sonication tests and subsequently accelerated sedimentation tests. The sonication process was carried out for 5 min and the behavior of the suspensions was visualized for 40 min. For the accelerated sedimentation process, special equipment manufactured in the laboratory was used, in which the suspensions were rotated at an angular velocity of $\omega = 10.68$ rad/s and lateral acceleration of $a = 29.66 m/s^2$. If it is considered that $1g = 9.81\ m/s^2$, the equipment causes an acceleration of approximately 3g. Each suspension was again subjected to ultrasonic vibration for 5 min before the accelerated sedimentation process.

Preparation of cementitious nanocomposites. The cement mortar was prepared using a water to cement ratio of 0.75 and a Cement to sand ratio of 1:3. A laboratory mortar mixer was used for the preparation of the mortar. The dosage of carbon nanotubes were varied in steps as 0.1, 0.05, 0.01 and 0.005% with respect to the weight of the cement. The mortar samples were tested at 2, 7 and 28 days of age for their compressive strength.

3 Results and Discussions

3.1 Characterization of the Nanoparticles

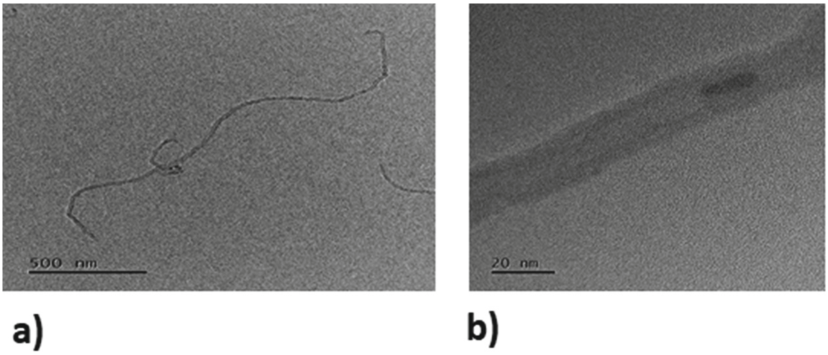

Fig. 1. TEM images of carbon nanotubes. (a) 500 nm and (b) 20 nm.

The transmission electron microscopy images are shown in Fig. 1. Carbon nanotubes of approximately 2 microns are visualized in Fig. 1a. While the diameter of the nanotubes reaches 20 nm (see Fig. 1b).

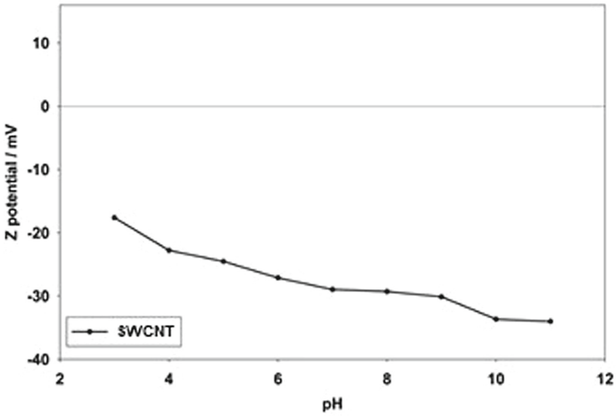

Fig. 2. Z potential of carbon nanotubes.

In Fig. 2, it was observed that the carbon nanotubes maintain a good dispersion in the pH range of 3–11. This indicates that the incorporation of carbon nanotubes will have a positive influence on the cementitious matrix, promoting an improvement in their mechanical properties.

The sample was analyzed in a range of 800–4000 cm^{-1} (see Fig. 3), using a diamond ATR device for solid samples. The FTIR pattern does not show signs of organic groups

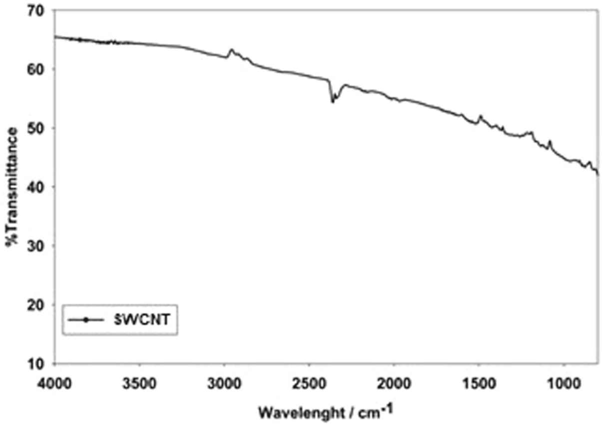

Fig. 3. FTIR of carbon nanotubes.

other than carbon, the signal obtained by the equipment is typical of non-oxidized carbon materials (Fig. 3).

3.2 Sonication of SWCNT/Surfactant Systems

The suspensions of SWCNT/surfactant systems were subjected to ultrasonic vibration for 5 min. In Figs. 4 and 5, the suspensions obtained, before and after sonication are shown. It is observed that there is no visually significant difference when a surfactant is used during sonication.

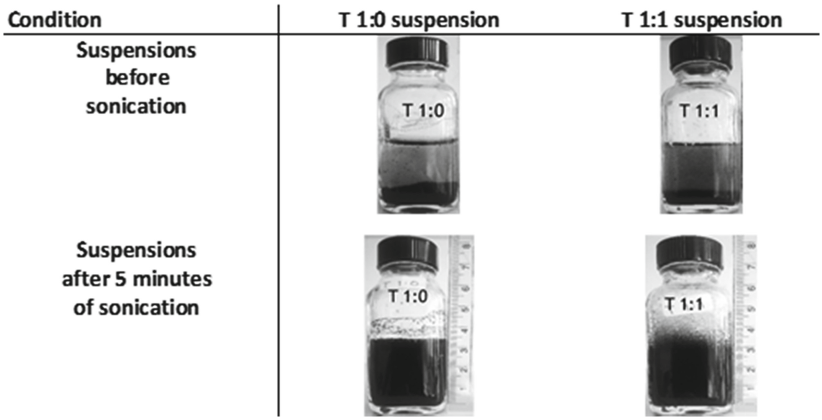

Fig. 4. Carbon nanotubes in suspension.

Sedimentation in suspensions after ultrasonic vibration. After sonication, the samples were visually monitored to observe the sedimentation of particles. There was no significant difference between the suspensions until 30 min from the end of the sonication in the sedimentation of particles. Unfortunately, the foam produced does not disappear in the suspension containing SDS. Therefore, the suspension without surfactant is emerging as a good candidate, if the time available for dosing SWCNT suspension into the cementitious mix is less than 30 min.

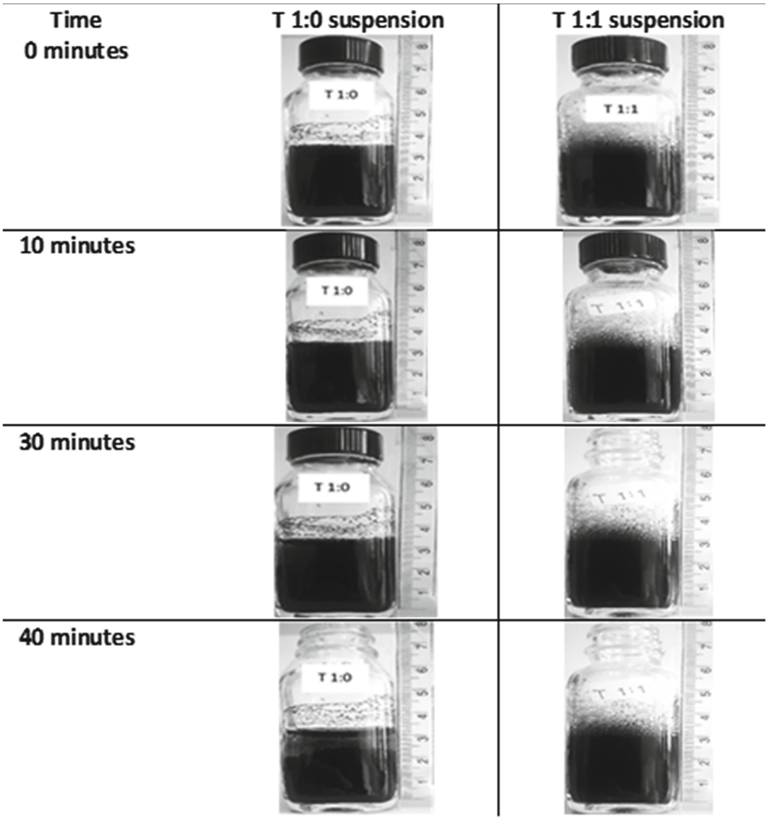

Fig. 5. Carbon nanotubes in suspension under sonication conditions.

3.3 Mechanical Testing of Cementite Compounds with Carbon Nanotubes

The compressive strength data obtained from the testing of mortar samples at the ages of 2, 7 and 28 days is plotted in Fig. 6 with the SWNCT dosage. It can be seen that at low concentrations of SWCNT (0.005 and 0.01%), the compressive strength is significantly improved with respect to the reference mortar. At higher dosages, a negative trend was observed at all ages. This indicates an optimum range of SWCNT dosage varying from 0.005 to 0.010% by weight of the cement to achieve better mechanical properties. The substantial improvement in mechanical properties obtained from the use of SWCNT can be further translated to a reduced cement content to achieve target properties.

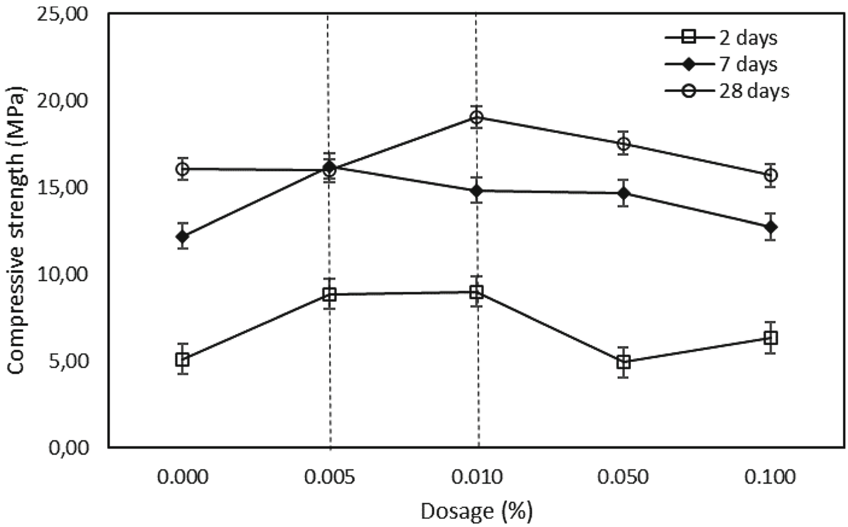

Fig. 6. Compressive strength of the mortar at different dosages of SWCNT.

4 Conclusions

This paper demonstrated the use of SWCNT in the cementitious matrix to enhance their mechanical properties. Expertise gained from this study, in the surface modification and dispersion of the SWCNT can be translated to engineering the properties of the cement concrete as desired.

- A specific dispersion protocol for the SWCNT in the cementitious matrix was developed in the study, which can also be adapted to the requirements of industrial-scale cement concrete production.
- The effect of SWCNT modification in the mechanical properties of the cementitious matrix was quantified and an optimum dosage range was identified for the target application in cement mortar.

The developed knowledge on nano modification can be applied to the production of high-performance concrete, multi-functional concrete and low clinker concrete. Specifically, with the production of cheaper nanomaterials like nano $CaCO_3$, this technology is worth pursuing for reducing the carbon footprint of the cement-concrete industry.

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