CHEMO/PIEZORESISTIVE HPFRCC CARRYING CARBON FIBER AND CARBON NANOTUBES FOR SENSING

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Abstract

High Performance Fiber reinforced Cementitious Composites (HPFRCC) based on conductive fibers, such as carbon, are both chemo- and piezo-resistive. Piezo-resistivity is a unique material property which allows materials to change its electrical resistance/impedance as a result of changes in the applied stress/strain and chemo-resistivity refers to change its electrical resistance/impedance as a result of changes in the chemical environment. HPFRCCs are therefore smart materials that can act as low-cost sensors. This paper discusses the piezo/chemo resistive properties of FRC and describe the development of cement-based sensors with carbon fibers and carbon nano-tubes. Emphasis is on strain measurement, but these sensors are equally useful as chemical sensors capable of detecting pH changes, carbonation profiles, chloride ingress and corrosion initiation in rebar.

1. INTRODUCTION

Bridges, buildings, turbines, aircrafts and many other engineering structures are susceptible to deficiencies due to strenuous loading and environmental conditions. In order to catch any deficiency in the structure’s performance before any serious loss of capacity occurs, a technology has recently emerged known as Structural Health Monitoring (SHM). The purpose of SHM is to accurately monitor the behavior of an engineering structure, constantly assess its performance and provide continuous data on its current conditions.

SHM is a multidisciplinary technology which involves structural and material design, development of sensors and actuators, signal processing, networking and communication, data mining and analysis, diagnostics and prognostics, management strategies, etc. (1).

The sensory system is a very important component of SHM systems. Sensing devices constituting the sensory system are responsible for measuring parameters such as time, load, displacement, strain, acceleration, temperature and moisture.
Because of their low cost, durability and compatibility with concrete structures, recently developed cement-based sensors would be a very efficient replacement for conventional sensors such as fiber optic sensors, MEMS, etc. The ultimate purpose is to mount these sensors on structures in NSM or embedded formats as part of a wireless SHM system that is capable of detecting strain, cracks and even corrosion (Figure 1). Made of structural material, this type of sensor can be regarded as an integral part of the structure as it does not alter the properties or appearance of the host structure. Cement-based sensors are designed to function based on the principle of piezoresistivity. In this research, smart cement-based materials are developed using either carbon fibers alone or in combination with carbon nanotubes.

2. NANOTECHNOLOGY AND CARBON NANOTUBES

Nanotechnology is the science and technology of developing materials at the atomic and molecular level and generating techniques to measure and use their unique and special electrical, mechanical and chemical properties. Discovered almost 20 years ago by (2), carbon nanotubes (CNT) are one of the most important materials employed in nanotechnology. Carbon nanotubes are allotropes of carbon with a nanostructure that can have a length-to-diameter ratio of up to 28,000,000:1, which is significantly larger than any other material. CNT can be visualized as a modified form of graphite, where a single sheet or several sheets of graphite are seamlessly rolled into a tube structure (3). Single sheets rolled up are referred to as single-walled carbon nanotubes (SWCNT), and multiple sheets rolled up are called multi-walled carbon nanotubes (MWCNT). Results from a study by Li et al. (4) indicate that the addition of CNT, treated or untreated, to cement paste leads to a notable decrease in volume electrical resistivity and a distinct enhancement in the pressure-sensitive properties for cement composites.

3. EXPERIMENTAL PROGRAM

The following materials were used in the preparation of cement-based sensors:
- GU (formerly Type 10) Portland cement with specific gravity of 3.15 (W/C ratio ≈ 0.3 to 0.4).
- Densified silica fume with a specific gravity of 2.27 at 20% of by weight of cement.
- Coal-tar based carbon fiber (Table 1).
- Purified MWCNT (Table 2).
- Methylcellulose to help disperse carbon fibers; in the amount of 0.4% by weight of cement.
- A water base defoamer at 0.2% by weight of cement.
- A polycarboxylate-based Superplasticizer with a specific gravity of 1.1.
- Copper electrodes.
Table 1. Properties of Carbon Fiber (CF)

<table>
<thead>
<tr>
<th>Length (mm)</th>
<th>$\phi$ (μm)</th>
<th>S.G.</th>
<th>T. S.</th>
<th>E (GPa)</th>
<th>Volume Resistivity (Ω-m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>11</td>
<td>2.12</td>
<td>2620</td>
<td>634</td>
<td>$2.3 \times 10^6$</td>
</tr>
</tbody>
</table>

Table 2. Properties of Multi-walled Carbon Nanotubes (MWCNT)

<table>
<thead>
<tr>
<th>Outer Diameter (nm)</th>
<th>Inside Diameter (nm)</th>
<th>Purity</th>
<th>Length (μm)</th>
<th>Specific Surface Area (m$^2$/g)</th>
<th>Specific Gravity</th>
<th>Electrical Conductivity (s/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-20</td>
<td>3-5</td>
<td>&gt; 95 wt%</td>
<td>10-30</td>
<td>233</td>
<td>≈ 1.5</td>
<td>&gt; $10^2$</td>
</tr>
</tbody>
</table>

3.1 Resistivity Measurements

150 mm long samples with 25 mm × 15 mm cross section and 70 mm inner-electrode spacing, as recommended by Banthia et. al. (5), were prepared using different volume fractions ($V_R$) of carbon fiber (CF) and MWCNT. Specimens were air cured for 24 hours before the moulds were carefully stripped.

Direct current (DC) measurement of electrical resistance has proven to be technically difficult because of the polarization effect, which causes an exponential rise in the measured resistivity (5). Therefore, resistivity measurements in this study are made using alternating current (AC). An Agilent 4263B LCR meter at 100 kHz AC frequency was used for resistance measurements.

There are two commonly used methods for resistance measurements, two-probe and four-probe. While the two-probe technique is much simpler, error sources such as lead inductance, lead resistance and stray capacitance between the two electrodes are incorporated in the measured resistance. In the four-probe method, on the other hand, the effect of lead impedances is reduced because the current and voltage paths are separate. In the two-probe technique, the measured voltage consists of voltages from the electrodes ($V_E$, which is almost negligible), cement-based sensor ($V_S$) and contact resistance ($V_C$). In the four-probe method, however, $V_E$ and $V_C$ are eliminated and the voltage measurement consists of only the sensor voltage, $V_S$. Figure 2 schematically displays the equivalent circuits for two-probe and four-probe measurement techniques.
Two-probe resistance measurements increase dramatically as the L/A (electrode spacing/electrode contact area) ratio increases, whereas the four-probe configuration is unaffected by specimen design. Therefore, the four-probe method was employed for resistivity measurements (6,7). The electrical resistivity $\rho$ of a material with a uniform cross section is measured as its resistance per unit length:

$$\rho = R \frac{A}{\ell} \quad (1)$$

Where: $\rho$ = electrical resistivity in ohm meters ($\Omega$ m); $R$ = electrical resistance of a uniform specimen in ohms ($\Omega$); $A$ = cross-sectional area of the specimen ($m^2$), and $\ell$ = length between the measurement electrodes (m)

3.2 Effect of Current Frequency

The current frequency is a crucial element to be considered. Many factors may have a role in the effect of current frequency: internal factors such as fiber content and specimen geometry and external factors such as moisture and temperature. It has been found that if DC or low frequency AC is used, the cement matrix plays a dominant role in the electrical conductivity, but as the AC frequency is increased the interface impedance decreases and thus the electrical conductivity of the composite is strongly governed by the conductive fibers (8).
In addition, cement-based composites are capacitive in nature and thus, using higher frequencies reduces the reactance part of impedance.

In order to experimentally investigate the effect of current frequency on the cement-based sensors, a frequency sweep between 1 Hz and 1 MHz was completed - using a Solartron 1260 impedance/gain-phase analyzer - for specimens with different fiber contents (Figure 3).

Purely resistive impedance occurs when the phase angle (θ) is zero. Therefore, phase angles at different current frequencies were compared to find the most efficient frequency. The results, plotted in Figure 3, show that phase angle is for the most part negative, which confirms the fact that these cement-based composites are capacitive rather than inductive. For samples with fiber contents in the 0.5%-7% VR range, phase angle values fluctuate, lowering at 1 Hz and about 10 kHz. Samples with 15% and 20% VR of carbon fiber, 3% MWCNT specimens and the hybrid samples (15% CF + 3% MWCNT), exhibit much lower phase angle values especially at frequencies of 100 kHz and below. These samples seem to show inductive characteristics at some frequencies (where θ>0). A 100 kHz frequency was chosen.

3.3 Effect of Fiber Content

The addition of even a small amount of carbon fibers to cement paste significantly reduces the resistivity of the material. Conductivity increases by several orders of magnitude when the volume fraction of carbon fiber reaches a certain critical value, referred to as the percolation threshold (9,10). Fiber size and shape are important factors in determining the percolation threshold; for example, longer fibers provide higher electrical conductivity at lower fiber volume fractions, whereas the conductivity of specimens containing very short fibers increases very gradually with volume fraction (6).

Resistivity measurements from samples with various fiber contents, illustrated in Figure 4, indicate that the resistivity values of samples with only 0.5% VR of carbon fiber dropped considerably (97%) compared with plain samples. The resistivity of the specimens with 0.5% VR to ~15% VR remained almost constant, which validates the existence of a percolation threshold. However, the resistivity values could yet be significantly decreased (up to a thousand times smaller than the values at percolation threshold) by adding more fiber to the mix; samples with 20% VR of fiber exhibited electrical resistivity values as low as 5 Ω·cm, which was expected while these specimens were being prepared, in that there was much less cement paste than fibers and it was very difficult to mix. In order to observe the interaction between fibers and their dispersion, a series of images was obtained using a scanning electron microscope (SEM). SEM images of specimens with three different fiber contents, displayed in Figure 5, show how the increase in fiber content affects the dispersion of the fibers and in turn the electrical properties of the specimens. The effect of different amounts of MWCNT and SWCNT is also illustrated in Figure 4. It was found that the addition of CNT at 1% or 3% VR slightly decreases the resistivity of the cement paste. Owing to the extremely high conductivity values reported for CNT, this reduction was expected to be much greater, but the dispersion of CNT was very difficult to achieve even though a sonication process was used. Moreover, even if the dispersion was perfect, the extremely small size of CNT would prevent any contact or network among them in such low volume fractions. This triggered the idea of creating hybrid specimens: 1% MWCNT + 15% CF and 3% MWCNT + 15% CF; these samples yielded a lower electrical resistivity than the 15% CF and 20% CF samples, respectively.
Although the “3% MWCNT + 15% CF” hybrid and the 20% CF samples had preferable resistivity values, more suitable for the sensing application, they each had their downfalls; the former was very soft and brittle and the latter was extremely hard to prepare. Therefore samples with 15% CF or 1% MWCNT + 15% CF were selected to be used as sensor material. The entire class of such materials are hereafter called piezoresistive fiber reinforced concrete (PFRC).

3.4 Effect of Chloride and Moisture

The electrical conductivity of cement-based sensors is through both the conductive fibers and the cementitious matrix. Conductivity of the matrix part of the conduction path is through the pore structure and is referred to as the electrolytic conductivity. The presence of moisture and chloride changes the chemical composition of the pore structure and therefore affects the electrical resistivity of cementitious composites.

To examine the effect of moisture and chloride on cement-based sensors, plain, 3.5% $V_f$, 7% $V_f$ and 15% $V_f$ samples were kept in chloride solution (100 g of NaCl dissolved in 1 L of water). Resistivity measurements were taken from the specimens at the start of the experiment, after one month of exposure and again after the specimens were completely dried using desiccators. Figure 6 shows the resistivity values of the specimens at these three stages.

While one month submersion in chloride solution caused a significant decrease in the electrical resistivities of all the specimens, the plain sample was the only one to recover most of its resistivity. The carbon fiber reinforced samples recovered only a small percentage of their original resistivity after completely drying out. The conduction path in 15% CF samples includes more fiber to fiber contact which makes them less sensitive to the presence of moisture and chloride.

It is important to take this effect into consideration if and where the sensors are employed in environments subjected to moisture and chloride. Coating the sensors with moisture resistant material may be a solution to this issue. It was also observed during this experiment that the plain and 3.5% CF specimens experienced some delamination and blemishes, whereas the other two samples remained unaffected, which indicates that carbon fiber reinforced cementitious composites with higher $V_f$ of fiber are more durable when subjected to chloride ingress.
4. PIEZORESISTIVITY

Changes in the electrical resistivity of piezoresistive fiber reinforced concrete (PFRC) was monitored under cyclic compression to examine their sensing abilities.

Cylindrical specimens containing either “15% CF” or “15% CF + 1% MWCNT” were prepared. 10mm strain gauges were attached to the samples to compare the results with measured strain. Specimens were loaded cyclically to 30 kN (approximately 30% of load capacity) while monitoring the response (Figure 7).

In order to evaluate the sensing ability of the developed sensors, fractional change in resistivity (FCR) was compared against applied load. Fractional change in resistivity is given by:

\[
FCR = \frac{\rho_t - \rho_0}{\rho_0}
\]

(2)

where, \(\rho_t\): Electrical resistivity at time \(t\) during the tests; and \(\rho_0\): Electrical resistivity at the beginning of the test (prior to loading)

Figure 6. Effect of Chloride Solution on Electrical Resistivity of Sensors

Figure 7. Sensor in Compression

Figure 8. A 15% CF Sensor Under Cyclic Compression (30kN amplitude)

Figure 10 (a) Comparing PFRC (15% Carbon Fiber) with Traditional Sensor
Figure 9. 15% CF +1% MWCNT sensor under cyclic compressive loading with 30kN amplitude

Figure 10 (b) Comparing PFRC (15% Carbon Fiber + 1% Multiwalled Carbon Nanotubes) with Traditional Sensor

Figure 8 and Figure 9 display the response of sensors to strain for 15% CF and 15% CF + 1% MWCNT specimens, respectively. Very good correlation between the measured FCR and strain is observed. During each loading cycle, the resistivity values decrease with the increase in compressive load, resulting in negative FCR values, and then increase to the initial value when the unloading branch of the cycle takes place. Closer examination shows that the hybrid sensors (containing both carbon fibers and carbon nanotubes) exhibit better sensitivity and repeatability to strain. Some calibration curves are given in Figure 10. Note a better gauge factor for sensor with nanotubes.

5. DYNAMIC SENSING

Concrete structures in most instances are loaded at strain rates ( $\dot{\varepsilon}$ ) approximated in our standardized tests. However, there are dynamic events in which the strain-rates may significantly exceed those obtained in standardized tests such as in fast moving traffic ($\dot{\varepsilon} = 10^{-4} - 10^{-2}\text{s}^{-1}$), gas explosions ($\dot{\varepsilon} = 5\times10^{-5} - 5\times10^{-4}\text{s}^{-1}$), earthquakes ($\dot{\varepsilon} = 5\times10^{-3} - 5\times10^{-2}\text{s}^{-1}$), pile driving ($\dot{\varepsilon} = 10^{-2} - 10^{0}\text{s}^{-1}$) and aircraft landing ($\dot{\varepsilon} = 5\times10^{0}\text{s}^{-1}$). Sensors when used on these structures should be able to record their responses in a rapid and accurate manner. Since cement-based materials are highly strain-rate sensitive, sensors based on these materials (PFRCs) must also depict rate-effects.

Figure 11 shows high strain-rate (impact) tests on PFRC sensors obtained by using an air-gun based impact setup (11,12). The specimen is held in the machine such that the top-half is stationary and the bottom half is pulled down at a high speed by an air-gun. The top half of the sensor specimen is suspended from a dynamic load cell of 5kN capacity with a resolution of 0.01 N. The displacement of the sensor specimen (ignoring the elastic deformations) during a test is measured by means of a single LVDT fixed to the moving bottom-half. The air gun operated at a peak pressure of 0.35 MPa and generated a displacement rate of 3000 mm/s.
In a test the applied impact impulse (load-time curve) and resistivity signals from the sensor were recorded and some preliminary results are given in Figure 12.

As the preliminary plots in Figure 12 indicated, while the sensor is capable of dynamic recording, there are a number of issues to be resolved. First of all, there is a lag in measurement of load and sensor response. Further, due to the lag, the FCR in the loading range remains very low. Significant amount of further work is required to derive useful information from these sensors under high strain-rate loads.

6. CONCLUSIONS

Cement-based sensors, also described as smart (self-monitoring) structural materials, have recently been developed for use in structural health monitoring (SHM) systems. These sensors are rather inexpensive, durable, very easy to manufacture and install, and best of all they possess mechanical properties similar to concrete, enabling them to perform in the same manner as the host structure. They do not alter the properties or appearance of concrete structures; hence, if integrated into the host structure, they can be regarded almost as an integral part of the structure.

The purpose of this study was to develop piezoresistive cement-based sensors for use in SHM systems by incorporating carbon fibers as well as both single-walled and multi-walled carbon nanotubes in a cement paste matrix.

The effect of fiber content, current frequency and the presence of moisture and chloride on electrical resistivity were investigated. Consequently, the piezoresistive quality of the sensors was confirmed through monitoring their response to cyclic compressive loading. The electrical resistivity of these sensors changed in response to change in strain; decreasing reversibly with the increase in compressive strain. The sensors with nano-tubes depicted a higher sensitivity than those with carbon fiber alone. Some dynamic sensing tests were carried out that showed promise, but also indicated that many issues need to be resolved before these sensors can be used for SHM during earthquakes.

REFERENCES