Elimination of polarization effect in DC measurement of resistivity of CNT-cement composites

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Abstract. Multi-walled carbon nanotubes (CNT) may serve as electrically conducting fillers for traditional cement-based materials. Introducing small amount of CNT in the matrix of concrete turns the latter into a smart piezoresistive material applicable for the structural health monitoring of reinforced concrete structures. CNT–cement composites are subject to polarization during direct current (DC) resistance measurement. This phenomenon results in increase of electrical resistance of composites hindering their practical application. Suggestions for dealing with polarization usually include using alternate current measurements or applying direct current until resistance readings stabilize. This paper presents simple two-probe resistance sensing technique with DC being applied to the specimens as single square waves. Suggested approach is experimentally validated on the samples of CNT–cement composites. No polarization was observed in tested specimens when the periods between measurements were larger than 3 min. Such frequency of measurements is quite acceptable for monitoring the stress state of structures under static loading.

1. Introduction

Since their first synthesis in 1991 [1] carbon nanotubes have become one of the most favorable classes of fillers for nano-reinforcement of materials [2]. The reason for this is that CNTs possess extremely high strength, Young's modulus, aspect ratio (ratio of length to diameter), ultimate strain capacity and ductility, excellent electrical conductivity [3, 4]. Multi-walled CNTs are metallic in character with electrical conductivities on the order of $10^5$–$10^6$ S/cm [5]. Introducing CNTs into the structure of concrete enhances its strength under compression and tension [6, 7] as well as ductility [8] and fracture toughness [9]. Incorporating CNTs into conventional concrete matrix also leads to its ability to sense the strain, stress, crack or damage [10, 11]. Appropriately dispersed CNTs create an extensive conductive network in concrete. Such composite is piezoresistive, i.e. self-sensible with respect to the applied force. Stressing or deforming of the composite results in the change of conductive network and affects resistivity of composite. Sensing property emerges from the change in intrinsic resistance of CNTs and the change in contact resistance between adjacent CNTs with the latter being the main contributing factor [12]. As such nanomodification of concrete can be a powerful tool for the aims of structural health monitoring of infrastructure [13–15]. Small units made of smart concrete having the size of coarse aggregate may be placed in the body of the structure of interest and serve as a strain sensor for the whole working life of the building [16, 17].
One of challenges in utilization of the cement-based sensors is managing their electric polarization under an applied direct current (DC). This phenomenon is observed in dielectric materials exposed to an electric field such as during electrical resistivity measurement [18]. Since the polarization-induced electric field in the material is opposite in direction from the applied electric field, polarization results in growth of measured resistivity with time during resistivity measurement [19]. Such effect is undesirable for the purposes of application of nanomodified concrete as a piezoresistive material for it causes difficulties in associating the changes in resistivity with strain condition [20]. Applying voltage signals to materials with alternating current (AC) signals with equal magnitudes of positive and negative peaks can reduce the polarization. But this effect is dependent on current frequency [21]. It is therefore necessary to establish the appropriate current frequency prior to resistivity measurement which complicates the procedure. Besides that AC measurements are made with more sophisticated equipment as compared to DC measurements.

Several approaches to treatment of the polarization can be found in the literature. One of these is to evaluate the electrical resistance after a certain period of constantly applied current necessary for achieving a stable level of polarization. Meoni et al. [22] fulfilled their tests on strain sensitivity and linearity of the sensors after 6000 s of exposure to DC with a 4-probe method. Smaller value of 1000 and 1500 s was chosen by Li et al. [23] as a time for initial resistance measurement of CNT-cement composites with acid-treated nanotubes. Kim et al. [24, 25] measured DC resistance of CNT-cement composites value after 2 hours of electrical current supply from the digital multimeter.

Another method to cancel out the effect of polarization is to estimate the growth of electrical resistivity of a unloaded control specimen and then subtract it from the measurements on the actual loaded specimen [20]. Han et al. [26, 27] consider CNT–cement composites as a material having both resistance and capacitance characteristics. Resistance of composites during DC measurement therefore exhibits increase due to the effect of capacitor charging. Measured growth of resistance caused by the capacitor charging is approximatively linear. It is suggested that pressure-sensitive responses of composites can be calculated by removing the linear component from the measured resistance. In the research of Konsta-Gdoutos et al. [28] polarization of CNT–cement was successfully eliminated by drying the specimens in an oven first at 60 °C for three days, and then for another three days at 95 °C. Similar approach was adopted by Monteiro et al. [29] to decrease the effect of influence on electrical conduction of concrete composites with carbon black particles.

This research studies the possibility of a resistivity measurement with DC pulse waves. The suggested approach is based on assumption that polarization can be eliminated by applying electric field of short duration with relatively large period of measurement. Method is tested on the specimens of CNT-cement composites with different nanotubes concentration levels.

## 2. Materials and experimental program

### 2.1. Materials and preparation of specimens

The specimens for the experiment were made of concrete with no coarse aggregate doped with CNT. Ordinary Portland cement produced by Eurocement was used as a binder material. Natural sand for concrete mix had a fineness module 2.3. Silica fume was introduced in the mix for it is known to decrease the van der Waals force among CNT and therefore contribute to their dispersion [24]. Sikament BV 3M superplasticizer based on sodium lignosulfonate was added in order to increase the workability of concrete mix. Multi-walled CNTs produced by Dealtom (Russia) were used as electrically conductive filler. The physical properties of the CNT for the experiment are listed in table 1. Multi-wall carbon nanotubes are reported to be more sensitive to stress changes than single-wall nanotubes [13].

The composition of concrete is shown in Table 2. Three series each consisting of three specimens were fabricated for this study. The carbon nanotubes concentration in these series was 0.05, 0.1 and 0.2% by weight of cement. Galvanized steel plates with the size 24 mm x 24 mm were used as electrodes.
Table 1. Properties of MWCNT

| Parameter             | Unit | Value       |
|-----------------------|------|-------------|
| Diameter              | nm   | 49 - 72     |
| Length                | μm   | 5           |
| Electric resistivity  | Ω·m  | 3500·10^{-8}|
| Specific surface area | m²/ g | 97.6        |

Table 2. Mix-design of the prepared samples.

| Components            | Content (wt % / cement) |
|-----------------------|-------------------------|
| Sand                  | 100                     |
| Water                 | 45                      |
| Silica fume           | 15                      |
| Superplasticizer      | 1                       |

Carbon nanotubes tend to aggregate into microscale bundles due to the presence of strong attractive forces originating from their polarizable, extended π-electron systems [2]. That is why disaggregation and uniform dispersion of CNTs in concrete are critical challenges for the successful fabrication CNT-cement composites [30]. In this study weighed CNTs, superplasticizer and silica fume were first dissolved in water by ultrasonication with a frequency of 42 kHz for 30 min. Then the suspension was added to cement and fine aggregate. Fresh mix was casted into oiled 40 x 40 x 40 mm molds (figure 1) and subjected to machine vibration to achieve the desired compactness. The hardened specimens were demoulded and cured for 28 days at 20°C. Then they were dried in an oven for three days to improve their sensitivity [30]. After that all specimens were covered by epoxy to prevent variation of their moisture level and consequent inaccuracies of resistivity readings [29].

2.2. Measurement

Resistance measurement of CNT-cement composites can be fulfilled by either two-probe or four probe-method. Although a four-electrode method can reduce the polarization effect, it is associated with more complex fix of electrodes and measurement of electrical resistance [26]. This particularly may be the issue in case of monitoring compressive stresses in cross-section of elements in bending. The small height of their compression zone demands the small size of a sensor which would be difficult to achieve with large number of electrodes. Therefore, the relatively simple two-probe method (figure 2) was employed to measure electrical resistance with two electrodes embedded in the center of the section of each specimen at a mutual distance of 20 mm.

Figure 1. Prepared specimens.
Figure 2. Electrical diagram of the test configuration.

Downey et al. [31] reversed polarization by reversing the direction of the sensing current flow. Material sensing was provided by a periodic measure/discharge square wave, where DC measurements were made during the measurement region of the square wave. In our study DC for resistance measurement was applied as unidirectional pulses. The sensing current was provided as single square waves 0 to 2 V with a length 24 ms by portable data logger (TML TDS-530). The period between measurements was firstly taken equal to 1h and then reduced until the growth of resistivity became apparent. Specimens were subjected to at least 300 measurements with each of these periods to make sure that the presence or absence of polarization was understood correctly. The period of measurement preceding to the one when the polarization began to manifest was thus regarded as a “safe” period which can be used for DC resistance measurement of specimen.

3. Results

As an example figures 3 - 5 show experimental variations of resistance over number of measurements for specimens with 0.05% concentration of CNT. Change of resistivity is expressed in $R/R_0$, where R and $R_0$ are respectively the current and initial values of electrical resistance. For the depicted case at the 1 and 3 min period between measurements growth of resistance is present throughout the whole test. The sharpest increase in resistance is experienced within first 100 - 400 measurements. Although thereafter resistance tends to level out the further growth keeps being evident up until 1100 measurements. For the considered case 5 min period between measurements was recognized as a “safe” one. As it can be seen it is the shortest period of those that provide constant resistance measurement.

The test results for all specimens are given in Table 3. Mean value of initial resistivity of specimens with 0.2 % concentration of CNT is 50% and 47 % of those with 0.05 % and 0.1 % respectively. The variation of resistivity is shown in $R_{ult}/R_0$, where $R_{ult}$ is the electrical resistance from the last measurement. The “safe” period between measurements for tested specimens with was similar for all considered CNT/cement ratios. There is a slight variation of values of $R_{ult}/R_0$ with specimens having CNT/cement ratio 0.05 % displaying smaller values than those with CNT/cement ratio 0.1% and 0.2 %.

Based on these results the proposed method can be recommended for the electrical resistivity measurements of CNT-cement composites. Considering the aforementioned observations there must be a preliminary stage at which “safe” period between measurements must be determined for the sensors with particular mix proportions.
Table 3. Variation of resistance over period between measurements.

| CNT/cement ratio (%) | Specimen | $R_0$ (kΩ) | 1 min | 3 min | 5 min | $R_{ult}/R_0$ |
|----------------------|----------|-------------|-------|-------|-------|---------------|
| 0.05                 | #1       | 1852.68     | 1.061 | 1.028 | 1.002 |
|                      | #2       | 1271.66     | 1.081 | 1.025 | 1.002 |
|                      | #3       | 1289.01     | 1.060 | 1.046 | 0.999 |
|                      | Mean     | 1471.12     | 1.067 | 1.033 | 1.001 |
| 0.1                  | #1       | 1448.99     | 1.096 | 1.046 | 1.001 |
|                      | #2       | 1489.35     | 1.092 | 1.031 | 1.002 |
|                      | #3       | 1783.32     | 1.093 | 1.016 | 1.001 |
|                      | Mean     | 1573.89     | 1.094 | 1.031 | 1.001 |
| 0.2                  | #1       | 639.53      | 1.098 | 1.035 | 0.998 |
|                      | #2       | 805.36      | 1.091 | 1.027 | 1.001 |
|                      | #3       | 773.33      | 1.092 | 1.028 | 0.999 |
|                      | Mean     | 739.41      | 1.094 | 1.030 | 0.999 |

4. Conclusions

The paper studied the possibility of CNT-cement composites DC resistivity measurements with a new relatively simple method. Material sensing is fulfilled by periodic measurements with a square wave of short length. Polarization of the samples is eliminated by establishing period between the measurements providing stable resistance readings. The “safe” period between the measurements for all CNT/cement ratios considered in the experiment was equal to 5 min. CNT-cement composites are often suggested to be used for production of smart sensors for structural health monitoring. For that matter sensing with a period of 5 min is quite applicable for monitoring the stress state of structures under static loading.

Further research is necessary to study the effect of voltage and wave length on the polarization of CNT-cement composites during resistivity measurements with the proposed method. During our experiments electrical resistance of CNT-cement composites was strongly influenced by their temperature. This issue also needs to be addressed with a targeted research because of its primary importance for practical application of CNT-cement composites as smart sensors.

Figure 3. Variation of $R / R_0$ measurements for specimens with CNT / cement ratio 0.05 % with period 1 min between measurements
**Figure 4.** Variation of $R/R_0$ measurements for specimens with CNT/cement ratio 0.05% with period 3 min between measurements

**Figure 5.** Variation of $R/R_0$ measurements for specimens with CNT/cement ratio 0.05% with period 5 min between measurements

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