NORTHLAND ADVANCED TRANSPORTATION SYSTEMS RESEARCH LABORATORIES

Seed Project Final Report

Development of Carbon-Nanotube/Cement Composite for Traffic Flow Detection

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Summary:

Traffic flow sensors are import devices to provide inputs for traffic management applications. This NATRL seed project explores the piezoresistive property of the CNT/cement composite and its feasibility as an embedded stress sensor for to detect traffic flow. The experimental results show that the electrical resistance of the CNT/cement composites changes proportionally to the compressive stress levels indicating the potential of using the CNT/cement composite as a stress sensor for civil structures. The piezoresistive responses of composite with two different fabrication methods and CNT doping levels were also studied. It is found that the CNT dispersion-assistant surfactant could block the contacts among carbon nanotubes thus impair the piezoresistive response of the composite, while a higher CNT doping level could improve the sensitivity of the composite stress response. Currently, the piezoresistive property of the CNT/cement composite is being applied to develop an in-pavement traffic flow sensor.

1. Introduction:

A traffic flow sensor is a device that detects the presence or passage of vehicles on a roadway. The data collected through such sensors becomes a crucial input for various on/off-line applications in traffic engineering, such as traffic signal control, freeway flow surveillance and management, planning and design of a road network.

A large number of researchers have investigated different kinds of traffic sensing technolgoies. These sensors can be categorized into two major classes [1-3]:

- **Intrusive (in-road) sensor**: it is embedded in the pavement such as inductive loop detectors and magnetometers.
- **Non-intrusive (over-road) sensor**: this kind of sensor is mounted over the roadway such as microwave radar sensors, ultrasonic sensors, laser radar sensors, infrared sensors, and video image processors.

Among these various sensors, inductive loop detectors are the predominant traffic flow sensors, due to their mature technology, insensitive to weather conditions, and relative low costs. The configuration of an inductive loop detector is shown in Fig. 1 [3], which typically consists of a coil that is embedded in the road, a pull box, a lead-in cable, and a controller. As the vehicle passes over the coil, the inductance of the coil will reduce, which will change the oscillation frequency of an oscillator.

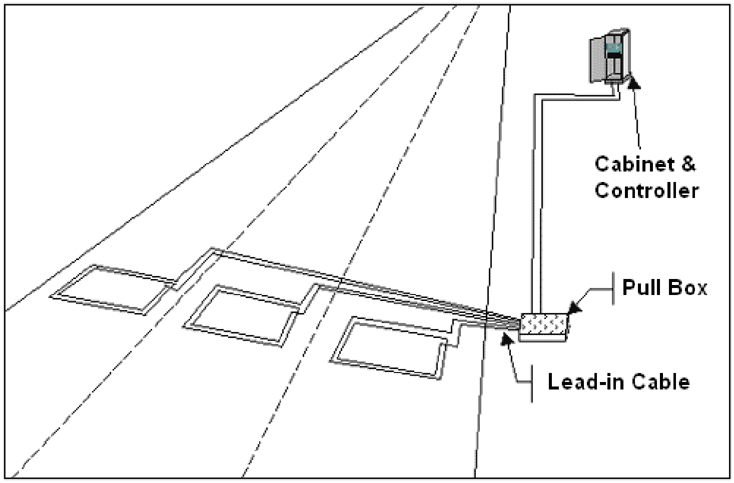

Fig. 1 Configuration of an inductive loop detector [3]

Inductive loop detector can accurately measure occupancy, vehicle speed, and gaps. However, there are several limitations with inductive loop detectors:

1) installation of inductive loops requires pavement cut (the typical size of a loop is 6 ft x 6 ft).
2) installation and maintenance require lane closure, which will bring sever traffic congestion and high maintenance cost.
3) wire coil suffer to the stresses of traffic and temperature.
4) if not properly installed, the inductive loop will decrease the pavement life.

Recent advances in computing and communication technologies have led to the development of non-intrusive detection technologies, such as microwave radars, infrared sensors, and video image processors. However, these non-intrusive sensors face limitations of high sensor costs, high maintenance cost, and poor performance in inclement weather conditions (rain, snow, and fog). Many of them also need additional mounting structures and need accurate calibration processes. These limitations make the intrusive sensors (mainly inductive loops) still are primarily used in traffic detection systems. The lack of low cost, low maintenance, long service, and reliable traffic detectors motivates this proposed research.

In this seed project, we aim to develop carbon nanotube (CNT)/cement composites that can detect traffic flow by detecting the change of electrical resistance of the composite when subject to the stress of vehicle. Being an integral part of the pavement and with strong mechanical strength, the proposed traffic sensor will provide several advantages over the inductive loop detectors:

- **Easy installation and maintenance**: the CNT/cement composite can be applied just like normal pavement.
- **Long service life and little maintenance**: the CNT/cement will have higher strength than cement concrete, and the composite can be seamlessly integrated and distributed into the pavement.
- **Wide detection area**: the CNT/cement could be paved on a large area for wide-area detection, in contrast to current sensors that could only detect the specific point where the sensor is installed.
- **The CNT/composite potentially could be used for structural health monitoring**: if implemented in critical structures such as bridges, the CNT/composite could detect the cracking of pavement, because cracking will dramatically *increase* the resistance of the composite (as will be discussed below, the compressive stress will *decrease* the resistance).

Carbon nanotubes (CNTs) are seamless tubular structures rolled up froming 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 μm.

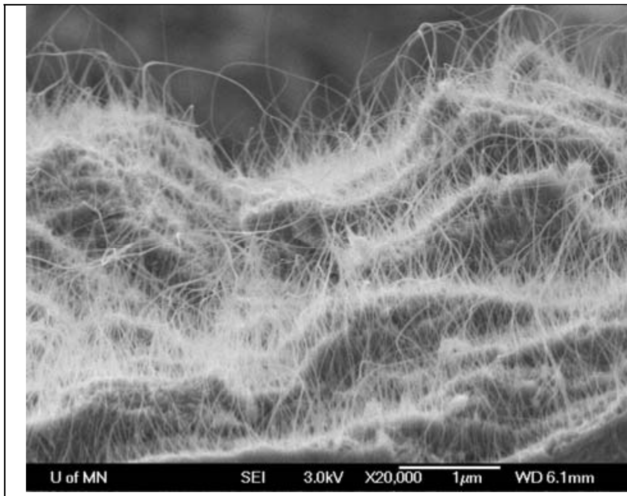

Fig. 2 A SEM (scanning electron microscope) picture of CNTs

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 charity [5]; and high aspect ratio (>500). The extremely high aspect ratio of CNTs makes them easy to form a conductive network and reinforcement network with doping level as low as 0.1% wt of CNTs [6-8]. Carbon nanotubes also have interesting electromechanical properties. 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 stain gage. These previous works show that CNT based composite could be a promising stress/strain sensor. However, no previous works have been performed on CNT/cement composites on the study of piezoresistive responses. 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 to investigate 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 $0.3/g (TimesNano, China). The decreasing price and the ultra low needed doping level of CNTs enable them possible to be used in large structures like concrete pavements, which had not been investigated by previous researches.

A literature survey reveals very few previous researches 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 are 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 did a similar mechanical reinforcement study but not piezoresistive behaviors [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 smaller 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 will be *irreversible* due to the fiber breakage when the strain is larger than 0.2% [16]. Therefore, CF/cement composite is not appropriate as a strain/stress sensor to heavy stressed detect traffic flow. On the contrary, Tombler *et. al.* found that the piezoresistive characteristics of CNTs are highly reversible even for a huge strain of 3.4% [9]. This proves CNT/cement could be a promising distributed stain/stress sensor for traffic flow detection.

2. Fabrication of CNT/cement composite

In this study, the high purity multi-walled carbon nanotubes (MWNTs) (<5 vol % impurity) were synthesized using the chemical vapor deposition (CVD) method (supplied by Timesnanoweb, Chengdu, China). Figure 3 shows a scanning electron microscope (SEM) picture of the received MWNTs.

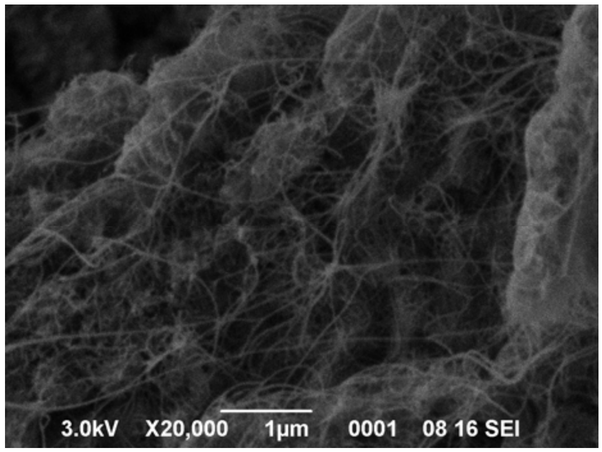

Fig. 3 SEM picture of as-received MWNTs

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 will be compared for both methods. As the controlled sample, the plain cement pastes without CNTs were also prepared with the water/cement ratio of 0.45.

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. 4 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 0.45 and MWNT is 0.1% weight of cement. The CNT/cement pastes were molded into 50.8 x 50.8 x 50.8 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. CNT/cement composite samples with 0.06 wt% MWNTs were also made in the same procedure as above.

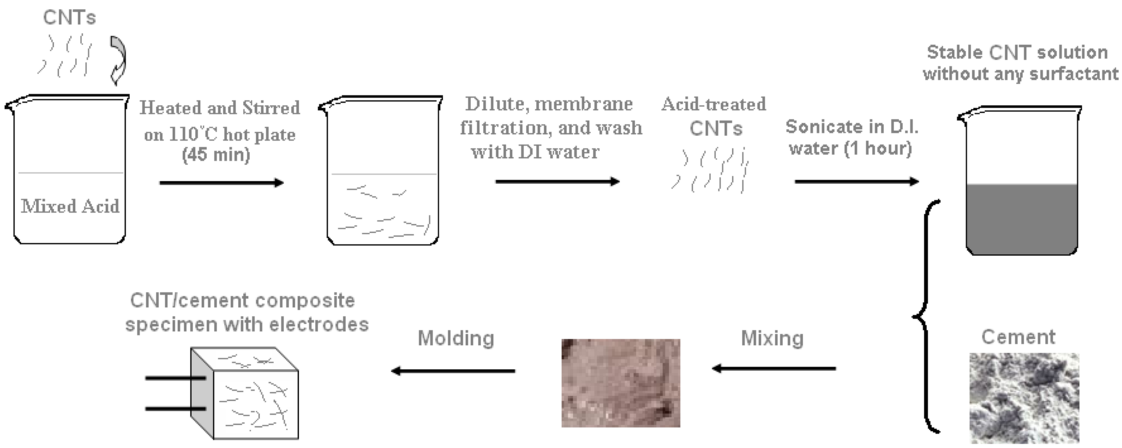

Fig. 4 Illustration of the CNT/cement fabrication process based on the acid treatment of CNTs

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 dodecyl sulfate (SDS) was used. MWNTs were dispersed in SDS solution and then mixed with cement, the water/cement ratio was 0.45, MWNT is 0.1% weight of cement, and SDS was 0.2% weight of cement. The composite sample was then prepared in the same manner as the method #1.

3. Results and discussion

Fig. 5 shows the SEM pictures of the CNT/cement composites made from Method 1 and Method 2, respectively. It shows that CNTs can form a network and be bonded to cement matrix.

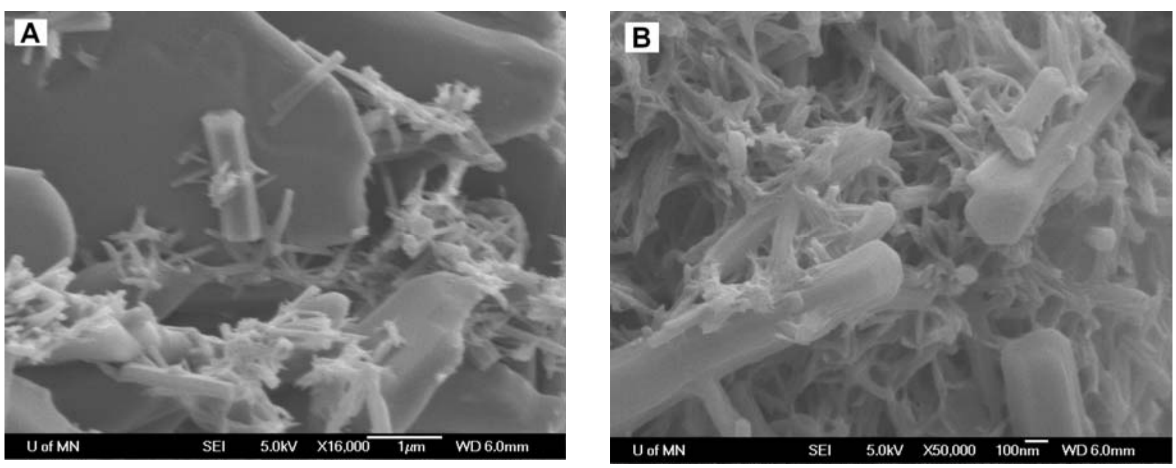

Fig. 5 SEM (scanning electron microscope) pictures of CNT/cement composites.

The piezoresistive responses of CNT/cement samples were tested with a MTS compressive testing machine by measuring the electrical resistances while varying the compressive loads on composite samples. The electrical resistance was measured by two-lead method with a digital multimeter (Keithley 2100, 6 ½-digit). Fig. 6 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 shows the resistance changes of the composite fabricated with the method #2 (SDS-assisted method) with 0.1wt% MWNTs. Although the resistance also changes corresponding to the stress load levels, the composite made with the method #2 has much lower signal/noise ratio on the measurement, compared to the results from the method #1 composite in Fig. 6. 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). Nanotube contacts could be blocked by the surfactant between nanotubes, which results in high signal noise especially in low stress levels.

The piezoresistive response of the composite with 0.06 wt% MWNT was also tested. It showed similar responses to the stress levels as from the 0.1% wt MWNT composite, but with lower sensitivity. Table 1 summarizes the resistance changes of the different CNT/cement composites. A higher CNT doping level can improve the piezoresistive sensitivity of the composite, but will increase the material cost.

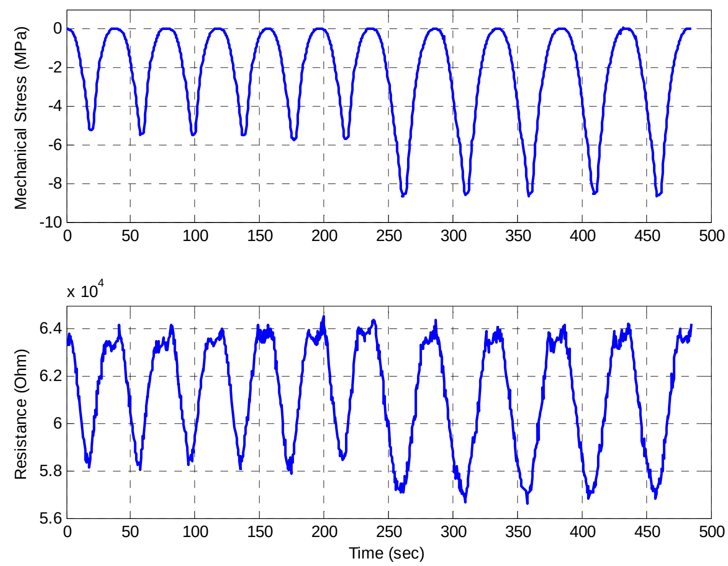

Fig. 6 Piezoresistive response of CNT/cement composite fabricated by method #1 (acid-treatment), MWNTs are 0.1 wt% of cement.

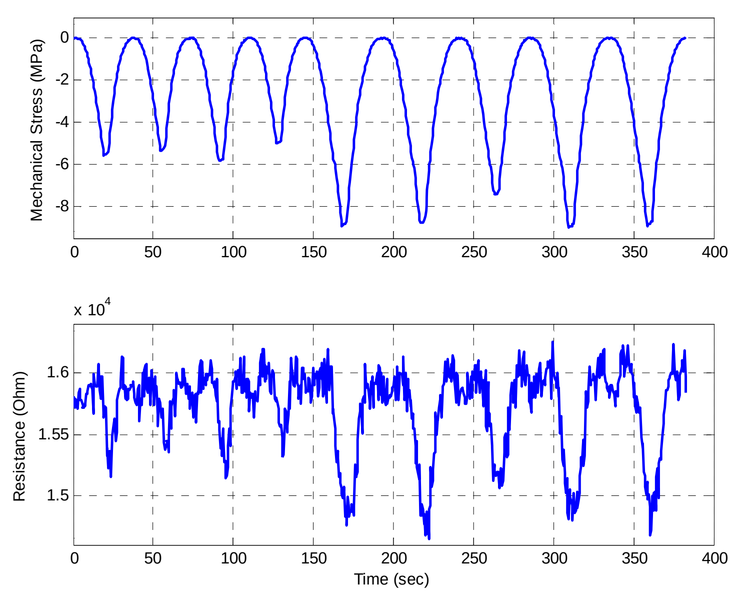

Fig. 7 Piezoresistive response of CNT/cement composite fabricated by method #2 (surfactant wrapping), MWNTs are 0.1 wt% of cement.

TABLE 1 Comparison of electrical resistance changes of CNT/cement composites with different CNT doping levels and under different compressive loads.

CNT/cement composites	Resistance change (5.2 MPa load)	Resistance change (8.6 MPa load)
Cement only	0%	0%
0.06 wt% MWNT (method #1)	8.8%	10.3%
0.1 wt% MWNT (method #1)	9.4%	11.4%
0.1 wt% MWNT (method #2)	~5.0%	~7.2%

These experimental results have demonstrated the linear peizoresistive responses of the CNT/cement composites, although the fabrication methods still need to be further optimized and the piezoresistive response of CNT enhanced concrete (which has 15~20% of cement) needs to be studied. The peizoresistive property of the CNT/cement composite has the potential to be used for many civil structure applications. For example, it can be used as intelligent pavement that can detect traffic flow in roadway or monitor the structure health of important civil infrastructures, such as bridges and levees. As illustrated in Fig. 8, the pavement strips of such CNT/cement could be installed on a roadway to make the roadway section itself a traffic flow detector. The CNT/cement stress sensor can be seamlessly integrated into the pavement with strong mechanical strength, thus is expect to have a long service life with little maintenance required.

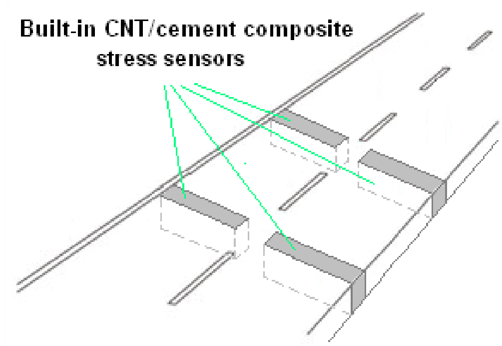

Fig. 8 Illustration of the CNT/cement composite as an embedded traffic flow detector

4. Conclusions

The piezoresistive property of the CNT/cement composites was investigated 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 and CNT doping levels have also been 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. A higher CNT doping level could improve the sensitivity of the composite stress response. These experimental results demonstrated the potential of using the CNT/cement composite as a stress sensor. Currently, the CNT/cement composite is being applied to develop an in-pavement traffic flow sensor.

Acknowledgments

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