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Mechanical properties of highly dispersed carbon nanotubes reinforced cement-based materials

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Abstract. Carbon nanotubes (CNTs) are considered as ideal candidates for preparation of high performance cement-based composites due to their remarkable mechanical properties. Dispersion of CNTs is the crucial step while using CNTs in cement-based materials, while poor dispersion could lead to performance reduction of materials. In this paper, an effective dispersion method of MWCNTs by applying ultrasonic energy and in combination with surfactants was developed. The effects of surfactant type on the dispersion of MWCNTs were systematically investigated. Additionally, experiments are carried out to investigate the influence of concentration of MWCNTs on the mechanical properties of cement paste. The results show that a stable MWCNTs suspensions could be manufactured via the addition of surfactants and the stability of MWCNTs suspensions appears to be related to the ionic nature of the surfactant. Furthermore, the addition of MWCNTs is justified to enhance the flexural strength and compressive strength of the cement-based materials remarkably.

1. Introduction

Cement-based composite is one of the most commonly used construction materials in the world due to its low cost and wide variety of sources. Cement-based materials present high compressive strength, elastic modulus and relatively low toughness and tensile strength. Fiber toughening is the most effective methods used to improve the toughness of cement-based materials. Recently, microfiber reinforcement is successfully applied to improve the mechanical properties of cement-based composite and achieve significant improvement. However, microfibers do not stop the initiation of microcracks, although they delay the development of formed microcracks. The utilization of nanoscale fibers will inhibit the formation of cracks at nanoscale level [1]. Therefore, the development of nanosized fibers has break a new field of nano-reinforcement of cementitious composites.

Due to the advantages such as the excellent electrical, mechanical, thermal properties and high resistance to corrosion, carbon nanotubes (CNTs) are considered one of the most beneficial nanomaterials for reinforcement [2-3]. The remarkable properties of CNTs make them preferred materials for reinforcement of composite materials [4-8]. Theoretically speaking, CNTs reinforced cement-based composites should exhibit high strength, high volume stability and high permeability. At the earlier research, CNTs have been added in cementitious composites at an amount ranging from 0.5 to 2.0 wt.% (by weight of cement) [7-13]. However, CNTs are prone to agglomerate or form tightly bound bundles due to the produced method. Therefore, poor dispersion is the major challenge in front of the incorporation of CNTs in cement-based materials [14-15]. Many defect sites occur in the nanocomposite if the CNTs are not dispersed well and the efficiency of the CNTs in the matrix is



limited. In the prior work, pre-treatment of CNTs surface by chemical modification were carried out to promote the dispersions of CNTs in liquid [8–12]. Therefore, improving the dispersibility of CNTs and reducing the aggregation of CNTs is crucial for preparing CNTs reinforced cement materials [16–17].

In this study, an effective dispersion method of MWCNTs in water was developed by sonication and surfactant. Six different types of surfactants were systematically compared, and the effect of surfactants on the dispersion of MWCNTs was investigated, by measuring the survival time of the MWCNTs suspension under centrifugation treatment. Finally, the influence of the concentration of MWCNTs on the mechanical properties of the cement-based materials were studied.

2. Experimental

2.1. Selection of materials

The cement used in this study was Type I 42.5R Portland cement manufactured by Tangshan Jidong Cement Co., Ltd. Multi-walled carbon nanotubes (MWCNTs) were supplied by Shenzhen Nanotech Port Co., Ltd., China, which were synthesized using the chemical vapor deposition (CVD) method. Its physical properties are shown in Table 1. Additionally, the following commercially available surfactants were also selected for the aqueous dispersion of MWCNTs: anionic surfactants including sodium dodecyl sulfate (SDS) and sodium dodecyl benzene sulfonate (SDBS), cationic surfactants including hexadecyl trimethyl ammonium bromide (HTAB) and hexadecyl trimethyl ammonium chloride (HTAC), nonionic surfactants including polyvinyl pyrrolidone (PVP) and Triton X-100 (TX-100).

Table 1. Properties of the MWCNTs used in this study.

Type	Diameter (nm)	Length (μm)	Purity	Specific Surface Area (m^2/g)
MWCNTs	10~20	5~15	>97	100~160

2.2. Manufacture and curing of specimens

Prior to preparing the CNT/cement material, the aqueous dispersion of MWCNTs was prepared. In this study, combination of ultrasonic and surfactant is used to disperse MWCNTs. Required amount of surfactant was added into water, stirring until it dissolves, followed by addition of MWCNTs and mixing for 10 min. The aqueous suspension of MWCNTs was then sonicated with an Ultrasonic Cell Disrupter (Scientz-1500F Ultrasonic cell disrupter, Ningbo Scientz Biotechnology Co., Ltd.) for 30 min. Required amount of cement was added into the aqueous dispersion, mixing for 5 min by a cement mixer to obtain fresh MWCNTs/cement pastes. The cement paste specimens were cast into $40 \times 40 \times 160$ mm size molds for flexural strength tests and $40 \times 40 \times 40$ mm size molds for compressive strength tests, respectively. After demolding at an age of 24 hours, the specimens cured under 20°C and relative humidity (RH) of 95% until testing. The water/cement ratio was 0.35 and the surfactant was 0.2% weight of cement.

2.3. Testing procedures

To evaluate the stability of MWCNTs aqueous suspensions, the suspensions were subjected to centrifuging treatment at centrifuging speed of 3000 r/min and observed every 5 minutes, record the centrifuging time when the stratification of the suspension occurs.

The tests of mechanical properties of specimens include compressive strength and flexural strength according to Chinese national standard (GB 50152-92).

3. Results and discussion

3.1. The effect of surfactant on the dispersibility of MWCNTs

Dispersion of CNTs is the first step and crucial step while using CNTs in cement-based materials and the degree of dispersion influences the properties of composite. Utilization of surfactant and sonication are commonly used and most efficient methods to disperse CNTs into water. Therefore, the effect of different types of surfactants on the stability of MWCNTs suspensions was investigated and the results were summarised in table 2.

Table 2. The effect of different types of surfactants on the stability of MWCNTs suspensions^a.

Number of specimens	Surfactants	Ionic nature	centrifuging time before stratification (min)
1	none	-	5
2	SDS	Anionic	55
3	SDBS	Anionic	65
4	HTAB	Cationic	100
5	HTAC	Cationic	105
6	PVP	Nonionic	160
7	Tx-100	Nonionic	145
8	HTAB + PVP (1:1)	Cationic + Nonionic	180
9	HTAC + PVP (1:1)	Cationic + Nonionic	175
10	HTAB + Tx-100 (1:1)	Cationic + Nonionic	150
11	HTAC + Tx-100 (1:1)	Cationic + Nonionic	155
12	PVP + Tx-100 (1:1)	Nonionic + Nonionic	150
13 ^b	HTAB + PVP (1:1)	Cationic + Nonionic	120

^a the mass ratio of MWCNT and surfactants was 1:4

^b at centrifuging speed of 5000 round/min.

As indicated in table 2, specimens treated with different type of surfactant exhibit more longer survival time than the specimens with no surfactant. MWCNT are difficult to disperse in water in the absence of surfactant. After centrifuging for 5 min at centrifuging speed of 3000 round/min, MWCNT suspension without addition of surfactant was not stable and stratification was observed (specimen 1). A more stable MWCNT suspension could be manufactured via the addition of surfactants and the stability of MWCNT suspension appears to be related to the ionic nature of the surfactant. More specifically, the stability of MWCNT suspension added with either cationic surfactants or nonionic surfactants (specimens 4~7) is relatively better than those added anionic surfactants (specimens 2~3). Furthermore, the cationic and nonionic surfactants were selected to prepare cationic + nonionic type of compound surfactants and/or nonionic + nonionic type of compound surfactants. The effect of the above type of compound surfactants on the stability of MWCNT suspension were further investigated and the obtained results show that MWCNT could be dispersed in compound surfactants solutions more easily (specimen 8~12). More specifically, suspension prepared by cationic + nonionic type compound surfactant are quite stable (specimen 8~11). Suspension with addition of HTAB and PVP survive for 120 min without stratification at a higher centrifuging speed of 5000 round/min (specimen 13), indicated that MWCNT were dispersed in water efficiently. Therefore, compound surfactants HTAB + PVP is the optimized surfactants for the dispersion of MWCNT and the prepared MWCNT suspension was selected for the preparation of MWCNT reinforced cement-based materials in this study.

3.2 Mechanical properties

The flexural and compressive strengths of cement paste specimens was studied at 28 days of curing. The average flexural and compressive strengths of cement pastes with MWCNTs at amounts of 0%, 0.05%, 0.08%, 0.1%, 0.12% and 0.15% (by weight of cement) were summarized in Table 3. It is evident from Table 3 that the addition of the MWCNTs result in increase in both the flexural and compressive strengths of Portland cement. Moreover, the flexural strength of cement composite increased with increasing amount of MWCNTs, and 0.08 wt% of MWCNT addition lead to maximum

enhancement of flexural strength around 23% to a maximum of 13.5 MPa (sample 3). However, the flexural strength decreases to 10.5 MPa (sample 6) while further increasing the MWCNT content to a dosage of 0.2%.

The compressive strength tests showed similar results as the flexural strength tests. The best performance was achieved to a maximum of 87.1 MPa at 0.1 wt% addition of MWCNTs, which maximum enhancement of compressive strength reach 13% (sample 4). However, increasing the dosage of MWCNTs to 0.2 wt% led to a strength decrease to 73.0 MPa.

It is established that the reinforcement effect of the MWCNTs on cement-based materials largely depends on the efficiency of dispersion. In this study, the remarkable enhancement of the flexural strength of the cement-based composites mainly attributed to the excellent dispersion of MWCNTs, the strong interfacial bond strength and the increase of the compactness [18]. Furthermore, effective dispersion of the MWCNTs in the cement paste also reduce the fiber free area in the material and improve the mechanical performance of the cement-based composite.

Table 3. The mechanical properties of different MWCNTs/CC after 28 days curing.

Sample	Admixture (%)	Compressive strength (mean value) (MPa)	Flexural strength (mean value) (MPa)	Compressive strength variation / %	Flexural strength variation / %
1	0	77.4	11.0	-	-
2	0.05	82.9	12.2	7	11
3	0.08	83.9	13.5	8	23
4	0.1	87.1	13.0	13	18
5	0.15	82.4	12.8	6	16
6	0.2	73.0	10.5	-6	-5

Compared to the specimens contain small fraction of MWCNTs, the case of inclusion of more quantity of MWCNTs lead to the reduction in strength due to poor dispersion and agglomeration. It indicates that higher concentration of MWCNTs in the cement matrix cause the poor dispersibility and therefore reduce the reinforcement of the cement. Furthermore, when the cement composite contains more MWCNTs, the number of interface defects between cement and MWCNTs increased, which may also cause the strength decreasing. Therefore, the concentration of MWCNTs should be controlled at a relatively low level.

4. conclusions

The experimental results presented in this paper lead us to draw the following conclusions:

a) MWCNTs can be dispersed in water efficiently by means of surfactant and sonication. The stability of MWCNTs suspension is related to the ionic nature of the surfactant and a stable MWCNT suspension can be manufactured by the addition of appropriate cationic + nonionic type of compound surfactants.

b) The flexural and compressive strength of cement-based materials can be greatly improved by addition of MWCNTs. The enhancement attribute to the prominent mechanical properties of MWCNTs, the highly effective dispersion of MWCNTs and the increase of compactness.

c) A relatively low concentration of effectively dispersed MWCNTs is preferred to achieve better reinforcing effect on the cement-based materials.

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