



# Mechanism of cement/carbon nanotube composites with enhanced mechanical properties achieved by interfacial strengthening



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## HIGHLIGHTS

- Carbon nanotubes disperse in cement paste with polyvinyl alcohol as bridging agent.
- The interaction among cement, PVA, and acid-treated carbon nanotube is studied.
- Flexural strength of cement/polyvinyl alcohol/carbon nanotube is enhanced.
- The enhancement is also found in cement/polyvinyl alcohol/graphene oxide composite.

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## ABSTRACT

The mixing of carbon nanotubes (CNTs) with cement or concrete to form cementitious composites has been practiced for decades. CNTs usually aggregate, and have very weak interfacial interaction with the cement matrix, which negates any benefits associated with the original properties of the CNTs. In this study, we present a novel method for interfacial enhancement between surface-treated CNTs and the cement matrix using polyvinyl alcohol (PVA) as the bridging agent. Compared with the slight enhancement effect of untreated CNTs, the flexural strength of cementitious composites containing 0.05 wt% surface-treated CNTs increased from 5.52 to 12.61 MPa with the interfacial strengthening of PVA. A similar flexural strengthening was also found by using graphene oxide (GO) to replace CNTs. Our findings demonstrate that the flexural strength of cement/CNT (or GO) composites can be clearly increased by interfacial strengthening between the CNTs (or GO) and the cement matrix.

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## 1. Introduction

Since their discovery in 1991 [1], carbon nanotubes (CNTs) have become a focus in chemistry, physics and material science due to their superior mechanical [2–4], electrical [5,6] and thermal [3,6] properties. Effective utilization of these exciting CNT properties in cementitious composites mainly depends on their dispersion and interfacial interaction with the inorganic matrix [7–10]. Normally, the strength and durability of cementitious materials depend primarily on the microstructure and chemical bonding of the cement matrix [7]. The importance of other major factors such as the type and amount of aggregates, microfillers and secondary binders varies with the type of cementitious materials and their applications [11,12]. The main drawback of all cementitious structural materials is their brittle nature and consequent tendency to cracking [7,13–15]. So, researchers have already tried to use CNTs

as the bridging filler in the cement matrix to improve the mechanical properties of the composite material [7–9,13,16–18]. However, because there are no chemical bonds formed between the CNTs and the cement matrix, and their surface tensions are quite different [19], the interface between the original CNTs and cement is very weak. CNTs are likely pulled out from cement matrix during cracking, leading to a slight increase of the mechanical strength in cement/CNT composites.

To overcome this problem, surface treatment of CNTs is important before being added into the cement matrix. Oxidation or fluorination [20], and covalent functionalization by organic molecules or polymers, are common ways to generate oxygenated functional groups on the surfaces of CNTs [21]. The functional groups (normally –COOH or –OH) generated by the surface treatment of CNTs, can improve the interface between the CNTs and cement. However, the excessive oxidation destroys the surface structure of the CNTs, leading to a decrease of the self-mechanical properties of the CNTs [5,6,22]. On the other hand, non-covalent surface treatment, such as using surfactants or polymers to modify CNTs [5],

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can only benefit the dispersion of CNTs in the matrix. However, even with a homogeneous dispersion, non-covalent modified CNTs barely contribute their mechanical properties to the composite as a whole, due to the absence of any chemical bonding between the CNTs and matrix.

In this study, we use a polymer to bridge the slightly surface-treated CNTs and cement. Here we chose polyvinyl alcohol (PVA), because it has been reported to crosslink well with cement, resulting in macro-defect free cement with extremely high mechanical strength [23]. In addition, the hydroxyl groups in the polymer chains have the possibility to connect with the carboxyl groups on the treated surfaces of CNTs. To do this, a covalent oxidized CNT suspension was mixed with PVA solution, and the mixed suspension was then directly added into the cement paste to form the cementitious composite. Further, another carbon nanomaterial used in cementitious composites, graphene oxide (GO) [13,24,25], was employed as a composite with cement, and PVA was also used as the interfacial strengthening agent. X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), Time-of-flight secondary ion mass spectrometry (ToF-SIMS), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and flexural tests were employed to characterize the chemical bonding, dispersion and flexural strength of the composites.

## 2. Materials and methods

### 2.1. Materials

Portland cement satisfying the requirements of BS EN197-1:2000 (a European standard that was adopted as a British Standard) for CEM I Portland cement of strength class 52.5 N (roughly equivalent to the requirements of ASTM C150 for Type I Portland cement) was used in this study. Polyvinyl alcohol (PVA) with Mw of 130,000 was purchased from Sigma-Aldrich. The CNTs used here were commercial baytubes C 150 P from Bayer, Germany, produced in a high-yield catalytic process based on chemical vapor deposition (CVD).

### 2.2. Methods

#### 2.2.1. Surface treatment of CNTs and preparation of GO

Firstly, 150 mL of concentrated  $H_2SO_4$  was cooled at  $0^\circ C$  in an ice bath for 30 min under slowly stirring. Then, 3 g of CNT powder was added into the cold  $H_2SO_4$  under stirring for 30 min. After that, 15 g of  $KMnO_4$  was added gradually and the water bath temperature was controlled not to exceed  $20^\circ C$ . The mixture was stirred for 8 h, filtered and washed by water until neutral. GO was prepared from graphite powder (Alfa-Aesar, 200 mesh) according to the modified Hummer method [26]. The detailed preparation process is described in our previous work [13].

#### 2.2.2. Preparation of cement/PVA/a-CNT composites

The acid-treated CNTs (a-CNTs) or GO was dispersed in water under ultrasonication, and then mixed with the PVA solution. The suspension was mixed with cement at a water/cement (W/C) weight ratio of 0.3. The paste was cast into molds to form specimens of size of  $4 \times 25 \times 80 \text{ mm}^3$ , and the specimens were maintained in condition of high humidity (95% humidity,  $20^\circ C$ ) for 28 days to complete the hydration process. The composites of cement/PVA, cement/a-CNTs (or GO), and cement/PVA/original CNTs were fabricated in same way.

#### 2.2.3. Characterization and tests of cement/PVA/a-CNT composites

The X-ray photoelectron spectroscopy (XPS) spectrometer (Axis Ultra DLD system, Kratos Analytical) was equipped with a monochromatic Al  $K\alpha$  X-ray source (1486.6 eV). The pass energy was 40 eV for high-resolution scans. Fourier transform infrared (FTIR) spectra were measured with a Vertex 70 Hyperion 1000 FTIR spectrometer (Bruker) in the range  $500\text{--}3800 \text{ cm}^{-1}$ . Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was used to demonstrate the existence of PVA characterization ions with the presence of CNTs or a-CNTs. Static ToF-SIMS spectra of PVA/CNTs and PVA/a-CNTs were obtained from a ToF-SIMS V spectrometer (ION-TOF GmbH, Münster, Germany). The samples were bombarded with  $Bi_3^+$  primary ions, which were accelerated at 25 kV with an average pulsed current of 0.3 pA. The raster area was  $200 \mu\text{m} \times 200 \mu\text{m}$ , and the acquisition time for each spectrum was 40 s, corresponding to an ion dose of  $<4 \times 10^{11} \text{ ion cm}^{-2}$ . Three positive and negative spectra were recorded for each specimen at different locations. Morphology and distribution of CNTs were characterized by a transmission electron microscopy (TEM; JEOL, JEM-2100, 200 kV). The structure and morphology of cement/CNT

and cement/PVA/a-CNT composites were characterized by an ultra-high resolution scanning electron microscope (SEM; JEOL, model JSM-6700F). Flexural tests were conducted at  $25^\circ C$  using an Instron 3365 testing machine, with a span between the two clamps of 40 mm and a crosshead speed of 0.5 mm/min. For each test, 5 specimens were tested and similar curves were obtained, and a representative curve was selected for further analysis.

## 3. Results and discussion

### 3.1. Surface treatment and interfacial bonding of CNTs

The oxidation of CNTs can be directly demonstrated by XPS C1s spectra, as shown in Fig. 1. The original CNTs have only one peak, at 285.0 eV, corresponding to the C atoms of the C–C groups (Fig. 1a). After the acid-treatment, as seen in Fig. 1b, we can find the appearance of a small peak at 287.5 eV, suggesting the formation of C=O groups [27]. The surface oxidation percentage of CNTs was calculated to be 22% from the ratio of the peak areas, indicating that a considerable number of functional groups formed on the surfaces of the a-CNTs after acid-treatment. We expected that such slight surface oxidation does not decrease the original mechanical properties of CNTs too much, and provides sufficient functional groups for the connection with PVA.

The adsorption of PVA on the surface of a-CNTs was characterized by FTIR tests. Normally, oxygenated groups such as hydroxyl and carboxylic groups are generated in the open ends and defect sites of the CNTs through acid treatment [28]. In the FTIR spectrum of a-CNTs (curve 1 in Fig. 2a), the bands at  $1720 \text{ cm}^{-1}$  and  $1580 \text{ cm}^{-1}$  are due to the carbonyl group (C=O) and C–O bond stretching of the carboxylic groups, respectively. To demonstrate the chemical connection between a-CNTs and PVA, a-CNT

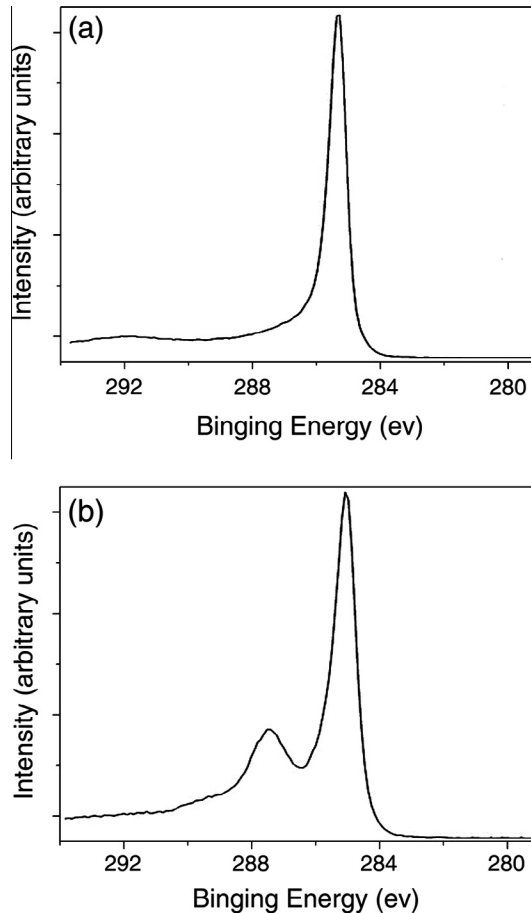


Fig. 1. XPS C1s spectra of (a) original CNTs; and (b) acid-treated CNTs (a-CNTs).

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