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# STRAIN-SENSING CARBON NANOTUBE CEMENT-BASED COMPOSITES FOR APPLICATIONS IN STRUCTURAL HEALTH MONITORING: PREPARATION AND MODELLING ISSUES

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**Abstract.** *The authors have recently explored the use of electrically conductive cement-based composites doped with carbon nanotubes for dynamic monitoring of strain in concrete structures. While the technology appears to be very promising for cost-effective structural health monitoring, some challenges still limit its applicability to full-scale constructions. The dispersion of the nanoparticles, typically based on sonic treatment and on other special procedures, is not compatible with distributed full-scale deployments and essentially limits the applications of the technology to the fabrication of embeddable sensors. Also, the electromechanical behaviour of the composites is complex and a proper analytical model linking electrical output to accurate strain measurements is yet to be established. This work discusses these open issues in fabrication and modelling of carbon nanotube composite concrete. A fabrication procedure with potential applicability to large casting volumes is presented and experimental results highlighting its effectiveness are discussed. Results cover analysis of nanoparticles dispersion, electrical percolation, strain sensitivity and polarization.*

## 1 INTRODUCTION

Conductive micro- and nano-fibers, such as carbon nanoinclusions, can be incorporated into cementitious matrices to provide electrical conductivity. The resulting composite materials exhibit self-sensing abilities, whereby their electrical response is modulated by their state of strain [1-8]. Unfortunately, large-scale applications of this sensing technology are still missing, owing to the difficulties in obtaining a good dispersion of particle additives. Dispersion typically requires special treatments, such as the sonic treatment, that cannot be applied in the case of large casting volumes. Nanoparticles are difficult to disperse because they tend to form agglomerates and bundles. In the case of Multi-Walled Carbon Nanotubes (MWCNTs), for example, the formation of agglomerates and bundles is caused by Van der Waals attraction forces among nanotubes due to the electronic configuration of tube walls and their high specific surface area. While most authors agree that ultrasonic treatment is the most effective way to achieve a satisfactory dispersion, the use of dispersing additives can also help preventing the formation of bundles in an aqueous solution containing MWCNTs.

This paper investigates electrical conductivity and strain sensitivity of concrete doped with MWCNTs and prepared using different fabrication processes. The objective of this study is to explore possible processing strategies suited for fabricating conductive concrete with improved scalability to large-scale applications. This will be achieved without sonication, by using dispersing additives and mechanical mixing.

## 2 SMART CONCRETE DOPED WITH CARBON NANOTUBES

MWCNTs belong to the structural family of Fullerene. Van der Waals attractive forces between nanotubes cause the formation of bundles. Because of these bundles, it is difficult to achieve a uniform dispersion of the nanoparticles within the cement matrix, provoking defects in the composites and insufficient mechanical properties. Dispersion of the nanotubes is typically accomplished in water, followed by the addition of the water-MWCNTs suspension to cement powder, aggregates and additives.

Different approaches used in dispersing nanotubes in water can be roughly classified into: (i) mechanical methods, where nanotubes are separated using mechanical mixers; (ii) physical methods, where nanotubes separation is obtained through non-covalent surface modifications based on the use of proper dispersants without altering the covalent bonds on the tube lattice; (iii) chemical methods, where covalent surface modifications are operated using aggressive chemicals, such as neat acids, that functionalize the surface of MWCNT but often result in defects or alterations due to the chemical nature of the treatment. In most cases, the sonic treatment, where mechanical agitation by ultrasonication produces temporary dispersion of nanotubes, is conducted to complement the chemical or physical methods. The mechanical processing methods and their possible combination with sonic treatment are the central focus of this study.

The ability of a nanocomposite to work as a sensing material is related to the piezoresistive effect. Namely, when concrete doped with MWCNTs is subjected to a variation in its internal state of strain, the distance between the nanoparticles is changed, which also alters their electrical interactions [4]. The resulting macroscopic variation in materials' electrical resistivity can be measured and correlated with the applied strain.

It should be noticed that nanocomposite concrete is not only resistive, but also capacitive, which complicates the characterization of its electromechanical behavior. Literature findings suggest that only the internal resistance is significantly influenced by the mechanical deformation. According to this simplification, a relationship between incremental variation in electrical resistance, $\Delta R$ , and axial strain, $\varepsilon$ (positive in compression), can be established, which, at a first order of approximation (small strain) can be modeled in analogy with electrical strain gauges as

$$\frac{\Delta R}{R_0} = -\lambda\varepsilon \tag{1}$$

where $R_0$ is the unstrained internal electrical resistance and $\lambda$ is the gauge factor of the material. From Eq. (1), the sensitivity, *S*, of nanocomposite concrete specimens is given by

$$S = \frac{\Delta R}{\varepsilon} = -\lambda R_0 \tag{2}$$

## 3 FABRICATION AND MODELLING ISSUES

Nanocomposite concrete specimens doped with MWCNTs were prepared by varying the type and amount of dispersant, and the mixing procedure. The resulting nanotube dispersion and quality of the fabricated composites were then experimentally assessed.

Conductive nanoparticles in the cementitious matrix were multi-walled carbon nanotubes type Graphistrength C100 from Arkema. Eight different types of dispersants were considered in the experiments, as summarized in Table 1.

First, an amount of 0.1 g of MWCNTs and a variable amount of chemical dispersant were added to 40 g of deionized water. Each dispersant was used in three different concentrations, namely 0.1:1, 1:1 and 10:1 to the mass of MWCNTs, corresponding to 0.01 g, 0.1 g and 1.0 g of dispersant. Premixing of deionized water, dispersant and MWCNTs was conducted manually. MWCNTs were then mixed in water by means of two different procedures, termed mixing procedure ME and mixing procedure SO. Mixing procedure ME was a simple mechanical mixing, while mixing procedure SO consisted of a sonication procedure. In mixing procedure ME, magnetic stirring was followed by 60 minutes of mechanical mixing, while, in mixing procedure SO, the water-dispersant-MWCNTs suspension was sonicated for 30 minutes. Figure 1 sketches the mechanical mixing procedure ME, also termed the scalable mixing procedure.

The following identification code was used for naming the different samples of MWCNTs-water dispersions prepared for the experiments: "MP_DN_DR", where MP denotes the mixing procedure, that can either be ME or SO, as described above, DN is the dispersant number (see Table 1) and DR is the ratio between dispersant and MWCNTs mass.

| No. | Name | No. | Name |
|---|---|---|---|
| 1 | BYK 154 | 5 | NaDDBS |
| 2 | G.SKY 624 | 6 | SLS |
| 3 | DISPERBYK 190 | 7 | PSS |
| 4 | BYK 9076 | 8 | PVA |

Table 1: Dispersants used in the experiments.

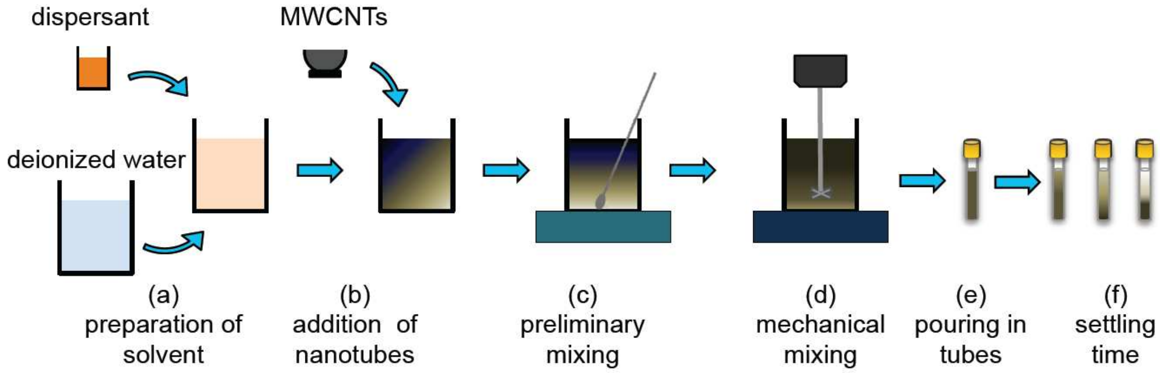


Figure 1: Scalable preparation procedure for dispersing MWCNTs in water.

Concrete nanocomposite specimens were fabricated using different concentrations of MWCNTs and the two different dispersion procedures presented in the previous section with a selected type of dispersing additive. Specimens were poured in cubes of 5.1x5.1x5.1 $cm^3$ with embedded net-shaped electrodes consisting of stainless steel nets inserted in the specimens along approximately 85% of their thickness (Figure 2).

The composite specimens were named using the following identification code: "CO_MP_N%_DN_DR", where CO stands for concrete, N% is the mass content of MWCNTs expressed as a percentage with respect to the mass of cement, while MP, DN and DR are as defined above.

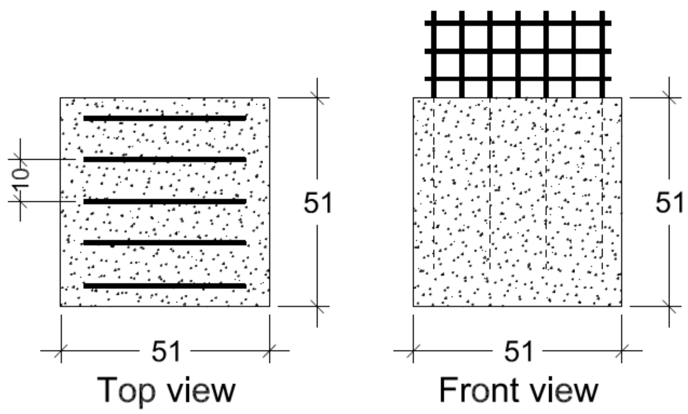


Figure 2: Sketch and dimensions (in mm) of fabricated nanocomposite concrete specimens

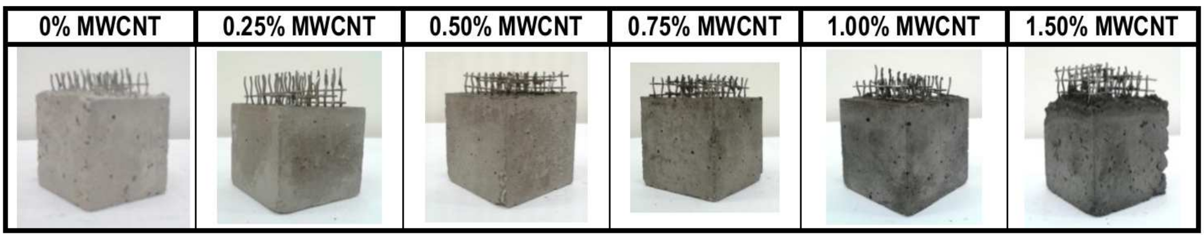


Figure 3: Photographs of fabricated concrete composite specimens using 10:1 concentration of SLS dispersant without sonication and with different mass contents of MWCNTs to the mass of cement (from 0 to 1.5% rightward).

Six different concentrations of MWCNTs were considered, from 0 to 1% with respect to the mass of cement, with step increments of 0.25%, and from 1 to 1.5% with a step increment of 0.5%. Figure 3 shows photographs of the composite specimens fabricated using the SLS dispersant at a concentration of 10:1 and considering different contents of MWCNTs. The change in color from the plain materials to the nanocomposites with increasing content of MWCNTs is apparent from the figure.

## 4 EXPERIMENTAL PROGRAM

A classification of the different specimens based on a dispersion performance index, *J*, ranging from 0 to 6 was performed (0 corresponding to the worst dispersion and 6 to the best dispersion) in order to investigate the quality of MWCNTs dispersion. The dispersion index was computed as:

$$J = S_1 + S_{28} + P \tag{3}$$

where $S_1$ denotes the "initial settling factor", $S_{28}$ denotes the "final settling factor" and $P$ is the "SEM picture factor".

$S_1$ and $S_{28}$ factors are derived from the transparency analysis of test tubes containing 1 ml of the MWCNTs suspension diluted in 10 ml of deionized water. The assessment of the settling conditions of the suspension in the test tube after 1 day gave the initial settling factor, $S_1$, a value of 0, 1 or 2 (2 for fully opaque and 0 for fully transparent suspension). The final settling factor, $S_{28}$, is attributed a value of 0, 1 or 2 following the same procedure adopted for $S_1$, but after 28 days.

SEM pictures of the specimens at different magnifications were used to assess the SEM picture factor *P*. The SEM analysis was conducted on a drop of the obtained solution, poured on a silicon wafer and taken after water evaporation. A value $P = 0$ was given when the picture first showed bundles of MWCNTs at a magnification factor of 100x. A value $P = 1$ corresponds to bundles first observable at a magnification factor of 500x. A value $P = 2$ is assigned when the SEM image does not show any bundles at 5000x.

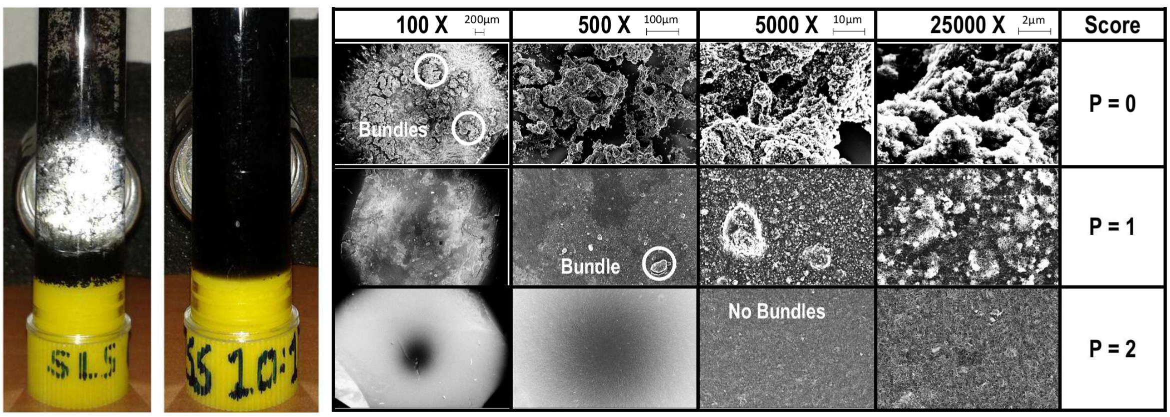


Figure 4: From left to right: Illustrative samples corresponding to initial settling factors of 0 and 2; SEM pictures corresponding to different SEM picture factors.

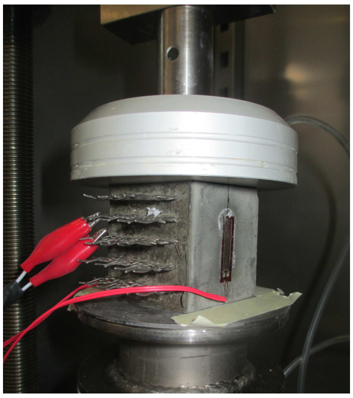

Figure 5: Detailed view of coaxial cables connected to the net electrodes of the sample under uniaxial compression test with strain gauges.

Typical pictures of retro illuminated test tubes corresponding to settling factors of 0 and 2, as well as SEM images taken at different magnification factors illustrating situations corresponding to SEM picture factors of 0, 1 and 2 are shown in Figure 4.

Electrical characterization of the composite materials was conducted using a high precision digital multimeter, model Keithley 6517B with resistivity text fixture model 8009. In particular, a constant voltage difference of 1.5 V was applied at the two external electrodes and the electrical resistance was indirectly obtained by measuring the current circulating through the specimens after 3 minutes to reduce the polarization process.

The strain-sensing capability of the composite concrete was assessed through axial compression tests using a servo-controlled pneumatic universal testing machine, model IPC Global UTM14P of 14 kN load capacity. Figure 5 is a photo of a specimen mounted on the machine. In the axial compression tests, the sensing specimens were first precompressed at 0.5 kN, and then subjected to loading-unloading cycles at constant speed of 0.5 kN/s and increasing amplitude of 1, 1.5 and 2 kN. Average compressive strain in the composites was obtained by using two resistive strain gauges, while strain sensitivity, $S$, Eq. (2), was obtained by measuring $\Delta R$ through a digital multimeter, model NI PXI4071.,installed into a NI PXIe1073. The NI PXIe1073 also hosted a source measure unit, model NI PXI4130, to provide a stabilized potential difference of 1.5 V in a single isolated channel, and a data acquisition card, model NI PXIe-4330, for strain gauges.

## 5 RESULTS

Scores obtained by the different specimens in MWCNTs dispersion tests are shown in Figure 6. These scores were computed according to Eq. (3) and only specimens qualifying for scores greater than zero are shown in the figure. The presented results outline excellent performances of dispersants number 3 (DISPERBYK190) and 6 (SLS): these dispersants, when complemented with sonication, attain the highest score even with a 1:1 concentration. Almost all types of dispersants provide very good results ( $J \geq 4$ ) when sonicated and used at the 10:1 concentration.

The results presented above suggest that a good dispersion can be obtained by sonication using the SLS dispersant of concentration ratios 1:1 and 10:1, or mechanical mixing using the same dispersant of concentration ratio 10:1. The SLS dispersant of concentration ratio 10:1 resulted in a high score ($J$=4) without sonication.

Figure 7 shows the effect of MWCNTs content on the electrical conductivity of the composites. The results show a clear percolation threshold around 1% of MWCNTs content for composite concrete specimens. Also, results show that sonicated and mechanically mixed specimens have similar percolation curves.

Figure 8 shows the time histories of the incremental variation of the electrical resistance, $\Delta R$, under the axial test results, for three different types of nanomodified concrete. The time drifts in the electrical resistance signals are associated with residual polarization effects in the materials. The experimental gauge factor, Eq. (1), and strain sensitivity $S$, Eq. (2), obtained from each test result are reported in Table 2.

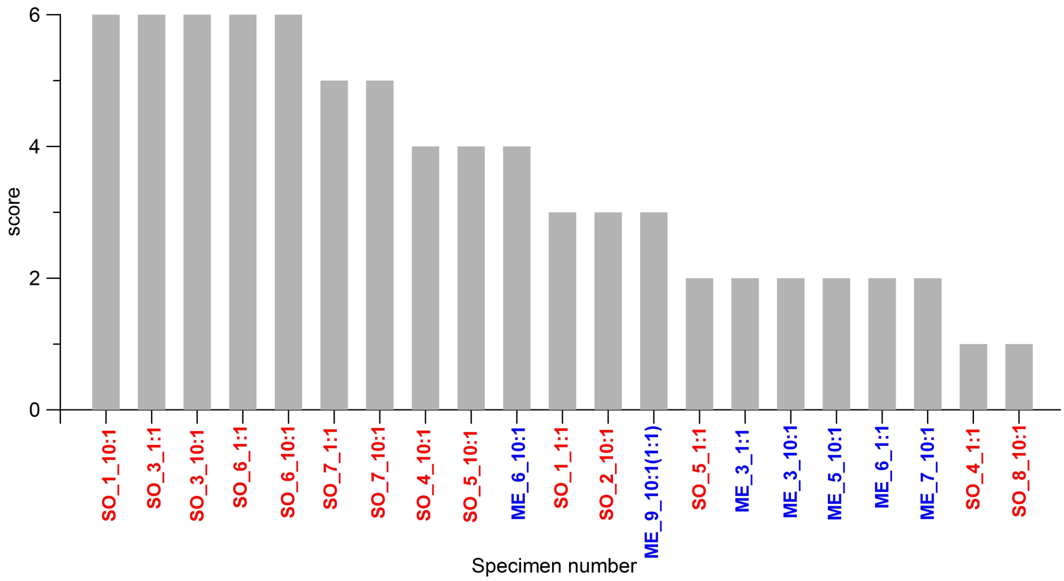


Figure 6 : Scores obtained by different specimens in MWCNTs dispersion tests using Eq. (3) (specimens with zero score are omitted, sonicated specimens are indicated in red, mechanically mixed specimens are indicated in blue)

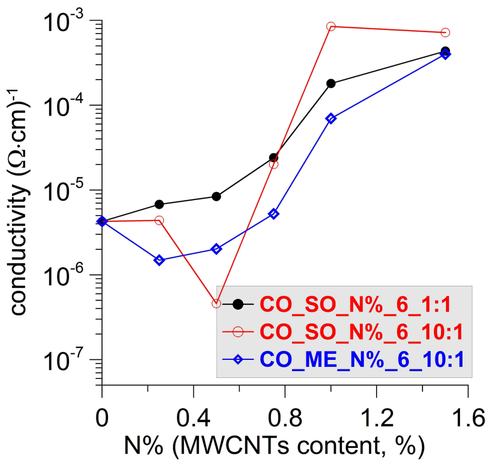


Figure 7: Electrical conductivity of composite specimens versus MWCNTs mass content expressed as a percentage with respect to the mass of cement (specimens identification codes are defined in Section 3) at different curing times

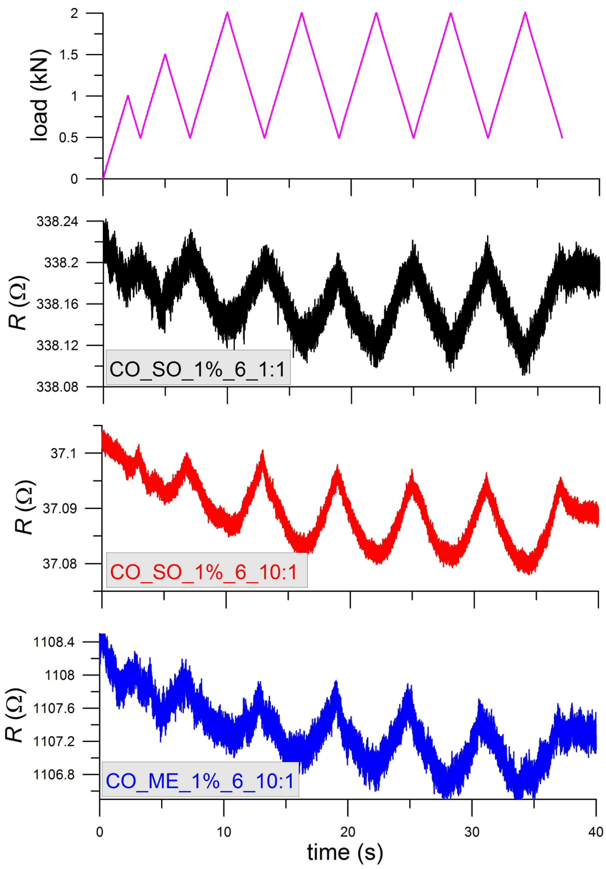


Figure 8: Results from strain sensing tests.

| Specimen | λ | S (Ω) |
|---|---|---|
| CO_SO_1_6_1:1 | 23 | 7790 |
| CO_SO_1_6_10:1 | 29 | 1074 |
| CO_ME_1_6_10:1 | 76 | 39480 |

Table 2: Gauge factor and strain sensitivity derived from axial compression tests.

Results from the axial compression tests demonstrate the strain sensing ability of the composites and, more importantly, the larger sensitivity of mechanically mixed concrete in comparison with sonicated concrete. This can be explained by both an increase in gauge factor and a substantial increase in the unstrained electrical resistance, $R_0$.

## 6 CONCLUSIONS

In this study, the effects of different preparation strategies over electrical conductivity, percolation and strain-sensing properties of nanocomposite concrete doped with multi-walled carbon nanotubes have been investigated.

The quality of nanotubes dispersion under different processing strategies has been evaluated based on the rate of separation of the nanotubes from the water and on the minimum magnification factor necessary to clearly detect the presence of MWCNTs bundles using scanning electron microscopy.

Nanocomposite concrete specimens with different concentrations of MWCNTs have been prepared using three preparation strategies. The first preparation strategy consists of using the best dispersant without sonication and is identified as the "scalable procedure". The remaining two strategies consider the same additive, at similar and lower concentrations, and include the sonic treatment.

The fabricated specimens have been subjected to axial compression tests measuring their electrical conductivity and assessing their strain-sensing properties. The results have highlighted that the scalable procedure provides composites with very similar percolation thresholds (around 1% of MWCNTs) and enhanced strain-sensitivity compared to sonicated concrete.

The scalable fabrication procedure is potentially suitable for casting full-scale self-sensing structural components and for large-scale deployment of self-sensing concrete.

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