

NANOCOMPOSITES PREPARED BY A DISPERSION OF CNTS ON CEMENT PARTICLES

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Abstract

The hydrophobic behaviour of carbon nanotubes (CNTs) is a main challenge for the incorporation in Portland cement (PC) composites. In this paper, multi-walled carbon nanotubes (MWCNTs) at proportions of 0%, 0.05% and 0.10% of cement weight, without any surface treatment, were mixed in a non-aqueous isopropanol media and unhydrated PC and were sonicated for 2 hours. Thereafter isopropanol was evaporated, water was added to the mixture of cement and carbon nanotubes, and pastes were prepared and moulded. After 28 days, the cement pastes were subjected to compressive and splitting tensile tests. Results indicated better performance of PC nanocomposites. Incorporation of 0.05 % of CNTs resulted in gains of approximately 50% in both compressive and splitting tensile strengths. The results suggest that reinforcement due to the presence of carbon nanotubes and/or the nanomaterial acted as nucleation sites for cement hydration product formation leading to a matrix densification.

Streszczenie

Hydrofobowe zachowanie się nanorurek węglowych (CNT) jest głównym problemem dla ich zastosowania w materiałach kompozytowych na bazie cementu portlandzkiego (PC). W tym artykule przedstawiono wyniki badań wielowarstwowych nanorurek węglowych (MWCNT), które w proporcji 0%, 0.05 % i 0.10 % masy cementu, bez żadnej obróbki powierzchniowej, mieszano w niewodnym medium izopropanolowym i bezwodnym cemencie portlandzkim, i sonikowano przez 2 godziny. Następnie odparowano izopropanol; do mieszaniny cementu i nanorurek węglowych dodawano wodę; przygotowywano zaczyny i uformowano próbki. Po upływie 28 dni, zaczyny cementowe poddano badaniom na ściskanie i rozciąganie przez rozłupanie. Wyniki badań wskazują na lepsze zachowanie nanokompozytów z cementu portlandzkiego. Dodatek w postaci 0.05% CNT przyniósł zysk w przybliżeniu 50% zarówno dla wytrzymałości na ściskanie jak i rozciąganie przez rozłupanie. Wyniki badań wskazują, że zbrojenie w postaci nanorurek węglowych i/lub nanomateriałów działało jako miejsca zarodkowania do tworzenia produktu hydratacji cementu, prowadząc do zagęszczenia matrycy cementowej.

Keywords: Cement paste; Carbon nanotubes; Dispersion; Isopropanol; Mechanical Properties.

1. INTRODUCTION

Carbon nanotubes (CNTs) are hollow tubular channels, formed by graphene laminated sheets. They can be classified as single-walled (SWCNTs) when they have a simple cylindrical layer of graphene or as multiple-walled (MWCNTs) formed by the joining of two or more single cylindrical layers.

Due to the extraordinary properties, as a high tensile strength, the incorporation of the CNTs in civil construction materials has been studied. Recent research has shown that the incorporation of this nanomaterial allows improvements in the mechanical properties of cementitious compounds [1–5]. However, the hydrophobic nature of CNTs makes the dispersion a

challenge to the cement pastes production. CNTs tend to agglomerate and form granules in the presence of water, and those clusters contribute to weakening the PC pastes mechanical properties. A good dispersion is crucial for the improvement of cement composites mechanical strength.

According to MELO *et al.* (2011) [1] there is an optimal range for the incorporation of CNTs in Portland cement particles. For a given dispersion technique there is an optimum CNT content and the excess of nanomaterial lead to granules formation that compromise the mechanical performance and durability of cement pastes. All optimal CNT contents in cement paste or mortar composites found in the literature were in the order of 0.01–0.5% in mass with respect to cement weight [1].

The CNTs can be surface-treated to achieve a better dispersion, resulting in an increase of the dispersive properties. According to FILHO and FAGAN (2007) [6] there is a treatment through noncovalent and covalent interactions, the so-called functionalization. The noncovalent interactions are weak bonds with CNTs, conversely, the covalent interactions are strong and can cause modifications in the CNTs properties. Non-covalent functionalization of CNTs can be achieved by the use of surfactants such as concrete admixtures [2]. However, the amount of surfactant necessary to achieve a good dispersion of CNTs may have negative effects on cement hydration which limits the quantity of CNTs to be incorporated in cement matrixes [3]. On the other hand, the most common covalent functionalization involves the use of strong acids in processes that are not suitable for large scale production that is needed for the application in cement based materials [7].

According to PAULA *et al.* (2014) [4], researchers have studied two methods of dispersion currently. The first one involves a previous dispersion in sonicating surfactant, allowing covalent interaction between the materials. The other method is an attempt to spread the CNTs in the cement or other grain particles. There are two known methods for this second way of dispersion: either by the in situ synthesis of the CNTs on ground PC clinker particles [8] or by suspending the CNTs in a non-aqueous medium, to avoid hydration of the cement, also with ultrasonic frequencies [5].

The in-situ synthesis on clinker produces lower quality nanotubes, but can be easily upgraded to industrial scale. The addition of this nanostructured clinker resulted in similar effects on the rheology of fresh paste [4], on the mechanical behaviour [8], and on the

microstructure [9] as the addition of high quality CNTs.

The research published by MAKAR and CHAN (2009) [5], using images obtained from a high resolution electron microscope, indicated good dispersion of SWCNTs on PC grains, after 2 hours sonication in non-aqueous isopropanol media. The authors [5] also observed that the dispersed CNTs in the cement matrix act as nucleation sites for calcium silicate hydrate (C-S-H) formation, which is responsible for the strength and durability of cement pastes, suggesting a good interaction between the C-S-H and CNTs.

Currently, there is no accepted method able to quantify the dispersion of carbon nanotubes in the cement matrix. An indirect method adopted by some researchers is the analysis of the mechanical behaviour of cementitious composites. Considering this information and the results obtained by MAKAR and CHAN (2009) [5], the present paper aims at evaluating the mechanical performance of PC pastes with 0%, 0.05% and 0.10% of non-functionalized MWCNTs in a non-aqueous isopropanol media and sonication for 2 hours.

2. MATERIALS AND METHODS

2.1. Materials

The nanotubes used were multi-walled type (MWCNTs), with estimated tube lengths between 5 μm and 30 μm , 99% of external diameter between 10 nm and 50 nm, and purity greater than 93%. CNTs were produced in the Nanomaterials Laboratory of the Physics Department of the Federal University of Minas Gerais (UFMG). Brazilian Type CP-V Portland cement was used because of the low percentage of mineral additions. The isopropanol used was absolute grade of EMFAL brand.

2.2. CNTs dispersion

The dispersion process began with the mix of CNTs and approximately 30 ml of isopropanol. The mixture was shaken and sonicated on ultrasonic apparatus with 42 Hz frequency for 30 minutes. In sequence, 300 grams of cement was added with further isopropanol (approximately 200 ml). The suspension was mechanically shaken at 500 rpm and sonicated for additional 2 hours. Fig. 1 illustrates this process.

After 24 hours, the isopropanol was completely evaporated, and the dry mixture of cement and CNTs were used for cement paste preparation.



Figure 1. Mixture of cement, CNTs and isopropanol in the ultrasonic bath being mechanically agitated

2.3. Cement Paste Preparation

The cement pastes were prepared in a mortar blender, as described in the Brazilian National Standard for the determination of consistency of cement pastes [10]. First the mixing water was placed in the batch, the CNTs dispersed on cement particles together with the remaining cement were added subsequently. Tab. 1 describes the proportion of materials used for the production of pastes with and without CNTs dispersed on unhydrated Portland cement particles. Three cement paste types were mixed with water cement ratio of 0.33. The first paste was the reference, using only cement and water (0% of CNTs). The second, in addition to cement and water, contained a proportion of 0.05% carbon nanotubes with respect to cement weight. The third type incorporated 0.10% of carbon nanotubes.

Table 1. Proportions of materials used to prepare cement pastes with CNTs dispersed on cement particles

Identification	Materials	Weight Composition (g)
REF-ISO-P	CP-V Cement	3 000.00
	Water	990
0.05%-ISO-P	CP-V Cement	3 000.00
	Water	990
	CNTs	1.5
0.10%-ISO-P	CP-V Cement	3 000.00
	Water	990
	CNTs	3

Following the paste preparation, prismatic specimen with 5 cm of diameter and 10 cm height were moulded and vibrated on a vibrating table for 1 minute. The moulds were demoulded after 24 hours and bathed in a tank of lime saturated water until reaching the age of 28 days. For each type, 8 cylindrical specimens were moulded: 4 for compressive strength test and 4 for splitting tensile strength test.

2.4. Compressive strength test and splitting tensile strength test

After 28 days, the test specimens' surfaces were regularized for uniform stress distribution in compressive strength test. After that, they were measured and tested on a universal EMIC brand test equipment with load cell of 300 kN for compressive strength test and 20 kN for splitting tensile strength test. The load increment was 0.20 MPa/sec and 1 mm/min respectively. Fig. 2a and Fig. 2b illustrate the compressive strength test and splitting tensile strength test setups, respectively.



Figure 2. a) compressive strength test setup; b) splitting tensile strength test using an apparatus specially developed for the test

Table 2.
Results obtained in the compressive and splitting tensile strength tests

Identification	Compressive strength			Splitting tensile strength		
	Average strength	Standard deviation	Strength gain	Average strength	Standard deviation	Strength gain
	(MPa)	(MPa)		(MPa)	(MPa)	
REF - ISO - P	38.24	6.84	-	2.13	0.18	-
0.05 - ISO - P	55.44	9.27	45%	3.17	0.47	49%
0.10 - ISO - P	51.74	5.91	35%	2.55	0.09	20%

The results of compressive strength test and splitting tensile strength test were obtained by the following equations:

$$fc = \frac{F}{\pi r^2} \tag{1}$$

fc = compressive strength (MPa);

F = maximum load applied (N);

r = test piece average radius (mm);

$$ft = \frac{2F}{\pi dh} \tag{2}$$

ft = splitting tensile strength (MPa);

F = maximum load applied (N);

d = test piece diameter (mm);

h = test piece height (mm).

For analysis, the one with the higher deviation among the 4 results of the same paste was discarded and the mean value of the remaining 3 results was considered.

3. RESULTS AND ANALYSIS

The dispersion process of CNTs on the cement particles surface using isopropanol resulted in visually homogenous dispersion. While in suspension, the CNTs were apparently well dispersed, without formation of clumps. During the paste preparation no significant effect of the CNT addition on paste workability was noticed.

Tab. 2, Fig. 3 and Fig. 4 describe the results obtained in the compressive and splitting tensile strength tests.

The presence of CNTs at the cement composites in both concentrations resulted in a better performance, when compared to the reference paste. 0.05-ISO-P paste had 45% higher compressive and 49% higher tensile strength than the reference. At the same time the gains for the 0.10-ISO-P paste were 35% and 20%, respectively. For an addition of 0.05% CNTs, however, the gain was greater than 0.10% in both

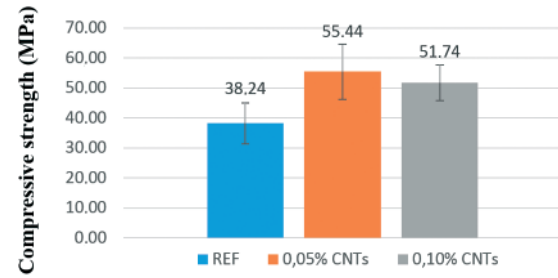


Figure 3.
Compressive strength test results

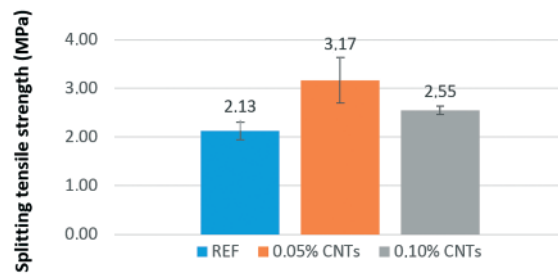


Figure 4.
Splitting tensile strength test results

compressive and splitting tensile tests.

A difference between the relation of gain in compressive and tensile strength was also observed. For 0.05-ISO-P paste the gain in tensile strength was slightly higher (49%) than in compressive strength (45%), meanwhile for 0.10% CNT content the relation was the opposite: higher compressive strength gain (35%) than tensile (20%). This phenomenon may be explained by the CNTs working more like fibre reinforcement when used in smaller content. The higher gain in compressive strength for the 0.10-ISO-P paste indicates that the CNTs in this case have less fibre reinforcement effect, acting rather as nucleation sites for cement hydration products.

These results may also indicate the existence of a dispersion limit of CNTs by this methodology between 0.05 and 0.10% pf CNT content. Despite the visually

good results using isopropanol, the dispersion of contents higher than 0.05% was less effective, which may have caused the agglomeration of CNTs and worse strength performance.

4. CONCLUSIONS

A method for the production of cement pastes based on the previous dispersion of CNTs on PC particles was presented in this work. The CNT content with respect to cement weight was 0.05 and 0.10%. A visually good dispersion was achieved without using any surfactant, or covalent functionalization of the nanotubes.

The described dispersion method allowed the incorporation of MWCNTs in cement matrix, at 0.05% and 0.10% proportion. The addition of CNTs resulted in improvement of the cement pastes' mechanical strength properties. Gains of up to 45% in compressive strength and up to 49% in splitting tensile strength were observed in the case of 0.05% CNT content. For higher CNT addition the gains were lower, but still had better behaviour than the reference paste without nanotubes.

The better performance of 0.05% than 0.10% CNTs incorporation may indicate a possible accumulation of nanomaterial at sites of cement hydration nucleation, compromising the good reaction. This fact corroborates the hypothesis that there is an optimal range for the incorporation of CNTs, and for the present method the ideal range is close to the 0.05% ratio.

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