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The critical role of nanotube shape in cement composites

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ABSTRACT

The growing availability of nanotubes and the increased knowledge about their loading in polymers have prompted the incorporation of nanotubes in cementitious matrices. The effects of loading straight tungsten di-sulfide nanotubes (WS_2NT) or waved carbon nanotubes (CNT) in cementitious matrices was explored. Their inclusion in these composites at exceptionally low concentrations (0.063 vol% and 0.15 vol% for WS_2NT and CNT, respectively) enhanced the composite's mechanical properties, including compressive and flexural strengths (25–38%). Thermal analysis and electron microscopy indicated that nanotube incorporation in cementitious matrices also accelerated hydration reaction kinetics. It was shown that straight WS_2NTs bridged pores and cracks more effectively than the waved CNTs, which resist crack propagation via an anchoring mechanism. A comparison to representative cement nanocomposite systems shows that nanotubes (aspect ratio $\gg 1$), offer better reinforcement efficiencies than particulate nanomaterials, yielding high mechanical properties enhancement at low concentration.

1. Introduction

The extraordinary mechanical properties possessed by nanotubes (NTs) have driven their use as additives in a large variety of nanocomposite products, including automotive parts, electromagnetic interference shielding packages and coatings, among others [1]. For the most part, the host matrix for nanocomposites comprises a polymer [2], but in light of the worldwide importance of cementitious systems (annual global production of 4.2×10^9 tons [3]), many studies have also explored the merits of incorporating NTs in cement systems. The principal motivation behind NT-loaded cement composites is to exploit the novel properties [2,4–6] and large specific surface area of NTs [7] to engineer cement nanocomposites (CNC) with enhanced mechanical [8–17], electrical [12,16,18], or piezoelectric [19,20] properties relative to plain cement systems.

Although NTs have proven to be an excellent reinforcing nanomaterial (NM) in other matrices, studies of their application in cement have failed to establish a consensus. Results have shown in some cases that the inclusion of NTs in cement composites substantially enhanced composite mechanical properties [8–17], while in other studies, the improvement was only minor [20–22]. This inconsistency stems from the difficulty associated with exfoliating the as-received NT agglomerates. For reinforcement purposes, it is crucial to use only individual NTs and to remove the NT agglomerates, which act as point of stress concentration [23], subsequently deteriorating the nanocomposite performance. NTs are frequently dispersed by sonication in the presence of dispersant (e.g., surfactant) solution, hence peeling off (or exfoliating) individual NTs from the agglomerates. However, this procedure is often not followed by precipitate (agglomerate) removal, and when loaded in the cement matrix results in scattered reinforcing effects [9–17,20–22].

The reinforcing effect of NT in cement system is usually attributed to its ability to inhibit crack propagation via bridging mechanism [9,24]. However, the scenarios in which these NTs fail in cementitious systems awaits consensus.

The inclusion of NTs in cement systems can also affect the hydration reaction kinetics of the cement, which, in turn, dictates the mechanical properties of the cement system [25]. Upon exposure to water, cement undergoes a hydration reaction that yields a variety

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Abbreviations: C-S-H, Calcium-Silicate-Hydrate; CNT, carbon nanotube; CNC, cement nano-composites; LVDT, linear variable differential transformer; NM, nanomaterial; NT, nanotube; PC, plain cement paste; SEM, scanning electron microscope; TEM, transmission electron microscopy; TGA, thermogravimetric analysis; WS_2NT, tungsten di sulfide nanotube.

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Table 1
NT dispersion parameters [29].

NT	Dispersant	Dispersant concentration [mg/mL]	NT concentration [mg/mL]	Sonication duration [min]	Sonication energy [33] [J]
CNT	Pluronic F-127	1.5	2.0	20	3150
WS_2NT	β-Lactoglobulin	2.0	6.0	30	540

of hydration products, both amorphous (e.g., calcium-silicate-hydrate (C-S-H) phase) and crystalline (e.g., calcium hydroxide and ettringite). The NTs can also function as nucleation sites that promote the formation of hydration products [26] in a manner similar to that observed for other fine particulate-based NM [27,28].

In this study the role of NTs in cement systems was explored using a dispersion method [29] that produced only individually dispersed NTs in the CNC [8,17]. The mechanical properties (flexural and compressive) of the obtained NT-loaded CNCs are then characterized, as well as their fractography and the hydration reaction kinetics. The effect of NT *shape* was studied by loading either *waved* carbon nanotubes (CNT) [30] or *straight* tungsten di-sulfide nanotubes (WS_2NT) in the cement systems.

2. Materials and methods

2.1. Materials

Portland cement CEM I 52.5 R (Nesher Israel Cement Enterprises Ltd), β-Lactoglobulin (CAS 9045-23-2, Sigma-Aldrich) and Pluronic F-127 (CAS 9003-11-6, Sigma–Aldrich) were used as received. Multi-wall CNT (10–20 nm in diameter, 233 m^2/g, Cheaptubes) and WS_2NT (30–130 nm in diameter, 8 m^2/g [31], batch no. TWPO-MB023, received as a gift from NanoMaterials Ltd), were further treated (see Section 2.2).

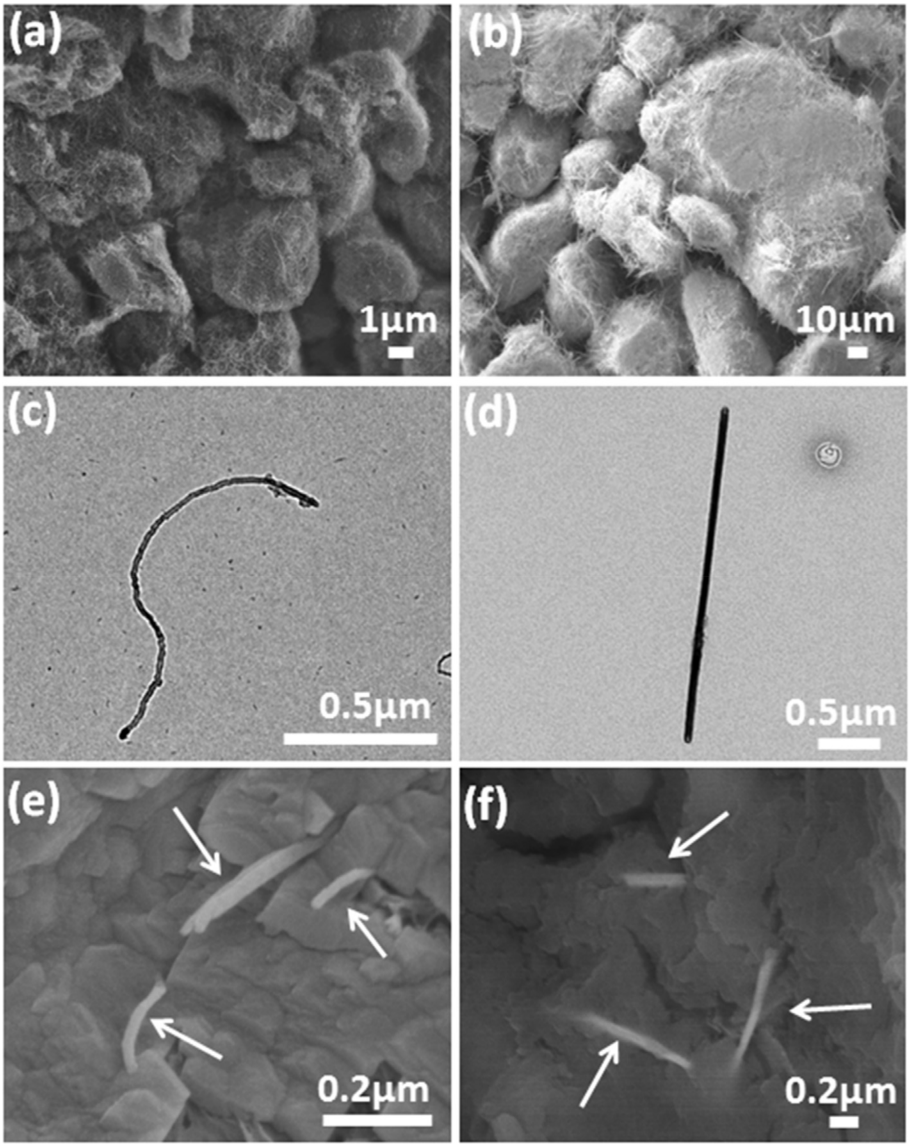

Fig. 1. NT imaging. SEM images of as received agglomerated (a) CNT and (b) WS_2NT. TEM images of individually dispersed (c) CNT and (d) WS_2NT following sonication, centrifugation and decantation. SEM images of fractured CNC (e) 0.15 vol% CNT-based and (f) 0.063 vol% WS_2NT-based; white arrows indicate well-dispersed NTs.