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Effect of water content on the piezoresistivity of MWNT/cement composites

Baoguo Han · Xun Yu · Jinping Ou

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Abstract The piezoresistive behaviors of multi-walled carbon nanotube (MWNT)/cement composites with different water contents under uniaxial compression are investigated. Experimental results indicate that the piezoresistive sensitivities of MWNT/cement composites with 0.1, 1.3, 3.3, 5.7, 7.6, and 9.9% of water content are 0.60, 0.61, 0.73, 0.68, 0.34, and 0.06 kΩ/MPa, respectively. These findings indicate that piezoresistive sensitivities of MWNT/cement composites strongly depend on the water content in the composites. The mechanism behind the nonlinear relationship between piezoresistivity and water content is also studied via the changes of contact resistance induced by field emission effect of MWNTs in the composites.

Introduction

Recent advances in nanotechnology research have led to the development of smart sensing composites that could improve the way we detect stress/strain, crack, and damage in structural components. Carbon nanotubes (CNTs) are being considered as one of the most promising fillers for fabricating smart and multifunctional composites due to their excellent mechanical, electrical, and other physical properties. These excellent properties represent a potential for developing low cost, low operating voltage, and smart sensitive composites/sensors as candidates for various applications such as aerospace structures, biomedical, and environmental engineering equipments [1–4]. One of the new potential applications of CNTs is in the area of health monitoring of civil infrastructure. The deterioration and aging of civil infrastructure have emphasized the urgent need for structural health monitoring to improve the performance and safety of structures and reduce their maintenance costs. Cement composites have long been used as structural materials for construction. CNTs can be incorporated into the cement-matrix to produce CNT/cement composites with improved mechanical properties and electrical conductivity. The electrical conductivity of such composites could vary with external stress levels or deformations, i.e., the composites have piezoresistivity; CNT/cement composites thus become intrinsic smart sensitive composites/sensors for structural health monitoring of concrete structures, i.e., the multifunctional self-sensing materials [4–11].

Li et al. first developed piezoresistive CNT/cement composites, using multi-walled carbon nanotubes (MWNTs) treated by a mixed solution of H_2SO_4 and HNO_3 to fabricate MWNT/cement composites, and measured the piezoresistivity of these composites under uniaxial compression [8]. Later, Azhari investigated the piezoresistivity of carbon fiber (CF) and MWNT hybrid cement-based composites with different CF/MWNT ratios under uniaxial compression, and studied the relationship between the fractional change in electrical resistance and compressive stress/strain [9]. Yu et al. modified MWNTs using surface acid treatment and surfactant (sodium dodecyl sulfate, SDS) to fabricate piezoresistive MWNT filled cement paste, and investigated

B. Han · X. Yu (✉)
Department of Mechanical and Industrial Engineering, University of Minnesota, Duluth, MN 55812, USA
e-mail: xunyu@d.umn.edu

B. Han · J. Ou
School of Civil Engineering, Harbin Institute of Technology, Harbin 150090, China

J. Ou
School of Civil and Hydraulic Engineering, Dalian University of Technology, Dalian 116024, China

the piezoresistive response of composites to compressive loading [10]. Saafi studied the piezoresistive response of single-walled CNT/cement composites under monotonic tensile load, and developed the piezoresistive single-walled CNTs/cement sensors for damage detection in concrete structures [4]. Han et al. modified MWNTs by using surfactant (sodium dodecylbenzene sulfonate, NaDDBS) to fabricate piezoresistive MWNT/cement composites, and investigated the feasibility of using these composites for traffic monitoring such as vehicle detection, weighing, and speed measurement [11]. Although much effort is being concentrated on research and application of the piezoresistive CNT/cement composites, the effect of water in CNT/cement composites on the piezoresistivity needs to be investigated for real road/civil applications. This also deserves sufficient and extensive scientific investigation because the water is a mainly raw material for fabrication of cement-based composites, and the water content in the cement-based composites fluctuates under internal hydration and external environmental effects [5, 12]. In addition, the adsorption of water gives rise to the change in the intrinsic resistance of nanotubes [13–16]. Especially, the water attracted to the nanotube tip makes the highly occupied molecular orbital unstable, thereby enhancing the field emission on the nanotube tip [17–19].

In this article, the effect of the water content in MWNT/cement composites on the piezoresistivity of composites is investigated. The electrical resistances of composites with different water contents, and their responses to compressive stress under repeated compressive loadings are studied. The mechanism of how water affects the composites' piezoresistivity is also studied via the CNT field emission effects for composites with different water contents.

Materials and experimental method

Materials

The cement used is Portland cement (ASTM Type I) provided by Holcim Inc., USA. The MWNTs used are carboxyl MWNTs provided by Timesnano, Chengdu Organic Chemicals Co. Ltd. of Chinese Academy of Sciences, China. Their properties are given in Table 1. The surfactant used for dispersing the MWNTs is NaDDBS, provided by Sigma-Aldrich Co., USA. Tributyl phosphate (Sigma-Aldrich Co., USA), which is used as defoamer to decrease the air bubble

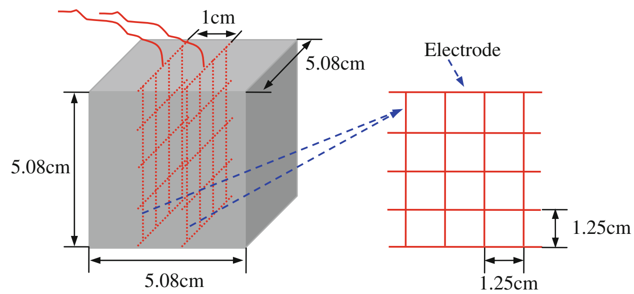


Fig. 1 Structure of MWNT/cement composites sample and arrangements of electrodes

in MWNT filled cement-based composites caused by the use of NaDDBS. Stainless steel gauzes with opening of 1.25 × 1.25 cm^2 are used as electrodes as shown in Fig. 1.

Sample preparation

The fabrication process of MWNT/cement composites is illustrated in Fig. 2. The NaDDBS (1.4×10^{-2}mol/L of concentration in water) was first mixed with water (the water/cement ratio is 0.6) using a magnetism stirrer (PC-210, Corning Inc., USA) for 3 min. Next, MWNTs (0.1% by weight of cement) were added into this aqueous solution and sonicated with an ultrasonicator (2510, Branson Ultrasonic Co., USA) for 2 h to make a uniformly dispersed suspension [10, 11]. Then, a mortar mixer was used to mix this suspension and cement for about 3 min. Finally, a defoamer in the amount of 0.25 vol% was added into the mixture and mixed for another 3 min. After the mixtures were poured into oiled molds (5.08 × 5.08 × 5.08 cm^3) and two stainless steel gauze electrodes with 1 cm apart were embedded, an electric vibrator was used to ensure good compaction. The samples as shown in Fig. 2 were then surface-smoothed, and covered with plastic films. All the samples were demolded 24 h after casing, then cured under the standard condition at a temperature of 20 °C and a relative humidity of 100% for 6 months to fully hydrate the cement. Thereafter, the samples were kept in a water bath case for 2 weeks. Finally, the samples were kept under the condition at a temperature of 20 °C and a relative humidity of 30% before testing.

Measurement

The water content and the piezoresistivity of samples were measured over a drying period of time ranging from 2 h to

Table 1 Properties of carboxyl multi-walled carbon nanotubes

Outside diameter	Inside diameter	–COOH content	Length	Special surface area	Electrical conductivity	Density
<8 nm	2–5 nm	3.86 wt%	10–30 μm	>500 m^2/g	>10^2 s/cm	~2.1 g/cm^3

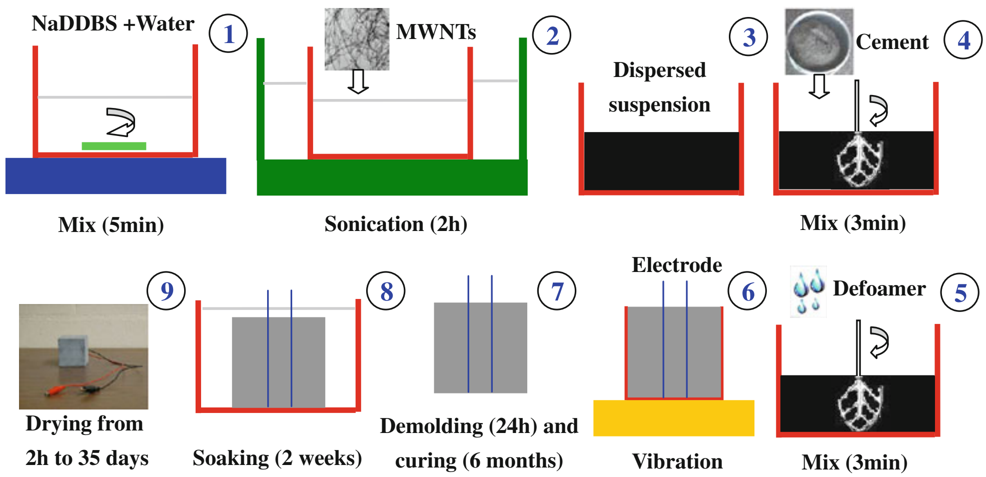


Fig. 2 Fabrication process of MWNT/cement composites samples

35 days. The water content measurement was measured using an electronic scale (PG5002-S, Mettler Toledo Inc., USA). The water content C_{w} can be denoted by

$$C_{\mathrm{w}} = \frac{W_{\mathrm{s}}^{t} - W_{\mathrm{s}}^{0}}{W_{\mathrm{s}}^{0}} \times 100\% \tag{1}$$

where W_{s}^{t} is the mass of samples, t is the time duration for drying, W_{s}^{0} is the constant mass of samples when the drying duration exceeds 28 days under the condition at a temperature of 20 °C and a relative humidity of 30%.

The lab test setup is illustrated in Fig. 3. Compressive loads were applied using a material testing machine (ATS 900, Applied Test Systems, Inc., USA). Electrical resistance was measured in the compressive stress direction perpendicular to electrodes under compressive loading. Electrical resistance measurements were made by a two-electrode method using a digital multimeter (Keithley 2100, Keithley Instruments Inc., USA). Piezoresistivity is that the electrical resistivity of MWNT/cement composites would be changed when they encounter some outside forces. According to Ohm law, the electrical resistivity ρ of samples can be expressed as

$$\rho = R \times \frac{S}{L} \tag{2}$$

where R is electrical resistance of samples, S is the sectional area of the sample, and L is the space between the two electrodes. Applying calculus mode of calculation in Eq. 2, we can obtain

$$\frac{\mathrm{d}\rho}{\rho} = \frac{\mathrm{d}R}{R} - (1 + 2\mu)\frac{\mathrm{d}L}{L} \tag{3}$$

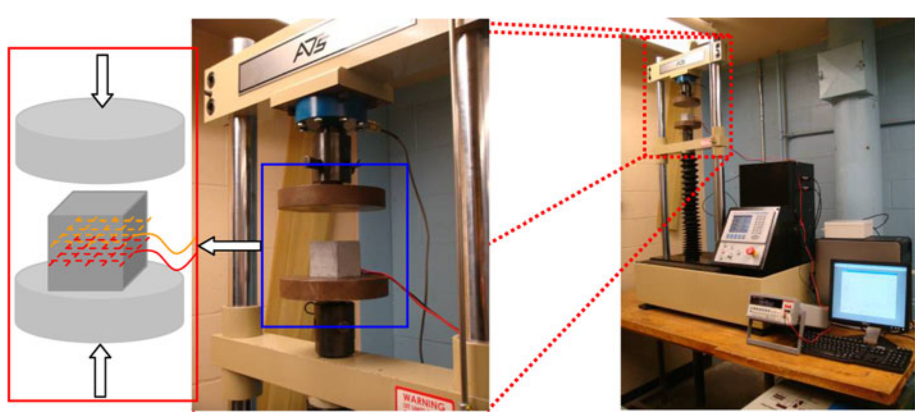
where μ is Poisson's ratio.

As the deformation of the samples under compression is very small, the changes in L can be neglected. Correspondingly the change of electrical resistivity can be denoted as

$$\Delta\rho/\rho = \Delta R/R \tag{4}$$

It can be seen from Eq. 4 that the change in electrical resistivity of samples is the same as the change in electrical resistance [20, 21]. In addition, the samples are within an elastic regime when the compressive loading amplitude is 6 MPa, so the relationship between compressive stress and compressive strain is linear [22, 23]. Because the electrical

Fig. 3 Experimental set up



resistance and compressive stress are convenient to obtain, the relationship between electrical resistance and compressive stress is taken to describe the piezoresistivity of MWNT/cement composites in this article.

All of the measurements being interfaced with a PC are automatically recorded.

Results and discussion

Figure 4 shows the piezoresistive responses of samples with different water contents under repeated compressive loading with amplitude of 6 MPa. The piezoresistive sensitivity values of k given by the formula $\left(k = \left|\frac{\Delta R}{\Delta \sigma}\right| \times 100\%\right)$ are fitted using a linear regression. As can be seen in this figure, the electrical resistance of MWNT/cement composites decreases linearly and reversibly on loading and increases linearly and reversibly on unloading in every cycle under compressive loading, exhibiting regular and stable piezoresistive responses, while composites with different water contents yield different levels of resistance changes.

The electrical resistance of CNT/cement composites comes from two sources, i.e., the intrinsic resistance of nanotubes and the contact resistance (i.e., the resistance of the matrix connecting the crossing nanotubes and through which electrical tunneling occurs) as shown in Fig. 5. The electric conductivity of individual CNTs is in the order of 10^4–10^7 s/m. However, the contact resistance at nanotube junctions is rather complicated and depends on physical characteristics of nanotubes, tunneling gap at contact points, and conductive properties of matrix filling the tunneling gap. The electrical resistance of MWNT/cement composites can be changed when they are deformed under applied loading. Several factors may contribute to the electrical resistance change. First, when MWNT/cement composites are deformed under external loading, the nanotube length and diameter will alter, resulting in the change of nanotube's intrinsic resistance, and hence, the electrical resistance of the nanotube network. However, this resistance change is expected to be negligible because of the extremely small elastic deformation in nanotubes. The second and more important factor contributing to the resistance change of the composites is the contact resistance. Under applied load, the thickness of the insulating matrix between adjacent nanotubes may be changed considerably. The compressive loading gives rise to the decrease of the gap at the contact area where electrical tunneling takes place and thus decreases the contact resistance [8, 24].

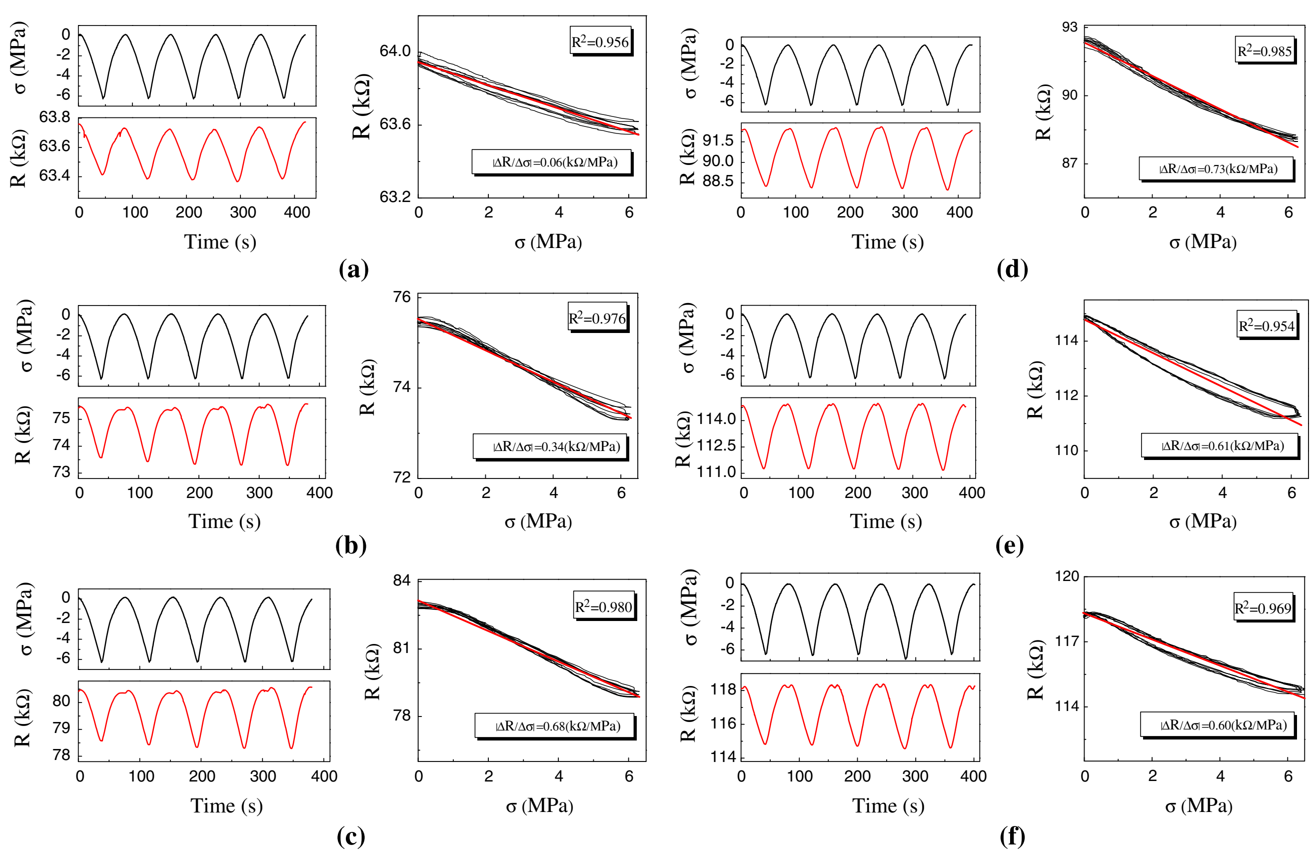


Fig. 4 Piezoresistivity of MWNT/cement composites with different water contents. **a** 9.9%, **b** 7.6%, **c** 5.7%, **d** 3.3%, **e** 1.3%, **f** 0.1%

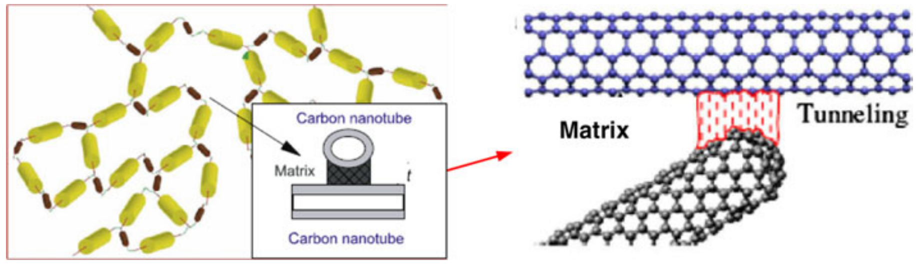


Fig. 5 A schematic diagram of conductive network in CNT/cement composites

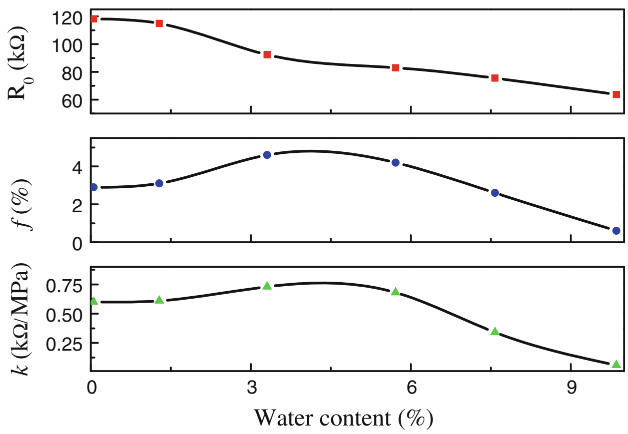


Fig. 6 Comparison of electrical resistances, maximum change in amplitudes of electrical resistance, and piezoresistive sensitivities of MWNT/cement composites with different water contents

Figure 6 shows the initial electrical resistances R_0, the maximum change amplitudes f ($f = |\frac{R_{6\,\mathrm{MPa}} - R_0}{R_0} \times 100\%|$, where $R_{6\,\mathrm{MPa}}$ is the electrical resistance of samples when the compressive stress is 6 MPa) of electrical resistance and piezoresistive sensitivities of samples with different water contents. It can be found from Fig. 6 that the maximum change amplitudes of electrical resistance and piezoresistive sensitivity of samples with 3.3% of water content are the highest among composites with different water contents. The above results indicate that the piezoresistive sensitivities of the composites first increase and then decrease with the increase of water content in the composites.

It is interesting to note that the piezoresistive sensitivity of the composites does not linearly increase with water content, but the electrical conductivity of the composites as shown in Fig. 6, increases with increasing water content. This phenomenon can be explained as follows.

Two factors would contribute to the effect of water content on the sensitivity of piezoresistive response: One, the electrical conductivity of matrix [25], and the other, the field emission effect on the nanotube tip. The electrical conductivity of matrix and the field emission effect on the nanotube tip can be enhanced by the adsorption of water molecules [17–19, 24]. When the water content is 0.1%, the electrical conductivity of matrix filling the tunneling gap is low (i.e., the contact resistance is high), and the field emission effect on the nanotube tip is weak. The conductive path is thus hard to form, even when an external force is applied to the composites. As a result, the composites possess high electrical resistance and low sensitivity to stress. With the increase of the water content to 3.3%, the electrical conductivity of matrix filling the tunneling gap increases (i.e., the contact resistance decreases) and the field emission effect on the nanotube tip is enhanced. This increases the electrical conductivity of composites. Furthermore, when the composites deform under compressive loading, the tunneling barrier of electrons will decrease and the field emission-induced tunneling can easily occur in the composites. These cause the composites to exhibit lower electrical resistance and higher piezoresistive sensitivity. With the continuous increase of water content to a higher level such as 9.9%, the electrical conductivity of matrix filling the tunneling gap further increases (i.e., the contact resistance further decreases), and the field emission effect on the nanotube tip is enhanced, and then the conductive network stabilizes and becomes hard to change under loading. As a result, a too higher water content will induce a much lower electrical resistance and a lower sensitivity to stress [22, 25–28]. Therefore, the sensitivity of piezoresistive response of MWNT/cement composites is highly influenced by the water content in the composites, as it first increases then decreases with the increase of water content in the composites.

Conclusions

The responses of electrical resistance of MWNT/cement composites with different water contents to compressive stress under repeated compressive loadings with amplitude of 6 MPa were compared. The piezoresistive sensitivities of MWNT/cement composites with 0.1, 1.3, 3.3, 5.7, 7.6, and 9.9% of water content first increase then decrease with the increase of water content in the composites. These findings indicate that the water content in MWNT/cement composites is a key factor in influencing the piezoresistivity of composites. The mechanism behind the non-linear relationship between piezoresistivity and water content was also studied via the changes of contact resistance induced by field emission effect of CNTs in the composites.

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