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WS_2 nanotube – Reinforced cement: Dispersion matters

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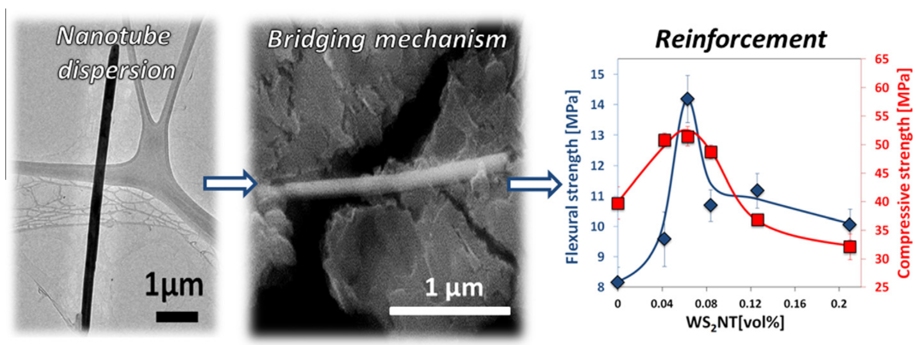
HIGHLIGHTS

- Tungsten di-Sulfide NanoTubes (WS_2NTs) enhance the cement flexural strength by 74%.
- We developed a method to disperse WS_2NT individually in cement paste.
- Optimal enhancement occurs at extremely low WS_2NT concentration (0.15 wt%).
- WS_2NTs inhibit crack propagation by bridging, and fail via pullout mechanism.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanotubes are considered as promising nano-reinforcement in cement-based materials. The main challenge towards achieving a significant enhancement in cement properties is an effective dispersion of the agglomerated nanotubes. In this paper, we demonstrate a novel dispersion method of Tungsten di-Sulfide NanoTubes (WS_2NTs) that results in substantial flexural and compressive strength enhancements at optimal nanotube concentration as low as 0.15 wt%. The reinforcement by WS_2NTs remains significant after a variety of curing processes, suggesting a genuine nanoscale reinforcing effect. Finally, by employing a comprehensive fractography we found that the WS_2NTs inhibit crack propagation by bridging with a pullout failure mechanism.

1. Introduction

Cement, one of the most widely used composite materials, is characterized by high compressive strength on the one hand and by low tensile, flexural and fracture toughness properties on the other [1,2]. The latter properties are expected to improve by loading appropriate Nano-Materials (NMs) into the cement paste matrix [3].

A wide range of NMs were used in Cement Nano-Composites (CNC), including nano-silica [4–6], nano-titanium dioxide [4,7,8],

Abbreviations: BSE, Back-Scattered Electron; CNT, Carbon NanoTube; CNC, Cement Nano-Composites; EDS, Energy-Dispersive X-ray Spectroscopy; NM, Nano-Material; NT, nanotube; PC, Plain Cement paste; SEM, Scanning Electron Microscope; TEM, Transmission Electron Microscope; WS_2NT, Tungsten di-Sulfide NanoTube.

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carbon nanofiber [9,10] and Carbon NanoTube (CNT) [10–18]. Tungsten di-Sulfide NanoTube (WS_2NT) [19,20], which possesses attractive mechanical and geometrical properties (Table 1) [21,22], may be a promising alternative for cement nano-reinforcement.

NMs tend to agglomerate due to strong interfacial van der Waals interactions [23–25], or to entangele due to their waved structure (e.g. CNT) [26,27]. Therefore, their effective surface area is reduced, leading to a decrease in stress transfer between the matrix and the NMs. Furthermore, NM agglomerate act as stress concentrators and may initiate crack propagation [28]. As such, it is essential to develop a dispersion method yielding individual NMs. WS_2NTs also tend to form agglomerates, however, their straight shape does not allow entanglements (in contrast to CNT) and, consequently, simplifies the dispersion process.

NMs may serve as nucleation sites in the cement hydration reaction and accelerate its kinetics [29–31]. Such acceleration insinuates a genuine, although short-term, mechanical properties enhancement in the early stages of the hydration. However, after a longer hydration time (>10 d), this increase vanishes almost completely [32]. As such, in order to observe signs of long-term nano-reinforcement, the mechanical properties should be evaluated after a longer period. Alternatively, hydration processes may be accelerated by heating [1] and the outcomes of this process predict the long-term mechanical properties of the CNC.

Recently, we have shown that WS_2NTs can potentially serve as nano-reinforcement in cement systems [33]. We now aim at expanding the study on the benefits of incorporating this nano-reinforcement. In this paper, we demonstrate a novel dispersion method, facilitating the integration of only individually dispersed WS_2NTs. The mechanical properties of the produced CNCs are measured and compared to the Plain Cement paste (PC) in a variety of curing ages, hence evaluating both WS_2NT's short and long term reinforcing effects. Concerning our methodology, we distinguish between structurally similar cement *ettringites* and the *WS_2NTs* by employing both quantitative and qualitative techniques to allow an accurate evaluation of both the toughening and failure mechanisms of WS_2NT-based CNCs.

2. Experimental section

2.1. Materials

Portland cement CEM I 52.5 R (Nesher Israel cement enterprises Ltd.), protein-based dispersant β-lactoglobulin (⩾90%, Sigma–Aldrich) and WS_2NT (batch no. TWPO-MB023, received as a gift from NanoMaterials Ltd.), were used as received.

2.2. Specimen preparation

2.2.1. WS_2NT dispersion [34]

WS_2NTs are mixed with deionized water (6.0 mg/ml) containing β-lactoglobulin (2.0 mg/ml). The solution is bath-sonicated (Elma, model S10; 30 W, 37 kHz, Singen) for 30 min (540 J). The vial (20 ml) is placed at the center of the sonicator and kept at 0 °C during the whole sonication process. To allow the precipitation of large agglomerates, a phase separation by decantation is conducted an hour after the sonication process. The WS_2NT concentration in the supernatant is then calculated using a combination of thermo-gravimetric and spectroscopic techniques [35]. The supernatant (exfoliated WS_2NT) is freeze-dried (Lobanco Freezone 2.5) in a 40 ml plastic flask for 72 h. The product of which is a sticky–fluffy powder of concentrated WS_2NTs wrapped in β-lactoglobulin dispersant. This product is a ready to use additive in any cement preparation technology.

Table 1
Properties of WS_2NT.

Property	Value
Young's modulus (TPa)	0.15–0.17 [21,22]
Tensile strength (GPa)	19.6 [22]
Diameter (nm)[a]	30–100
Length (μm)[a]	1–4 μm

[a] Measured by electron microscopy (WS_2NT counts = 180).

2.2.2. CNC preparation

The lyophilized WS_2NTs are mixed in water and bath-sonicated for 2 min. The cement is then gradually added and manually mixed into the solution using a spatula (water/cement ratio of 0.4). To reach a uniform dispersion, the mixture is mechanically mixed for 4 min (800 rpm, R50D overhead stirrer, CAT). Finally, this CNC mixture is cast in silicone molds (specimen's dimensions are $8 \times 8 \times 60\ mm^3$ and $12 \times 12 \times 12\ mm^3$ for flexural strength and compressive strength, respectively). The molds are placed inside a vibration machine (Lab Line Orbital Shaker) for 4 min to remove large air bubbles. The CNC samples are removed from the molds (24 h after casting) and cured in water vessel (33.7 mg/l calcium) in a maintenance room (23 °C, 60% humidity) for either 14 or 28 days. An accelerated aging process is performed by immersing CNC samples (after 14 d of normal curing at room temperature) in a hot bath (50 °C) for an additional 21 d, to evaluate the CNC durability and the WS_2NT's effect on the composite's properties over time [36–38]. The effect of the ionic strength of the curing medium on the CNC performances has been studied by replacing the water curing medium by a lime saturated one. CNC samples without dispersant (Section 2.2.1) were also prepared for control.

2.3. Characterization

2.3.1. Dispersion characterization

The WS_2NT dispersion quality is examined by the use of a Transmission Electron Microscope (TEM) (FEI Tecnai 12 G2 TWIN TEM operated at 120 kV). The TEM samples are prepared by placing a droplet of dispersion on carbon-coated copper grids (Ted Pella, lacey carbon, 300 mesh), followed by drying at 80 °C for 2 h before TEM examination.

2.3.2. Measurements of mechanical properties

The flexural strength of the WS_2NT-based CNC and PC is determined by performing a three-point bending test, using prism-shaped specimens. These measurements are performed by a LRX, LLOYD instrument (capacity of 5 kN) at a constant extension rate of 0.5 mm/min (>5 specimens for each wt%). The compressive strength is determined by compression measurements of cube specimens, performed by an Instron 5982 instrument (capacity of 100 kN), with a constant extension rate of 2 mm/min (>5 specimens for each wt%).

2.3.3. Fractographic characterization

To understand the role of WS_2NT in both toughening and failure mechanisms of WS_2NT-based CNC, it is essential to distinguish between WS_2NT and other cement components with similar morphologies.

A fractographic study is carried out on the specimens' fractured surfaces using a high-resolution field-emission gun-SEM (JEOL, JSM-7400F) equipped with Energy-Dispersive X-ray Spectroscopy (EDS) instrument (Noran Vantage) and a Back-Scattered Electron (BSE) detector (AutraDet, AUTORATA YAG) operated at 20 keV. The samples are Pt-coated (few Ångstroms) with Sputter Coater (Emitech K575X). The WS_2NTs are qualitatively identified (1) using BSE imaging mode, which increases mass contrast, since heavy elements (e.g., tungsten $Z = 74$) backscatter electrons stronger than lighter elements in the matrix (e.g., calcium $Z = 20$). Thus, in BSE imaging mode, WS_2NT appears brighter than ettringite in comparison with secondary electron imaging mode (Fig. 1).

(2) WS_2NT and ettringite have different elemental compositions. As such, when a suspected WS_2NT is found (Fig. 2a), tungsten identification by EDS also confirms its presence (white coloration in Fig. 2b).

The EDS elemental spectrum provides a sulfide-to-tungsten atom ratio of ~2, in agreement with the WS_2 composition (Fig. 2c) as opposed to spectrum of CNC without WS_2NT, which does not show evidence of tungsten atoms (Fig. 2d).

3. Results and discussion

3.1. Dispersion method and characterization

As stated above, the major challenge in achieving a significant properties enhancement of CNC by means of nanotubes (NTs) nano-reinforcement is their efficient dispersion. Therefore, a novel dispersion method, based on sonication, decantation and lyophilization is implemented (Section 2.2), yielding only individually dispersed WS_2NTs in the cement matrix.

The WS_2NTs' structural integrity and dispersion quality were monitored by electron microscopy throughout the dispersion procedure to verify that only individual and defect-free NTs are integrated into the CNC. The as-received WS_2NTs (Fig. 3a) are in an agglomerated state (~0.1 mm in diameter), which calls for both sonication and decantation steps. The individually dispersed