Construction and Building Materials 168 (2018) 459–470

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

On the mechanical and shrinkage behavior of cement mortars reinforced with carbon nanotubes

A. Hawreen [a,*], J.A. Bogas [a], A.P.S. Dias [b]

[a] CERIS-ICIST, DECivil, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisbon, Portugal
[b] LAETA, IDMEC, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisbon, Portugal

HIGHLIGHTS

- CNTs aspect ratio and dispersion process highly affect the CNT-mortar performance.
- CNTs are more effective in mortars with low w/c and early testing ages.
- Shrinkage and fracture toughness of mortars highly improve with CNT incorporation.
- Increment in compression, flexion and elastic modulus of CNT-mortars.
- CNTs provide efficient crack bridging and enhance quality of aggregate-paste ITZ.

ARTICLE INFO

Article history:
Received 8 November 2017
Received in revised form 28 January 2018
Accepted 21 February 2018

Keywords:
Carbon nanotube
Mortar
Mechanical strength
Toughness
Shrinkage
Microstructure

ABSTRACT

This paper investigates the reinforcement efficiency of mortars produced with different types of carbon nanotubes (CNTs) in terms of their mechanical strength, ultrasonic pulse velocity, elastic modulus, fracture toughness, shrinkage and microstructure. The incorporation of 0.05–0.1% of CNTs was able to reduce the early shrinkage up to 62% and increase the flexural strength and fracture energy up to 33% and 65%, respectively. Well-dispersed CNTs could improve the post-cracking resistance of mortars, being able to effectively bridge microcracks up to around 1 μm wide. Microscopic analysis shows that CNTs can potentially improve the quality of the cement matrix in the aggregate-paste interfacial transition zone.

1. Introduction

The first polymer nanocomposite using CNTs as fillers was reported in 1994 by Ajayan [1]. Since then, CNT/polymer [2,3] and CNT/metal [4,5] composites have been widely investigated for Young's modulus, tensile strength, fracture toughness and strain/stress sensing. The positive effect of the incorporation of CNTs in the mechanical properties of ceramic matrices has also been reported [6–8]. These findings suggest that cementitious materials can also benefit from the incorporation of CNTs due to their significant mechanical properties [9]. In fact, some studies have shown the contribution of CNTs towards improving the initial shrinkage [6,10], mechanical properties [6,11], durability [12] and microstructure [6,7,13] of cementitious matrices. Nonetheless, research concerning cementitious composites reinforced with CNTs is still recent.

Some research investigations on mechanical characterization have been recently conducted, especially concerning the incorporation of up to 1% of CNTs by weight of binder in cement pastes [6,7,10,11,13,14]. Li et al. [7] investigated the mechanical behaviour of cement pastes reinforced with 0.4–0.5% of surface modified CNTs and reported 19–25% improvements in the flexural and compressive strength. Incorporation of pristine CNTs led to lower compressive strengths as compared to plain mixes. The low effectiveness of CNTs in mechanical strength reinforcement of cement pastes [11,15] or mortars [16] was also reported by other researchers. Nevertheless, some authors could attain strength improvements as high as 35% when CNTs were well dispersed in the cement matrix [6,17,18]. Konsta et al. [10] found up to 35% lower shrinkage in cement pastes with 0.028–0.048% of CNTs as compared to plain pastes. A greater contribution of CNTs was found in the toughness of cement pastes and mortars. Zou et al. [19], Li

* Corresponding author.
E-mail addresses: hawreen.a@gmail.com (A. Hawreen), abogas@civil.ist.utl.pt (J.A. Bogas), apsoares@tecnico.ulisboa.pt (A.P.S. Dias).

https://doi.org/10.1016/j.conbuildmat.2018.02.146
0950-0618/© 2018 Published by Elsevier Ltd.

et al. [20] and Stynoski et al. [21] found that the addition of 0.033–0.125% of CNTs resulted in fracture load, fracture toughness index and crack mouth opening displacement up to 51%, 19% and 52% higher than those of specimens without CNTs, respectively.

To sum up, depending on the type, amount and dispersion procedure of CNTs, as well as the studied property, different efficiency of CNTs-reinforced cement based materials has been reported in literature. Further research is thus necessary to better understand the CNTs potential in reinforcing cementitious matrices. In addition, studies have been essentially focused on the reinforcement of cement pastes, with less knowledge about the efficiency of CNTs in mortars and concretes, where aggregates are also present. That said, this paper aims the mechanical behaviour of cement mortars with different types of CNTs and a wide range of distinct compositions. Mortars were characterized in terms of mechanical and shrinkage behaviour. The dispersion efficiency and participation of CNTs in the reinforcement of mortars were analysed by means of scanning electron microscopy (SEM).

2. Experimental programme

2.1. Materials

Five types of CNTs were supplied by Timesnano Company (Table 1). CNTSL and CNTSS, with distinct aspect ratios, were supplied in suspension form at CNT concentrations of 5% and 9%, respectively. They were previously dispersed in water with the aid of a polyethylene glycol aromatic imidazole surfactant-TNWDIS. Pristine CNTPL had the same aspect ratio of CNTSL, but it was supplied in powder form. CNTCOOH and CNTOH, also supplied in powder form, were initially acid treated to render –COOH and –OH sidewalls functionalization, respectively. CNTOH presented the highest aspect ratio. The CNTs were selected in order to cover and study the influence of different factors, namely the aspect ratio, the surface functionalisation and the deliver condition (powder form or previously dispersed in aqueous suspension). Aspect ratios considered in this study are in the range of those usually considered in literature [17,22].

To disperse the powder form CNTs (CNTPL, CNTCOOH and CNTOH), the anionic commercial surfactant Dolapix PC67 (Zschimmer-Schwarz) was used. This surfactant was selected based on a previous study [23]. Portland cement type I 42.5R according to EN197-1 [24] and a polycarboxylate based superplasticizer, SP (MasterGlenium SKY 548) were used in mortar production. Aggregates consisted of 0.25/3.35 coarse sand and 0.125/1.0 fine sand.

2.2. Carbon nanotubes dispersion

The dispersion of powder CNTs in water was performed according to Guedes et al. [23]. The required CNT content was mixed with 70% of the mixing water and Dolapix PC67 (CNT:Dolapix of 1:1 for CNTPL, 1:0.5 for CNTCOOH and 1:0.25 for CNTOH), by means of a mechanical procedure consisting of 4 h of magnetic stirring, followed by about 30 min of sonication. The chemical method was not considered for CNTSS and CNTSL, since these products were previously supplied in aqueous suspensions, but they were also subjected to stirring and sonication.

2.3. Mix compositions and sample preparations

Mortars with different w/c (0.35, 0.45, 0.5 and 0.55) were produced to cover a wide spectrum of cementitious compositions. From a previous study [6] concerning the mechanical characterization of cement pastes with 0.015–1%, by weight of cement, of the same CNTs used in this study, the optimal amount of CNTs was achieved for 0.1% of CNTSS of lower aspect ratio and 0.05% of the other types of CNTs with higher aspect ratios (CNTPL, CNTSL, CNTCOOH and CNTOH). Based on this previous study, mortars were produced with the same optimum CNTs content. For shrinkage tests, the amount of CNTs varied between 0.1 and 1% in order to analyse the effect of higher CNT contents. Mortars were produced with 1:3 cement to sand ratio, in which siliceous natural sand consisted of 70% coarse and 30% fine sand, for better granular packing. Mortars with w/c of 0.35 and 0.45 were produced with 1.2% and 0.15% of SP (by weight of cement), respectively. In parallel, reference cement mortars (RCM) without CNTs were also produced.

Mortars were produced in a traditional multi-speed planetary mortar mixer. The dispersed CNT suspension was gradually added to the cement and mixed for 3 min. For mortars with w/c of 0.35 and 0.45, SP was added to the cement paste after mixing 1 min. In another mixer, fine and coarse sands were mixed and saturated with the remaining 30% of mixing water. Then, the cement paste was added to the saturated aggregates and mixed for more 2 min. For each composition, test and curing age (see 2.4), three prismatic specimens of 40 × 40 × 160 mm were produced. For shrinkage test, steel pins were incorporated at the centre of both ending surfaces of each prism, to allow the shrinkage measurements.

The specimens were compacted in a common mortar moulding compaction table and then covered with a plastic film until 24 h. After demolding, all the specimens, except those for shrinkage test, were water-cured in a chamber with relative humidity over 95% and temperature of 20 ± 2 °C until testing. The specimens used for shrinkage tests were placed in a controlled chamber with a temperature of 22 ± 2 °C and a relative humidity of 50 ± 5%, based on LNEC E398 [25].

2.4. Testing procedures

For compressive and flexural tests, samples were tested at 7, 28 and 90 d according to EN 1015-11 [26]. The samples for compressive strength test were obtained from the two remaining parts of

Table 1
Characteristics of CNTs (provided by supplier).

Notation	CNTSS	CNTSL	CNTPL	CNTCOOH	CNTOH
Commercial name	TNIM8	TNIM6	TNIM6	TNIMC6	TNIMH4
Form as supplied	Suspension	Suspension	Powder	Powder	Powder
Purity (%)	>90	>90	>90	>90	>90
Outer diameter (nm)	>50	20–40	20–40	20–40	10–30
Inner diameter (nm)	5–15	5–10	5–10	5–10	5–10
Length (μm)	10–20	10–30	10–30	10–30	10–30
Aspect ratio	~300	~667	~667	~667	~1000
True density (g/cm^3)	~2.1	~2.1	~2.1	~2.1	~2.1
COOH (%)				1.36–1.5	
OH (%)					2.48