Role of Carbon Nanofiber on the Electrical Resistivity of Mortar under Compressive Load

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Abstract
A nanomodified cement consisting of particles with in situ synthesized carbon nanofibers was developed to introduce a strong load-sensing capability of the hydrated binder matrix. The material was produced using chemical vapor deposition. The nanomodified cement contained 2.71 wt% of carbon nanofibers (CNFs). The electrical properties of the composite were determined. Several mortar samples were prepared by partially substituting ordinary Portland cement with 2, 4, 6, 8, and 10 wt% of the nanomodified cement. Additionally an ordinary Portland cement mortar was used as reference. The results show that the strongest piezoresistive response and therefore the best load-sensing was obtained for the mortar containing the highest amount of CNFs. This mortar contained 10 wt% of nanomodified cement. The fractional change in electrical resistivity of this mortar was 82% and this mortar had a compressive strength of 28 MPa.

In general, structural health monitoring (SHM) in civil engineering is defined as a process that aims to detect a change in the structural properties as a way of identifying damaged structures (1). Many methods that monitor concrete structures in SHM systems commonly use strain gauges mounted on the concrete surface or embedded fiber optic sensors. Most of the systems currently in use are prone to mechanical damage and have poor durability and thus a short lifespan. A novel solution is based on smart Portland cements, which after solidification have a strong sensing capability. The main advantage of cement-based sensors is their full material compatibility with the material used to build the structure being monitored. These sensors are expected to have a long service life, easy installation, and limited maintenance. Self-monitoring Portland cement-based materials are becoming more attractive for civil engineering applications. This self-monitoring or so-called self-sensing is made possible by changes in the electrical resistivity of a material. Electrical resistivity is a fundamental material property that shows how strongly the material opposes the flow of an electric current. The self-sensing phenomena in a material is based on the property of an electrically conductive material to show a change in its electrical resistivity if a deformation load is applied. This phenomenon is called piezoresistivity. To provide a cement-based material with this load-sensing capability various types of conductive materials need to be incorporated into the cementitious matrix.

Studies showed that the addition of carbon nanofibers (CNFs) and carbon nanotubes (CNTs) improve physical, mechanical, chemical, and electrical properties (2–5). For example, Cwirzen et al. found that an addition of 0.045 wt% of multi-walled carbon nanotubes (MWCNTs) to a cement paste increased the compressive strength by nearly 50% (6). Konsta-Gdoutou et al. (7) produced pastes containing 0.048 wt% of MWCNTs and achieved 30% to 40% higher flexural strengths values. The presence of long MWCNTs appeared to decrease the autogenous shrinkage. Konsta-Gdoutou and Aza (8) studied the piezoresistive behavior of a cementitious matrix with CNFs subjected to cyclic compression load in the elastic regime. The electrical resistivity tended to decrease during the loading and to increase while unloading. Similar results were obtained by Yu and Kwon (9) where a change in the electrical resistivity of a CNT/cement composite under different compressive loading was observed.

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Specimens reinforced with functionalized CNTs showed a stronger piezoresistive response. A sufficient amount of conductive materials is required to create a continuous interconnected network. The fibers must be evenly distributed throughout the binder matrix. Unfortunately, because of the hydrophobic nature and the tendency of carbon-based materials to agglomerate, it is crucial to ensure their uniform dispersion into the matrix. The nanomodified cement was developed to address the dispersion problem of carbon-based materials in cementitious matrices. The nanomodified cement was produced by synthesizing CNFs directly on the surface of pristine Portland cement particles in a chemical vapor deposition (CVD) reactor. In the processed synthesis, the Fe2O3 present in Portland cement acted as a natural catalytic substrate while the other phases supported the growth of CNFs ($10^{10}$–$10^{12}$). Acetylene ($C_2H_2$) was used as the main carbon source with synthesis temperatures between 525°C and 600°C. Solidified matrices produced from the modified cement showed a very good dispersion of the CNFs ($13$). Recently, Buasiri et al. reported pilot studies on the sensing capability of the nanomodified cement which showed an excellent load sensitivity of those materials ($14$). The studied mortars containing around 0.2 wt% of CNFs showed a high sensitivity, reaching around 90%.

The research described in this article aimed to determine the effects of the replacement of Portland cement with various amounts of nanomodified cement on the mechanical properties and the changes in the electrical resistivity under compression loading.

**Methods**

**Synthesis of the Nanomodified Cement**

The nanomodified cement was produced using a Carbon Chemical Vapor Deposition (CCVD) reactor located at the Silesian University of Technology in Poland. For the syntheses, pure ethylene ($C_2H_4$, 99.9999%) was used as a main carbon source, pure hydrogen ($H_2$, 99.999999%) as the reducer and Argon (Ar) as the transporting media. All of the gases were industrial grade. A schematic diagram of the CVD process and the synthesis procedure of the nanomodified cement are shown in Figure 1.

**Materials and Sample Preparation**

An ordinary Portland cement CEM I 42.5 provided by Cementa-Sweden was used for the synthesis of the nanomodified cement and for the production of the test mortars. Sand with maximum particle size of 150 μm was used as fine aggregate. The nanomodified cement was synthesized by the CVD method shown in Figure 1. The surface morphology of the pristine and modified cements is shown in Figure 2. The quantitative analysis of the carbon nanomaterials formed in the nanomodified cement was done by thermogravimetry (TG). The total amount of CNFs and other carbon containing phases calculated by percentage of the mass loss was approximately 2.71 wt%. The visually estimated diameters were around 10–50 nm and the lengths between 3 μm and 20 μm with a very curly shape.

All mortar samples had the same water to binder ratio (w/b) of 0.35, sand to binder ratio (s/b) of 1% and 0.8% of the super plasticizer admixture by weight of the binder. The admixture type Glenium produced by Grace Chemical was used to control the workability of fresh mixes. The nanomodified cement replaced 0% (Ref), 2% (S2), 4% (S4), 6% (S6), 8% (S8), and 10% (S10) of the pristine cement by weight of the binder. The proportions of the mortars produced are shown in Table 1. Because of the very limited amount of available nanomodified cement only two samples were produced for each mix.

![Figure 1](https://example.com)
amount of the trapped air. The mortars were cast into Teflon molds and subsequently cured in water. Before testing, all samples were stored in laboratory conditions at 20°C ± 2°C for 72 h to exclude any possible effects of moisture or temperature variations on the measured electrical properties. The specimens had dimensions of 12 mm × 12 mm × 60 mm with four copper electrodes embedded vertically. The 0.25 mm thick copper electrodes had a width of 5 mm and a height of 15 mm. The electrodes were spaced as shown in Figure 3a.

**Load-Sensing Determination**

The load-sensing capability in the present research was based on the determination of changes in the electrical resistivity of the samples when subjected to an increasing compression load. Sensing behavior of the cement-based materials under loading can be described by the fractional change in the electrical resistivity (FCR) which can be calculated using Equation 1:

\[
\text{FCR} = \frac{\Delta \rho}{\rho_0}
\]  

where \(\Delta \rho\) is the change in electrical resistivity and \(\rho_0\) is the initial electrical resistivity of the sensing cementitious matrix. The electrical resistivity \(\rho\) was calculated following Equation 2:

\[
\rho = \frac{R \cdot A}{L}
\]

where

- \(R = V/I\) is the measured resistance determined by the change of the voltage \(V\) across the specimen when applied the current \(I\),
- \(A\) is the electrode area, and
- \(L\) is the internal electrode distance.

The electrical resistance of the produced mortars was measured using the four-probe method during the application of the compressive load. This configuration showed the lowest variation coefficient and smallest scatter of the data (15). The 60 cm long electrical wires connected the copper electrodes with a digital multimeter of type Keysight 34465A. The direct current (DC) was applied between the two outer electrodes while the two inner electrodes were used to measure the potential difference. The compressive load with the rate of 0.05 cm/min was applied to the mortar beams. The experimental setup is shown in Figure 3b.

In moist matrices, including cement-based ones, the polarization effect causes chemical reactions liberating hydrogen and oxygen, which deposit around the measuring electrodes as a thin film and cause changes to the electrical response (16). To eliminate or minimize this effect, the specimens should be dry, and a high-frequency alternating current should be applied (17). In this study,
which used DC current, the polarization effects were limited by an additional calibration measurement \((18)\) to establish a stable initial reading of the resistance of the solidified matrix before the actual measurement was done.

**Results and Discussion**

Changes in the electrical resistivity under compressive load were determined on 28-day-old mortar samples containing various amounts of the nanomodified cement; Ref, S2, S4, S6, S8, and S10.

The load-sensing capability is directly related to the piezoresistive response. The conductivity is governed by the concentration of the CNFs and the so-called percolation threshold. The percolation threshold marks an abruptly increasing electrical conductivity when the concentration of the nanomodified cement reaches a certain critical value, the so-called percolation threshold value. The electrical resistivity changes depending on the amount of the conductive filler and creates three consecutive zones; an insulation zone, a percolation zone, and a conduction zone, Figure 4a \((19)\). Below the percolation zone, the amount of conductive filler is too small to achieve a conductive material. Furthermore, the electrical conductivity will be altered by any mechanical deformation causing changes in the contact area between CNFs, the binder matrix, or both. This leads to a rearrangement of the CNFs and the formation of effective conductive paths thus altering the measurable electrical conductivity, Figure 4c.

The observed curves also showed non-linear behavior, which could be related to microcracking of the binder matrix, Figure 5. Other possible factors also include variations of humidity and temperature. However, those factors were assumed insignificant because of the experimental setup used.

The results in Figure 5 showed that the fractional change in electrical resistivity decreased with increasing compressive stress for the samples containing different amounts of the nanomodified cement. This decrease continued until failure occurred. The partial substitution of the pristine cement by the nanomodified cement has affected the piezoresistive response of the mortar samples. There are three groups of piezoresistive response within the sample range, while the reference sample remained unchanged. In the first group, S2 and S4 showed very small piezoresistive effects to the applied load. This could be explained by several factors including the small amount of the nanomodified cement leading to the inter-particle distance of the conductive cement particles being too large. Because of this large inter-particle distance, no electrically conductive path through the sample can be formed. In the following group, the sensitivity of the solidified matrix containing 6 wt% of the nanomodified cement increased moderately to approximately 20%. In the last group, both measured samples S8 and S10 showed a strong piezoresistive response with similar trends. The highest sensitivity was achieved in the samples containing 10 wt% of the nanomodified cement which corresponded to a decrease by 82\% of the fractional change of electrical resistivity.

Mortar beams showed a piezoresistive response within two stages of nearly linear relationships. In the first stage, all samples had very high sensitivity to the applied compressive load up to around 6 MPa. In the second loading stage, from 6 MPa until failure, the change was less extensive. The piezoresistive response can be related to the intrinsic piezoresistive property of the CNFs. The applied compressive load leads to a deformation-induced formation of effective conductive paths as well as changes in the tunneling distance and the contact points between CNFs on the nanomodified cement particles.
The load-sensing capability could be related to the amount of CNFs present in the matrix and thus to the percolation threshold. Based on the results obtained the percolation threshold values of the nanomodified cement were around 7 wt%, Figure 4b. The measured values indicate that samples containing 2 wt%, 4 wt%, and 6 wt% of the nanomodified cement are still under the percolation threshold while samples containing 8 wt% and 10 wt% are above it.

**Conclusion**

The electrical response during compressive loading of a pristine cement sample and samples containing nanomodified cement was recorded to determine the load-sensing capability of the nanomodified cement. A replacement by 10 wt% of the untreated cement by the nanomodified cement showed an extremely strong piezoresistive response to the applied load. The fractional change in the electrical resistivity reached 82% at 28 MPa. The strong piezoresistive response was related to the intrinsic piezoresistive property of the CNFs themselves and to changes of the electrical resistance of the contact points between the nanofibers under the applied load. The results obtained indicate that the nanomodified cement-based material gives a clear piezoresistive response under loading which could be utilized as in-built sensors in structures.
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Author Contributions
The authors confirm contribution to the paper as follows: study conception and design: Thanyarat Buasiri, Karin Habermehl-Cwirzen, Lukasz Krzeminski, Andrzej Cwirzen; data collection: Thanyarat Buasiri; analysis and interpretation of results: Thanyarat Buasiri, Karin Habermehl-Cwirzen, Lukasz Krzeminski, Andrzej Cwirzen; draft manuscript preparation: Thanyarat Buasiri, Karin Habermehl-Cwirzen, Lukasz Krzeminski, Andrzej Cwirzen. All authors reviewed the results and approved the final version of the manuscript.

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