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Effect of highly dispersed carbon nanotubes on the flexural toughness of cement-based composites

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HIGHLIGHTS

• The addition of MWCNTs improved flexural toughness of cement-based composites.

• Fracture energy increased to a maximum of 312.2 N/m for a 0.08 wt.% addition of MWCNTs.

• Flexural toughness index increased by up to 57.5% for a 0.08 wt.% addition of MWCNTs.

• Composites with MWCNTs had lower porosity and a more uniform pore size distribution.

• MWCNTs act as bridge across crack and form a network that transfers load in tension.

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) modified by anionic gum arabic have been incorporated into Portland cement pastes to investigate the effect on flexural toughness. The flexural toughness of the cement composites were investigated, and the results showed that the addition of treated nanotubes significantly improved both the fracture energy and flexural toughness index of Portland cement pastes. The porosity and pore size distribution of the composites were measured using mercury intrusion porosimetry, and the results indicate that cement paste containing MWCNTs had lower porosity and a more uniform pore size distribution. The microstructure of samples was investigated using field emission scanning electron microscopy. This showed that MWCNTs act as bridges across cracks and voids and form a network that transfers the load in tension.

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1. Introduction

Carbon nanotubes (CNTs) have the best comprehensive properties among carbon materials and present several distinct advantages as a reinforcing material for high strength and performance cementitious composites compared to other traditional fibers. CNTs have generated tremendous interest among the world's scientific community, and their use has led to the development of completely novel nano-composites. CNTs are long, slender fullerene, in which the walls of the tubes are hexagonal carbon with a graphite-like structure, with the end caps containing pentagonal rings [1–3]. The attractive properties of CNTs make them potential candidates for use in a wide range of applications, such as CNT reinforcement materials [4–8], hydrogen containers [9–11], field emission sources [12,13], super-capacitors [14], molecular sensors [15] and scanning probe tips [16,17].

Cement is the most widely used construction material for its low cost, room temperature setting, wide availability and well documented properties for design and construction [18–20]. Although cementitious materials have relatively high compressive strengths the flexural strengths are relative low. Various methods have been used to improve the toughness of cements and concrete, and the most effective is fiber reinforcement. Carbon filaments are most commonly used fillers to improve both mechanical and electrical behaviors of cement-based composites.

Previous research shows that the addition of multi-walled carbon nanotubes (MWCNTs) can enhance the strength of cement matrix materials. Li et al. [5] found that a 25% enhancement in flexural strength of mortar was obtained. Konsta-Gdoutos et al. [21] observed a similar gain in the flexural strength, using a smaller CNTs concentration. The research completed by Musso et al. [22] and Chaipanich et al. [23] presented that a higher concentration of CNTs (about 5–10 times higher) can increase the compressive strength by nearly 20%. The results obtained by Cwirzen et al.







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Table 1Physical parameters of MWCNTs.

Products	Outer di (nm)	ameter	Length (µm)	Purity (%)	Specific surf $(m^2 g^{-1})$	ace area
MWCNTs	20-40		5–15	>97	90–120	
Table 2 Chemical co	mposition c	of cement.				
CaO (%)	SiO ₂ (%)	$Al_{2}O_{3}$ (%)	Fe ₂ O ₃ (%)	SO ₃ (%)	MgO (%)	Na ₂ O (%)
61.13	21.45	5.24	2.89	2.50	2.08	0.77

Table 3			
The mix	proportion	of	MWI

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Sample	Water-cement ratio	Mix proportions (wt.%)		
		MWCNTs	GA	TBP
РО	0.35	0	0	0.13
T1	0.35	0.05	0.30	0.13
T2	0.35	0.08	0.48	0.13
T3	0.35	0.10	0.60	0.13
T4	0.35	0.12	0.72	0.13
T5	0.35	0.15	0.90	0.13

[24] shown that, despite an increase in the compressive strength of nearly 50%, the flexural strength of the cement paste increased by only 10%.

In this paper, the effect of highly dispersed MWCNTs on the flexural toughness of cement-based composites were investigated. At the same time, the microstructure of the newly formed composites were studied. Field emission scanning electron microscope (FE SEM) was employed to study the morphology and the microstructure of the cement-based composites. A determination of the porosity of the composites was carried out through mercury intrusion porosimetry (MIP).

2. Experimental

2.1. Materials

The MWCNTs provided by Shenzhen NANO-Technology Co. Ltd. in China were all treated firstly by a surfactant-ultrasonic method with a commercial available surfactant Gum Aribic (GA) (supplied by Shanghai SINOPHARM Chemical Reagent Co., Ltd.). The defoamer was liquid tributyl phosphate (TBP) (supplied by Tianjin Chemical Reagent Plant, China), which was added in 0.13% by mass fraction of cement. MWCNTs were added to aqueous GA solutions; the mixture was ultrasonicated by a ultrasonic treatment (DS-3510DT) for 30 min at room temperature. The physical parameters of MWCNTs are shown in Table 1. The cement was brought from Dalian Onoda Cement Plant, the chemical composition of cement is shown in Table 2.

2.2. Dispersion of MWCNTs

MWCNTs were dispersed by using a surfactant-ultrasonic method with GA, a commercial available surfactant. According to the previous test results [25,26], the mass ratio of MWCNTs to dispersant was 1:6 and the relevant dispersant was first dissolved by four-fifths of the total water in each mixture. And then, the weighed MWCNTs were put into the aqueous dispersant solutions and dispersed sufficiently in an ultrasound processor (DS-3510DT) for 30 min at room temperature. Finally, the defoamer in the amount of 0.13 wt.% was used to eliminate the air bubbles in the solutions.

Table	4
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Mechanical properties of different samples after 28 days curing.

Sample	MWCNTs content (wt.%)	Fracture energy (N/m)	Flexural toughness index
PO	0	51.93	1.74
T1	0.05	54.47	2.28
T2	0.08	312.16	2.74
T3	0.10	232.13	2.56
T4	0.12	151.57	2.29
T5	0.15	69.60	1.92





Typical morphologic TEM images of MWCNTs in aqueous solution with the dispersion of GA are shown in Fig. 1. The MWCNTs disperse in the suspension with many of the MWCNTs existing as single forms. GA weakens the van der Waals attraction among MWCNTs through adsorption. At the same time, the hydrophilic groups of ionic GA can undergo ionization. In this way, it changes the surface electric potential of MWCNTs, strengthens the effect of electrostatic repulsion, enhances the dissolubility of MWCNTs, then improves the hydrophily of MWCNTs and enhances the evenness of MWCNTs in suspensions [27,28].



Fig. 1. TEM images of MWCNTs in suspensions after being dispersed by GA.

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