Piezoresistive behavior of mortars loaded with graphene and carbon fibers for the development of self-sensing composites

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ABSTRACT: Structural monitoring systems are gaining increasing interest in the field of civil engineering research, due to the recent commitment for the preservation of building heritage, for the saving of resources and for an eco-friendly construction industry. Recent researches show that the addition of conductive fillers and fibers within cement materials could originate cement-composites able to diagnose their own state of strain and tension, measuring the variation of their electrical characteristics (resistance). In this work, resistivity and piezoresistivity of mortars added with graphene nanoplatelets (GNP), and carbon fibers (CF) were evaluated. The variations in electrical resistivity as a function of strain were analyzed under cyclic uniaxial compression of the mortars samples. The results shown a high piezoresistivity behavior of the mortars with an optimal dispersion of GNP and CF, with a quite reversible relation between fractional change in resistivity (FCR) and compressive strain.

1 INTRODUCTION

In the last decades, infrastructures have acquired increasing importance within modern society. These regulate resources supply and the proper functioning of communication technologies and modes of transport. In the field of reinforced concrete structures, civil engineering is increasingly focusing on innovative control systems that guarantee safety in their use and an efficient operation (Brownjohn, 2007). This aims to introduce non-destructive systems, able to investigate the health of concrete, such as the detection of deformations through piezoresistivity.

Piezoresistivity is a physical characteristic of electrically conductive materials which leads to a variation in the electrical resistivity of the material subjected to strain stress (Zhu et al., 2007). Since the 1990s, studies have been carried out to implement cementitious materials through piezoresistive properties, to obtain an effective reading of the state of health of a concrete structure (Chung et al., 1993).

Material engineering contributes to this field of study, thanks to the development of innovative, multifunctional and high-performance materials, such as graphene. The electrical properties of graphene make it an interesting material to increase the electrical conductivity of cement-based materials and to develop their piezoresistive behavior. Graphene, dispersed in a cement-based mixture, forms an effective network of electrically conductive particles. When the composite is subjected to compressive deformation, the particles move closer, changing the conductive paths and giving the material piezoresistive properties (Chung et al., 1993).

However, there are few studies performed on piezoresistive cements with graphene addition. In this work, the electrical behavior of cementitious composites (structural mortars) with graphene nanoplatelets (GNP) and carbon fibers (CF) addition was investigated. Furthermore, the combined effect of these two materials on both mechanical properties and piezoresistive behavior of mixtures was investigated.

2 MATERIALS AND METHODS

2.1 *Mixtures*

In order to study the effects of GNP and CF in cement-based materials, mortars made of CEM II 32.5N cement and silica sand (diameter <1 mm) with an aggregate/cement ratio equal to 3 and a water/cement ratio equal to 0.5 were realized. GNP (Pentagraf, Pentachem S.r.l.) were added in two different quantities: 4% and 7% by cement weight; as well as CF (Apply carbon): 0.05% and 0.2% by mortar volume. For a better comparison of performances, a reference mixture without the addition of fillers and fibers was also produced (Tab. 1).

A polycarboxylate ether agent (Melflux 4930F, Basf S.E.) as superplasticizer (SP) was also used in order to improve the dispersion of the filler and the workability of the mixture.

Table 1. Mix proportions and slump flow values of tested mortars.

Mixtures	Cement (g/L)	Water (g/L)	Sand (g/L)	GNP (g/L)	CF (g/L)	SP (g/L)	Flow value (mm)
REF	512	256	1535	-	-	-	185
GNP4	512	256	1535	20	-	1	173
GNP7	512	256	1535	36	-	2	200
0.05CF	512	256	1535	-	2	-	177
0.2CF	512	256	1535	-	7	-	170
GNP4 + 0.05CF	512	256	1535	20	2	1	200
GNP4 + 0.2CF	512	256	1535	20	7	2	177

2.2 *Mechanical characterization*

In order to verify the influence of the additions on the mechanical properties of the composites, 3-point flexural strength tests and compressive strength tests were carried out on the 40x40x160 mm samples at 2, 7 and 28 days of curing (UNI EN 1015-11:2007).

2.3 *Electrical characterization and piezoresistivity tests*

The electrical conductivity of the mortars was investigated through the measurement of the electrical resistivity of the samples at 7, 14, 21 and 28 days of curing and in the specimens in dried conditions. For the tests, a power supply (Protek) and a data acquisition device (DAQ, Data Taker DT80) were used. A potential difference was applied in the external electrodes of the samples, in order to apply well defined values of current $I_{(t)}$ to the material. The voltage U_s between the two inner electrodes was detected by the DAQ, and the resistivity ρ_s is thus calculated through the first and the second Ohm's law, From which (eq. 1):

$$\rho_s = \frac{U_s}{I_s}\frac{A}{l} \tag{1}$$

Where I_s = current measured between the outer electrodes; A = contact area between the electrodes and the material; l = spacing between the inner electrodes. For piezoresistivity tests, a continuous acquisition of the resistivity of the material subjected to compression load cycles was carried out. After 28 days of curing, samples were dried at 60°C until a constant mass was reached, thus eliminate the influence of the samples humidity during the tests. For the measurement of compression deformation, a 15 mm, 120 Ω strain gauge connected to the DAQ was applied in the middle of the sample. A potential difference of ≈ 20V was applied to the outer electrodes until the stabilization of the resistivity value. A Shimadzu AG-IC press applied a pressure increase of 250 $N\cdot s^{-1}$ to the sample, up to a maximum of 25 kN (15.6 MPa) and a related decrease until 2kN. The piezoresistive properties of the materials were evaluated through the calculation of the fractional change in resistivity (FCR) according to equation (eq. 2):

$$FCR = \frac{\rho_{(t)} - \rho_0}{\rho_0} \tag{2}$$

Where $\rho_{(t)}$ = maximum load sample resistivity; ρ_0 = initial sample resistivity.
The correlation between FCR and strain, defined as sensitivity, was evaluated as (eq. 3):

$$sensitivity = \frac{FCR}{\mu\varepsilon} \tag{3}$$

3 RESULTS AND DISCUSSIONS

3.1 *Mechanical properties*

The mechanical strength tests demonstrated that the additions do not significantly improve the mechanical strength of the mixtures. On the contrary, high quantity of GNP, lead to a decrease in mechanical compressive strength (22% less for GNP7, compared to REF). This is due to the hydrophobicity of graphene and its physical characteristics (specific surface area and bulk density) and to the consequent difficulty in mixing during the samples preparation (Li et al., 2017). This leads to an increase in porosity in the hardened mortar.

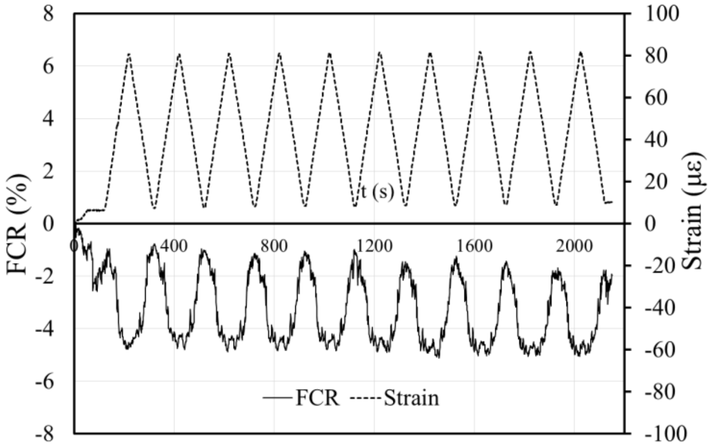
Best results in terms of mechanical performance were obtained on samples containing CF (with increments of 10% compared to REF). This is related to bridging action of fibers (Mastali et al., 2016). This effect offers more resistance to crack opening in cement-based materials, with transferring stress from fibers to the cement matrix regard to interfacial shear strength.

3.2 *Electrical properties and piezoresistivity*

The high amount of voids of the mortars with GNP also affects their electrical properties, since the samples with GNP show higher values compared to the reference (260% of the REF value for the mortar GNP4-0.05CF).

On the contrary, two of the realized mixtures show very low resistivity values, even after the samples drying. 0.2CF and GNP4-0.2CF mortars show a resistivity of 328 Ω·m (87% less than REF) and 5.3 Ω·m (three orders of magnitude less than REF) respectively. The high conductivity of these mixtures is probably due to an optimal distribution of the additions within the matrix, which form an extremely effective conductive network within the material (Han et al 2011). 0.2CF and GNP4-0.2CF mixtures, thanks to their high conductivity, showed also interesting piezoresistive properties. 0.2CF shows a very high sensitivity (613.5 MPa^{-1} and 5% of FCR), and the change in resistivity is constant and repeatable. However, the reading has some noise, as can be seen from the irregularity of the FCR-Time curve (Fig. 1).

On the contrary, GNP4-0.2CF shows a lower sensitivity (295.4 MPa^{-1} and 2.2% of FCR with similar strain values), but a very high regularity of reading, as seen by the trendline of the FCR-Strain points (Fig. 2). The high repeatability is due to the high conductivity of the material, which shows a piezoresistive behavior more similar to a traditional strain gauge.



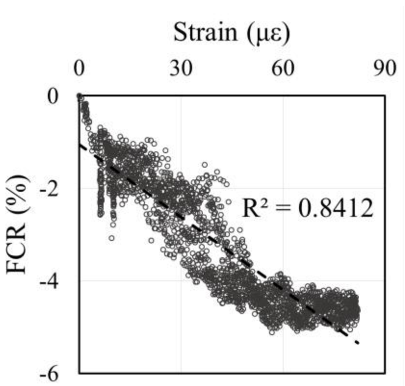


Figure 1. FCR and Strain vs. time of 0.2CF under cyclic loading and FCR-Strain trendline.

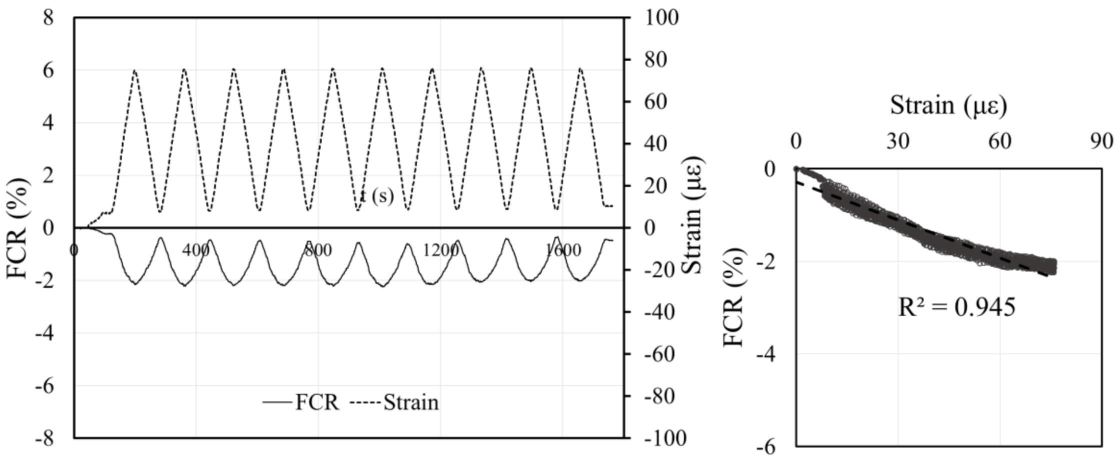


Figure 2. FCR and Strain vs. time of GNP4-0.2CF under cyclic loading and FCR-Strain trendline.

4 CONCLUSIONS

In this work, the electrical and mechanical properties of mortars with GNP and CF have been studied for the development of cement-based sensors for self-sensing systems.

Experimental results show that GNP decrease the homogeneity of composites, thus increasing the number of voids of the mortars. This leads to a decrease in mechanical strength and to an increase in resistivity. This demonstrates that the electrical properties of graphene are less influential than its effects on the cement matrix and the voids amount.

On the contrary, 0.2CF and GNP4-0.2CF mixtures show a very high electrical conductivity, and clear piezoresistive properties. Although the resistivity of the 0.2CF was two orders of magnitude greater compared to GNP4-0.2CF, the first shows a greater electrical sensitivity during load application. This demonstrate that greater electrical conductivity does not always leads to better piezoresistivity.

The interesting electrical properties of these two mixtures demonstrate the importance of the distribution of conductive additions within the mortars. In future studies, techniques for a better dispersion of GNP and CF in the composites will be investigated in order to improve their effectiveness as piezoresistive sensors.

5 REFERENCES

Brownjohn, J.M.W. 2007. *Structural health monitoring of civil infrastructure*, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 365, 589-622.

Chung D.D.L., Pu-Woei C. 1993. *Carbon fiber reinforced concrete for smart structures capable of non-destructive flaw detection*. Smart Materials and Structures. 2(1): p. 22.

Han B., Yu X., Ou J., 2011. *Multifunctional and smart nanotube reinforced cement-based materials. Nanotechnology in Civil Infrastructure. A Paradigm shift*. Gipalakrishnan K., Birgisson B., Taylor P., Attoh-Okine N. Editors – Springer, 1-48.

Li X., Liu Y.M., Li W.G., Li C.Y., Sanjayan J.G., Duan W.H., Li Z. 2017. *Effects of graphene oxide agglomerates on workability, hydration, microstructure and compressive strength of cement paste*. Construction and Building Materials 145 402–410.

Mastali M, Dalvand A. 2016. *The impact resistance and mechanical properties of self-compacting concrete reinforced with recycled CFRP pieces*. Composites Part B 92. 360-376.

Zhu S., Chung D.D.L 2007. *Analytical model of piezoresistivity for strain sensing in carbon fiber polymerematrix structural composite under flexure,* Carbon 45 (8) 1606-1613.