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Performance of cementitious materials produced by incorporating surface treated multiwall carbon nanotubes and silica fume

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HIGHLIGHTS

- Use of functionalized CNTs improve compressive and flexural strength of cement mortar.
- Using CNT-COOH with silica fumes increased compressive strength by 50%.
- Addition of silica fume enables better dispersion of CNTs in mortar samples.
- SEM results revealed that the CNTs were able to fill the voids in the mortar.

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ABSTRACT

The outstanding mechanical properties of carbon nanotubes (CNTs) highlight them as potential candidates for cementitious material reinforcement. However, their low surface friction and the Van der Waals forces of attraction between them, cause the CNTs to aggregate with each other rather than bind with the cement matrix. A number of methods have been investigated by researchers to reduce the aggregation, improve dispersion and activate the graphite surface to enhance its interfacial interaction. These methods involve surface functionalization and coating, optimal physical blending, use of surfactant and other admixtures. This research investigates the use of silica fumes (an admixture), surface functionalized CNTs and cement paste to overcome those obstacles. CNTs with polar impurities end groups OH and COOH were examined. Mortar samples with non-functionalized CNTs dispersed in water solution, another with non-dispersed, non-functionalized CNTs, and a third batch with no CNTs (as control) was used also studied. Silica fumes volume fraction was varied from 0 to 30% to determine its effect. Compressive and flexural strengths of the different mixes were measured and compared. Qualitative analysis using Scanning Electron Microscope (SEM) and Energy-Dispersive Spectroscopy (EDS) were carried out to study the morphology of each mix. Results reveal a much higher enhancement in strength both compressive and flexural strengths for the functionalized CNTs with 30% silica fumes over the other samples.

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1. Introduction

The use of nanomaterials has grown significantly since the first time it was discovered in 1959 [1]. Similar to other industries, the construction industry can benefit from nanotechnology in order to produce a more desirable outcome. One of the important aspects of the construction industry, which can take advantage of nanotechnology, is concrete production. The properties and characteristics of carbon nanotubes (CNT) provide great prospects to improve the properties of concrete when the CNTs are incorporated to the concrete mixture. CNTs can work as nano filler in concrete and has the potential to improve the strength and durability of concrete. The sizes of CNT are much smaller compared with the typical components in cement, and thus can improve mechanical properties at the nano scale [2]. The outstanding mechanical properties of carbon nanotubes (CNTs) highlight them as potential candidates for concrete reinforcement as well. The strength of the CNTs is directly related to the strong C═C bond and the relatively small number of defects present in the tubes. It is said to possess "a hundred times the strength of steel at one sixth of the weight" [3]. Young modulus is estimated to vary between 1 and 5 TPa, density is around 2000 kg/m^3, elongation to failure of 20–30%, which

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correlate to a tensile strength of well above 100 GPa. The CNTs are characterized by thermal stability up to 2800 °C [4]. Previous studies have shown that the compressive strength of concrete can increase with the addition of CNTs [5].

Despite the obvious advantages of adding CNTs in concrete, there are two major problems associated with its use. CNTs have a tendency to agglomerate due to the Van der Waals attraction force between CNT crystalline ropes when it is produced. The triangular network formed by these ropes tends to aggregate and reduce the dispersion of the CNTs in the water that is added to concrete. The second major drawback associated with CNTs is their very low surface friction, making it difficult for them to bind together or with the cement matrix material. The bonding between cement and CNT is often weak and only the hydration products can anchor a few CNTs. However, knowledge in this field is still limited [6]. Different techniques, such as use of silica fume [7,8], sonication [9] and surfactant addition [10] have been tried to disperse CNT in the mortar mix. Each of these methods has its own limitations and drawbacks. Sonication alone can break the CNT tubes resulting in a weaker reinforcement. Sonication and surfactant use can increase the air volume in the mix resulting in a voided structure. Additionally, although hydration product such as cal cium–silicate–hydrates (C–S–H), calcium hydroxide (CH) have same or larger dimensions than CNTs, only few of them are anchored in hydration products. Consequently, they don't provide effective reinforcement of cement composite. A study by [11] investigated how the length of CNT affects the property of the cement mortar. Sonication and surfactants were used to disperse the CNTs. Flexural test results show that sonication does not have an effect on surfactant performance since the flexural strength for all the samples were the same. Effective flexural strength can be achieved with high percentage of shorter CNTs, or less percentage of longer CNTs.

A study by [7] showed that incorporating a small amount of silica fume to the mix can improve dispersion of CNT and improve its compressive strength. Because of very small particle size of silica fume (in range of 10–500 nm), which is close to the size of CNTs, silica fume can be mixed with agglomerated CNTs and effectively disperse them. Moreover, silica fume particles intermixed with CNTs gets hydrated by Ca^{2+} ions from the cement due to their high pozzolanic activity. Hydration products of silica fume effectively anchor CNTs, and interfacial interaction between CNTs and the hydration products was thereby enhanced. A study by [12] observed that silica fume and silica functional groups improved the fracture performance of mixtures containing carbon nanotubes and carbon fibers, but further optimization of dosage, size, and interface strength is required to fully utilize carbon nanotubes in cementitious composites [12]. Improvements in flexural strength and fracture toughness are more significant at a later age in mixtures containing silica fume, although higher volumes of silica may lead to an adverse effect by concentrating the dispersed CNT in the silica fume fields [12,13].

Li et al. [14] investigated the mechanical properties of cement composite that contained functionalized CNTs. Results showed that surface treated CNTs exhibited better compressive and flexural strength due to the interfacial interaction with hydration

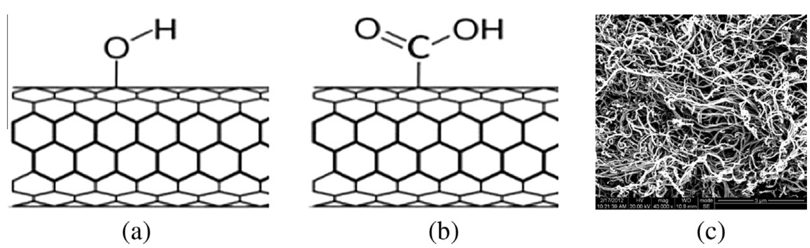

Fig. 1. Schematic of functionalized CNTs used in the study (a) CNT-OH, (b) CNT-COOH and (c) SEM of MWNTs [17].

Table 1
Mix proportions of CNTs-silica fumes mortars.

Set [#]	Mix name	CNT type	Silica fumes%	CNT (% wt of cement)	Cement (kg/m^3)	Silica (kg/m^3)	CNTs (kg/m^3)	Sand before water correction (kg/m^3)	Water before water correction (kg/m^3)	w/c [a]	s/c [b]
1	*No CNT 0*	–	0	0.00	467.0	0	0.0	607	140	0.3	1.3
2	*CNT-0*	CNT [c]	0	0.15	466.3	0	0.7	606	140	0.3	1.3
3	*CNT-OH-0*	CNT-OH [d]	0	0.15	466.3	0	0.7	606	140	0.3	1.3
4	*CNT-COOH-0*	CNT-COOH [e]	0	0.15	466.3	0	0.7	606	140	0.3	1.3
5	*CNT-H2O-0*	CNT-H_2O [f]	0	0.15	466.3	0	0.7	606	140	0.3	1.3
6	*No CNT-15*	–	15%	0.00	397.0	70	0.0	516	140	0.3	1.3
7	*CNT-15*	CNT	15%	0.15	396.4	70	0.6	515	140	0.3	1.3
8	*CNT-OH-15*	CNT-OH	15%	0.15	396.4	70	0.6	515	140	0.3	1.3
9	*CNT-COOH-15*	CNT-COOH	15%	0.15	396.4	70	0.6	515	140	0.3	1.3
10	*CNT-H2O-15*	CNT-H_2O	15%	0.15	396.4	70	0.6	515	140	0.3	1.3
11	*No CNT-30*	–	30%	0.00	327.0	140	0.0	425	140	0.3	1.3
12	*CNT-30*	CNT	30%	0.15	326.5	140	0.5	424	140	0.3	1.3
13	*CNT-OH-30*	CNT-OH	30%	0.15	326.5	140	0.5	424	140	0.3	1.3
14	*CNT-COOH-30*	CNT-COOH	30%	0.15	326.5	140	0.5	424	140	0.3	1.3
15	*CNT-H2O-30*	CNT-H_2O	30%	0.15	326.5	140	0.5	424	140	0.3	1.3

[a] w/c: water to cement ratio.
[b] s/c: sand to cement ratio.
[c] CNT: Industrial grade MWCNTs.
[d] CNT-OH: Industrial grade MWCNTs functionalized with hydroxyl group.
[e] CNT-COOH: Industrial grade MWCNTs functionalized with carboxyl group.
[f] CNT-H_2O: MWCNT dispersed in water.

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