

Design of smart cementitious composites based on multi-walled carbon nanotubes (MWCNTs) using probe ultrasonicator for dispersion

Shaban Shahzad^{1*}, Ahmed Toumi¹, Jean-Paul Balayssac¹, and Anaclét Turatsinze¹

¹LMDC, Université de Toulouse, INSA, UPS Génie Civil, 135 Avenue de Rangueil, 31077, Toulouse Cedex 04, France

Abstract: The purpose of this study is to develop smart cementitious material by incorporating multi-walled carbon nanotubes (MWCNTs). Two different types of carbon nanotubes (CNT) were dispersed using probe ultrasonicator; (i) Pristine CNT (P-CNT), and (ii) Functionalized CNT through annealing (A-CNT). Percolation threshold and optimum content of CNTs were determined by measuring electrical resistivity, porosity, compressive and flexural strengths at various contents of CNTs (0, 0.5 %, 0.75 %, and 1 % with respect to mass of cement). Self-sensing study was also carried out on smart material by relating the electrical properties with cyclic compressive loading. For this purpose, the electrical response was recorded with Wheatstone Bridge (WSB) circuit. The effect of curing and saturation degree of specimens on the resistivity pattern was also discussed. The results of electrical resistivity and mechanical properties showed that the content of CNTs should be at least 0.75 % to develop smart cementitious materials with a significant sensitivity and without detrimental effect on the mechanical properties. Moreover, smart material incorporating pristine CNT provides better sensitivity of self-sensing response as compared to the annealed CNT. Self-sensing test results also showed that with the increase in the content of CNT, sensitivity and repeatability of the sensing response were improved.

1 Introduction

Most of the civil infrastructures including highways, residential and commercial buildings, and dams are exposed to the severe and changing environment, chemical and physical agents, and thermal stresses. In addition, cementitious materials are under self-degradation due to aging, shrinkage cracking and construction defects. So, in the recent developments, monitoring of concrete structure is of prime concern to avoid catastrophic impact on humanity. For this purpose, traditional non-intrinsic based sensors such as strain gauges, optical fibers, shape memory alloys, and piezoelectric materials were used to monitor the behavior of the structure under external loading. Although these non-intrinsic sensors are easy to install, they are very sensitive, and can provide misleading information due to electromagnetic interference and lower sensitivity to the response. Moreover, non-intrinsic sensor and cementitious composites, being different materials, poses serious concern over the long term monitoring and high maintenance cost [1].

In the past few decades, the development of a cement-based intrinsic piezo-resistive sensor has reshaped the field of Structural Health Monitoring (SHM) in the construction industry. In line with the piezo-resistivity phenomenon, cement-based sensors can be used to monitor the health of the structures (mechanical strain or stress variation) by measuring the variation in the concrete electrical resistivity with external loading. However, the

cementitious materials offer high electrical resistance. So, to develop a smart cementitious material, inclusion of conductive material is essential to reduce the electrical resistance of the composite material.

Various types of conductive materials are used to prepare the smart cementitious materials including steel fibers, carbon fibers, carbon nanotubes (CNTs), slag, and carbon powder. Since after the discovery of carbon nanotubes by Iijima in 1991 [2], they have been extensively used in smart cementitious composites due to their high electrical conductivity.

Due to the large specific surface area of CNTs, they develop strong Van der Waals attractive forces resulting in the agglomeration of CNTs in aqueous medium [3]. Moreover, increase in the concentration of CNTs within the solution resulting in the formation of CNTs agglomeration to greater extent [4], [5]. So, optimum concentration and suitable method of dispersion is very important for uniform dispersion of CNTs.

There are various dispersion techniques which are being used by different researchers for the uniform dispersion of CNT within the solution first, and then in the cementitious matrix. Broadly, they are categorized into physical, chemical, and mechanical methods of dispersion which depend on non-covalent and covalent functionalization, and mechanical mixing respectively [6].

Current study investigated the effect of P-CNT and A-CNT dispersed by probe sonicator for dispersion on various properties of cementitious composites. Moreover,

*Corresponding author: shahzad@insa-toulouse.fr

effect of various concentrations on the sensitivity of self-sensing response is also studied.

2 Experimental program

2-1 Materials

Portland cement (CEM I 52.5R, provided by Lafarge Holcim) and normalized sand was used to prepare mortar. The conductive material used was multi-walled carbon nanotubes (MWCNTs) provided by Nanocyl, and having an average diameter of 9.5 nm with average length of 1.5 μm . The resistivity of used CNTs is $10^{-4} \Omega\cdot\text{cm}$, with specific surface area of 250-300 m^2/g . Master Glenium 27 from BASF was used as superplasticizer.

2-2 Preparation of specimens

Pristine and Annealed CNT are used for the preparation of specimens. Annealed CNTs are prepared by heating the CNT at 500 $^{\circ}\text{C}$ for 30 minutes. During the process of annealing, CNTs are modified in terms of increase in crystallinity, reduction of wall defects and removal of impurities such as metal oxides [7]–[9]. This modification in structure of CNT through annealing improves the hydrophilicity of CNT.

After preparation of annealed CNT, both annealed CNT and Pristine CNT are mixed with water separately. Then the solution is sonicated using the ultrasonicator provided by Hielscher Ultrasound Technology. The time of sonication depends on volume of solutions and the ratio

of CNT. So, after extensive experimentation, it is observed that the solution required 1 minute/liter of sonication based on the maximum content of CNT (1 minute of sonication is required to homogenize the 1 liter of water solution

containing 20g CNTs) to get the homogenized mixture. If sonication is continued beyond this time, solution containing CNT is losing its workability very fast and it starts to get stiffen as time of sonication is increased. So, 1 minute/liter rate of sonication was found to be optimum.

Seven different types of mortar mix with composition as shown in Table 1 were prepared using a mixer conforming to EN 196-3 [10]. Initially, cement and sand were homogeneously blended. Then, the dispersed CNT solution and superplasticizer were added gradually to the dry mixture and mixed until the dry mixture had become a fresh mixture. Prismatic specimens of 40 x 40 x 160 mm^3 for resistivity and flexural tests. After conducting the flexure test on prismatic specimens, cubes of 40 mm from same samples were prepared for compressive test. Fresh mixture was poured into the mold in two layers followed by compaction using a vibrating table. After the preparation of the specimens, they were placed in curing chamber at 20 $^{\circ}\text{C}$ and relative humidity of 100%. Detail of the samples cast can be seen in the Table 1.

Table 1. Mix Composition and nomenclature for mortar specimens

Designation	Type of CNT	Cement kg/m^3	Sand kg/m^3	Water kg/m^3	Dosage of CNT %	Superplasticizer
-	-					
PM	-				0.0	0.0
CNT0.5A	Annealed	500	1600	250	0.5	1.0
CNT0.75A					0.75	1.5
CNT1A					1.0	2.0
CNT0.5P					Pristine	0.5
CNT0.75P	0.75	1.5				
CNT1P	1.0	2.0				

A nomenclature has been adopted for the ease of referencing each mix. For example, in CNT0.5A, CNT refers to carbon nanotubes, 0.5 refers to the dosage of CNT, and A refers to annealed

2-3 Test Method

2-3-1 Resistivity test

To test the efficiency of the different solutions of CNT dispersion, the electrical resistivity of mortar specimen was measured using uni-axial method of measurement [11] as shown in Fig. 1. Potentiostat/galvanostat provided by Gamry Instrument was used and galvanostatic pulse method was followed to measure the electrical resistance of the material. The direct current was injected from the electrodes, instantaneous change

in the voltage was measured between two current peaks, and corresponding resistance was calculated using Ohm's law. By measuring the contact area and length of the specimen, resistivity is calculated using the following equation.

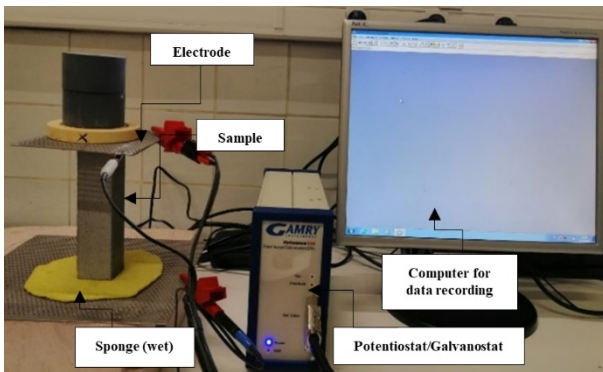


Fig. 1. Test setup for resistivity test

$$V = IR \quad (1)$$

$$\rho = R \frac{A}{L} \quad (2)$$

Where, I is the current injected, V is the voltage measured and R is the electrical resistance. ρ is the electrical resistivity, A is the contact area of specimen and electrodes and L is the distance between two electrodes.

2-3-2 Physical & Mechanical test

In order to analyze the mechanical properties of cementitious material, 40 mm cubes and prisms (40 mm x 40 mm x 160 mm) were prepared. The compressive and flexural tests were conducted at 28-days of curing in humidity chamber.

It has been reported that the annealing of CNT at high temperature increases the porosity of CNT due to the variation in the structural configuration [13]. To study the impact of CNT on the porosity of cementitious material, porosity was measured according to BS EN 1936 standard [14].

2-3-3 Self-Sensing test under compression

Self-sensing is the reactive behavior of smart material under the change in its own condition such as stress, strain or damage [15]. These properties are based on measuring the piezo-resistivity of the material. Under uni-axial compression loading, conductive materials start to get closer each other making the conductive path easier for the current to flow and under un-loading condition, electrical measurement come back to initial stage due to relaxation of the material. Self-sensing assessment of smart material is carried out under uni-axial loading cycle. Piezo-resistive response is measured using Wheatstone bridge (WSB) circuit which converts the variation of resistance into a variation of voltage. Alternating voltage of 20V with the frequency of 10 Hz is applied as an input. A specimen is connected to one arm of WSB circuit and potentiometers are connected to other three arms of the bridge to adjust the resistance to get balanced condition as shown in Fig. 2. Five cycles of loading/unloading were monitored with WSB circuit. Cyclic loading is applied on the specimen

between 0.6 to 10 MPa at a loading rate of 0.3 MPa/s using MTS press. Schematic diagram of testing arrangement is shown in Fig. 3. Two strain gauges were mounted on the surface of the specimen to measure the deformation during the experiment. Stainless steel plates were used as electrodes to measure the change in voltage and conductive paint provided by Bare Conductive is applied on the interface of specimens and electrode to minimize the interface resistance.

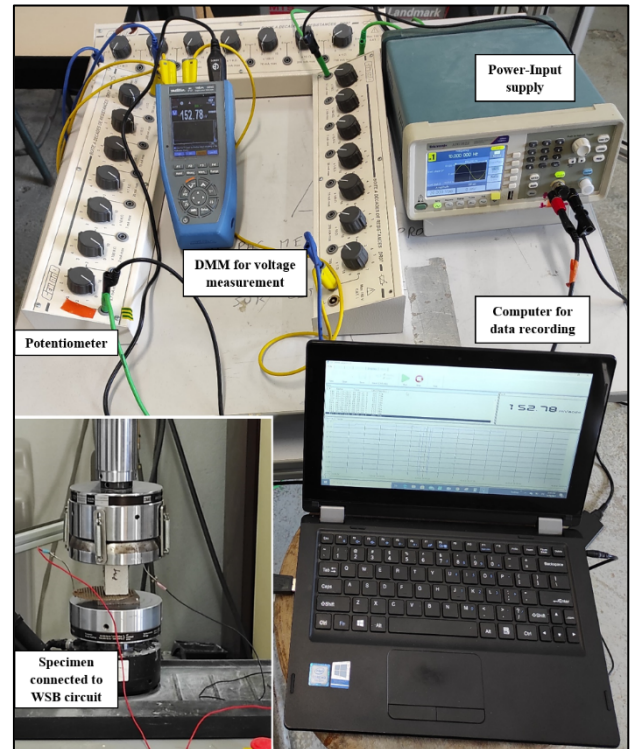


Fig. 2. Wheatstone bridge (WSB) circuit setup for self-sensing test [12]

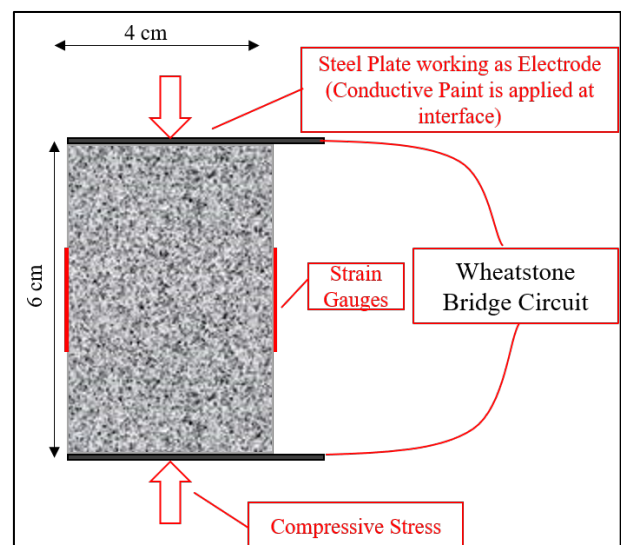


Fig. 3. Self-sensing test setup [12]

3 Results & Discussions

3-1 Electrical Properties

The electrical resistivity of cementitious composites containing two different types of CNT at different concentrations were presented in Fig. 4. The resistivity was measured at different curing times to evaluate its variation with of hydration progress.

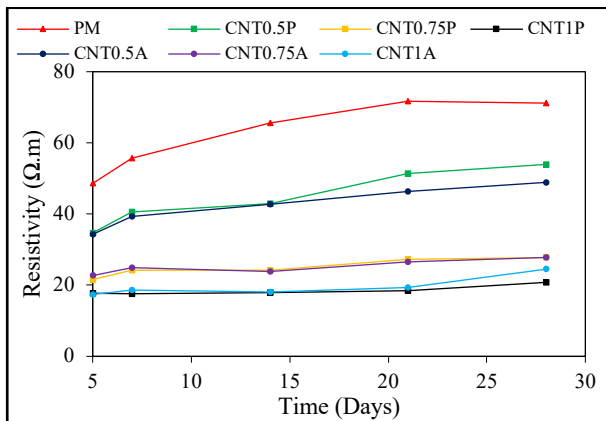


Fig. 4. Evolution of electrical resistivity with curing period for plain mortar, and mortar containing A-CNT & P-CNT

From Fig. 4, it can be observed that the resistivity responses of specimens having 0.75 % and 1 % dosages of Pristine and Annealed CNT are constant irrespective of the age of specimens. However, for 0.5 % of CNT, electrical resistivity increases with the time, but this increase is less steep as compared to plain mortar. In literature, it is explained that the percolation theory is the main reason behind the resistivity trends. Percolation threshold is the content of conductive material at which conductive filler start to form continuous conductive path within the composites that leads towards reduction in resistivity [16]–[18].

In order to analyze the drying effect on the resistivity evolution, samples were placed in oven at 40 °C and resistivity test was performed on the samples at different duration of drying as shown in Fig. 5.

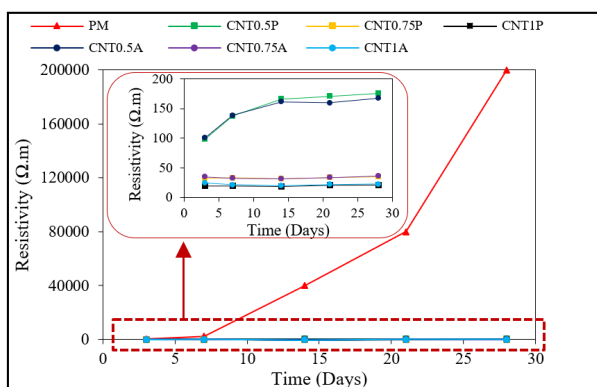


Fig. 5. Evolution of electrical resistivity with drying period (40 °C) for plain mortar, and mortar containing A-CNT & P-CNT

Cementitious materials with 0.75 % and 1 % dosages of CNT show stable resistivity response regardless of

the duration of drying as shown in Fig. 5 indicating the achievement of percolation threshold at 0.75 % and beyond. However, for the plain mortar, there is large increase in the resistivity evolution as the drying period is increased giving the information that saturation degree is mainly responsible for the conduction in plain mortar.

From resistivity results, no significant difference was observed between pristine and annealed CNT even at different dosage of CNT.

3-2 Physical & Mechanical Properties

Compressive and bending tests were carried out at 28-days of curing to assess the mechanical properties. In parallel, a porosity test was also carried out to determine the porosity of cementitious materials. Figs. 6, 7 and 8 show compressive, flexural strength and porosity of the cementitious composites incorporating annealed CNT and pristine CNT respectively. Compressive and flexural strength of all the composites containing CNT either annealed or pristine are less as compared to plain mortar, result in agreement with the previous findings [19].

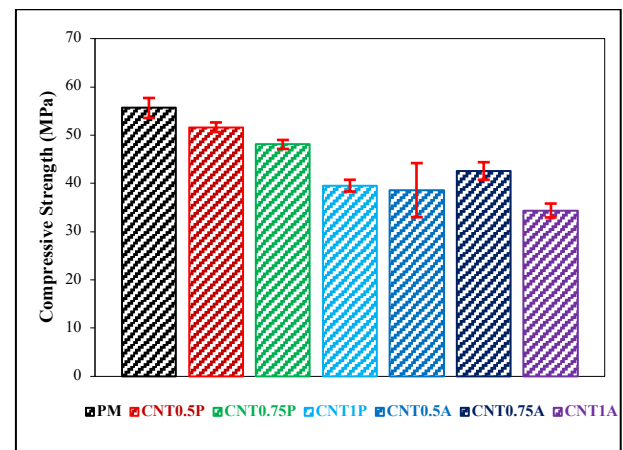


Fig. 6. Evolution of compressive strength of cementitious composites at different contents of pristine CNT (P-CNT) & annealed CNT (A-CNT)

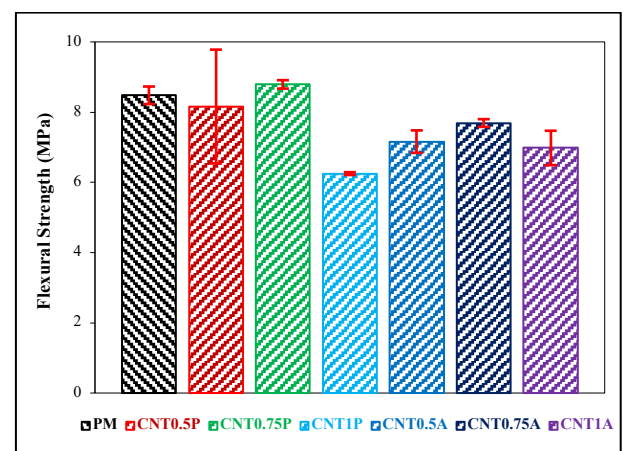


Fig. 7. Evolution of flexural strength of cementitious composites at different contents of pristine CNT (P-CNT) & annealed CNT (A-CNT)

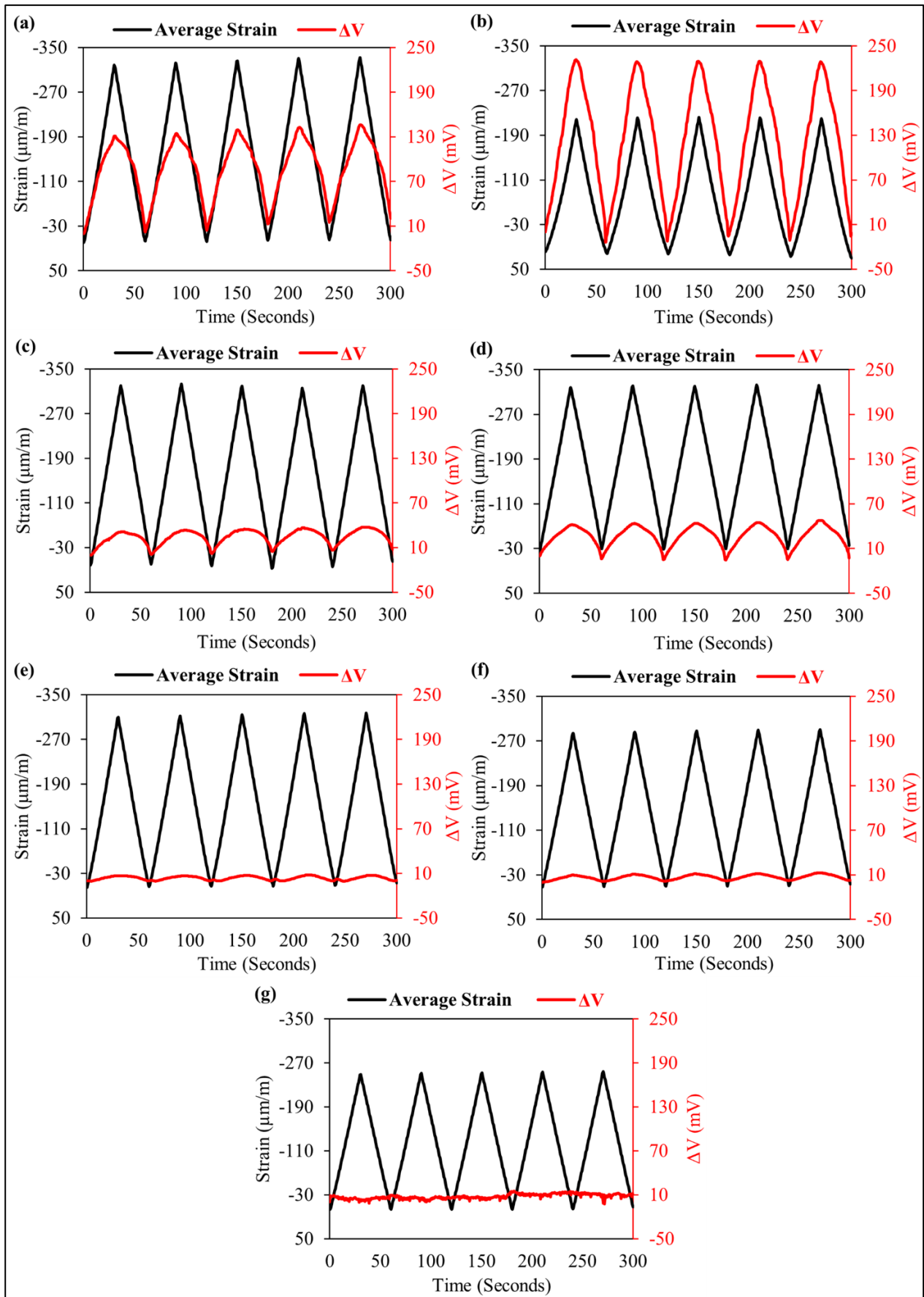


Fig. 9. Self-Sensing response of material under cyclic compressive loading, (a) CNT1A, (b) CNT1P, (c) CNT0.75A, (d) CNT0.75P, (e) CNT0.5A, (f) CNT0.5P, (g) PM

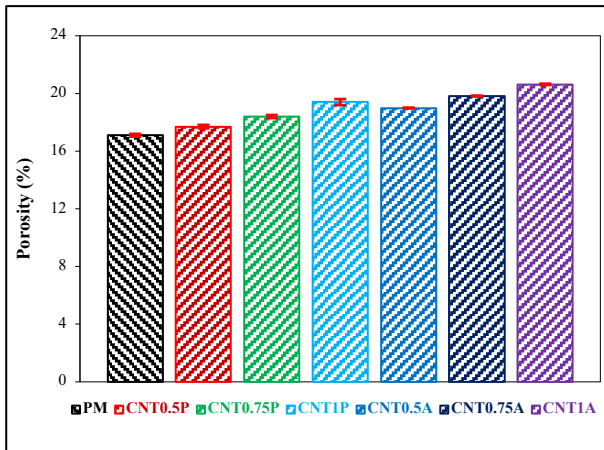


Fig. 8. Evolution of porosity of cementitious composites at different contents of pristine CNT (P-CNT) & annealed CNT (A-CNT)

From the results of compression and flexural tests, the reduction in mechanical properties is more in annealed CNT as compared to pristine CNT due to the slight increase in porosity. It is also observed that the porosity of specimens containing annealed CNT is slightly more as compared to the pristine one. This is evident that during heating of CNTs, porosity of CNT increases [16] and hence overall porosity of the specimen is increased.

So, based on the mechanical, physical and electrical properties of cementitious composites discussed earlier, it is concluded that 0.75 % content of P-CNT is the optimum content to develop smart cementitious composite to monitor the health of structures.

3-3 Self-Sensing Properties

Self-sensing response of the material under cyclic compressive loading is measured by measuring the change in the voltage (ΔV) at WSB circuit. ΔV is measured using the following equation.

$$\Delta V = V - V_0 \quad (3)$$

where, V is the voltage measured during loading, and V_0 is the voltage at so-called balanced condition at stress of 0.6 MPa (Ideally, it should be zero to have a balanced condition, However, with one arm of WSB representing a mortar is not possible to achieve zero voltage at balance. So, the resistance from the potentiometer is adjusted in such a way to get minimum voltage at so-called balanced condition). Resistance for three potentiometers and corresponding so called balanced voltage (V_0) for each material are presented in Table 2.

Specimens were partially saturated and had been kept in air dry condition for three weeks before the test. In Fig. 9, each material shows piezo-resistive response under cyclic loading (from 0.6 MPa as minimum stress to 10 MPa as peak) except plain mortar. From Fig. 9, it is observed that smart cementitious material at various concentrations of CNT show self-sensing response in line with strain. However, with the increase in the content of CNT, repeatability and sensitivity of self-

sensing response is improved. ΔV for CNT1A and CNT1P is 155 mV and 225 mV respectively, while for CNT0.5A and CNT0.5P, it is less than 20mV. These results indicate the decrease in the electrical resistance with the increase in the content of CNT due to which ΔV is also increased.

Table 2. Voltage and resistance at so-called balance condition of WSB circuit

Specimen	V_0	Resistance at Potentiometer
-	mV	k Ω
PM	680	4020
CNT0.5A	11.22	6.5
CNT0.75A	10.9	1.2
CNT1A	14.5	0.7
CNT0.5P	10.1	7.3
CNT0.75P	5.0	1.2
CNT1P	10	0.6

4 Conclusion

The results presented in this paper illustrated physical and mechanical properties as well as the self-sensing response of carbon nanotubes based smart cementitious materials. Following conclusions can be drawn from the results.

- Probe sonicator is an efficient device for the dispersion of CNT either pristine or annealed.
- Increase in porosity of cementitious composites containing annealed CNT is slightly more as compared to the pristine CNT.
- 0.75% content of pristine CNT can be adopted to develop smart cementitious material for monitoring of the structures.
- High electrical resistance offered by plain mortar indicate the no self-sensing response of the material under cyclic compression test.
- Self-sensing test results indicate that smart cementitious materials show piezoresistive response. Moreover, with the increase in content of CNT, sensitivity, and repeatability of the measurement is improved to the significant level.

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