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Electrical characteristics and pressure-sensitive response measurements of carboxyl MWNT/cement composites

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ABSTRACT

In this study, electrical characteristics of pressure-sensitive carboxyl multi-walled carbon nanotube (MWNT)/cement composites with and without compressive loading were investigated. Experimental results indicate that the carboxyl MWNT/cement composites have both resistance and capacitance characteristics. Capacitance is insensitive to compressive loading, but the charging of the capacitor causes a linear increase in the measured resistance during DC measurement. The reversible pressure-sensitive responses of resistance to compressive loading can be extracted by removing the linear increase component. An AC measurement method can also be used to eliminate the effect of capacitor charging and discharging on the pressure-sensitive responses of carboxyl MWNT/cement composites.

1. Introduction

Recent advances in nanotechnology have opened a door for developing new cement-based composites. Carbon nanotubes (CNTs) are molecular-scale tubes of graphitic carbon with outstanding properties. They are among the stiffest and strongest fibers known, and have remarkable electrical properties and other unique characteristics. As a result of these properties coupled with high aspect ratio, small diameter, lightness, and excellent chemical and thermal stability, CNT can be used as reinforcement to produce multifunctional cement-based composites [1]. The CNT/cement composites present superior mechanical properties (e.g. high compressive, tensile and flexural strengths, and fracture toughness) [1], electrical conductivity [1], thermal conductivity [2] and damping properties [3]. The electrical behavior of CNT/cement composites is relevant to the use of these composites for developing intrinsically self-sensing composites (i.e. composites themselves are also sensors), which can be used for civil structural health monitoring, smart structures, highway traffic monitoring, border security, building facility management, etc. [4–6].

The sensing ability of CNT/cement composites is related to their pressure-sensitivity, i.e., the change of resistance with external force or deformation. Li et al. [4] firstly used multi-walled carbon nanotube (MWNT) treated by a mixture of H_2SO_4 and HNO_3 to fabricate pressure-sensitive MWNT/cement composites, and measured the pressure-sensitivity of this composite under uniaxial compression. Azhari [7] investigated the pressure-sensitivity of carbon fiber and MWNT hybrid cement composites with different CF/MWNT ratios under uniaxial compression, and setup the relationship between the fractional change in resistance and compressive stress/strain. Yu and Kwon [5] modified MWNT by using surface acid treatment and surfactant (sodium dodecyl sulfate, SDS) to fabricate pressure-sensitive MWNT/cement composites, and investigated the pressure-sensitive response of these composites to compressive loading. Han et al. [6] modified MWNT by using sodium dodecylbenzene sulfonate (NaDDBS) as surfactant to fabricate pressure-sensitive CNT/cement composites for traffic monitoring.

When measuring pressure-sensitive response of CNT/cement composites, the authors found that CNT/cement composites have complex electrical properties including resistance, capacitance and impedance characteristics. This is because there are two basic types of electrical conduction in CNT/cement composites: electronic conduction and ionic conduction. Electrons move freely within CNT, while ion movement occurs mainly in the pore solution of hydrated cement [7–13]. The pressure-sensitive response of CNT/cement composites results from electronic conduction, while ionic conduction will cause electrical polarization and affect pressure-sensitive

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response measurement of CNT/cement composites [7,14,15]. Much research effort has been concentrated on pressure-sensitive response of CNT/cement composites in recent years. However, to the best of our knowledge, work has not been reported on the measurement methods of pressure-sensitive response of CNT/cement composites under polarization effect.

The aim of this study is to investigate the electrical characteristics of CNT/cement composites and obtain effective measurement methods for pressure-sensitive response of the composites under polarization effect. Resistance and capacitance characteristics of cement composites with different concentrations of carboxyl MWNT are experimentally investigated, and two measurement methods for pressure-sensitive response of carboxyl MWNT/cement composites are proposed.

2. Materials and experimental method

2.1. Materials

The cement used is Portland cement (ASTM Type I) provided by Holcim Inc., USA. The CNT used are carboxyl MWNT provided by Timesnano, Chengdu Organic Chemicals Co. Ltd., China. The surfactant used for dispersing the MWNT is sodium dodecylbenzene sulfonate (NaDDBS) provided by Sigma–Aldrich Co., USA. Tributyl phosphate (Sigma–Aldrich Co., USA) was used as defoamer to decrease the air bubble in carboxyl MWNT/cement composites caused by use of NaDDBS. Stainless steel gauzes with opening of 1.25×1.25 cm were used as embedded electrodes.

2.2. Specimen preparation

The mixing process of carboxyl MWNT/cement composites is as follows. The NaDDBS (1.4×10^{-2}mol/L of concentration in water) was firstly mixed with water (the water/cement ratio is 0.4) using a magnetism stirrer (PC-210, Corning Inc., USA) for 3 min. Next, carboxyl MWNT (0.1% and 0.5% by weight of cement) were added into this aqueous solution and sonicated with an ultrasonicator (2510, Branson Ultrasonic Co., USA) for 3 h to make a uniformly dispersed suspension. Then, a mortar mixer was used to mix this suspension and cement for about 3 min. Finally, defoamer in an amount of 0.25 vol.% was added into the mixture and mixed for another 1 min.

After the mixes were poured into oiled molds ($5.08 \times 5.08 \times 5.08$ cm) and two electrodes (5.08×5.08 cm) were embedded with 1.5 cm apart, an electric vibrator was used to ensure good compaction. The specimens were then surface-smoothed, and covered with plastic films. All specimens were demolded 24 h after casting. Thereafter, they were cured under the standard condition at a temperature of 20°C and a relative humidity of 100% for 28 days. All specimens were dried at a room temperature and a relative humidity of about 48% for 60 days before testing.

The reduction effect of the conductive fillers on electrical resistivity of cement composites is due to the formation of a good three-dimensional conductive network in cement-matrix. As a result, the electrical resistance of electrically conductive cement composites depends upon the conductive network inside the composites. The dispersion of CNT in cement-matrix will directly affect the conductive network inside composites, thus the electrical resistance of composites and its discreteness. The composites with well dispersed CNT would present smaller resistance discreteness. Therefore, resistance discreteness of the composites can be taken as indicators to evaluate the dispersion of CNT in the cement matrix. The relative standard deviation of electrical resistance of both types of specimens with 0.1% and 0.5% of carboxyl MWNT are less than 8%. This indicates that carboxyl MWNT are uniformly dispersed in cement-matrix.

2.3. Measurement

The test setup in lab is illustrated in Fig. 1. Resistance and capacitance of the specimens without loading were measured by using a handheld LCR meter (U1732A, Agilent Technologies, Inc., USA). Since cement composites are usually taken as pressure-bearing part of engineering structures in real applications, the pressure-sensitivity of carboxyl MWNT/cement composites is investigated under compressive loading in this study. A repeated compressive loading with stress amplitude of 6 MPa was applied using a material testing machine (ATS 900, Applied Test Systems, Inc., USA). Under the compressive loading, resistance and capacitance of the specimens in compressive stress direction perpendicular to electrodes were measured by using a digital multimeter (Keithley Instruments Inc., USA) and the Agilent U1732A LCR meter, respectively.

When an AC measurement method is used, pressure-sensitive carboxyl MWNT/cement composites are series-connected with a constant reference resistance as shown in Fig. 1 and we have

$$\frac{V'_C}{R'_C} = \frac{V_P - V'_C}{R_R} \quad (1)$$

where R'_C and R_R are the resistance of the cement composites and the constant reference resistance respectively. V'_C is the measured voltage at both ends of the cement composites. V_P is the voltage supplied by an external AC stabilified-voltage power.

Eq. (2) can be further derived as

$$R'_C = \frac{V'_C}{V_P - V'_C} R_R \quad (2)$$

If the composites are subjected to compressive loading, their resistance will vary. The change in resistance of the composites $\Delta R'_C$ can be expressed as

$$R'_C + \Delta R'_C = \frac{V'_C + \Delta V'_C}{V_P - (V'_C + \Delta V'_C)} R_R \quad (3)$$

where $\Delta V'_C$ is the change in the voltage at both ends of the composites.

Since $\Delta V'_C$ is much smaller than $(V_P - V'_C)$, Eqs. (2) and (3) can be combined and derived as

$$\frac{R'_C + \Delta R'_C}{R'_C} = \frac{V'_C + \Delta V'_C}{V_P - (V'_C + \Delta V'_C)} \times \frac{V_P - V'_C}{V'_C} \approx \frac{V'_C + \Delta V'_C}{V'_C} \quad (4)$$

Eq. (4) can be further rewritten as

$$\frac{\Delta R_C}{R_C} \approx \frac{\Delta V'_C}{V'_C} \quad (5)$$

It can be seen from Eqs. (1) and (5) that the change in resistance signal of composites caused by compressive loading is approximatively equal to that in voltage signal at both ends of the composites. Because the voltage signal is convenient to acquire, the AC voltage at both ends of the composites is taken as indices for describing pressure-sensitive response during the AC measurement. The voltage in circuit as shown in Fig. 1 was provided by an AC stabilified-voltage power (15VAC, Cui Inc., USA). The AC voltage signal at both ends of the composites was measured with a Keithley 2100 digital multimeter. All the experiments were conducted at room temperature.

3. Results and discussion

3.1. Resistance and capacitance of carboxyl MWNT/cement composites without compressive loading

Fig. 2 shows the electrical resistivity and capacitance of carboxyl MWNT/cement composites under different test frequencies.

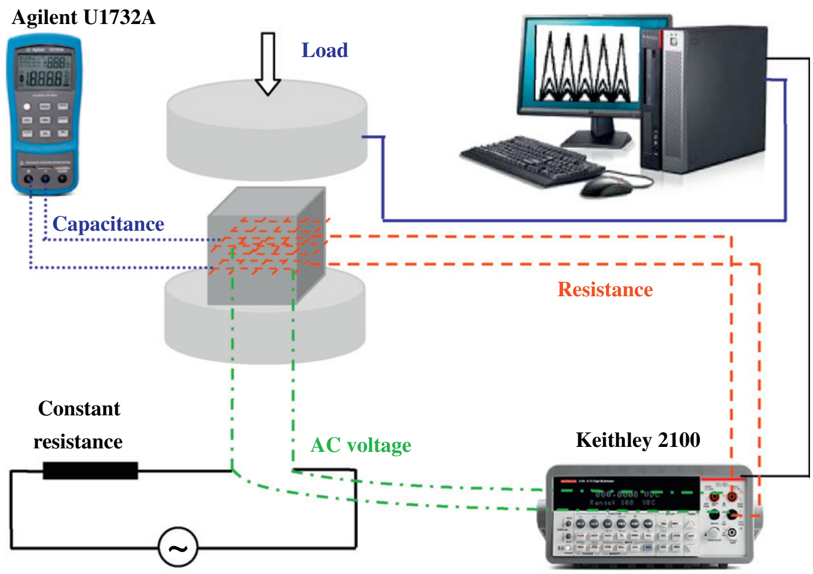

Fig. 1. Sketch of loading test and three measurement circuits.

It can be seen from Fig. 2a that the electrical resistivity of the specimens with different CNT concentrations both decreases with the increase of test frequency. This can be attributed to the effect of the capacitance characteristic of carboxyl MWNT/cement composites as shown in Fig. 2b. Additionally, a higher test frequency leads to a lower capacitance, which is consistent with the conventional capacitive mechanism. The above results indicate that the carboxyl MWNT/cement composites have both resistance and capacitance characteristics. Furthermore, according to the conductive model of CNT/cement composites as shown in Fig. 3, the cement composites with 0.5% CNT have better CNT conductive network (i.e. lower R_C) and larger number of interface capacitance (i.e. higher C_{int}) than those with 0.1% CNT. As a result, the composites with 0.5% CNT have lower electrical resistivity than those with 0.1% CNT, while the former present higher capacitance.

Fig. 4 depicts the variation of DC resistance with test time for carboxyl MWNT/cement composites without loading. As shown in Fig. 4, the measured resistance increases rapidly during the initial stage of measurement. After that, the measured resistance first quickly and then slowly increases with test time. This phenomenon can be explained as below. The specimens with capacitance characteristic like capacitor, and will be charged during the measurement of resistance. This will generate a current opposite to the current within multimeter when a multimeter is used to measure the resistance of specimens as shown in Fig. 5. The resistance R'_A (i.e., apparent resistance, to be distinguished from the true resistance R'_C) of specimens can be expressed as

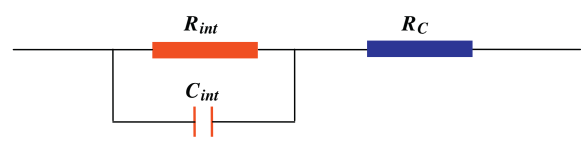

Fig. 3. Conductive model of CNT/cement composites [16], R_C is the resistance of CNT in CNT/cement composites, R_{int} and C_{int} are the interface resistance and the interface capacitance in CNT/cement composites respectively.

$$R'_A = \frac{V}{I - I_C(t)} \tag{6}$$

where V and I are respectively voltage and current in the circuit within multimeter. $I_C(t)$ is the charging current of capacitor.

The charging of capacitor during the initial test stage is faster than that during the subsequent test stages, so the measured resistance exhibits a three-stage variation trend of rapid increase, fast increase and low increase as shown in Fig. 4.

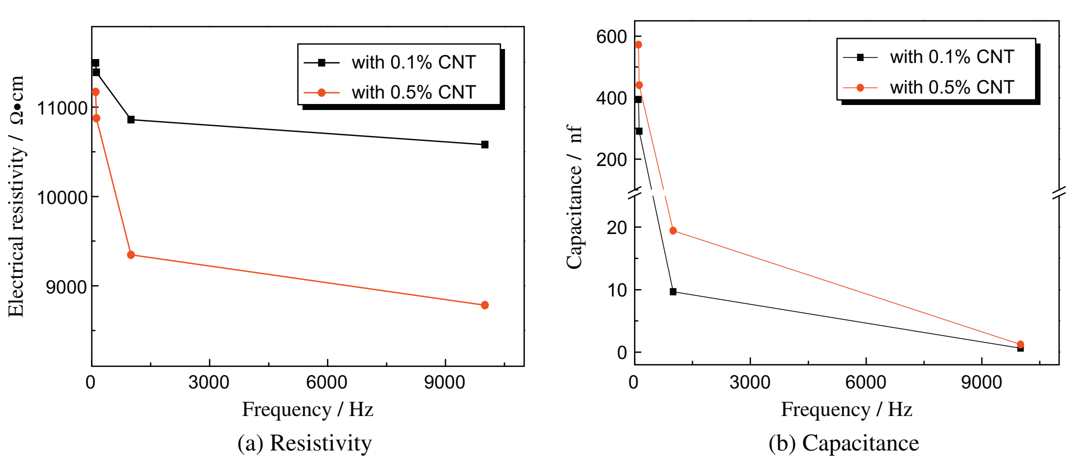

Fig. 2. Electrical resistivity and capacitance of carboxyl MWNT/cement composites with different CNT concentrations.

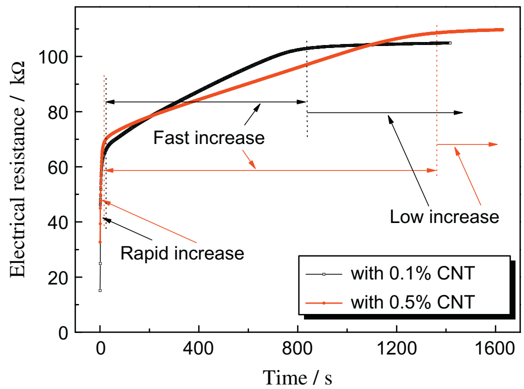

Fig. 4. Variation of measured resistance with test time for carboxyl MWNT/cement composites.

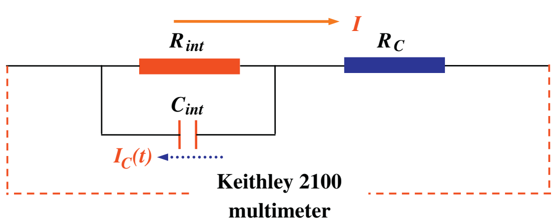

Fig. 5. Equivalent circuit during DC measurement.

3.2. Response of capacitance of carboxyl MWNT/cement composites to compressive loading

Fig. 6 shows the variation of capacitance of carboxyl MWNT/cement composites under compressive loading. It can be seen from Fig. 6 that the capacitance of the specimens increases slightly during both loading and unloading under different test frequencies. There is not regular corresponding relationship between compressive stress and capacitance of the specimens. This indicates that the compressive loading only causes a little insensitive and irregular change in capacitance.

3.3. Response of resistance of carboxyl MWNT/cement composites to compressive loading

Since the change in resistance trends to be stable in the 'low increase' stage as shown in Fig. 4, we measure the response of resistance of carboxyl MWNT/cement composites to compressive loading at this stage. The relationship curves between resistance (R'_A) and compressive stress (σ) are illustrated in Fig. 7. This figure shows that the measured resistance of the specimens decreases upon loading and increases upon unloading in every cycle under the repeated compressive loading with amplitude of 6 MPa. However, the initial value of resistance in each loading and unloading cycle increases with the number of cycles. Because compressive loading hardly cause any change in capacitance of specimens, the compressive loading only leads to the reversible change of the true resistance of specimens (R'_C). In addition, as can be seen from Fig. 7, the increase in measured resistance caused by the capacitor charging is approximately linear. Therefore, we remove the linear component in the measured resistance to obtain the pressure-sensitive response of the composites. The resistance signals after removing the linear component are given in the two top traces in Fig. 7. The two subfigures show that the change of resistance ($\Delta R'_C$) decreases reversibly during compressive loading and increases reversibly during unloading in every cycle. This further proves that the pressure-sensitive responses of carboxyl MWNT/cement composites can be extracted by eliminating the linear increase component in the measured resistance.

3.4. Response of AC voltage of pressure-sensitive carboxyl MWNT/cement composites to compressive loading

Fig. 8 gives the response of AC voltage of pressure-sensitive carboxyl MWNT/cement composites to compressive loading. As shown in this figure, the AC voltages (V'_C) of the two kinds of specimens both present stable and reversible pressure-sensitivity. This is because the capacitor allows the alternating current to pass as shown in Fig. 9. The AC measurement method avoids the effect of capacitor charging and discharging on the pressure-sensitive response of the composites. Therefore, the AC voltage signals can be directly used to describe the pressure-sensitive responses of carboxyl MWNT/cement composites.

3.5. Effect of AC voltage amplitude on pressure-sensitive sensitivity of carboxyl MWNT/cement composites

When the pressure-sensitive carboxyl MWNT/cement composites are series-connected to different values of constant resistance, the amplitude of the measured AC voltage at both ends of the CNT/cement composites is different. Fig. 10 shows the pressure-sensitive responses of specimens with 0.5% CNT under different amplitudes of measured AC voltage. It can be seen from Fig. 10a–e that

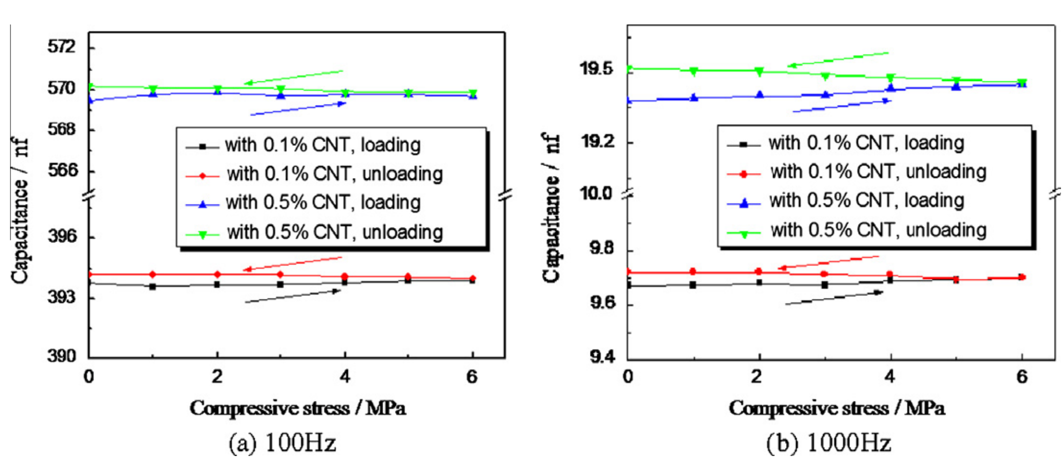

Fig. 6. Response of capacitance of carboxyl MWNT/cement composites to compressive loading.

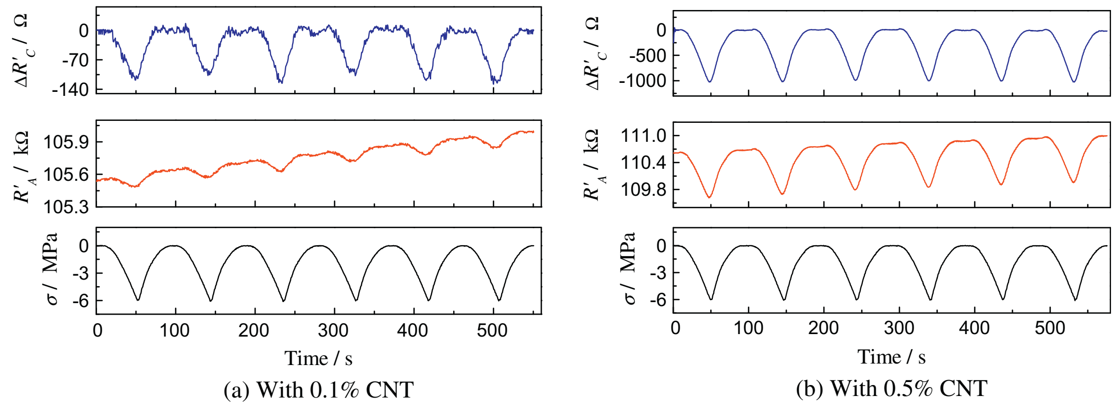

Fig. 7. Response of resistance of pressure-sensitive carboxyl MWNT/cement composites to compressive loading.

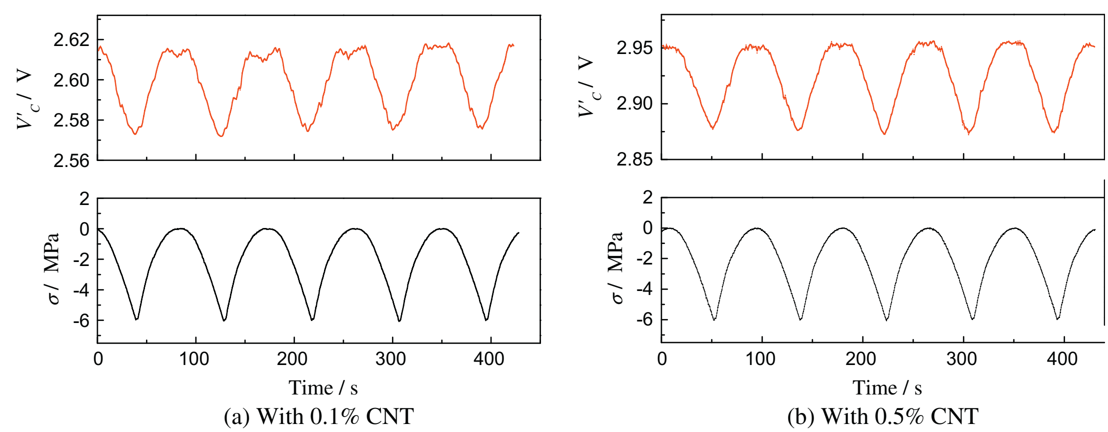

Fig. 8. Response of AC voltage of pressure-sensitive carboxyl MWNT/cement composites to compressive loading.

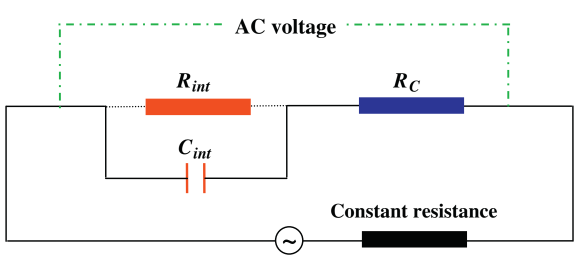

Fig. 9. Equivalent circuit during AC measurement.

the change trends of pressure-sensitivity under different voltage amplitudes are similar, but the pressure-sensitive curves are smoother and more regular at lower voltage amplitudes. This indicates that the smaller AC voltage signals have higher signal to noise ratio. In addition, it is noted from Fig. 10a–e that the same compressive stress yields different levels of change in AC voltage signals. Fig. 10f summarizes the fractional change in voltage at different amplitudes of AC voltages. This subfigure shows that the fractional change in voltage, i.e. the sensitivity of pressure-sensitive response of specimens, increases with the decrease of AC voltage amplitude. This is because higher voltage amplitude at both ends of the cement-based composites is easier to induce capacitor charging and discharging during the test. As a result, the lower amplitude of AC voltage is more beneficial for eliminating the effect of capacitance on the pressure-sensitive responses of carboxyl MWNT/cement composites.

4. Conclusions

The electrical properties of cement composites with 0.1% and 0.5% of carboxyl MWNT were experimentally studied, and two measurement methods for pressure-sensitive responses of carboxyl MWNT/cement composites were proposed. The research results show that the carboxyl MWNT/cement composites have both resistance and capacitance characteristics. The resistance of the composites is sensitive to compressive loading, but the capacitance is insensitive. Due to the effect of capacitor charging, the resistance of composites exhibits a three-stage variation trend of rapid increase, fast increase and low increase during the DC resistance measurement. The reversible pressure-sensitive responses of resistance to compressive loading can be extracted by removing the linear increase component in the measured resistance, which is caused by the capacitor charging. In the DC method, resistance can be directly measured. However, one disadvantage of the DC measurement method is that a pre-power time is needed to let resistance reach its linear increase stage. The AC measurement method is more convenient than the DC one. It can directly eliminate the effect of capacitor charging and discharging on the pressure-sensitive responses of carboxyl MWNT/cement composites, since the capacitor allows the alternating current to pass. A low-amplitude AC voltage is helpful for improving the pressure-sensitive sensitivity of the composites.

The measurement of pressure-sensitive response is a basic issue not only for pressure-sensitive CNT/cement composites, but also for pressure-sensitive cement composites with other fillers. This paper addresses this issue and seeks to provide effective measurement methods for pressure-sensitive cement composites under

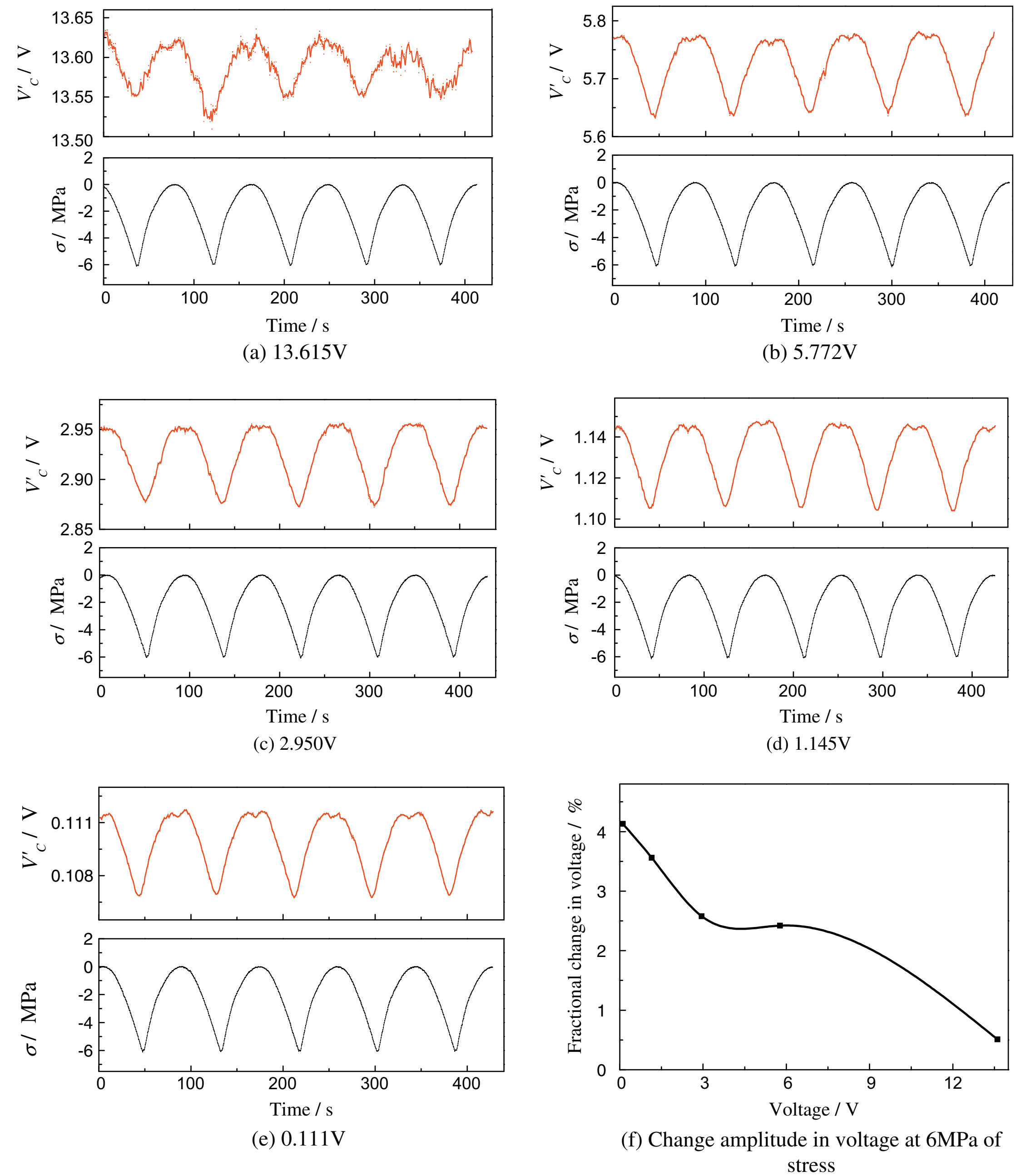

Fig. 10. Comparison of pressure-sensitive responses of carboxyl MWNT/cement composites under different amplitudes of measured AC voltages.

polarization effect. The proposed measurement methods in this study can lay foundation for research and application of this kind of cement composites.

Acknowledgments

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