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Fracture toughness enhancement of cement paste with multi-walled carbon nanotubes

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HIGHLIGHTS

- Carbon nanotubes were uniformly dispersed into cement pastes.
- MWCNTs and MWCNTs-COOH improved fracture toughness of cement-based composites.
- MWCNTs-COOH improved composites' fracture and compression properties better than MWCNTs.
- Number of micropores reduced with nanotubes addition, especially MWCNTs-COOH.
- Nanotubes can bridge cement particles and form a network that transfers load.

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) have been incorporated into cement pastes to investigate the effect on compressive strength and fracture toughness. Cement-based composites have been prepared from Portland cement with various amounts of common MWCNTs or MWCNTs with a carboxyl group (MWCNTs-COOH), ranging from 0% to 0.1% by weight. Nanotubes were uniformly dispersed into cement paste by applying ultrasonic energy in combination with the use of surfactants. Results indicated that fracture toughness of composites increased by the addition of common MWCNTs, while compressive strengths showed no significant increase. However, MWCNTs-COOH significantly improved fracture energy, fracture toughness and compressive strengths of cement pastes. The porosity and pore size distribution of composites were measured by Mercury Intrusion Porosimetry, and the microstructure of samples was analyzed using a Scanning Electron Microscope. The number of micropores with diameters of 25–50 nm was found to reduce significantly with the addition of MWCNTs, especially MWCNTs-COOH, and the nanotubes bridged the cement particles.

1. Introduction

Cement is the most widely used construction material in the world. Cementitious materials are typically characterized as quasi-brittle materials with low tensile strength and low toughness, which lead to cracking in concrete structures [1]. For instance, cracks can be found in the vast majority of concrete dams [2]. Fiber reinforcement is a typical and effective method to control cracking in cementitious materials. The most frequently used reinforcing fibers are organic fibers (such as polypropylene and nylon), natural cellulose (such as hardwood and softwood pulps), and inorganic fibers (such as steel, glass and carbon) [3]. However, macro- and micro-fibers in cementitious materials can delay the development of microcracks but they do not stop their formation.

Recently, carbon nanotubes (CNTs) have gained the interest of concrete researchers because of their extremely high mechanical, thermal and electrical properties, which may help prevent micro-crack formation in cementitious materials [4]. Typical mechanical properties of CNTs include an average Young's modulus approaching 1000 GPa, exceptional tensile strengths in the range of 20–100 GPa, and an ultimate strain of 12% [5]. The attractive properties of CNTs make them potential candidates for reinforcement of cementitious materials. Related studies have shown that the strength of cement-based materials could be improved by mixing CNTs into cement-based materials [6–15].

Campillo et al. [6] used both multi-wall carbon nanotubes (MWCNTs) and single-wall carbon nanotubes (SWCNTs) to study their enhancement effects on the compressive strength of cement pastes. They showed that the composite containing MWCNTs had

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a significantly higher compressive strength than their counterparts containing SWCNTs. Li et al. [7,8] employed a carboxylation procedure to improve the bonding between MWCNTs and a cement matrix. They obtained a 25% increase in flexural strength and a 19% increase in compressive strength. Cwirzen et al. [9,10] reported the 50% increase in compressive strength of cement paste specimens using MWCNTs that were 0.045–0.15% of the cement weight. Yakovlev et al. [11] added CNTs (0.05% by mass) to foamed concrete. The result showed a significant reduction in the average pore diameter of the composite, and compressive strength increased by 70%, from 0.18 MPa to 0.306 MPa. Makar et al. [12] found that SWCNTs could accelerate the hydration reaction of C_3S in ordinary Portland cement (OPC). The results obtained by Abu Al-Rub et al. [16] showed that the flexural strength of cement samples containing short 0.2 wt% MWCNTs and long 0.1 wt% MWCNTs increased by 26.9% and 65%, respectively, compared with a plain cement sample at 28*d*. Wang et al. [17] presented that the flexural toughness index increased by up to 57.5% for a 0.08 wt% addition of MWCNTs. These researches have shown that the incorporation of CNTs in OPC is a novel way of embellishing the mechanical properties of OPC. However, the problems related to nanomaterial dispersion also exist in case of cementitious composites, and the effect of CNTs on pore structures and microstructure of a cement matrix still remains unclear. What is more, the studies concerning the fracture properties of CNTs-OPC composites are insufficient.

In this work, dispersion technologies of CNTs in aqueous solution were discussed, and cement-based composites have been fabricated from OPC with various amounts of MWCNTs and MWCNTs-COOH ranging from 0% to 0.1% by weight. The strength and fracture toughness of MWCNTs-cement composites were investigated. Concurrently, the pore distributions of the composites were tested by using Mercury Intrusion Porosimetry (MIP), and Scanning Electron Microscope (SEM) was employed to analyze composite microstructure.

2. Materials and experimental program

2.1. Materials

Ordinary Portland cement of LAFARGE SHUI ON CEMENT LIMITED with chemical composition shown in Table 1 was used in the mixtures. The MWCNTs were sourced by Chengdu Organic Chemicals Co. Ltd., Chengdu, China. The properties of two types of MWCNTs used in the experiments are shown in Table 2. The following chemical admixtures were chosen for the preparation of MWCNTs dispersions and fresh composite mix in this investigation:

- Sodium Dodecyl Sulfate (SDS): an anionic surfactant with the formula CH3(CH2)11OSO3Na, white powder, soluble in water.
- Gum Arabic Powder (GAP): colorless and odorless powder, slightly soluble in water.
- Polyethylene glycol: Macrogol 400 (PEG400), a kind of stabilizer that helps dissolve, colorless viscous liquid, soluble in water.
- Polycarboxylate superplasticizer: water reduction efficiency of 40%.
- Antifoaming agent: white milky liquid.

2.2. Dispersion technologies of CNTs in aqueous solution

CNTs always tend to form agglomerations because of high van der Waals forces between CNT surfaces, so the dispersion of CNTs in aqueous media is the major challenge to fabricate a MWCNT/cement composite. Physical and chemical dispersion are two main dispersion methods [18–22]. Physical dispersion mainly employs ultrasonication and magnetic stirring to separate CNTs from each other. Chemical dispersion uses surfactants or functionalization to change the surface of CNTs. In this study, both physical and chemical methods were used to separate MWCNTs in aqueous solution. Effective dispersion of CNTs in aqueous solution was achieved by using commercially available surfactants and the application of ultrasonication.

In the initial attempt, the MWCNTs ground by hand were put into 1% SDS or GAP solution. Grinding is beneficial for the dispersion of CNTs and avoiding stratification. However, the suspensions were unstable, and sediments of CNTs were observed after only 3 h. Then, stable CNTs aqueous solutions were obtained by means of ultrasonication using a frequency of 80 kHz for 3, 5 and 7 h. The CNT aqueous solutions after standing for 15*d* are shown in Fig. 1. A Tecnai TF20 200 kV FEG high resolution Transmission Electron Microscope (TEM) provided by the Tsinghua-Foxconn Nanotechnology Research Center was employed to observe the dispersion effect of MWCNTs in aqueous solution. The TEM micrographs of three kinds of CNTs, including untreated MWCNTs, MWCNTs coated with surfactants, and MWCNTs coated with surfactants and treated by ultrasonication, are shown in Fig. 2. Untreated MWCNTs in aqueous solution that are similar with insoluble particles at the macro-level are tangled by each other (Fig. 2a). The agglomerates of MWCNTs coated with surfactants in aqueous solution had been decreased (Fig. 2b). The dispersion effect of MWCNTs coated with surfactants and treated by ultrasonication are very good (Fig. 2c). In addition, the MWCNTs disperse in the aqueous solution with a number of MWCNTs existing in singular forms.

The dispersion effect of MWCNTs in aqueous solution is associated with ultrasonication time. Fig. 3 compares TEM micrographs of MWCNTs dispersion treated with ultrasonic time of 6, 14 and 24 h under a given frequency. The dispersion effect of MWCNTs in aqueous solution was improved with an increase in ultrasonication time. The agglomerates of MWCNTs were quite dispersed when ultrasonic time reached 24 h. MWCNTs-COOH is soluble in water because of the carboxyl group, so the dispersion of MWCNTs-COOH in aqueous solution is easily obtained without the help of a surfactant.

Table 1
Chemical composition of OPC.

Constituent	Content (%)
CaO	53.55
SiO_2	26.44
Al_2O_3	9.09
Fe_2O_3	4.33
SO_3	3.44
MgO	1.77
K_2O	0.97
Ti_2O	0.02
Na_2O	0.09
P_2O_5	0.09
SrO	0.08
Cr_2O_3	0.07
MnO	0.06

Table 2
Properties of MWCNTs.

Parameter	Unit	MWCNTs-TNM3	MWCNTs-TNMC1
Purity	wt%	>95	>95
Outer diameter	nm	10–20	<8
Length	μm	10–30	10–30
Special surface area	m^2/g	>200	>500
ASH	wt%	<1.5	<1.5
Density	g/cm^3	0.22	0.27
–COOH content	wt%		3.86

Fig. 1. CNT aqueous solutions after standing for 15*d* (The ultrasonication time from left to right is 3, 5 and 7 h).