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16. Abstract This research project developed self-sensing carbon-nanotube (CNT)/cement composites. The piezoresistive property of carbon nanotubes enables the composite to detect the stress/stain inside the pavement. Meanwhile, CNTs can also work as the reinforcement elements to improve the strength and toughness of the concrete pavement. Experimental results show that the electrical resistance of the composite changed proportionally to the compressive stress levels. The piezoresistive responses of the composite with different fabrication methods are also studied. Lab tests and road tests were performed to test the self-sensing concrete. Controlled dynamical loads were applied on the sensors. Experimental results demonstrated that the CNT/cement composite function as excellent stress/strain sensors.			
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Carbon Nanotube Based Self-sensing Concrete for Pavement Structural Health Monitoring

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Final Report

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Executive Summary

This project report summarizes the development of self-sensing carbon-nanotube (CNT)/cement composites. The piezoresistive property of carbon nanotubes enables the composite to detect the stress/strain inside the pavement. Meanwhile, CNTs can also work as the reinforcement elements to improve the strength and toughness of the concrete pavement.

Piezoresistive CNT/cement composites are developed and tested in this study. Experimental results show that the electrical resistance of the composite changed proportionally to the compressive stress levels. The piezoresistive responses of the composite with different fabrication methods are also studied. The CNT acid-treated method showed stronger piezoresistive response and higher signal-to-noise ratio than the surfactant-assistant dispersion method, in which the surfactant could block the contacts among nanotubes thus impairing the piezoresistive response of the composite. However, the acid-treatment of CNTs is difficult to scale up for larger samples. The involvement of strong acids also makes it hard to be implemented in the field. The surfactant wrapping of CNTs is also effective to disperse CNTs into the cement matrix and give promising piezoresistive properties.

A set of lab and road tests were performed to test the effectiveness of the self-sensing concrete by applying dynamic loads under the controlled environment. Experimental results demonstrated that the CNT/cement composite function as excellent stress/strain sensors.

Chapter 1 Introduction

Highway structures, such as concrete pavement and bridges, continuously deteriorate as a result of strain/stress, cracking, delamination and other damages. The capability to detect such damages in civil infrastructures as early as possible is critical for the safety of public. While various methods have been developed to monitor the performance and state of the pavement structure, there is still no effective and low cost method to continuously monitor the structural health of a large pavement area. Currently, most methods developed to date for concrete pavement structural health monitoring use embedded sensors, such as electric-resistance strain gauges, optic sensors and piezoelectric ceramic sensors that are inserted in key structural positions [1-3]. However, these sensors are for localized point monitoring only and have the drawbacks of poor durability, high cost and expensive analysis equipments, low survival rate, low sensitivity, and unfavorable compatibility with concrete structures. This research will focus on developing a new nanotechnology based self-sensing concrete for monitoring the structural health conditions of the pavement. In the new pavement structure, the concrete is mixed with carbon nanotubes (CNTs), which form an internal electrical network and the piezoresistive properties of the carbon nanotubes will enable the concrete to detect the changes of mechanical stress. CNTs can also work as the concrete reinforcement element that could enhance the strength and durability of the pavement structures. This new sensor and concrete are homogeneous cement-based material, so the resulting sensing system will have the same service life as a concrete structure and possess good compatibility with the concrete pavement structure.

Carbon nanotubes (CNTs) are seamless tubular structures rolled up forming a one-atom sheet of graphite, with diameter in the order of a nanometer (10^{-9} m). The nanotubes may consist of one shell of carbons (single-walled carbon nanotubes (SWNTs)), or up to tens of concentric shells of carbons (multi-walled carbon nanotubes (MWNTs)). The diameters of CNTs are in the range of 1~20 nm, and the lengths are in the range of 0.2~5 μ m.

Since the discovery of CNTs by S. Iijima in 1991 [4], carbon nanotubes have been widely used for a variety of applications due to their excellent physical properties: high strength (the Young's modulus of individual CNTs is about 1.8 TPa) [5], metallic or semi-conductive electrical properties depending on their roll up chirality [5]; and high aspect ratio (>500). The extremely high aspect ratio of CNTs makes them easy to form a conductive and reinforcement network with doping level as low as 0.1% wt of CNTs [6-8]. Carbon nanotubes also have interesting electromechanical properties.

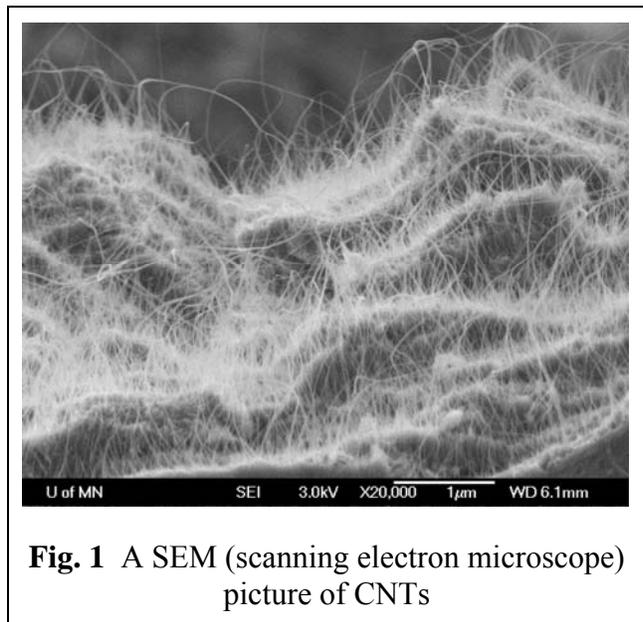


Fig. 1 A SEM (scanning electron microscope) picture of CNTs

When subject to stress/strain, the electrical properties of CNTs will change with the level of stress/strain, expressing a linear and reversible piezoresistive response [9-12, 25]. Most of those prior works were performed with individual nanotubes or nanotube membranes. Recently, CNT/polymer composites have also been investigated for strain/stress sensing [13, 26-27]; their results also show linear electrical resistance changes with respect to the strain/stress and the sensitivity is 3.5 times of regular strain gage. These previous works show that CNT based composite could be a promising stress/strain sensor. However, no study to date has been performed on the piezoresistive responses of the CNT/cement composites. Since the properties of cement are much different from polymers, it would be very interesting to investigate the electromechanical property of the CNT/cement composite, and how the interface between CNTs and cement will influence the electromechanical property of the composite.

On the other hand, with the advances of CNT synthesis techniques, the price of CNTs has decreased dramatically in recent years. For example, MWNT can be purchased at \$0.2/g (TimesNano, China). The decreasing price and the ultra low needed doping level of CNTs enable them possible to be used in large structures, e.g., concrete pavements, which had not been investigated by previous studies.

A literature survey reveals very few previous research efforts on the CNT/cement composites. Li *et. al.* studied the mechanical properties of CNT/cement composites [14]. They found that the compressive strength and flexural strength of the 0.5% CNT cement composites were increased by 19% and 25% respectively, compared to the un-reinforced cement. However, they did not study the piezoresistive properties of CNT/cement composites. Another research group in Canada conducted a similar mechanical reinforcement study but not the piezoresistive behavior of the composites [20].

It should be noted that another class of carbon material – carbon fibers (CFs), have been extensively studied as reinforce elements in cement concrete. CFs are different from CNTs with much larger diameters (1~15 μm), smaller Young's modulus (~560 MPa) and aspect ratio [15]. The piezoresistivity and piezoelectric properties of CF/cement have also been investigated by Chung *et. al.* [16-18] and Sun *et. al.*[19]. However, it was found that the piezoresistivity and piezoelectric of the CFs would be *irreversible* due to the fiber breakage when the strain was larger than 0.2% [16]. Therefore, CF/cement composite is not appropriate as a strain/stress sensor to detect heavy stresses of traffic flows. On the contrary, Tombler *et. al.* found that the piezoresistive characteristics of CNTs were highly reversible even for a huge strain of 3.4% [9]. This indicates CNT/cement could be a promising distributed strain/stress sensor for structural health monitoring of civil infrastructures.

Chapter 2

Fabrication of CNT/Cement Composites

In order to form a conductive network and explore their physical properties, CNTs need to be fully dispersed in cement matrix. However, CNTs tend to aggregate together in most solvents, due to van der Waal's forces, and form nanotube clusters and bundles. To be dispersed in aqueous solvent, CNTs' surfaces have to be modified such as by using surfactants (e.g. sodium dodecyl sulfate (SDS) and Triton X-100) or by surface acid-treatment. In this research, we used two CNT surface modification methods to functionalize and disperse CNTs for the fabrication of CNT/cement composites, the composite properties were compared for both methods.

In this study, 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. Figure 2 shows a scanning electron microscope (SEM) picture of the received MWNTs.

Table 1. Properties of carboxyl multi-wall carbon nanotubes

Parameters	Values
Outside diameter	<8nm
Inside diameter	2~5nm
-COOH content	3.86 wt.%
Length	10~30 μ m
Purity	>95%
Ash	<1.5 wt.%
Special surface area	>500 m ² /g
Electrical conductivity	>10 ² s/cm
Density	~2.1 g/cm ³

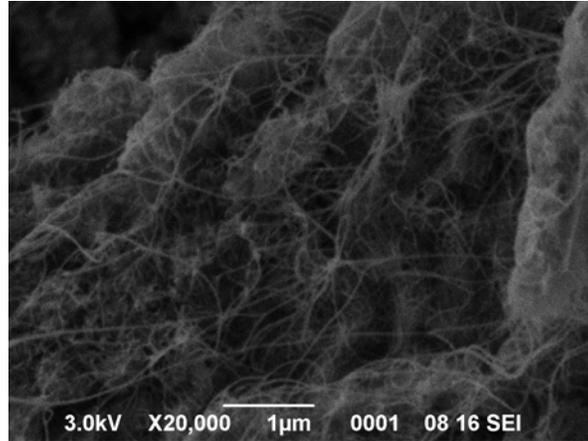


Fig. 2 SEM picture of as-received MWNTs

Method #1: In our previous studies on the fabricating transparent conductive CNT thin films [21, 22], CNTs have been successfully dispersed in water by treating CNTs with a mixture of sulfuric acid and nitric acid for an adequate length of time. It is well known that, during acid treatment, oxygen atoms from acids react with carbon atoms on the nanotubes, especially on the ends, curvatures, and defects of the nanotubes where carbon atoms are more reactive [23]. Negatively charged carboxylic groups will be introduced on the SWNT surfaces as a result of the oxidation (covalent surface modification). The electrostatic repulsion force between these negative charges can be utilized to disperse SWNTs in water without any surfactant. Fig. 3 shows a diagram of this proposed fabrication process for CNT/cement composites. Acid-treated MWNTs were dispersed in water and then mixed with Portland cement (Type I) without adding sand or aggregate, the water/cement ratio was 0.6 and MWNT is 0.1% weight of cement. The CNT/cement pastes were molded into $50.8 \times 50.8 \times 50.8 \text{ mm}^3$ shapes. The sample was de-molded in one day, cured in water for 20 days, and then dried in air at room temperature for 10 days.

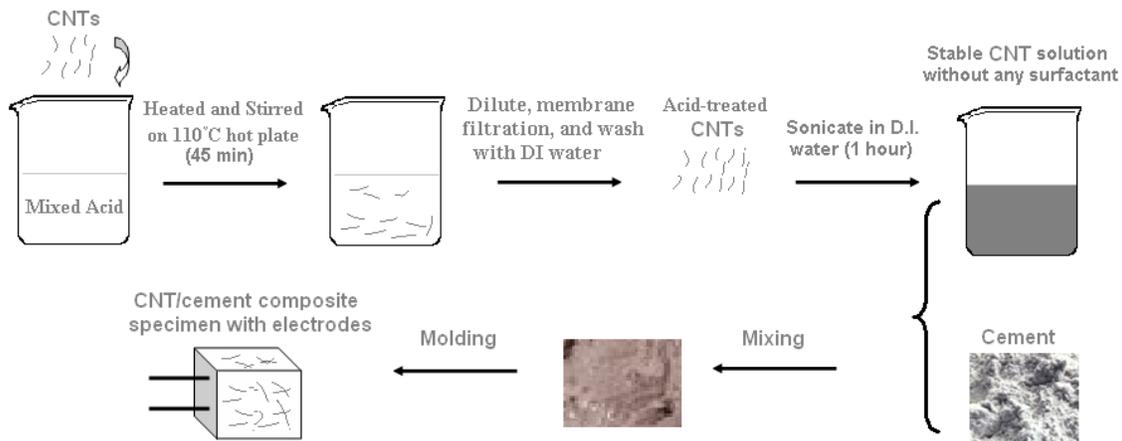


Fig. 3 Illustration of the CNT/cement fabrication process based on the acid treatment of CNTs

Method #2: An alternative method of dispersing CNTs in cement matrices is to use non-covalent surface modification for CNT surfaces, as opposed to the above covalent surface modification. With non-covalent interactions, surfactants can be wrapped around the nanotubes, which in turn can render CNTs to be dispersed in aqueous solution and mixable with cement. In this project, surfactant sodium dodecylbenzene sulfonate (NaDDBS) was used. The critical micelle concentration of 1.4×10^{-2} mol/L of NaDDBS was used as the input surfactant concentration. The surfactant was firstly mixed with water (the water/cement ratio is 0.6:1) using a magnetism stirrer (PC-210, Corning Inc., USA) for 3 minutes. 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 hours to make a uniformly dispersed suspension. Then, a mortar mixer was used to mix this suspension and cement for about 3 minutes. Finally, a defoamer in the amount of 0.25 vol. % of cement was added into the mixture and mixed for another 3 minutes. After pouring the mixes into molds and embedding two electrodes with 1cm 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 hours 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 temperature of 50°C for five days before testing.

Fig. 4 shows the picture of the fabricated CNT/cement composite samples and the illustration of the electrodes. Fig. 5 shows a SEM picture of the microstructure of the CNT/cement sample.

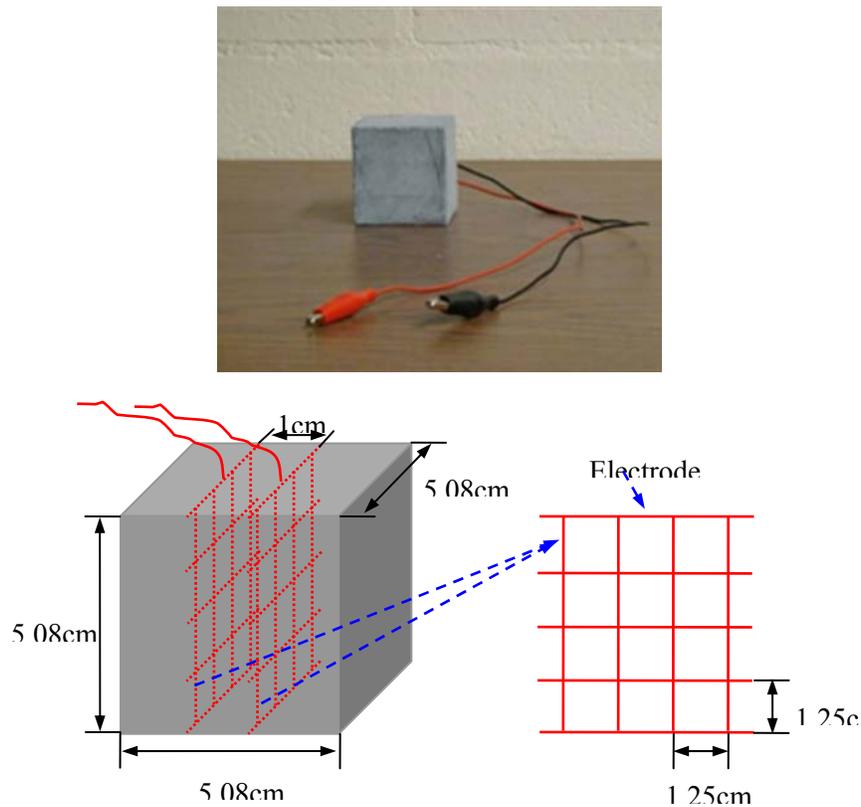


Fig. 4 Picture of CNT/cement composite sample and the illustration of electrodes

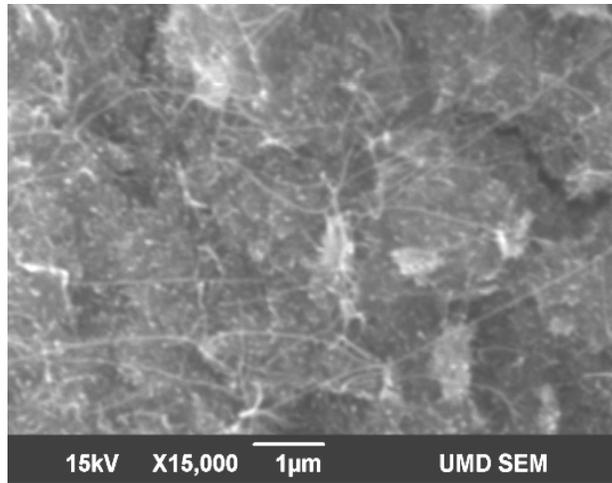


Fig. 5 SEM Picture of the microstructure of the CNT/cement composite sample

Chapter 3

Piezoresistive Properties of CNT/Cement Composites

The piezoresistive responses of the CNT/cement composite were first tested in the laboratory before being tested for traffic flow detection. The lab test setup is illustrated in Fig. 6. Compressive loads were applied using a material testing machine (ATS 900, Applied Test Systems, Inc., USA). Electrical resistance is measured in the compressive stress direction perpendicular to electrodes under repeated compressive loading and impulsive loading. Electrical resistance measurements were made by a two-electrode method using a digital multimeter (Keithley 2100, Keithley Instruments Inc., USA). All of the measurements interfaced with a PC are automatically recorded.

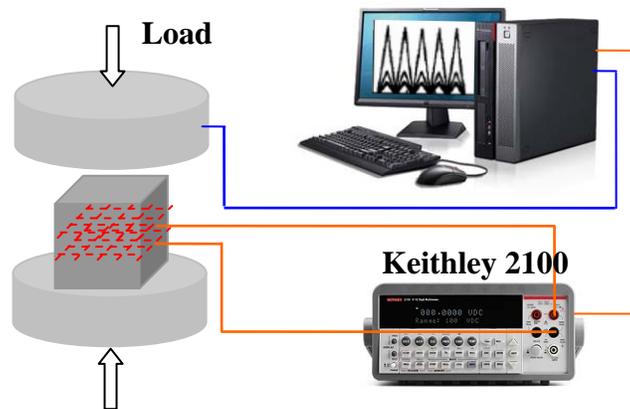


Fig. 6 Sketch of experimental equipments for repeated compressive loading and impulsive loading

3.1. Piezoresitivity of CNT/cement composite made by Method #1 (acid-treatment of CNTs)

Fig. 7 shows the piezoresistive responses of the composite fabricated with method #1(acid-treatment method) with 0.1 wt% MWNTs. As can be seen, the electrical resistance changes linearly with the compressive stress and the changes are proportional to the stress levels.

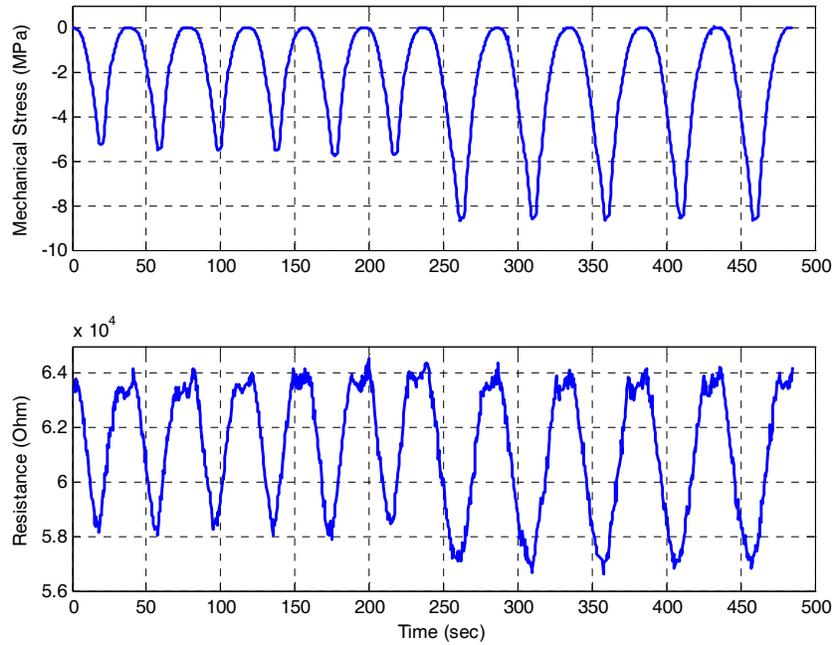
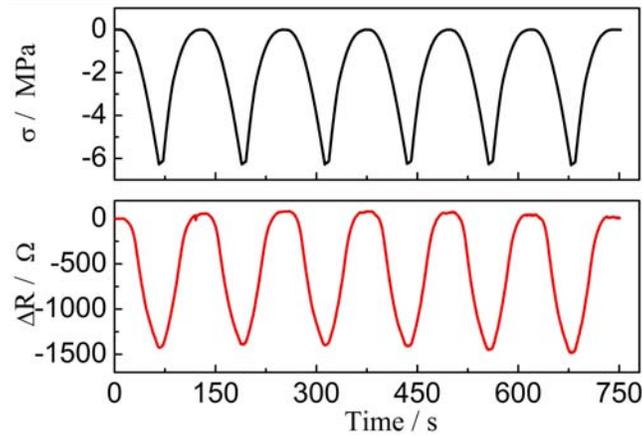


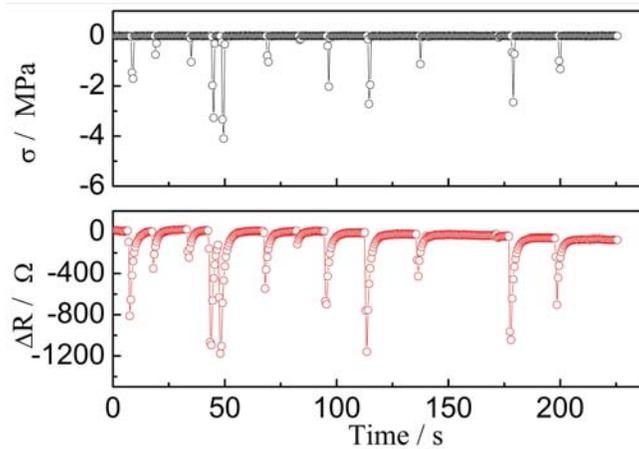
Fig. 7 Piezoresistive response of CNT/cement composite fabricated by method #1 (acid-treatment).

3.2 Piezoresitivity of CNT/cement composite made by Method #2 (surfactant wrapping of CNTs)

Fig. 8 depicts the variation of the electrical resistance R of the self-sensing CNT/cement composite under repeated compressive loading and impulsive loading. Fig. 8a) shows that the electrical resistance of the composite decreases upon loading and increases upon unloading in every cycle under repeated compressive loading with amplitude up to 6MPa. It indicates that the response of electrical resistance of this composite to compressive stress σ is regular under repeated compressive loading. The change in electrical resistance ΔR (i.e. $R - R_0$, where R_0 is the initial electrical resistance of specimens without compressive loading) reaches about 1500 Ω maximum as compressive stress is 6MPa. As shown in Fig. 8b), the impulsive loadings also cause regular changes in the electrical resistance of self-sensing CNT/cement composite. According to these results, it can be seen that the response of electrical resistance of self-sensing CNT/cement composite to compressive stress is reversible and sensitive, which means that the self-sensing CNT/cement composite has excellent sensing capability.



a) Under repeated compressive loading with amplitude of 6MPa



c) Under impulsive loading

Fig. 8 Relationships between compressive stress and electrical resistance of the self-sensing CNT/cement composite.

3.3 Discussion on the piezoresistive mechanism of the CNT/cement composite

The piezoresistivity for the composites with CNTs is caused by the following four reasons. (1) the electrical conductivity of CNTs varies under external stress (according to Tomblar et. al.[24], the electrical resistance of CNTs will increase 100 times when strain changes from 0.0% to 3.2% under tensile loading. CNT's resistance thus will decrease under compressive loads); (2) the number of contact points of CNTs increases with the increase of compressive loading, which can cause an enhancement of conductivity; (3) the separation distance between CNTs decreases under compressive loading, which can cause an enhancement in tunneling effect conduction; (4) the field induced tunneling effect enhances due to compressive loading [25-29]. According to the Fowler-Nordheim theory, CNTs have a strong field emission effect under electric field [27]. The smaller the diameter of CNTs, the higher the field emission effect (CNTs used in this study is the MWNTs with the smallest diameter, which is smaller than 8nm). The local high electrical

field in composites increases the potential energy of electrons through tunneling barrier between CNTs, which causes the enhancement in tunneling effect conduction. Furthermore, when the composites are deformed under compressive loading the separation between CNTs will be reduced, i.e. the tunneling barrier to be transited by electrons will decrease and the field induced tunneling can more easily occur in the composites [30, 31]. As a result, the piezoresistivity of MWNTs filled cement-based composites are strongly influenced by the conductive network in composites.

Comparing the experimental results in Fig. 7 and Fig. 8, it can be seen that the composite made by Method #1 has higher piezoresistive response than those from Method #2. This difference of piezoresistive response between two composites made with different methods could be attributed to the different nanotube to nanotube interfaces. In the Method #1, CNTs are dispersed in cement matrix without any surfactant. Therefore the nanotubes could contact directly with each other in the CNT network. However, for the Method #2, the nanotube surfaces are wrapped with surfactants (SDS). Therefore, nanotube contacts could be blocked by the surfactant between nanotubes, which impedes the piezoresistive response levels.

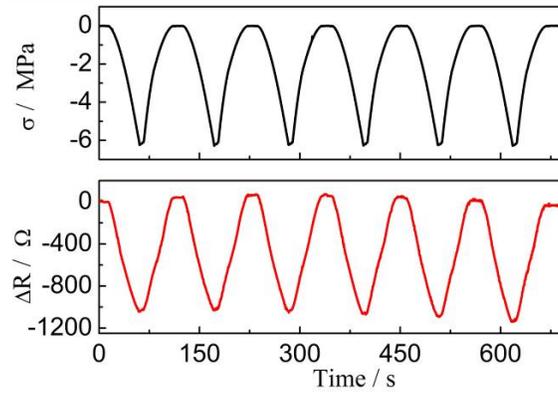
3.4 The effect of CNT concentration level on the piezoresistivity of CNT/cement composites

To study the effects of the CNT concentration level on the piezoresistive sensitivity, CNT/cement composites with different MWNT concentration levels are fabricated and their electrical responses to compressive stress are studied. Table 2 describes the mix proportions of the three types of CNT/cement composites in this study. The experiment is designed to find the effect of CNT concentration level from samples #1, #2, #3.

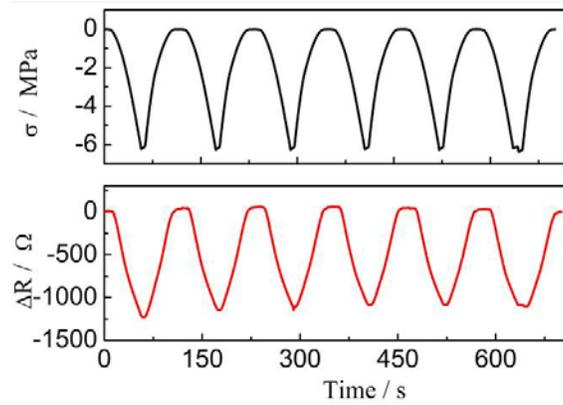
Table 2. Mix proportions of three types of CNT/cement composites

Sample	CNT/cement ratio	Water/cement ratio	Surfactant		Defoamer vol. %
			Type	Concentration	
#1	0.05%	0.45	NaDDBS	1.4×10^{-2} mol/L	0.25
#2	0.1%	0.45	NaDDBS	1.4×10^{-2} mol/L	0.25
#3	1%	0.45	NaDDBS	1.4×10^{-2} mol/L	0.25

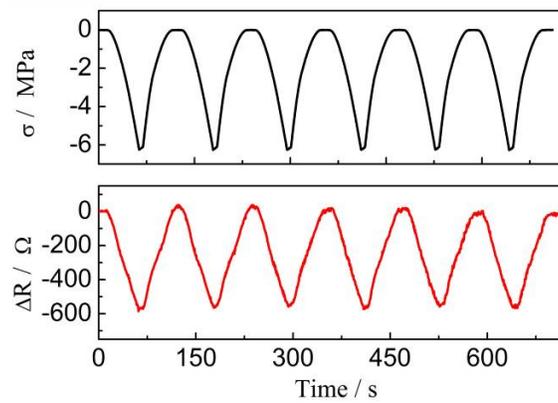
Fig. 9 shows the piezoresistive responses under repeated compressive loading with amplitude of 6MPa for samples #1, #2 and #3. As can be seen in Fig9, the electrical resistance R of all the three types of CNT/cement composites decreases upon loading and increases upon unloading in every cycle under compressive loading, expressing stable and regular piezoresistive responses.



a) With 0.05 wt.% of MWNT (Sample #1)



b) With 0.1 wt.% of MWNT (Sample #2)



c) With 1 wt.% of MWNT (Sample #3)

Fig. 9 Piezoresistivity of CNT/cement composites with different MWNT concentration levels

Fig.10 depicts the change amplitudes of the electrical resistance for samples #1, #2 and #3 as the compressive stress is 6MPa. As shown in Fig.10, we find that the change in electrical resistance

of samples #1, #2 and #3 reaches about 1000Ω , 1150Ω and 600Ω respectively as compressive stress is 6MPa. This indicates that the CNT/cement composite with 0.1 wt. % of MWNT has the most sensitive response to compressive loading among the three types of CNT/cement composites. It is interesting to note that the composite's piezoresistive sensitivity does not linearly increase with CNT concentration levels. This phenomenon can be explained below. The concentration level of MWNT influences and reflects the situation of network formed in the composites. When the MWNT concentration level is 0.05 wt. %, the thickness of the insulating matrix between adjacent nanotubes is large and the amount of conducted tunneling junction under external loading is low. With the increase of the concentration level of MWNT to 0.1 wt. %, the thickness of the insulating matrix between adjacent nanotubes decreases and the electronic transition by tunneling conduction becomes easy. With the continuous increase of MWNT, the tunneling gap would be further shortened, and then the CNT network stabilizes and becomes hardly to change under loading. This can be proved by SEM photographs as shown in Fig.11. Comparing Fig.11 b) with Fig.11 a), it can be found that the CNT network in CNT/cement composite with 1 wt. % of MWNT is more widespread than that in CNT/cement composite with 0.1 wt. % of MWNT. As a result, the contact resistance of CNT/cement composites with 0.1 wt. % of MWNT is the most sensitive to compressive loading among the fabricated CNT/cement composites. Therefore, the sensitivity of the piezoresistive response of CNT/cement composites first increases then decreases with the increase of MWNT concentration levels.

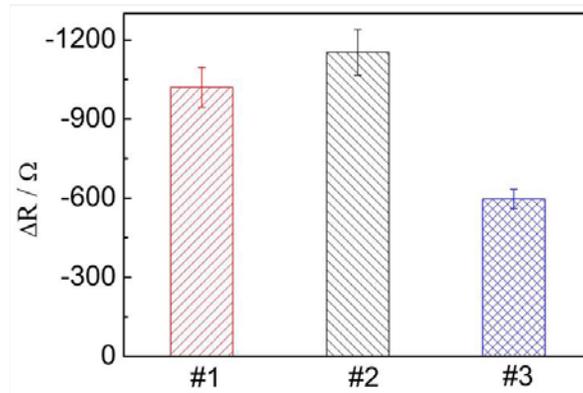
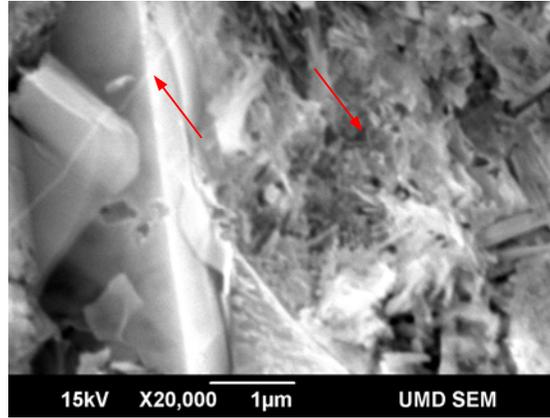
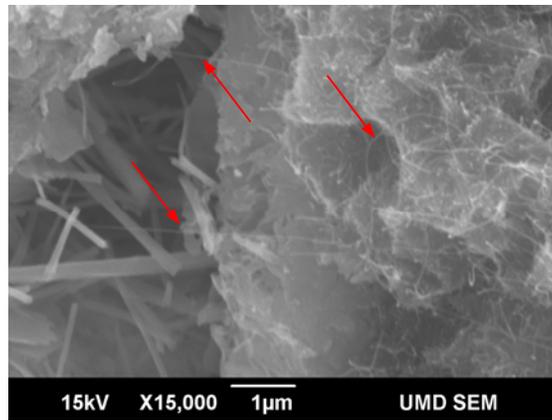


Fig. 10 Comparison of electrical resistance changes of CNT/cement composites with different MWNT concentration levels (#1: 0.05 wt. %, #2: 0.1 wt. %, #3: 1 wt. %)



a) With 0.1 wt.% of MWNT (Sample #2)



b) With 1 wt.% of MWNT (Sample #3)

Fig.11 SEM photographs of CNT/cement composites

3.5 The effect of water content on the piezoresistivity of CNT/cement composites

For the CNT/cement composites to be used in real civil structures, the effect of the water content on the piezoresistivity of composites also needs to be investigated. In this project, the electrical resistances of composites with different water contents and their responses to compressive stress under repeated compressive loading are therefore also studied. For this study, the CNT/cement composite with 0.1wt% CNT is used.

Fig.12 shows the initial electrical resistance R_0 , the maximum change amplitudes f

$$\left(f = \left| \frac{R_{6MPa} - R_0}{R_0} \times 100\% \right| \right), \text{ where } R_{6MPa} \text{ is the electrical resistance of samples when the}$$

compressive stress is 6MPa) 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 the samples with 3.3% of water content are the highest among the 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 the water content in the composites.

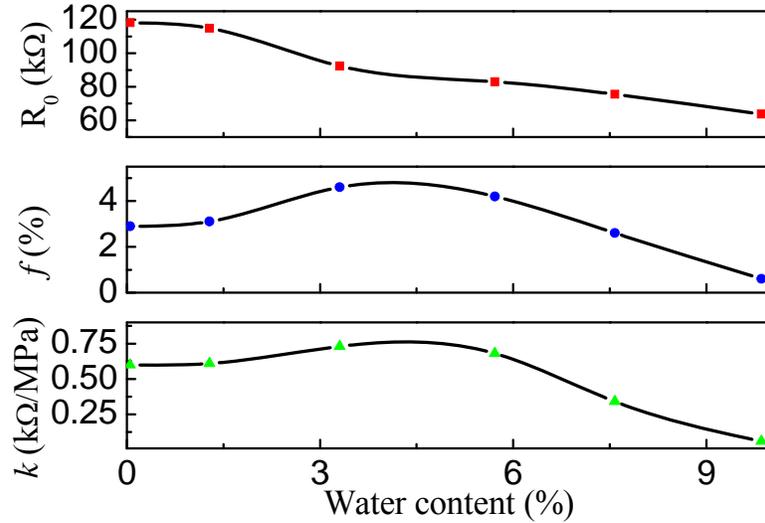


Fig. 12 Comparison of electrical resistances, maximum change amplitudes of electrical resistance and piezoresistive sensitivities of CNT/cement composites with different water contents

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 water content. This phenomenon can be explained below.

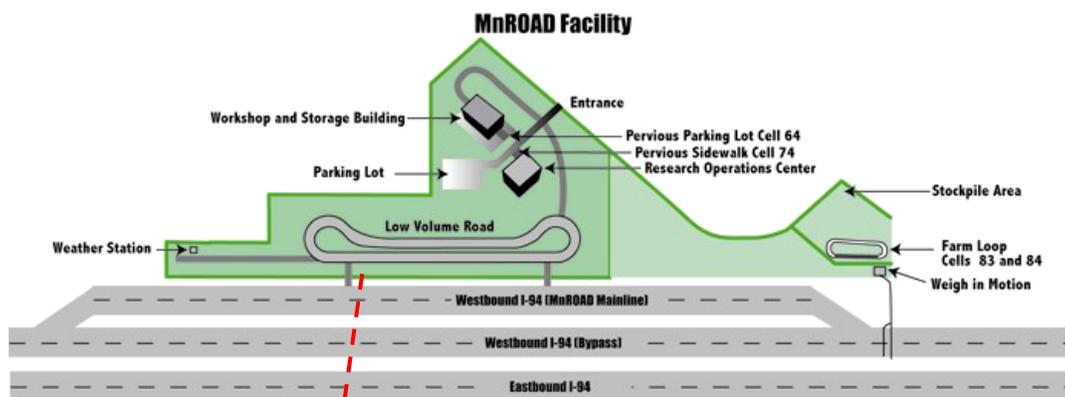
Two factors would contribute to the effect of water content on the sensitivity of piezoresistive response. One is the electrical conductivity of matrix [32], and the other is the field emission effect on the nanotube tip. The electrical conductivity of matrix and the field emission effect on the nanotube tip can be enhanced by the adsorption of water molecules [33-36]. 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 present 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 hardly to change under loading. As a result, too high level of the water content will induce a much lower electrical resistance and a lower sensitivity to stress [37-40]. Therefore, the sensitivity of the piezoresistive response of CNT/cement composites is influenced by the water content in the composites, and it initially increases then decreases with the increase of water content in the composites.

Chapter 4 Road Tests

4.1 Construction of self-sensing CNT concrete pavement

Two self-sensing CNT concrete sensors, a pre-cast sensor and a cast-in-place sensor, were integrated into a concrete test section at the Minnesota Road Research Facility (MnROAD) of the Minnesota Department of Transportation, USA. MnROAD is located near Albertville, Minnesota (40 miles northwest of Minneapolis). It is a pavement test track using various research materials and pavements. The layout of the MnROAD is shown in Fig.13 a). It consists of a test section of I-94 carrying interstate traffic, a low volume roadway that simulates conditions on rural roads, and thousands of sensors that record load and environmental data.



a) Layout of MnROAD testing facility



b) Construction process of self-sensing CNT concrete pavement

Fig.13. Location and construction of self-sensing CNT concrete pavement

As shown in Fig.13 b), two grooves were firstly cut in the existing concrete pavement. The spacing between the two grooves is about 1.8m. For the pre-cast case, the CNT cement mortar mixture was poured into a wood mold of 160×23×10cm with three reinforcing steel bars, three strain gauges (PML-60-2LT, Tokyo Sokki Kenkyujo Co., Ltd, Japan) and two mesh electrodes arranged as shown in Fig.14. The structure and specification of the strain gauges are given in Fig. 15 and Table 3 [41]. A vibration table was used to ensure good compaction. The CNT concrete sensor was then surface-smoothed, and covered with plastic film to prevent water evaporation. After that, the sensor was cured at room temperature for 28 days before installed into the road pavement. Finally, the sensor was fixed in one of the cutting grooves using concrete mortar. For the cast-in-place sensor, common patch mix concrete was firstly poured into the bottom of the other cutting groove until level with the bottom of the pre-cast CNT concrete sensor. Then, the CNT cement mortar mixture was poured into the groove, in which three reinforcing steel bars, three strain gauges and the bottom mesh electrode were preinstalled as shown in Fig. 16. The upper mesh electrode was put in when the poured mixture is 5cm thick over the bottom electrode. After all the mixture was poured into the groove, the cast-in-place CNT concrete sensor was then surface-smoothed. Finally, the two CNT concrete sensors were covered with plastic film for curing. Road tests began after one month of curing.

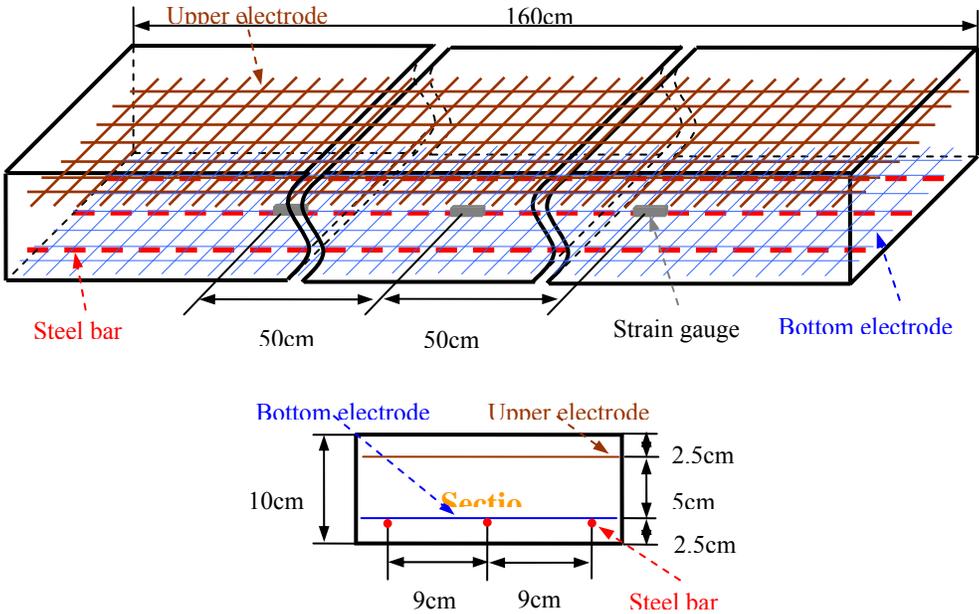


Fig.14 Structure of the self-sensing CNT concrete sensors

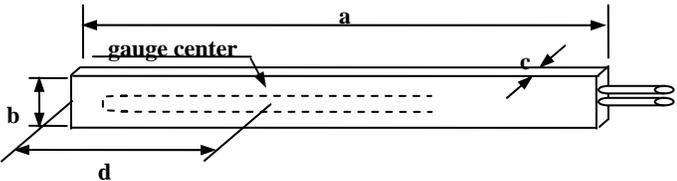


Fig.15. Structure of the strain gauges

Table 3. Specification of the strain gauges

Gauge length	Gauge width	Backing				Resistance
		a	b	c	d	
60mm	1mm	125mm	13mm	5mm	40mm	120Ω

4.2. Preparation of CNT concrete

The cement used was Portland cement (ASTM Type I) provided by Holcim Inc., USA. The sand used was commercial grade fine sand provided by Quikrete International Inc., USA. The multi-wall carbon nanotubes (MWNT) used were carboxyl MWNT provided by Timesnano, Chengdu Organic Chemicals Co. Ltd. of Chinese Academy of Sciences, China. Their properties are given in Table 1 (Page 3). 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 the CNT filled cement mortar composites caused by use of NaDDBS. Stainless steel meshes with opening of 1.25×1.25cm were used as electrodes. Steel bars of 6 mm diameter were used as reinforcement.

1.4×10^{-2} mol/L of the critical micelle concentrations was taken as the input surfactant concentration of NaDDBS in water. The surfactant was firstly mixed with water (the water to cement ratio is 0.46:1) by hand stir for about 2 minutes. Next, MWNT (1% by weight of cement) were added into this aqueous solution and sonicated with an ultrasonicator (8510, Branson Ultrasonic Co., USA) for 2 hours to make a uniformly dispersed suspension. Then, a 5 cubic feet cement mortar mixer was used to mix this suspension, cement and sand (the ratio of sand to cement is 1.5:1) for about 15 minutes. Finally, the defoamer in the amount of 0.25 vol. % was added into the mixture and mixed for another 5 minutes.

4.3 Road tests set-up

Fig.18 shows the set-up of the road test with the road-side data collection unit. During the test, a MnROAD 5-axle semi-trailer tractor truck and a van were driven to pass over the self-sensing pavement. The detailed parameters of the truck and the van are given in Fig.17 and Table 5, respectively. The measurement circuit diagram of the CNT concrete sensors and strain gauges is depicted in Fig.18. The voltages at both ends of the CNT concrete sensors and the strain gauges were taken as indices for detecting the passing vehicles, since the electrical resistance of both the CNT concrete sensors and the strain gauges would change when the vehicles pass. As shown in Fig.16, a MnROAD signal acquisition system was used to collect the sensing signals of the two CNT concrete sensors and the six strain gauges. The sampling rate of the voltage signals is 1000Hz. In addition, in order to decrease the effect of measurement noise, a low-pass filter was used to post-process the measured sensing signals of the CNT concrete sensors and the strain gauges.



Fig.16. Road test of self-sensing CNT concrete pavement

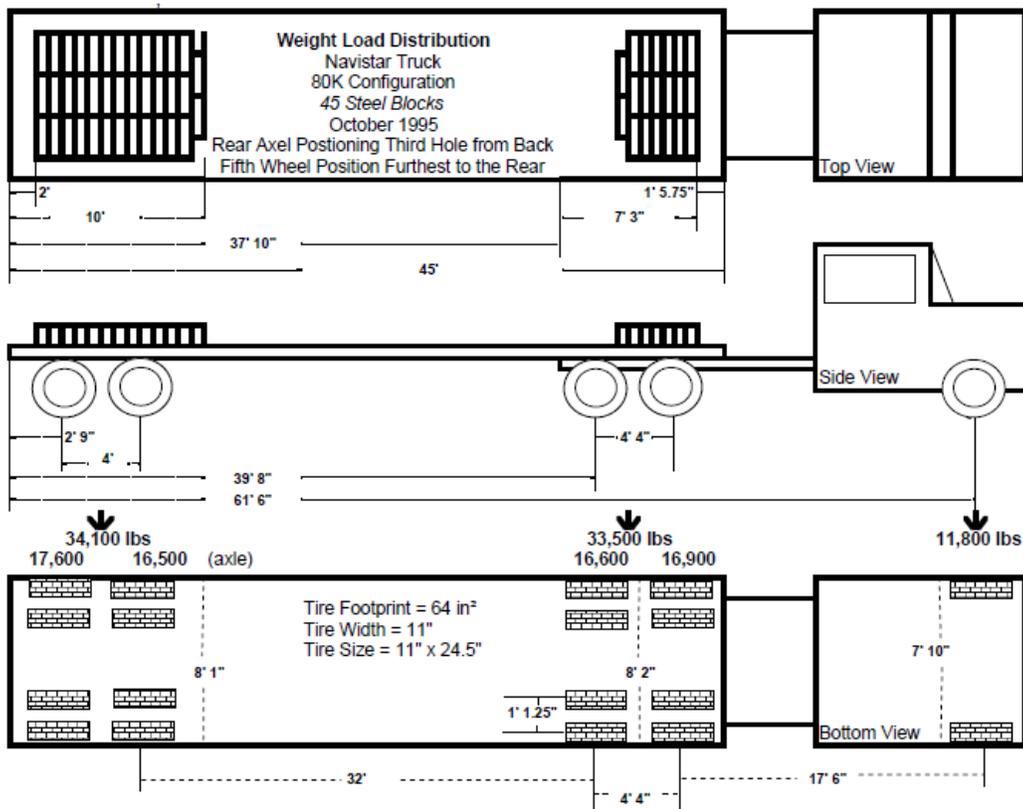


Fig.17. The MnROAD 5-axle semi-tractor trailer truck

Table 5. Parameters of the van

Van model	Weight	Wheelbase
1999 Ford Econoline Van E-250	~2500kg	3.5m

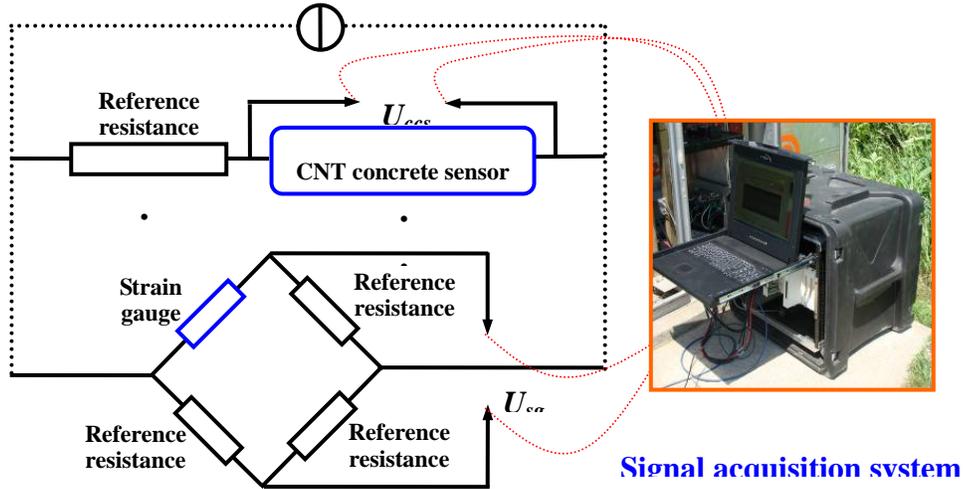


Fig.18. Measurement circuit diagram of the CNT concrete sensors and strain gauges

4.4. Test results and discussion

4.4.1. Detection of truck passing

Detection results of truck passing at low and higher speeds are illustrated in Fig.19 and Fig.20, respectively. As shown in Fig.19 a), Fig.19 b), Fig.20 a) and Fig.20 b), abrupt changes occurred in the voltage signal curves when the truck passes over the cast-in-place and pre-cast CNT concrete sensors. Each peak indicates a passing wheel, which is well corresponding to the structure of the truck as shown in Fig.17. In addition, because truck wheels pass over the middle region of the CNT concrete sensors during test, only strain gauges in the middle of the two concrete sensors have some responses to the truck passing (the voltage signal curves of the strain gauges are also given in Fig.19 and Fig.20). A comparison between the voltage signals of the CNT concrete sensors and those of the strain gauges indicates that generally the CNT concrete sensors have higher detection accuracy than the strain gauges (as shown in Fig. 19(d) and Fig. 20 (d), there were missed measurements on the strain gauge). This is due to the larger sensing area of the CNT pavement sensors.

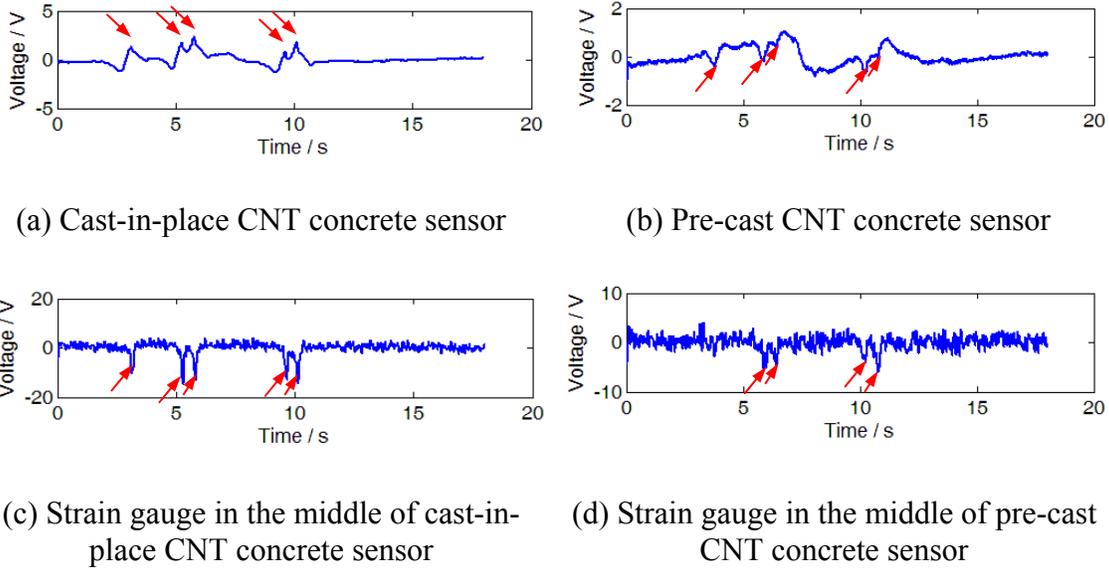


Fig.19. Detection results of truck passing at low speed

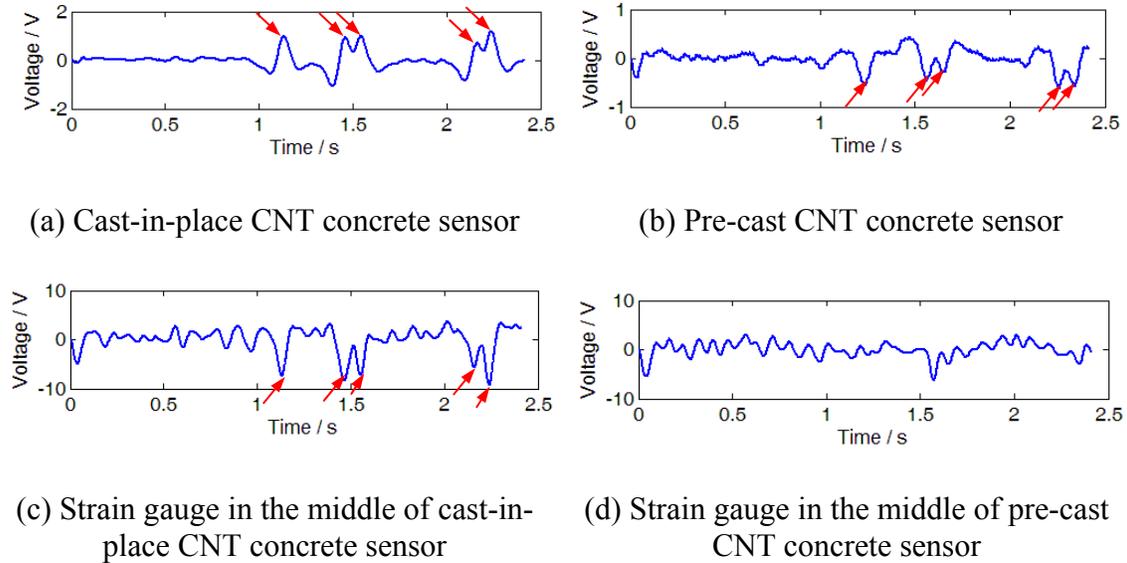


Fig.20. Detection results of truck passing at higher speed

Fig. 21 illustrates the truck passing detection results in another two tests of the cast-in-place CNT concrete sensor and the strain gauge. It is found that the detection results shown in Fig.21 are very similar to those shown in Figs. 19 and 20. This indicates that the CNT concrete sensors have stable and repeatable traffic detection capability.

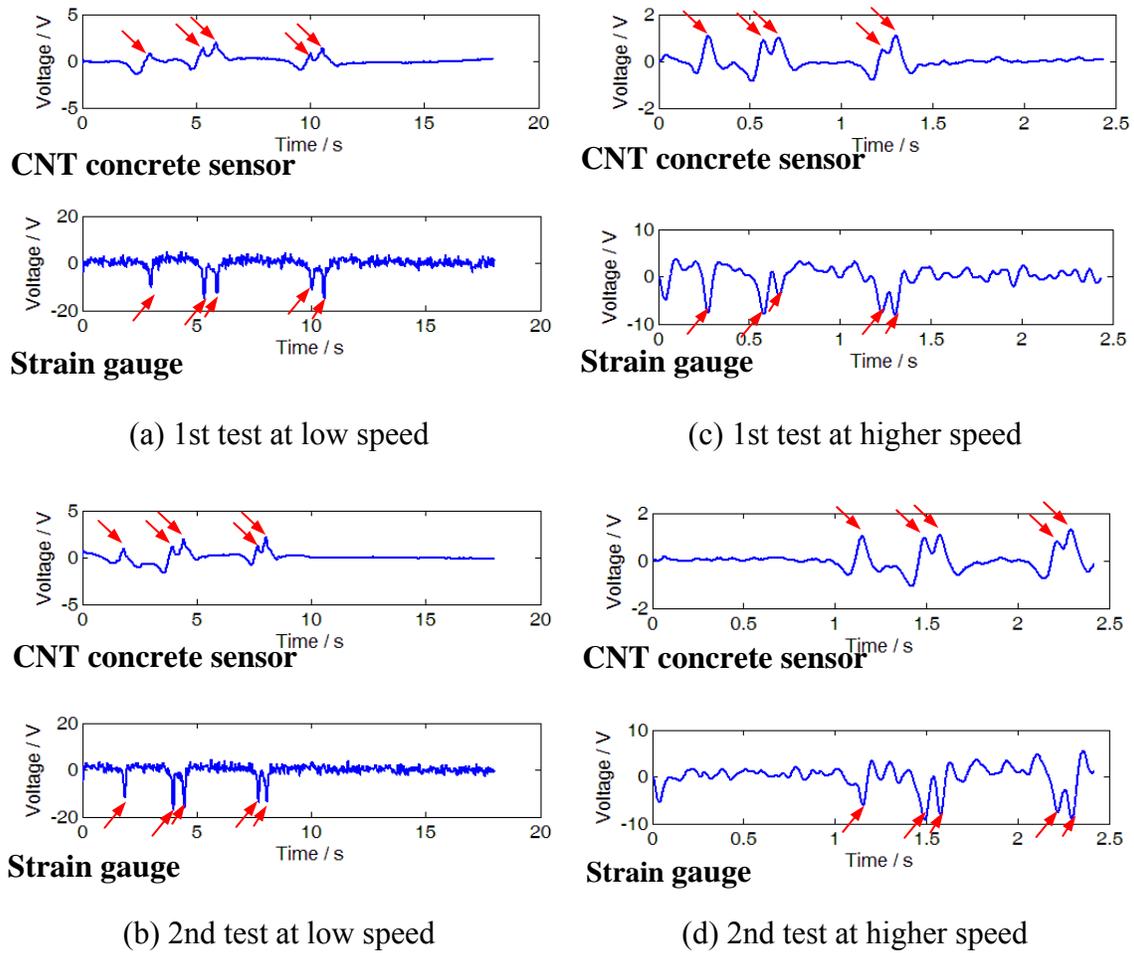
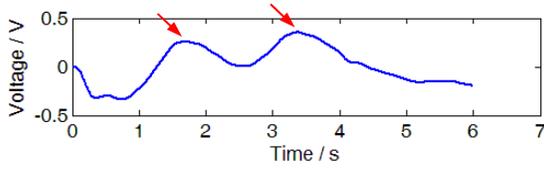


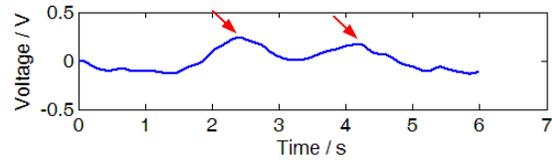
Fig.21. Detection results of cast-in-place CNT concrete sensor and the strain gauge in multi-tests for truck passing

4.4.2. Detection of Van passing

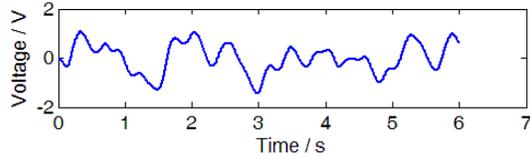
Fig.22 and Fig.23 give the detection results of the van passing at low and higher speeds. It can be seen from Fig.22 a), Fig.22 b), Fig.23 a) and Fig.23 b) that changes occur in the voltage signal curves of the cast-in-place and pre-cast CNT concrete sensors when the van passes over them. This indicates that the CNT concrete sensors can identify the front wheel and the rear wheel passing of the van. However, as shown in Fig.22 c), Fig.22 d), Fig.23 c) and Fig.23 d), the van passing cannot be detected by the strain gauges. This is because the van loading is much lower than the truck loading.



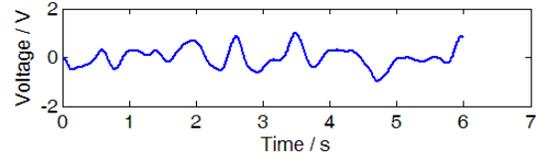
(a) Cast-in-place CNT concrete sensor



(b) Pre-cast CNT concrete sensor

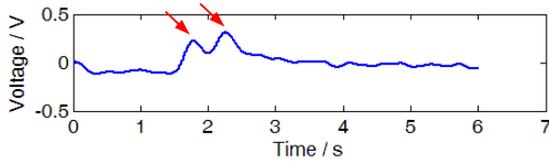


(c) Strain gauge in the middle of cast-in-place CNT concrete sensor

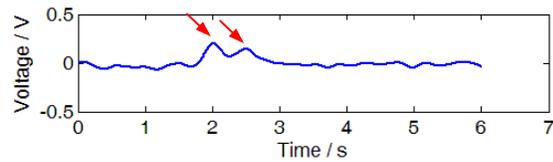


(d) Strain gauge in the middle of pre-cast CNT concrete sensor

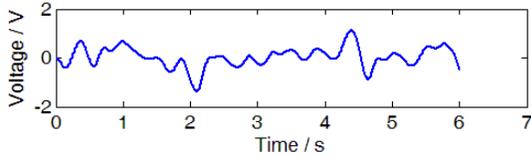
Fig.22. Detection results of van passing at low speed



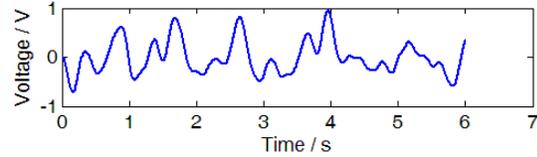
(a) Cast-in-place CNT concrete sensor



(b) Pre-cast CNT concrete sensor



(c) Strain gauge in the middle of cast-in-place CNT concrete sensor



(d) Strain gauge in the middle of pre-cast CNT concrete sensor

Fig.23. Detection results of van passing at higher speed

In the road tests, both the polarization of CNT concrete under external electrical field [42] and the changes in environmental temperature and humidity (i.e. the moisture content of the sensors)[43] are found to have some effects on the electrical resistivity of the CNT concrete sensors. However, the changes in electrical resistivity signals (i.e. voltage signals) caused by the polarization and environmental factors, are continuous and gradual, while those caused by vehicular loading are transient and abrupt. Therefore, the former can be filtered out in the post-

processing of measured voltage signals, and they will not influence the detection accuracy of the CNT concrete sensors. In addition, it should be mentioned that the detection of truck passing was performed under relatively cold temperatures (temperature: 3.5°C), while the van passing was detected in much warmer environment (temperature: 23°C). Additionally, the detection results in Figs.19-23 were collected at different test time after current was applied, corresponding to different polarization conditions inside the CNT concrete sensors. It can be seen from Figs.19-23 that the CNT concrete sensors can accurately detect vehicle passing under different polarization conditions and test environments. It therefore can be concluded that the self-sensing CNT concrete pavement features excellent robustness to the polarization inside CNT concrete sensors and the changes of external environments.

Chapter 5

Summary and Discussion

New piezoresistive CNT/cement composites were developed and tested in this study. Experimental results showed that the electrical resistance of the composite changed proportionally to the compressive stress levels. The piezoresistive responses of the composite with different fabrication methods have also been studied. The CNT acid-treated method showed stronger piezoresistive response and higher signal-to-noise ratio than those from the surfactant-assistant dispersion method, in which the surfactant could block the contacts among nanotubes thus impairing the piezoresistive response of the composite. However, the acid-treatment of CNTs is difficult to scale up for larger samples. The involvement of strong acids also makes it hard to be implemented in the field. The surfactant wrapping of CNTs is also effective to disperse CNTs into the cement matrix and give promising piezoresistive properties. The experimental results, including the lab and road tests, have demonstrated the potential of using the CNT/cement composite as the structural health monitoring stress/strain sensors for civil infrastructure.

References

- [1] K. P. Chong, E. J. Garboczi, and G. Washer “Health monitoring of civil infrastructures”, *Prog. Smart. Mater. Struct.*, vol. 12, pp. 483-493, 2003.
- [2] K. P. Chong, and E. J. Garboczi, “Smart and designer structural materials systems”, *Prog. Struct. Engng. Mater.*, vol. 4, pp. 417-430, 2002.
- [3] H. V. d. Auweraer, and B. Peeters, “Sensors and Systems for Structural Health Monitoring” *Journal of Structural Control*, vol. 10, pp.117-125, 2003.
- [4] S. Iijima, “Helical microtubes of graphitic carbon,” *Nature*, vol.354, pp. 56-58, 1991.
- [5] M. Meyyappan, edit, “Carbon Nanotubes – Science and applications”, *CRC Press*, 2005.
- [6] J. C. Grunlan, A. R. Mehrabi, M. V. Bannon, and J. L. Bahr, “Water-based single-walled-nanotube-filled polymer composite with an exceptionally low percolation threshold,” *Advanced Materials*, vol.16, pp. 150-153, 2004.
- [7] G. B. Blanchet, S. Subramoney, R. K. Bailey, G. D. Jaycox, and C. Nuckolls, “Sel-assembled three-dimensional conducting network of single-wall carbon nanotubes,” *Applied Physics Letters*, vol. 85, pp.828-830, 2004.
- [8] Y. J. Kim, T. S. Shin, H. D. Choi, J. H. Kwon, Y.-C. Chung, and H. G. Yoon, “Electrical conductivity of chemically modified multiwalled carbon nanotube/epoxy composites,” *Carbon*, vol. 43, pp.23-30, 2005.
- [9] T. W. Tomblor, C. Zhou, L. Alexseyev, J. Kong, H. Dai, L. Liu, C. S. Jayanthi, M. Tang, and S.-Y. Wu, “Reversible electromechanical characteristics of carbon nanotubes under local-probe manipulation,” *Nature*, vol. 405, pp.769-772, 2000.
- [10] J. Cao, Q. Wang, and H. Dai, “Electromechanical properties of metallic, quasimetallic, and semiconducting carbon nanotubes under stretching,” *Physical Review Letters*, vol. 90, pp.157601-157604, 2003.
- [11] R. J. Grow, Q. Wang, J. Cao, D. Wang, and H. Dai, “Piezoresistance of carbon nanotubes on deformable thin-film membranes,” *Applied Physics Letters*, vol.86, pp.093104 – 093104-3, 2005.
- [12] P. Dharap, Z. Li, S. Nagarajaiah, and E. V. Barrera, “Nanotube film based on single-wall carbon nanotubes for strain sensing,” *Nanotechnology*, vol. 15, pp. 379-382, 2004.
- [13] I. Kang, M. J. Schulz, J. H. Kim, V. Shanov, and D. Shi, “A carbon nanotube strain sensor for structural health monitoring,” *Smart Mater. Struct.*, vol. 15, pp.737-748, 2006.
- [14] G. Y. Li, P. M. Wang, and X. Zhao, “Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes,” *Carbon*, vol. 43, pp.1239-1245, 2005.
- [15] R. L. Jacobsen, T. M. Tritt, J. R. Guth, A. C. Ehrlich, and D. J. Gillespie, “Mechanical properties of vapor-grown carbon fiber,” *Carbon*, vol. 33., pp. 1217-1221, 1995.
- [16] S. Wen, and D. D. L. Chung, “Piezoresistivity in continuous carbon fiber cement-matrix composite,” *Cement and Concrete Research*, vol. 29, pp.445-449, 1999.
- [17] S. Wen, S. Wang, and D. D. L. Chung, “Piezoresistivity in continuous carbon fiber polymer-matrix and cement-matrix composite,” *Journal of Materials Science*, vol. 35, pp.3669-3675, 2000.
- [18] D. D. L. Chung, “Piezoresistive cement-based materials for strain sensing,” *Journal of Intelligent Material Systems and Structures*, vol. 13, pp.599-609, 2002.

- [19] M. Sun, Q. Liu, Z. Li, and Y. Hu, "A study of piezoelectric properties of carbon fiber reinforced concrete and plain cement paste during dynamic loading," *Cement and Concrete Research*, vol. 30, pp.1593-1595, 2000.
- [20] J. Makar, J. Margeson, and J. Luh, "Carbon nanotube/cement composite – early results and potential applications," *3rd International Conference on Construction Materials: Performance, Innovations and Structural Implications*, Vancouver, B. B., pp. 1-10, Aug. 22-24, 2005
- [21] X. Yu, R. Rajamani, K. A. Stelson, and T. Cui, "Carbon nanotube based transparent acoustic actuators and sensors," *Sensors and Actuators A: Physical*, vol.132, 2006, pp. 626-631.
- [22] X. Yu, R. Rajamani, K. A. Stelson, and T. Cui, "Carbon nanotube based transparent conductive thin film," *Journal of Nanoscience and Nanotechnology*, vol.6 (7), 2006, pp.1939-1944.
- [23] Z. Jia, Z. Wang, J. Liang, B. Wei, and D. Wu, "Production of short multi-walled carbon nanotubes," *Carbon*, vol. 37, 1999, pp.903-906.
- [24] T. W. Tomblor, C. Zhou, L. Alexseyev, J. Kong, H. Dai, L. Liu, C. S. Jayanthi, M. Tang, S.Y. Wu, Reversible electromechanical characteristics of carbon nanotubes under local-probe manipulation, *Nature*, vol. 405, 2000, pp.769-772.
- [25] Z. M. Dang, M. J. Jian, D. Xie, S. H. Yao, L. Q. Zhang, J. B. Bai, Supersensitive linear piezoresistive property in carbon nanotubes/silicone rubber nanocomposites, *Journal of Applied Physics*, vol. 104, 2008, pp.024114.
- [26] C. Gau, H. S. Ko, H. T. Chen, Piezoresistive characteristics of MWNTs nanocomposites and fabrication as polymer pressure sensor, *Nanotechnology*, vol. 20, 2009, 2009, pp.185503.
- [27] M. Meyyappan, *Carbon Nanotubes Science and Applications*, CRC Press., Boca Raton, 2005.
- [28] L. Vaisman, H. D. Wagner, G. Marom, The role of surfactants in dispersion of carbon nanotubes, *Advances in Colloid and Interface Science* vol. 128-130, 2006, pp.37-46.
- [29] G.Y. Li, P.M. Wang, X.H. Zhao, Pressure-sensitive properties and microstructure of carbon nanotube reinforced cement composites. *Cement and Concrete Composites*, vol. 29, 2007, pp.377-382
- [30] B. Chen, K.R.,Wu, W. Yao, Piezoresistivity in carbon fiber reinforced cement based composites, *Journal of Materials Science and Technology*, vol.20, 2004, pp.746-750.
- [31] Y. Wan, D.J. Wen, Conducting polymer composites and their special effects, *Chin. J. Nat.* vol. 21, 1999, 149-153.
- [32] C. Tashiro, H. Ishida, S. Shimamura. Dependence of the electrical resistivity on evaporable water content in hardened cement pastes. *Journal of Materials Science Letters*. 6, 1987, 1379-1381.
- [33] M. Grujicic, G. Gao, B. Gersten. Enhancement of field emission in carbon nanotubes through adsorption of polar molecules. *Applied Surface Science*. 206, 2003, 167-177.
- [34] C.W. Chen, M.H. Lee, S.J. Clark. Gas molecule effects on field emission properties of single-walled carbon nanotube. *Diamond and Related Materials*. 13, 2004, 1306-1313.
- [35] L. Qiao, W. T. Zheng, Q. B. Wen, Q. Jiang. First-principles density-functional investigation of the effect of water on the field emission of carbon nanotubes. *Nanotechnology*. 18, 2007, 155707(5pp).
- [36] C.Y. Li, T.W. Chou. Modeling of damage sensing in fiber composites using carbon nanotube networks. *Composites Science and Technology*. 68, 2008, 3373-3379.

- [37] Q.Z. Mao, B.Y. Zhao, D.R. Sheng, Z.Q. Li. Resistance changement of compression sensible cement specimen under different stresses. *Journal of Wuhan University of Technology*. 11, 1996, 41-45.
- [38] J.R. Lu, X.F. Chen, W. Lu, G.H. Chen. The piezoresistive behaviors of polyethylene/foliated graphite nanocomposites. *European Polymer Journal*. 42, 2006, 1015-1021.
- [39] L.H. Wang, T.H. Ding, P. Wang. Influence of carbon black concentration on piezoresistivity for carbon-black-filled silicone rubber composite. *Carbon*. 47, 2009, 3151-3157.
- [40] K. Chen, C.X. Xiong, L.B. Li, L. Zhou, Y. Lei, L.J. Dong. Conductive mechanism of antistatic poly (ethylene terephthalate)/ZnOw composites. *Polymer Composites*. 30, 2008, 226-231.
- [41] http://www.tml.jp/e/product/strain_gauge/gauge_list/pm_list.html
- [42] B.G. Han, X. Yu, J.P. Ou. Chapter 1: Multifunctional and smart carbon nanotube reinforced cement-based materials. Book: Nanotechnology in Civil Infrastructure: A Paradigm Shift, Publisher: Springer, Editors: K. Gopalakrishnan, B. Birgisson, P. Taylor, N.O. Attoh-Okine. 1-47. 2011
- [43] B.G. Han, X. Yu, J.P. Ou. Effect of water content on the piezoresistivity of CNTs/cement composites. *Journal of Materials Science*. 2010, 45: 3714-3719.