Electrical properties of cement-based composites with highly dispersed carbon nanotubes

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Abstract. In this paper, the effects of dispersion of multi-walled carbon nanotubes (MWCNTs) on the electrical properties of cement-based composites were systematically investigated. Six different types of surfactants were selected to disperse MWCNTs in cement by sonication, and the effect of ionic nature of surfactants on the electrical resistivity of cement-based composites was investigated. Additionally, experiments were carried out to investigate the effect of dosage of MWCNTs on the piezoresistivity of cement composite under cyclic compressive loading. The results show that the ionic nature of the surfactant influence the electrical resistivity of cement-based composites obviously. Furthermore, adding MWCNTs into cement-based composites is justified to improve their conductivity and the repeatability of piezoresistivity.

1. Introduction

Concrete structures are widely used in industrial and civil constructions, roads and bridges, airports and hydraulic projects. It is of great significance to implement structural health monitoring (SHM) on these important civil infrastructures. High performance intelligent sensors are the most important constituent of SHM of concrete structures. Among the currently available types of sensors of SHM, cement-based piezoresistive sensor has attracted more attention from engineers and researchers due to its good compatibility with concrete structure, good durability and low price [1-5]. The main principle of cement-based sensors is incorporating conductive fillers into the cement matrix to produce cement-based materials with electrical conductivity and monitor the change of electrical resistivity of composite when suffering from external stress.

Carbon nanotubes (CNTs) is identified as one of the most effective nanomaterials for high performance structural composite materials due to its admirable mechanical, electrical and thermal properties [6-9]. Earlier researchers have attempted to add CNTs in polymer composites to investigate the strain sensing properties [10-11].

In order to explore their electrical properties, fully dispersion of CNTs in the cement matrix to form a conductive network is required. However, CNTs is liable to agglomerate or generate tightly bound bundles in most solvents due to strong van der Waals forces and huge aspect ratio. To be dispersed in an aqueous solvent, modification of the surface of CNTs is necessary [12-13]. In this work, MWCNTs are dispersed in water effectively by utilization of surfactant and sonication. Systematic comparison of six different types of surfactants were carried out, and their effect on the electrical property of cement-based composite with MWCNTs was investigated, by testing the electrical resistivity of MWCNTs/CC. Finally, the influences of the dosage of MWCNTs on the piezoresistivity of the cement-based materials were investigated.
2. Experimental

2.1. Selection of materials
The cement used in this work was P.O 42.5R Portland cement supplied by Tangshan Jidong Cement Co., Ltd. China. Carboxyl multi-walled carbon nanotubes (MWCNTs) were manufactured by Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences, China. The physical properties of MWCNTs are listed in Table 1. Furthermore, the following three types of surfactants are selected: anionic surfactants: sodium dodecyl benzene sulfonate (SDBS) and sodium dodecyl sulfate (SDS); cationic surfactants: hexadecyl trimethyl ammonium chloride (HTAC), hexadecyl trimethyl ammonium bromide (HTAB); and nonionic surfactants: Triton X-100 (TX-100), polyvinyl pyrrolidone (PVP).

| Type            | Outer Diameter | Length  | Purity | Specific Surface Area | -COOH content | Electric Conductivity |
|-----------------|----------------|---------|--------|-----------------------|---------------|----------------------|
| MWCNTs          | 5~15 nm        | 10~30 μm | >98    | 220~300 m²/g          | 3.86 wt%      | >100 s/cm            |

2.2. Sample preparation
Firstly, required amount of surfactant were added into water and mixed by magnetic stirrer for 10 min, then MWCNTs was added and further mixing for 10 min. After sonication for 30 min by an Ultrasonic Cell Disrupter (Scientz-1500F, Ningbo Scientz Biotechnology Co., Ltd.), cement was added into the aqueous suspension of MWCNTs followed by mixing with a cement mixer for 5 min to obtain fresh MWCNTs/cement pastes (the water/cement ratio was 0.35). The cement pastes were cast into 40 × 40 × 160 mm size molds, and four stainless steel gauze as electrodes were embedded along the length of the specimen, as shown in Figure 1. The specimens were demolded after 24 hours and cured under 20 °C and relative humidity (RH) of 95% for 28 days.

2.3. Testing procedures
Electrical resistivity measurements were tested by a four-electrode method using digital multimeter (DMM6500, 6 1/2-digit, Keithley Instruments Inc., USA). The piezoresistive responses of the composites were tested using a hydraulic mechanical testing system.

To evaluate the piezoresistive property of cement-based composites with MWCNTs, the fractional change of the resistivity was determined as follows:

\[ \Delta \rho = (\rho - \rho_0) / \rho_0 \]  

where \( \rho \) is the resistivity of cement-based composites under compressive load and \( \rho_0 \) is the initial resistivity of the cement-based composites.

3. Results and discussion

3.1. The effect of surfactant on the electrical resistivity of MWCNTs/CC
Dispersion of CNTs is a crucial step in the preparation of cement-based composites with MWCNTs and influences the properties of composites. Among the dispersion methods of MWCNTs in water, combined application of surfactant and ultrasonic usually present a better effect. In our previous study, we found that the change in the type of surfactant in cement-based composite with MWCNTs has significant influences on the dispersibility of MWCNTs in cement matrix and the mechanical properties of MWCNTs/CC. Herein, the effect of surfactant on the electrical resistivity of cement-based composites with MWCNTs were systematically investigated and the results were listed in Table 2.

| Number of specimens | Surfactants     | Mass ratio of MWCNTs/surfactants | Electrical resistivity (ohm.cm) |
|---------------------|-----------------|----------------------------------|--------------------------------|
| 1                   | none            | -                                | 43678                          |
| 2                   | SDS 1:4         | -                                | 6547                           |
| 3                   | SDBS 1:4        | -                                | 6123                           |
| 4                   | HTAB 1:4        | -                                | 5632                           |
| 5                   | HTAC 1:4        | -                                | 4435                           |
| 6                   | PVP 1:4         | -                                | 4132                           |
| 7                   | Tx-100 1:4      | -                                | 4512                           |
| 8                   | HTAB + PVP (1:1)| 1:4                              | 4009                           |
| 9                   | HTAC + PVP (1:1)| 1:4                              | 3976                           |
| 10                  | HTAB + Tx-100 (1:1)| 1:4                            | 4210                           |
| 11                  | HTAC + Tx-100 (1:1)| 1:4                        | 4321                           |
| 12                  | PVP + Tx-100 (1:1)| 1:4                         | 3654                           |
| 13                  | PVP + Tx-100 (1:1)| 1:3                         | 3367                           |
| 14                  | PVP + Tx-100 (1:1)| 1:2                         | 3212                           |
| 15                  | PVP + Tx-100 (1:1)| 1:1                         | 4980                           |

As shown in Table 2, specimens with 0.3% dosage of MWCNTs treated with different type of surfactant exhibit better electrical conductivity than the specimens without surfactant treatment. For instance, the electrical resistivity of MWCNTs/CC with surfactant SDS treatment is 6547 ohm.cm, which is an order of magnitude lower than that of MWCNTs/CC without surfactant treatment (43678 ohm.cm). Generally speaking, MWCNTs are not easy to disperse in water effectively without any surfactant and thus a conductive network in the cement matrix could not be formed efficiently. Evidently, a lower electrical resistivity could be observed via the addition of surfactants and the ionic nature of the surfactant appears to affect the electrical conductivity of MWCNTs/CC. More specifically, the electrical resistivity of MWCNTs/CC treated with either nonionic surfactants or cationic surfactants was relatively lower than the specimens that anionic surfactants were added. Therefore, the nonionic and cationic surfactants were selected to prepare (nonionic/nonionic) compound surfactants and (cationic/nonionic) compound surfactants. The obtained results show that composites with MWCNTs dispersed with those compound surfactants showed lower electrical resistivity. For example, specimens prepared by (nonionic/nonionic) compound surfactant exhibit better electrical conductivity. The electrical resistivity of composites with MWCNTs dispersed by PVP + Tx-100 is 3654 ohm.cm, which is 8% of MWCNTs/CC without surfactant treatment, indicated that MWCNTs were efficiently dispersed in cement composites and a good conductive network was established in the cement matrix. Furthermore, the electrical resistivity of MWCNTs/CC decreased with the concentration of compound surfactant. However, a further decrease in the amount of surfactant lead to an increase in electrical resistivity, which may due to inefficient dispersion of MWCNTs at such low concentration of surfactant.

3.2 Piezoresistivity of MWCNTs/CC

Figure 2 shows the piezoresistive responses of the MWCNTs/CC with 0.1 wt%, 0.3 wt%, 0.5 wt% and 1.0 wt% of MWCNTs. It is obvious that cement-based composites with well dispersed MWCNTs
exhibited good self-sensing capacity under a cyclic compressive load. The electrical resistivity changes synchronously with the compressive stress while the electrical resistivity decreased with increase of compressive load. Thus, the values of fractional change of the resistivity were negative in this work. Furthermore, it can be seen from Fig.2 that the fractional change of the resistivity varies with the amount of MWCNTs in cement-based composites. The fractional change of resistivity of MWCNTs/CC with 0.1 wt%, 0.3 wt%, 0.5 wt% and 1.0 wt% MWNTs were about 2%, 6%, 9% and 5%, respectively. On the whole, the fractional change of the resistivity increased with increasing content of MWCNTs, and composites incorporating 0.5 wt% of MWCNTs exhibited the best self-sensing capacity for a repeated compressive load with lower signal/noise ratio. Composite with 0.1 wt% MWNTs showed similar responses to the repeated compressive load as from the 0.5 wt% MWNTs composite, however, much lower sensitivity was obtained. When the dosage of the MWCNTs is lower (0.1 wt %), the distances between MWCNTs was far and could not contact with each other under compressive load. Thus, efficient conductive pathway cannot be formed and the change of electrical resistivity of composite was small. With the increasing of dosage of MWCNTs, MWCNTs may become closer and have more opportunity to connect directly to each other on a compressive loading, generating a lower electrical resistivity by forming more conductive pathways. In addition, when the MWCNTs become closer under the external compressive load, although they are not directly in contact with each other, the electrons can transfer between MWCNTs through a tunneling effect [14-15]. However, without external compressive load, a stable connection between MWCNTs and sufficient conductive pathway can form when the composites incorporating high dosage of MWCNTs. Therefore, the effect of elastic deformation of composite on the connection of MWCNTs and the electrical resistivity of MWCNTs/CC is weak.

Figure 2. The fractional change of resistivity under cyclic compressive loading with different mixing amount of MWCNTs. (a) 0.1 wt%, (b) 0.3 wt%, (c) 0.5 wt% and (d) 1.0 wt%.

4. conclusions
The following conclusions could be drawn from the above results in this study:

a) The ionic nature of the surfactant is proven to affect the electrical conductivity of MWCNTs/CC and a lower electrical resistivity can be obtained by the addition of appropriate (nonionic/nonionic) compound surfactants.

b) The incorporation of MWCNTs can greatly increase the conductivity of cement-based composites. MWCNTs/CC showed good piezoresistive response under a cyclic compressive load. A better sensitivity on stress response of composite can be obtained at a higher MWCNTs doping level.
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