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Dispersion of multi-walled carbon nanotubes and its effects on the properties of cement composites

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ABSTRACT

In this study, two types of multi-walled carbon nanotubes (pristine, p-CNT and functionalized, f-CNT) were dispersed in water by sonication and then added to cement mortar. The purpose of this study was to characterize the dispersion degree of the CNTs in aqueous suspension and to investigate whether achieving dispersion in water would also result in dispersion inside mortar. Dispersion of the CNTs in water was investigated by means of UV–vis spectroscopy, using different CNT concentrations and sonication durations. Dispersion of the CNTs in cement mortar was investigated by measuring the compressive and flexural strength and fracture toughness as well as the microstructural characterizations of scanning electron microscopy and mercury intrusion porosimetry. The effects of the CNT addition on drying shrinkage and cement hydration were also investigated for cement pastes. The results of UV–vis spectroscopy showed that by increasing the sonication time to 120 min, the dispersion degree of the f-CNT suspension increased progressively, while for p-CNT, a maximum was reached with 60 min of sonication. The compressive and flexural strength and fracture toughness of mortars containing f- and p-CNTs were not significantly improved either by increasing the amount of CNT or imposing sonication in mixing water. High CNT dispersion in cement matrix was not equally obtained by utilizing highly dispersed CNT suspension. Sonication of f- and p-CNT led to a remarkable deceleration of cement hydration in the first hour of hydration and drying shrinkage of the cement composites was found to be reduced by f- and p-CNT addition.

1. Introduction

Multi-walled carbon nanotubes (CNT) are carbon ordered structure and have unique mechanical properties. Young's modulus is estimated to be as high as 0.45 TPa and their tensile strength may reach 3.6 GPa [1]. Because of these outstanding mechanical properties, addition of CNTs as reinforcement to cementitious materials can potentially improve their properties and has received much interest among researchers.

Pristine CNTs are insoluble in water and are hydrophobic which causes difficulties for dispersion in water. Agglomeration of CNTs originates from several causes. Due to their nano-scale diameter, the surface area of CNTs as well as the surface attraction between CNTs is high. Dispersion difficulties also stem from the CNT propensity to form bundles that are tightly bound by high van der Waals forces. In addition, the high CNT aspect ratio (length/diameter) combined with their flexibility causes highly entangled agglomerates in liquid phases. Incorporation of CNTs into cement also confronts two main challenges: bonding and dispersion. Strong bonding between CNTs and the cement matrix as well as effective dispersion of CNTs is essential for an effective load-transfer to the CNTs which may act as reinforcement to improve mechanical properties of cement composites. It is also believed that if bonding between CNTs and the cement matrix can be controlled, the CNTs can provide substantial mechanical reinforcement [2] and can thus bridge microcracks and improve the ability of the cement composite to withstand fracture. Conversely, agglomeration of CNT inside cementitious materials could function as a local defect and might be detrimental to the reinforcing role of CNTs. A combination of physical (sonication) and chemical (surfactant usage) dispersion methods is the most recommended way to exfoliate CNT agglomerates in mixing water of cement composites [3]. Surfactants not only aid with exfoliation of CNT bundles, but may also play a role in

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bonding with the cement matrix. Li et al. [4] claim that interfacial interactions between surface-modified CNTs and hydration products will produce high bonding strength, and increase the load-transfer efficiency from the cement matrix to the reinforcement.

Although sonication provides an efficient way to suspend CNTs in aqueous media, it is always related to a certain degree of damage on CNT surfaces [5] and may also cause rupture to shorten CNTs. An optimum sonication duration and, correspondingly, delivered ultrasound power to a unit volume of suspension is introduced as a compromise between the dispersion degree and the level of damage to CNT surfaces. There is still an open question concerning the optimum sonication duration, that leads to the best performance of CNT incorporation into cement composites from the aspect of mechanical properties. CNTs have been dispersed in mixing water by sonication for widely varying durations, from a few minutes [6–9] to a few hours [4,10–12]; investigation of its optimum, however, has received less attention.

To date, many researchers have applied combinations of dispersion with different surfactants followed by sonication to fabricate cement composites containing CNTs, but have obtained conflicting results. Many works, for instance [4,7,10,13–17], reported improvement, while other studies [8,12,18–21] reported a lack of improvement in the mechanical properties of CNT-containing cement composites. The scatter of the results implies that dispersion of CNTs in aqueous suspensions could be reached by usage of surfactant and sonication, but effective dispersion of CNTs in the cement matrix could not necessarily be guaranteed. It is likely that CNTs randomly re-agglomerated after mixing with solid phase (cement and aggregates). A systematic investigation of this CNT re-agglomeration after mixing with cement is presently lacking in the literature. A study is needed to shed light on the re-agglomeration concept by characterizing the degree of dispersion of CNTs in the mixing water and in the cement matrix of cement composites.

Green [22] outlined several methods for characterization of CNT dispersion in suspensions: AFM (most commonly used), Cryo-TEM and UV–vis spectroscopy (as a bulk method). Prior data by Paredes et al. [23] showed that for a sonicated and surfactant-stabilized CNT suspension, as characterized by AFM, dispersion up to very high extent could be reached. Regarding dispersion in cement composites, Yazdanbakhsh et al. [24] suggested that even if nano-objects (e.g. CNTs) are well dispersed in the mixing water, geometry dependent clustering would still prevent their uniform dispersion in cementitious materials. Some researchers [2,3] believe that high dispersion of CNTs inside cement composites mostly influence flexural strength and toughness rather than compressive strength, thus mechanical testing could be an indirect way to characterize CNT dispersion inside cement composites.

In this study, suspensions containing pristine or functionalized CNTs were sonicated for various durations and were used for dispersion characterization via UV–vis spectroscopy. Then, they were used as mixing water for cement composites, where verification of the effective CNT dispersion was performed by mechanical testing. The compressive and flexural strength of mortars containing various CNT contents (of both types) was evaluated and the optimum content, having the highest compressive and flexural strength, was determined. Then, the optimum sonication duration for both CNT types, which resulted in the highest strength, and the optimum CNT content were determined to fabricate specimens for fracture toughness and drying shrinkage tests. In addition, the effects of CNTs on the kinetics of early stage hydration of cement were studied by isothermal calorimetry. Porosity analysis and morphology observation were performed on fragments collected from the specimens to provide further information of the microstructure of cement composites.

2. Materials and experimental methods

Ordinary portland cement CEM I 42.5R was used in this study and two types of commercial multi-walled carbon nanotubes were used: pristine (labelled p-CNT) and functionalized (labelled f-CNT). The specifications of p-CNT and f-CNT are presented in Table 1. Standard silica sand with minimum and maximum particle sizes of 0.08 mm and 2 mm and distilled water were used for composite mixtures.

2.1. Characterization of CNT dispersion

Individual carbon nanotubes are active in the ultraviolet–visible (UV–vis) region and show characteristic bands in a wavelength range of 200–1200 nm, with a characteristic peak, in this study at 260 nm, while CNT bundles are not active in this range [5,25–27]. It is therefore possible to detect exfoliation of CNT in aqueous media due to the dispersion process by measuring UV–vis absorbance spectra for CNT suspensions in relation to individual CNT concentration by the Beer-Lambert law. According to Beer-Lambert's law, the absorbance A in a certain wavelength for a suspension is proportional to the concentration of individual CNTs in the suspension:

$$A = -\log(I/I_0) = \varepsilon \cdot c \cdot d, \tag{1}$$

where ε (in $cm^2\ g^{-1}$) is a material specific extinction coefficient for the specific wavelength, c is the concentration of individual CNTs, d is the thickness of the substance exposed to the UV light, and I and I_0 are the transmitted and incident intensity of radiation (for the specific wavelength), respectively. Accordingly, the observed UV–vis spectra absorbance in the characteristic bands increases with the increasing CNT dispersion degree in aqueous suspension. The characterization of CNT dispersion was performed by comparing the absorbance of each CNT suspension with and without functional groups and with varying sonication duration.

CNTs of both types p and f were added at two contents of 0.22% and 0.45% by mass, into 70 ml of distilled water and manually mixed. The mixture was sonicated by a probe sonicator (Ultrasonic Homogenizer, model JY92-IIN, Ningbo Scientz Biotechnology Co.) with a 6 mm cylindrical tip and the power was set to deliver 1 W for 1 ml of the suspension. A suitable vessel was employed to fulfil requirements given by the sonicator manufacturer regarding the location of the tip between the surface of water and the bottom of the vessel. The sonicator was setup to deliver ultrasonic energy for 3 s followed by 3 s clearance to avoid heating up the suspension. During sonication no agitation or magnetic stirrer was employed and at predefined time intervals (0, 30, 60, and 120 min, corresponding to energy delivery of 0, 1800, 3600 and 7200 W ml^{-1} (W for each ml of suspension), 1 ml of the suspension was taken and diluted by a factor of 1:40 with distilled water and tested by UV–vis spectroscopy. The tested substances therefore had nominal CNT concentrations of 0.0055% and 0.011% by water mass.

Table 1
Properties of MWCNTs.

Parameter	Unit	Pristine MWCNT	Functionalized MWCNT
Outer diameter	nm	10–20	10–20
Length	μm	10–30	10–30
Purity	wt%	>95	>95
Ash	wt%	<1.5	<1.5
Specific surface area	m^2/g	>200	>200
-COOH content	wt%	0	2
Designation	–	p-CNT	f-CNT