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Durability of multi-walled carbon nanotube reinforced concrete

A. Carriço [a], J.A. Bogas [a,*], A. Hawreen [a], M. Guedes [b]

[a] DECivil, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisbon, Portugal
[b] DEM, Instituto Politécnico de Setúbal, Campus IPS, Estefanilha, 2914-761 Setúbal, Portugal

HIGHLIGHTS

- Durability of concrete with different types of carbon nanotubes (CNTs) was analysed.
- Mechanical strength and durability properties could be improved as much as 25%.
- CNTs were more efficient in tested properties under cracking conditions.
- Oxidized CNTs showed lower to similar behaviour of pristine CNTs.
- Nucleation and microcrack bridging of CNTs were shown by SEM and TG analysis.

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ABSTRACT

In this study the durability of concrete reinforced with different types of multi-walled carbon nanotubes (CNTs) is analysed. One type of acid treated CNTs and two types of pristine CNTs with distinct aspect ratios were analysed. Common structural concrete with various w/c ratios were produced and characterized regarding immersion and capillary water absorption and carbonation and chloride penetration resistance. Results show the potential of CNTs contribution to the enhancement of mechanical and durability properties of concrete, regardless of the type of CNTs and w/c ratio. The incorporation of 0.05–0.1% CNTs, by weight of cement, improved mechanical strength and durability properties up to 21% and 25%, respectively. The incorporation of CNTs was more effective when concrete was subjected to cracking conditions. In general, the best performance was found in concrete with higher amounts of CNTs of lower aspect ratio. Functionalized CNTs showed lower to similar behaviour to pristine CNTs of identical aspect ratio. The crack bridging and nucleation effect provided by CNTs was confirmed by SEM and thermogravimetric analysis.

1. Introduction

In the past decade carbon nanotubes (CNTs) have been extensively studied as a reinforcement material for cement-based composites. The growing interest in this field comes from the desire to modify the cement matrix at the scale of their main compounds, taking advantage of the outstanding properties of CNTs. On the one hand, CNTs have ultra-high strength and stiffness, with Young's modulus up to 1 TPa and exceptional tensile strength in the range of 20–100 GPa [1]. On the other hand, they possess extremely high aspect ratios (1:1000) and surface area (200–300 m^2/g), as well as very low density (1500 kg/m^3) [2]. Therefore, CNTs are ideal candidates for cement nano-reinforcement, being potentially able to retain the propagation of small nano-cracks and improving some negative features of cement based materials, such as the low tensile strength and low strain capacity. In fact, CNTs have proven to enhance the fracture properties and early age strain capacity of cement pastes and mortars, reducing or preventing crack initiation [3,4].

The reinforcing efficiency of CNTs depends on various factors, such as CNT type, and the quality of their dispersion, interaction and bond strength with the cement matrix [5]. CNTs tend to agglomerate due to their hydrophobic properties, high surface area and strong van der Waals forces between adjacent tubes. These intrinsic characteristics make their separation and dispersion a challenge. Various authors have proposed different methods to disperse CNTs in the cement matrix [6,7]. The preparation of stable aqueous suspensions that are subsequently combined with the cement paste is usually the most common route. In this case, the dispersion is often achieved through a combination of ultrasonic energy and a compatible surfactant [8–10]. CNT functionalization

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* Corresponding author.
E-mail address: abogas@civil.ist.utl.pt (J.A. Bogas).

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with hydroxyl (–OH) and carboxyl (–COOH) groups is also common, as it is believed to reduce the hydrophobicity of nanotubes and increase the interfacial bond with the cement matrix [11,12]. However, despite the current research effort, a methodology that can guarantee high levels of CNTs dispersion in cement based materials has still not been found. Different types and amount of CNTs, dispersion techniques and target reinforcement composites have led to contradictory results reported in the literature. Compressive strength increases over 50% when compared to non-reinforced mixtures were found [6,7], but also no significant improvement have been reported [13,14]. Flexural toughness improvement of as much as 57.5% [15], together with no significant influence [16] were found. Strength increment has been essentially attributed to the filler, nucleation and bridging effect provided by CNTs. The filler effect basically consists on pore filling with CNTs, especially in the spaces between the hydration products [17,18]. CNTs can also work as nucleation sites for the growth of C–S–H, promoting faster and more uniform hydration of cement compounds. Various authors have confirmed the development of hydration products on CNTs walls by scanning electron microscopy (SEM) [18,19]. Finally, the bridging effect provided by CNTs crossing microcracks may counteract their progression and the subsequent growth to the macroscale [20]. Evidence of CNTs crack bridging has also been observed by SEM [21,22]. Konsta et al. [3] found a great increment in the stiffness of C–S–H, showing that CNTs can provide stronger links between hydration products, as the result of the synergetic contribution of nucleation and bridging effects.

Although many studies have focused on the mechanical characterization of CNT-reinforced cement pastes or mortars, smaller emphasis has been put on their outcome on durability. Han et al. [23] did a comprehensive study on the transport properties of CNT-reinforced mortars. Water sorptivity, water permeability, and gas permeability were thoroughly improved with the incorporation of 0.2 wt% of CNTs. From rapid chloride migration tests Wang et al. [24] reported that pastes with different amounts of CNTs exhibited lower migration coefficients than non-reinforced pastes, confirming that CNTs are able to improve the microstructure of cement-based materials. Li et al. [25] analysed the compressive strength degradation after subjecting both reference and CNT reinforced mortar samples to 90 freezing and thawing cycles. Reinforced mortars exhibited better performance, which the authors attributed to the pore refinement and bridging provided by CNTs.

So far, only few works have been published concerning the characterization of concretes reinforced with CNTs. Noteworthy are the works of Kerienė et al. [26] and Wille and Loh [27], which essentially focus on the mechanical behaviour of CNT-reinforced concretes. Once more, contradictory results were reported in literature. Kerienė et al. [26] studied the influence of CNTs on non-autoclaved and autoclaved aerated concretes. CNTs were added in amounts ranging from 0.0008% to 0.06%wtc, which resulted in a maximum enhancement of 11% of both 28-day compressive and flexural strength. Wille and Loh [27] added 0.022% of multi-walled CNTs to ultra-high-performance concrete and concluded that their addition did not influence the 28 days compressive strength. Moreover, to the best of the authors' knowledge a comprehensive study on the durability of concrete reinforced with CNTs has never been done. Bearing this in mind, this study aims to investigate the durability behaviour of CNT-reinforced concretes produced with different types of treated and untreated CNTs. To this end, concretes with different w/c were characterized regarding relevant transport properties (capillary absorption and absorption by immersion) and carbonation and chloride ion penetration resistance. The influence of functionalized and two types of pristine multi-walled CNTs with distinct aspect ratios was studied. In addition, SEM and thermogravimetric analysis were carried out to better interpret the interaction of CNTs with the cement matrix.

2. Experimental program

2.1. Materials

Three types of industrial multi-walled carbon nanotubes purchased from *Timesnano* were tested: pristine nanotubes (CNTPL) and carboxyl-functionalized nanotubes (CNTCOOH), both with aspect ratio ~667, in powder form; lower aspect ratio (~300) pristine nanotubes (CNTSS) in aqueous suspension. Their main properties are listed in Table 1. A sodium salt of a poly(carboxylic acid) anionic surfactant with commercial name Dolapix PC67 (–COONa) was adopted to assist the dispersion of powder CNTs. For concrete production, cement type I 42.5 R according to EN 197-1, two crushed limestone coarse aggregates with D_{max} of 10 mm and two natural siliceous sands were selected. For low water/cement (w/c) ratios, a polycarboxylate based superplasticizer (SP) was also used.

2.2. Dispersion of multi-walled CNTs

Multi-walled CNTs supplied in the powder form were dispersed by a physical and chemical procedure involving sonication to deagglomerate CNT bundles, as well as the incorporation of Dolapix PC67 anionic surfactant to ensure the long-term stability of the dispersion. The stabilisation process differed for each type of CNT; the amount of dispersant and sonication duration were selected according to a previous research [9]. The optimum mass ratio of CNTs to dispersant was 1:1 for CNTPL, and 1:0.5 for CNTCOOH. Sonication time was 30 min for both types of suspensions. CNTSS was already supplied in aqueous suspension, previously stabilised by the manufacturer using a polyethylene-based dispersant. In this case, the dispersion procedure involved only 45 min of sonication. The dispersion procedure in cement was as follows: CNTs and surfactant were first mixed by magnetic stirring with 40% of the mixing water during 1 h; the CNTs suspension was afterwards subjected to two or three 15 min periods of sonication, in the case of powder CNTs or CNTSS, respectively.

2.3. Mixture compositions, concrete mixing and tests

To analyse the efficiency of different types of CNTs in concrete reinforcement, four concretes with w/c of 0.55 were produced with similar composition, differing only in the type and amount of CNTs. Reference concrete without CNTs was produced for comparison purposes. Mixture compositions are presented in Table 2. The appropriate dispersion in concrete mixes was only achieved at low CNT contents, determined in a previous work [28]. The optimal amount of CNTs by weigh of cement (%wtc) was determined considering the results of mechanical characterization of cement pastes with 0.015–0.1%wtc of the same type of CNTs used in this study: 0.05%wtc was determined in the case of CNTPL and CNTCOOH mixtures, and 0.1%wtc for CNTSS mixtures. According to the literature [22,29], higher concentrations of low aspect ratio CNTs (CNTSS) are needed to attain the same reinforcement level of longer CNTs. On the one hand, short CNTs with lower aspect ratios are easier to disperse, being possible to effectively incorporate higher amounts without excessive agglomeration. On the other hand, low aspect ratio results in higher theoretical spacing between neighbour CNTs and in fewer available fibers at crack surfaces, together with lower CNT-matrix bonding strength.

In order to analyse the influence of cement paste composition and to include the more common structural concrete, mixtures