Matériaux & Techniques **110**, 104 (2022)

https://doi.org/10.1051/mattech/2022020

Matériaux & Techniques

Available online at:
www.mattech-journal.org

Regular Article

Open Access

Cementitious composites incorporating Multi-Walled Carbon Nanotubes (MWCNTs): effects of annealing and other dispersion methods on the electrical and mechanical properties

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Received: 16 November 2021 / Accepted: 23 February 2022

Abstract. This study focuses on different techniques for dispersing Multi-Walled Carbon Nanotubes (MWCNTs) in cementitious materials. The impact of dispersion is observed through electrical resistivity and mechanical properties of cementitious composites. Two contents (0.5 and 1% by mass of cement) of MWCNTs are investigated and three different techniques were used to disperse CNTs in water by sonication: (i) pristine, P-CNT, (ii) functionalized carbon nanotubes by classical approach (dispersive agent, D-CNT), and (iii) by an innovative approach (annealing, A-CNT). Self-sensing response of the material under cyclic compressive loading is measured with Wheatstone Bridge (WSB) circuit. Results showed a detrimental effect of dispersive agent on the resistivity and mechanical properties of cementitious composites irrespective of the content of CNTs. However, the impact of P-CNT and A-CNT on the reduction of mechanical properties is slight. With the use of 1% content of A-CNTs, a stable resistivity response of the material is observed irrespective of the saturation degree. This indicates that content higher than 1% of A-CNTs is not required for the development of smart cementitious composites for structural health monitoring (SHM). The test results of self sensing measurements indicate a poor repeatability of the electrical response for plain mortar under each loading cycle while, stable response is noticed with specimens incorporating 1% of A-CNTs. The maximum variation in fractional change in voltage (FCV) shown by plain mortar is 6.3% indicating high electrical resistance of plain mortar, while in case of mortar containing 1% A-CNTs, variation in FCV is 35% indicating lower electrical resistance and better sensitivity of the material.

Keywords: cementitious composites / carbon nanotubes dispersion / annealing / electrical resistivity / self-sensing / wheatstone bridge

1 Introduction

Nowadays, most of infrastructures are being constructed with cementitious materials including social infrastructures such as residential and commercial buildings, network of transport system such as highways, runway at airports and large structures such as dams and barrages. The demand of the cement is increasing because concrete materials start to deteriorate not only under mechanical stress but also under harsh environmental impacts such as the action of weathering, chemical attack, abrasion, corrosion, or other processes that compromise its durability [1]. Therefore, there is a huge demand of constructing the new infrastructures for the need of ever growing population of the world as well as the re-construction of the existing structures. One cannot avoid the construction of new infrastructures to meet the requirement of population.

As the production of cement is increasing day-by-day, it is leaving negative impact on the environment. It is roughly estimated that cement industry produces around 5% of global greenhouse gas emissions [2]. However, proper monitoring of the existing infrastructures and timely repairing of the damage part of structures help to minimize the requirement of cement production for the re-construction. In Europe, it is estimated that about 50% of construction sector budget is utilized for the rehabilitation and maintenance of existing infrastructure [3]. Therefore, it is now considered judicious to monitor the condition of a structure continuously before it loses its serviceability.

Traditional non-intrinsic based sensors such as strain gauges, optical fibers, shape memory alloys [4] were used to monitor responses of the structure like stress, strain under external loading. However, heterogeneity in the material of sensor and cementitious material poses serious concern over the long-term application of these sensors. Non-intrinsic sensors are expensive for monitoring and

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susceptible to damage under different environmental conditions. To overcome the problem of non-compatibility of the non-intrinsic sensor with cementitious materials, the development of intrinsic piezo-resistive sensor made with cementitious composites in the past few decades has reshaped the field of Structural Health Monitoring (SHM).

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 such as mechanical, thermal or dynamic loading. However, the cementitious materials offer large resistance to current and hence it is not possible to make the cementitious materials a sensor without the inclusion of the conductive material to make cementitious material "a smart material".

Various types of conductive materials which are being used to design the smart cementitious materials including steel fibers, carbon fibers, carbon nanotubes, slag, and carbon powder. Among them, carbon nanotubes are most frequently used conductive materials for the development of smart cementitious composites. In order to have the best sensing properties of composite, optimum dosage and uniform dispersion of conductive materials within the cementitious matrix is very important.

Carbon nanotubes (CNTs) possess high electrical and thermal conductivity, highly flexible having higher tensile strength [5–9]. Pristine CNTs are hydrophobic in nature and causes difficulties during dispersion within water. There are several reasons of development of agglomeration in CNTs while mixing with water. Van der Waals interaction, π-π stacking and hydrophobic nature are the primary parameters, but not limited to, which affect the dispersion of carbon nanotubes according to researchers. Due to the large specific surface area of CNTs, they develop strong attractive forces called Vander Waals forces resulting in the agglomeration of CNT [10] as well as their nano-scale size. Therefore, in order to develop the smart cementitious material using carbon nanotubes, it is very important to have a good dispersion of CNT within the cementitious matrix with optimum dosage to get better sensitivity of smart material.

There are various dispersion techniques which are being used by different researchers for the uniform dispersion of CNT within the solution first then in the cementitious matrix. A combination of physical (mechanical mixing or sonication) and chemical (functionalization of CNT by the use of surfactant, by oxidation through acid treatment, ozone treatment and annealing) dispersion techniques is the most adopted way of dispersing CNTs in mixing water for cementitious composites.

Sonication proves to be an efficient way of dispersing CNTs in the aqueous solution. However, it leads to significant degradation of CNTs structure affecting its mechanical properties [11]. Optimum duration and energy of sonication is still a concern for the researchers to get the uniform dispersion with minimum loss of structural integrity of CNTs. A large variation in the duration of sonication for the dispersion of CNT, from few minutes [12–14] to several hours [15,16] has been found in literature. However, it is not limited to the duration of sonication, rather than many other factors, type of sonication (bath of probe type), temperature, energy, quantities of CNTs and of water [17].

In the recent studies, researchers used combination of sonication (bath or probe type) with functionalization (by surfactant or oxidation) for the dispersion of CNTs within the cementitious composites. However, conflicting results were found in the literature, for instance [18–21] reported improvement in mechanical properties and [22–24] reported reduction in mechanical properties with addition of CNT. Inconsistency in the results reveals that use of dispersion technique plays an important role to achieve the best and consistence result of CNTs reinforced cementitious composites.

Several studies have focused on the use of surfactant along sonication for the uniform dispersion of CNTs within the cementitious composites. However, selection of suitable surfactant is very important for the uniform dispersion of CNT. The effectiveness of surfactant depends on many factors reported in the literature; compatibility of surfactant with hydration products and duration of sonication [25], and amount of surfactant [26].

Sindu et al. [27] studied the effect of different surfactants on mechanical properties of cementitious composites reinforced with CNTs. Five different surfactants including, sodium lauryl sulfate (SLSD), Sodium dodecylbenzene sulphonate (SDB), Triton X-100 (TX-100), Gum Arabic (GA), and Cetyltrimethylammonium bromide (CTB) were used for the dispersion of CNTs, followed by the sonication for 1 h. They found the dispersion results in the sequence from best to worst as follows: SLDS, SDB, GA, CTB, TX-100 respectively by conducting UV-Vis absorbance studies and particle size analysis. However, the addition of surfactant has detrimental effect on the mechanical properties beyond 0.1% content of CNTs by weight of cement. With the content of CNTs up to 0.1%, CNT-cement composites prepared with Arabic gum (GA) showed improvement in mechanical properties than control one. Reduction in the mechanical properties may be due to the hindrance in the hydration reaction induced by surfactant or due to the increase in the porosity of material.

Similarly, Shao et al. [28] observed the effect of surfactant on dispersion and mechanical properties of CNT reinforced cementitious materials. They used three different surfactants including, Sodium Dodecyl Sulfonate (SDS), Tween-20 (T-20) and Triton X-100 (TX-100) with 1.5% content of CNTs. Based on Dynamic Light Scattering (DLS) test results, T-20 surfactant shows the best dispersion among other followed by T-100 and SDS respectively. However, with addition of SDS and T-100 along CNT, compressive strength reduced by 5–6 times than the control specimens, which is mainly due to the formation of foam with use of these surfactants resulting in creation of weak zone within the cementitious matrix. Notwithstanding, the decrease in the compressive strength is less while using T-20 (3 times lesser than control) indicating the formation of lesser air bubbles. Authors concluded that the good dispersion of CNT in water does not ensure the good dispersion in cementitious matrix.

Table 1. Physical properties and chemical composition of Portland cement (CEM I 52.5R).

Physical properties		
Properties	**Unit**	**Value**
Specific gravity	g/cm^3	3.15
Fineness	cm^2/g	4160
Water demand	%	28.6
Compressive strength of cement at 28 days	MPa	> 50

Chemical composition (%)							
$C_3S + C_2S$	CaO/SiO_2	MgO	C_3S	C_2S	C_3A	C_4AF	Gypsum
79	3.1	0.8	66	13	8	8	4.8

Table 2. Physical properties and chemical composition of normalized sand.

Characteristics of sand		
Properties	**Unit**	**Value**
Maximum particle size	mm	1.6
Minimum particle size	mm	0.08
Real density	kg/m^3	2640
Apparent density	kg/m^3	1620
Fineness modulus	–	> 2.7 and < 26
Water absorption	%	0.20

Chemical composition (%)			
Al_2O_3	Fe_2O_3	P_2O_5	SiO_2
0.54	0.07	0.00	98.07

There are several chemical treatments, which are used for the functionalization of nanoparticles like acid oxidation, ozone treatment or annealing. Thermal treatment of carbon nanotubes was carried out for the purification at elevated temperature. However, limited study is available for the functionalization of CNTs by thermal treatment. Chen et al. [29] studied the effect of thermal treatment on nanoparticles at elevated temperature in the presence of air and, they found it to be very effective technique in terms of dispersion quality. This thermal treatment at elevated temperature is also called annealing of nanoparticles. This method is more efficient and less time consuming and environmental friendly [30,31] as compare to other methods of functionalization.

Current study deals with the development and characterization of smart cementitious materials, which can be used for structural monitoring under different environmental and loading conditions. In this study, comparison is carried out between physical and chemical methods of dispersion based on classical and innovative approaches of functionalization. The dispersion of CNTs within the cementitious composites is assessed through the resistivity and mechanical results. The best, and reliable solution of dispersion of nanoparticle in cementitious material is proposed.

2 Materials and methods

2.1 Materials

Portland cement (CEM I 52.5R) in conformity with EN197-1:2011 [32] (provided by Lafarge) and normalized sand in conformity with EN 196-1 [33] were used. Physical properties and chemical composition of the cement and sand are shown in Tables 1 and 2, respectively. The conductive material used was multi-walled carbon nanotubes (MWCNTs) provided by Nanocyl. The properties of MWCNTs are shown in Table 3. Master Glenium 27 from BASF was used as superplasticizer. The surfactant was Dispex Ultra PX 4585 from BASF.

2.2 Methods adopted for dispersion

In this study, three different types of specimens were prepared, based on non-covalent and covalent functionalization (classical and innovative approaches) followed by sonication. Sonication for 20 minutes was carried out for each composition using bath sonicator. A study was carried out to analyze the impact of different treatments on the dispersion quality of MWCNT solution as well as the resistivity of the mortar. For non-covalent functionalization, a surfactant (Dispex Ultra PX 4585) was used for the dispersion of CNT. For covalent functionalization, annealing was used to functionalize the CNT. Annealed CNTs are prepared by heating the CNT at 500 °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 [34–36]. 70–80% yield of functionalized CNTs was obtained after annealing. Modification in the structure of CNT through annealing improves the hydrophilicity of CNT. A bath sonicator was chosen for the sonication of MWCNTs (for non-covalent and covalent functionalization of CNT).

2.3 Preparation of specimens

Mortar specimens with a cement/sand ratio of 1:3.2 were prepared using a mixer complying with EN 196-3 [37]. Initially, cement and sand were homogeneously blended using a Hobart mixer. 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. The water/cement ratio used in this study used was 0.5 and prismatic specimens of $40 \times 40 \times 160\,\mathrm{mm}^3$ for resistivity and flexural tests, and cubes of 40 mm were prepared for compressive test. Fresh mixture was poured into the mould in two layers followed by compaction using a vibrating table. The specimens were then cured in a chamber at 20 °C with a Relative humidity of 100%. Details of the samples prepared can be found in Table 4. Contents of CNT, superplasticizer, and dispersive agent are expressed with respect to the mass of the cement. A nomenclature has been adopted for the ease of referencing each mix. For example, in CNTM0.5A, CNT refers to carbon nanotubes, M refers to Mortar, and 0.5A refers to the dosage of CNT functionalized through annealing.

3 Testing procedures

3.1 Assessment of dispersion of CNT in solution

Visual observations were made to evaluate the dispersion quality at different times after sonication, and sedimentation of CNT within the water was monitored, as shown in Figure 1. The samples shown in Figure 1 were prepared with the aim of visualizing the sedimentation of CNT by preparing a solution with water, sonicating this solution for 20 minutes, and keeping the solutions for 90 days. No suspension was observed for the pristine CNT, where nanoparticles accumulated at the bottom. For the annealed CNT, very little sedimentation was observed. However, a uniform black suspension was obtained using CNT dispersed with dispersive agent. From the visual observation, the best dispersion was obtained by the use of dispersive agent. To analyze the dispersion within the cement-based composites and impact of different dispersion techniques on electrical and mechanical properties, mortar specimens were prepared to measure the resistivity as well as mechanical properties of the materials.

Table 3. Properties of MWCNTs.

Properties	Unit	Value
Average diameter	nm	9.5
Average length	µm	1.5
Carbon purity	%	90
Specific surface area	m^2/g	250–300
Volume resistivity (CNT powder)	Ω.cm	$_{10}$−4

3.2 Resistivity assessment on mortars

In order to analyze the dispersion quality, a resistivity test was carried out on the mortar specimens using the uni-axial method of measurement [38] as shown in Figure 2. A potentiostat/galvanostat provided by Gamry Instruments was used and the galvanostatic pulse method was adopted to measure the electrical resistance of the material. The current was injected from the electrodes, the instantaneous drop in voltage between two current peaks was measured as shown in Figure 3, and the corresponding electrical resistance was calculated using Ohm s law. By measuring the contact area and the length of the specimen, electrical resistivity was calculated using the following equations.

$$V = IR, \tag{1}$$

$$\rho = R\left(\frac{A}{L}\right), \tag{2}$$

where I (A) is the current injected, V (V) is the voltage measured and R is the electrical resistance calculated in Ohm (Ω). ρ is the electrical resistivity (Ω.m), A is the contact area of specimen and electrodes in m^2 and L is the distance between two electrodes in meter.

3.3 Mechanical properties

In order to analyze the mechanical properties of cementitious composites, 40 mm cubes and prisms ($40 \times 40 \times 160$ mm) were prepared for the compressive and flexural strength tests respectively. These tests were conducted after 28-days of curing described in Section 2.3.

3.4 Self-sensing test

Self-sensing is the responsive behavior of smart material under the change in its own condition such as stress, strain or damage [39]. These properties are based on measuring the piezoresistivity of the material. Piezoresistivity is defined as the change in the electrical resistivity of the material under the application of mechanical strain. 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 comes back to initial stage due to relaxation of the material. Self-sensing assessment of smart material is carried out under uni-axial loading cycle. Piezoresistive response in terms of variation in voltage is

Table 4. Nomenclature of the mortar specimens.

Designation	Dispersion technique	Content of CNT %	Superplasticizer %	Dispersive agent %
PM	–	–	0.25	
CNTM0.5P	–	0.5	0.5	
CNTM1P	–	1	0.5	
CNTM0.5DA	Dispersive agent	0.5		0.5
CNTM1DA	Dispersive agent	1		0.5
CNTM0.5A	Annealing	0.5	0.5	
CNTM1A	Annealing	1	0.5	

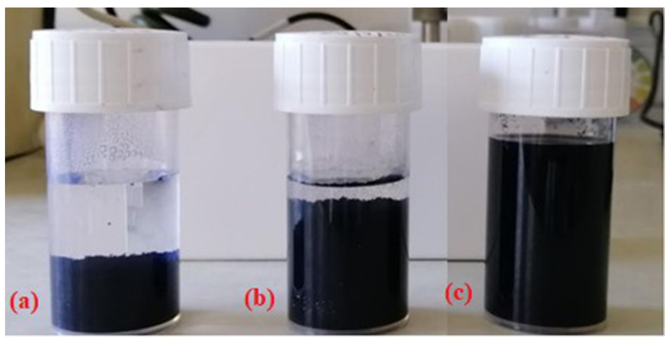

Fig. 1. Suspension of CNT in water after 3 months of preparation of solution: (a) pristine CNT (0.2 g/20 mL), (b) annealed CNT (0.2 g/20 mL), and (c) CNT with 0.2 g of dispersive agent (0.2 g/25 mL).

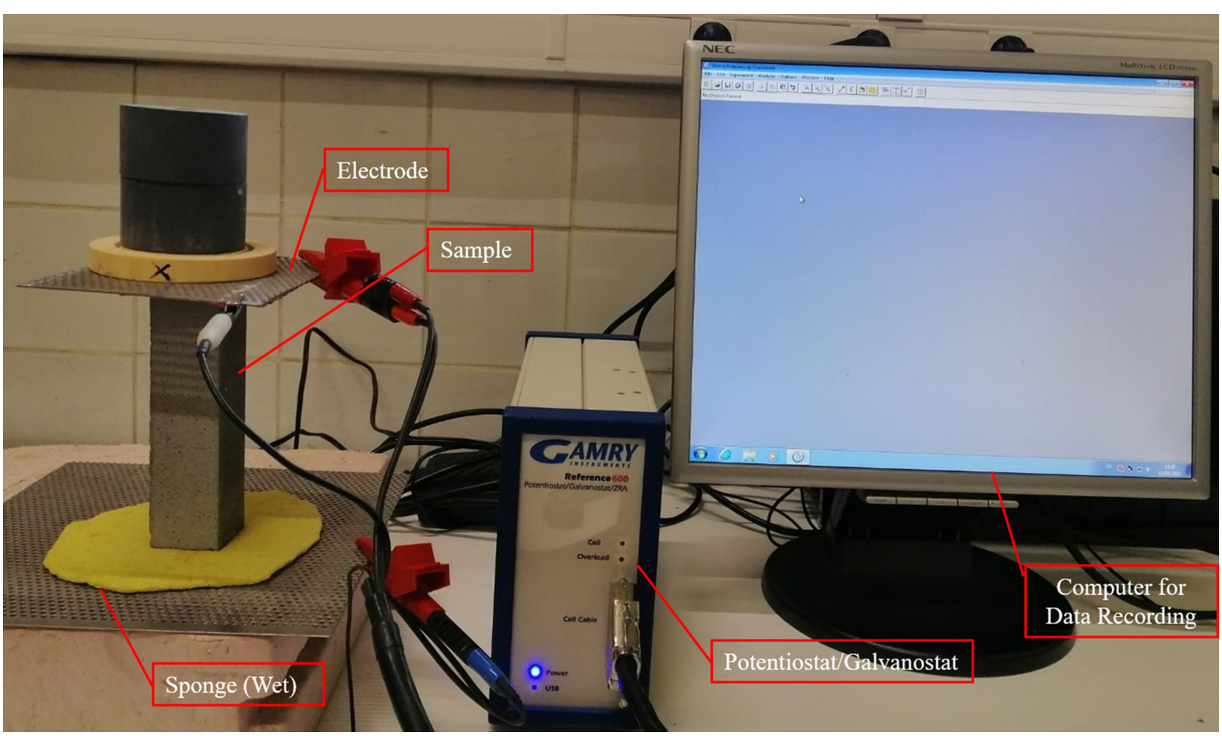

Fig. 2. Setup for resistivity test.

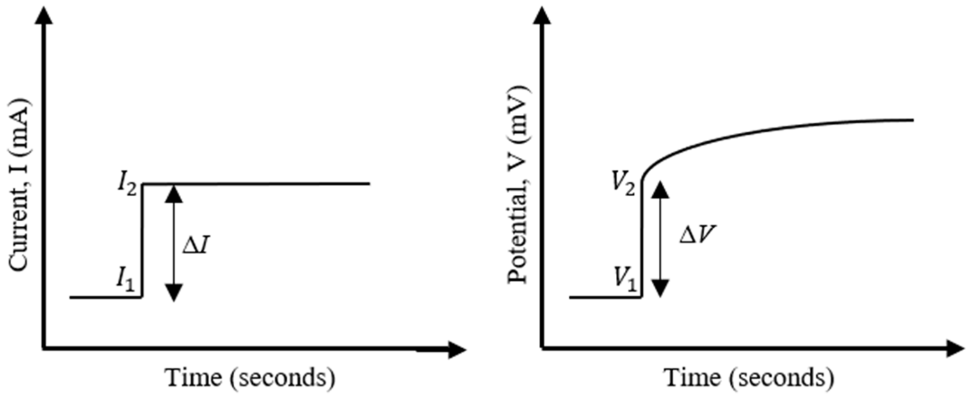

Fig. 3. Schematic view of galvanostatic pulse technique.

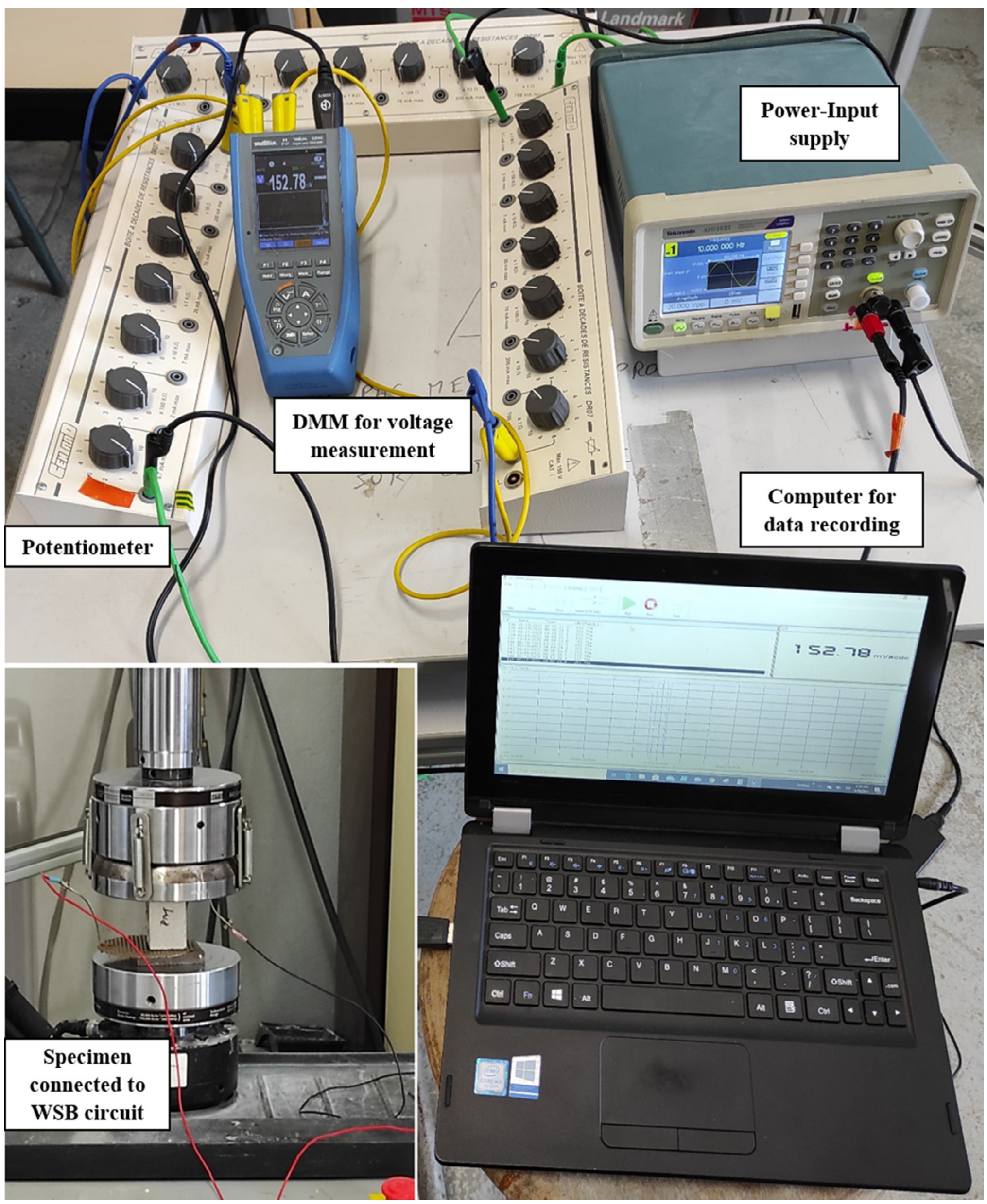

Fig. 4. Wheatstone bridge circuit setup for sensing test.

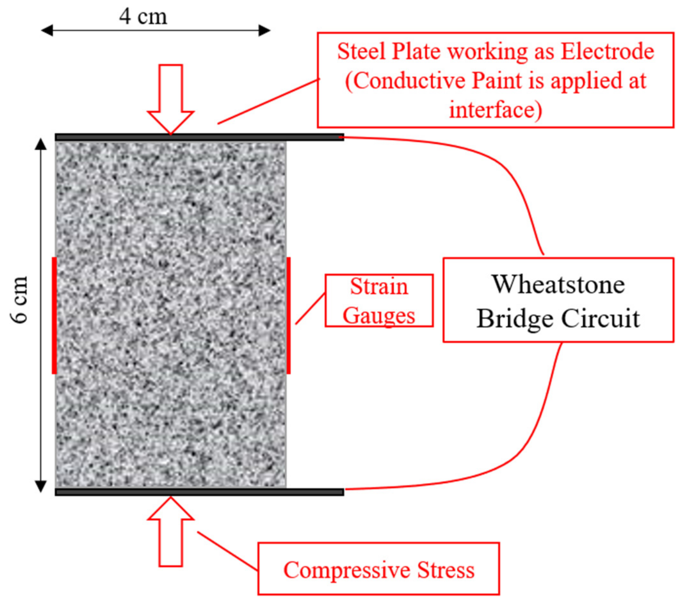

Fig. 5. Schematic representation of test setup.

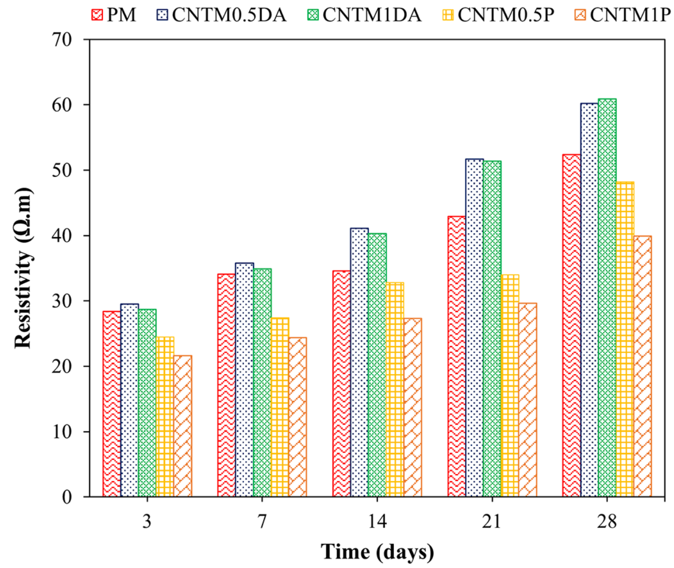

Fig. 6. Resistivity values of saturated specimens after various curing times for plain mortar and mortar with 0.5 and 1% dosage of CNT.

measured using wheatstone bridge (WSB) circuit. 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 Figure 4. 20 V peak-peak voltage and 10 Hz frequency of AC source has been applied as an input to measure the potential difference across the bridge of the circuit against applied mechanical loading. It has been concluded by Ferdiansyah et al. [40] that the WSB system is an efficient system to amplify the self-sensing response of concrete materials. He has studied the efficiency of the system by varying the frequency to 10 Hz, 1 kHz and 10 kHz and input voltage to 10, 15 and 20 V. They found that the system operated at 10 Hz and 20 V provides the better results in terms of the sensitivity and repeatability under mechanical loading. 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 machine. Schematic diagram of testing arrangement is shown in Figure 5. Two strain gauges were mounted on the surface of the specimen to measure the deformation during the experiment. Stainless steel plate was used as electrode to measure the change in voltage and conductive paint is applied on the interface of specimens and electrode in order to minimize the interface resistance.

4 Results and discussion

4.1 Electrical properties

4.1.1 Influence of dispersive agent on resistivity

The resistivity of plain mortar specimens, samples containing 0.5 and 1% of CNT prepared with pristine CNT dispersed by sonication only, and CNT dispersed using a dispersive agent followed by sonication was measured with potentiostat/galvanostat. Figure 6 shows the resistivity results of the specimens after various curing times. From the results presented in Figure 6, it can be observed that the specimens having CNT dispersed with dispersive agent show higher resistivity than the specimens of plain mortar. It can also be seen that the resistivity of each specimen increases with time as a result of the hydration process. Generally speaking, electrical conduction can be classified as either ionic or electronic [41]. Ionic conduction is the result of the movement of the ionic charge, whereas electronic conduction occurs through the movement of electrons in the conductive pathways formed by conductive materials within the cementitious matrix. The resistivity of specimens with higher contents of Pristine CNT is slightly less than those with lower content. However, it increases with time indicating the conduction is mainly through ions, which is affected due to utilization of free water by hydration reactions. Increase in the resistivity also indicates the poor dispersion of pristine CNT within cementitious composites.

The resistivity of specimens with dispersive agents is the same regardless of the CNT content (0.5 or 1%) and higher than specimens without CNT. Figure 7 shows the resistivity pattern at different contents of CNT after 28 days of curing in water. In the Figure 7, it can be observed that resistivity of mortar specimens containing dispersive agent is higher than that of plain mortar, irrespective of the CNT content. This indicates the negative effect of dispersive agent on the resistivity of material used in this study. In the case of mortar specimens without dispersive agent, resistivity decreases slightly with the increase of CNT content from 0.5 to 1%, due to poor formation of conductive pathways because pristine CNTs are hydrophobic and tend to agglomerate very quickly after the sonication. In order to assess the effect of water content on the resistivity, the samples were placed in two conditions after curing: in a room with RH of 50–70%, at a temperature of 23 °C and Oven Dried at 40 °C. The

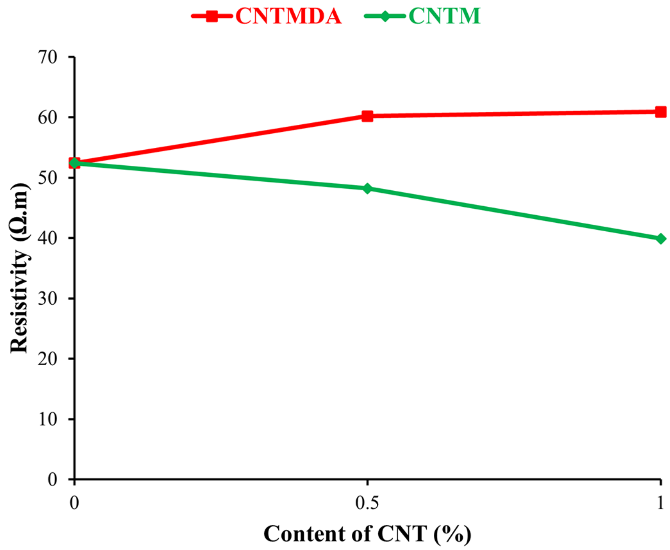

Fig. 7. Resistivity versus content of CNT after 28 days of curing.

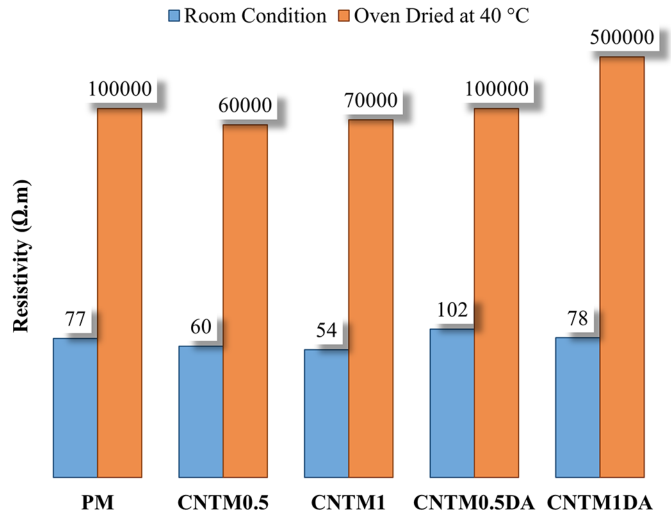

Fig. 8. Resistivity values of specimens after 3 weeks under different saturation conditions.

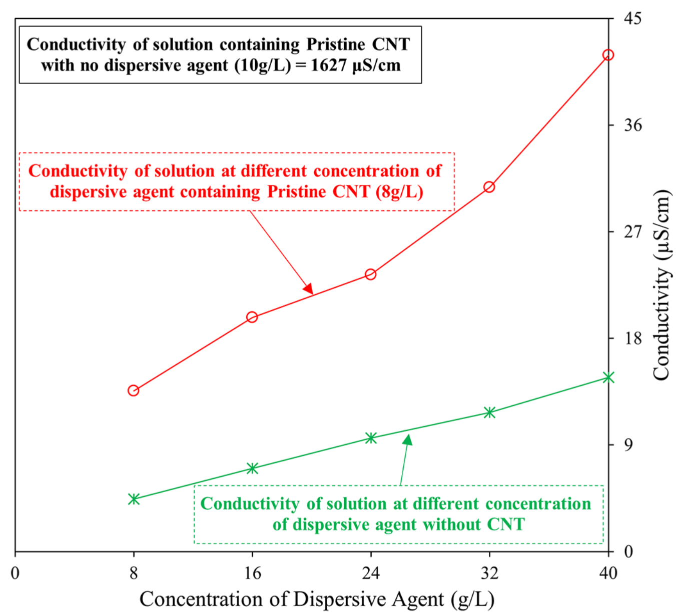

Fig. 9. Conductivity of solutions containing CNTs at various concentrations of dispersive agent.

results are presented in Figure 8. Figure 8 gives the resistivity values of the specimens in the room and in oven-dried conditions. It can be concluded that the use of dispersive agent is not effective to reduce resistivity as it affects the conductivity of carbon nanotubes. The use of pristine CNT dispersed with sonication is also not effective because CNTs tend to agglomerate during mixing with cement and sand.

In order to analyze the effect of dispersive agent on the conductivity of CNT, different water solutions containing dispersive agent and CNT were prepared and the conductivity of the solution was measured with a Conductivity Meter. The solutions were sonicated for 20 minutes to make the suspension uniform prior to the measurement. The conductivity of the solution was measured at different concentrations of dispersive agent as shown in Figure 9. Figure 9 shows that the solution without the addition of CNT has lower conductivity than the one containing Pristine CNTs. However, with increasing concentrations of dispersive agent, the conductivity of both solutions increases. The increase in conductivity is greater in a solution containing CNT and this variation in conductivity could be due to the formation of weak chemical bonds between the dispersive agent and the CNT as observed by Hauptman et al. [42]. The conductivity of the solutions containing pristine CNT (1627 μS/cm) is very high compared to that of the solution containing dispersive agent, regardless of the addition of CNTs. The conductivity of the solution is around 45 μS/cm at the highest concentration of dispersive agent containing pristine CNT, which is 35 times less than with no dispersive agent. Therefore, a negative effect of the dispersive agent on the conductivity of material is observed even though it gives better dispersion in solution (Fig. 1).

65% increase in conductivity of the solution is observed with 80% increase in concentration of dispersive agent. However, detrimental effect on mechanical properties were observed with the addition of 10 g/L concentration of dispersive agent in mortars containing CNTs as discussed in Section 4.2. So, the dispersive agent (Dispex Ultra PX 4585) is not appropriate for the development of smart cementitious material using CNT.

4.1.2 Effect of annealing on resistivity

Since annealing appeared effective for CNT dispersion (Fig. 1), samples were prepared with CNT functionalized by this way to analyze the effect on the resistivity of materials. Specimens were placed in a room with a controlled atmosphere (20 °C and RH of 100%). Figure 10 shows the results of resistivity tests after different periods of curing. From the results of Figure 10, the following points can be noted:

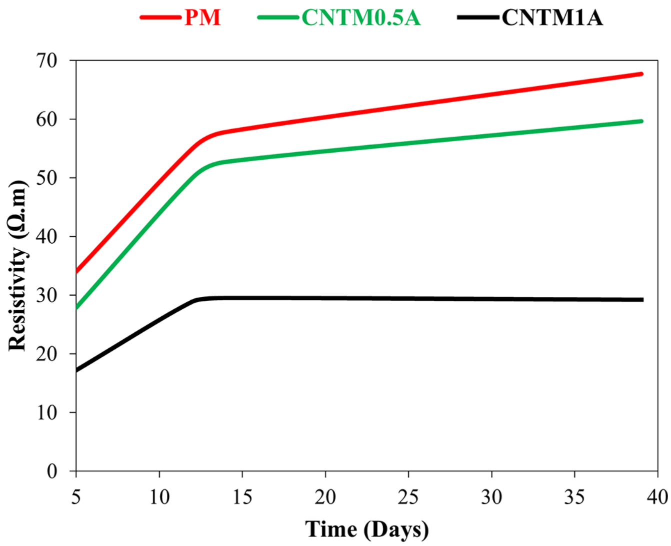

Fig. 10. Evolution of resistivity with curing period for plain mortar and mortar reinforced with 0.5% and 1% of annealed CNT.

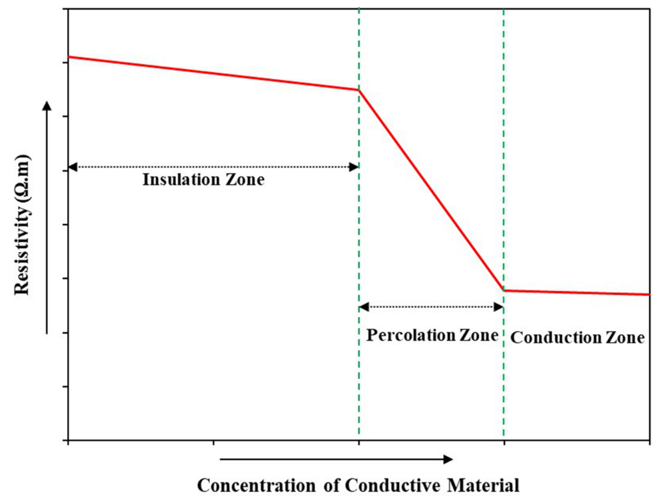

Fig. 11. Schematic representation of various conductive zones.

- The resistivity of mortar increases as the material ages, because water present in the sample is consumed by the hydration reaction [43]. Due to hydration, the movement of ions within the matrix is limited by the reduced availability of pore solution and movement of ions is mainly responsible for the conduction in plain mortar or cement-based composites [41];
- The resistivity of the mortar containing 0.5% of CNT is approximately the same as that of plain mortar, with a minute difference. The major conduction is ionic conduction through the pore solution with CNT contributing little. At 0.5% CNT, conduction paths are not formed and the distance between particles in most of the volume is such that electrons could not cross the barrier known as the tunneling distance for conduction [44]. 0.5% CNT content may fall in the percolation zone but this content is close to the insulation zone [44] as described in Figure 11;
- With the increase of CNT content to 1%, it is observed that there is no change in resistivity values after 2 weeks of curing, and resistivity becomes constant regardless of the hydration process. There is a slight increase of resistivity during the first two weeks of curing due to the hydration process, as conduction also takes place through the pore solution. After the maximum utilization of water during hydration, conduction through the direct path formed by CNT becomes stable. This CNT content falls well within the conduction zone [44].

After the specimens had been kept in the room with controlled atmosphere for more than 28 days, samples were placed under three different conditions of saturation in order to assess the effect of saturation degree on the resistivity of material. The following three conditions were considered:

- SSD – Samples were submerged in water and surface water was wiped off with clothes so that the specimen was in a saturated surface dry (SSD) state before the experiment;
- RC – Samples were placed in room conditions (RC) with a temperature of 23 °C and relative humidity of 50–70%. As the relative humidity was less than 100%, water evaporated from the samples [45];
- OD – Samples were placed in the oven at 40 °C and the experiment was performed at a partial saturation degree with more water loss than in the samples placed in room conditions.

Figure 12 presents the evolution of resistivity of specimens placed under different conditions of conservation. Figure 12a shows that saturated plain mortar has a stable resistivity response with time. In the saturated condition, conduction takes place through the movement of ions in pore solution. Samples with 0.5% of CNT showed slight reduction in resistivity after saturation. Both ionic conduction and tunneling conduction may take place simultaneously with the effect of ionic conduction being more pronounced. For samples with 1% of CNT, the resistivity response is observed to be stable with time. 1% content of CNT may be in the conduction zone, and the direct conduction effect is more pronounced than ionic one. Such findings are in agreement with conclusion from other studies [44].

In Figure 12b, as water is lost from the specimens due to the lower humidity (less than 100%), ionic conduction becomes mainly responsible for the conduction in specimens without CNT and with 0.5% CNT content. Due to the loss of water, resistivity increases with time. With 1% CNT content, resistivity is stable and does not change over time.

In Figure 12c trends observed that are similar to those for the specimens at room conditions. However, the resistivity of PM and of CNTM0.5A is much higher as compared to the one of CNTM1A specimens.

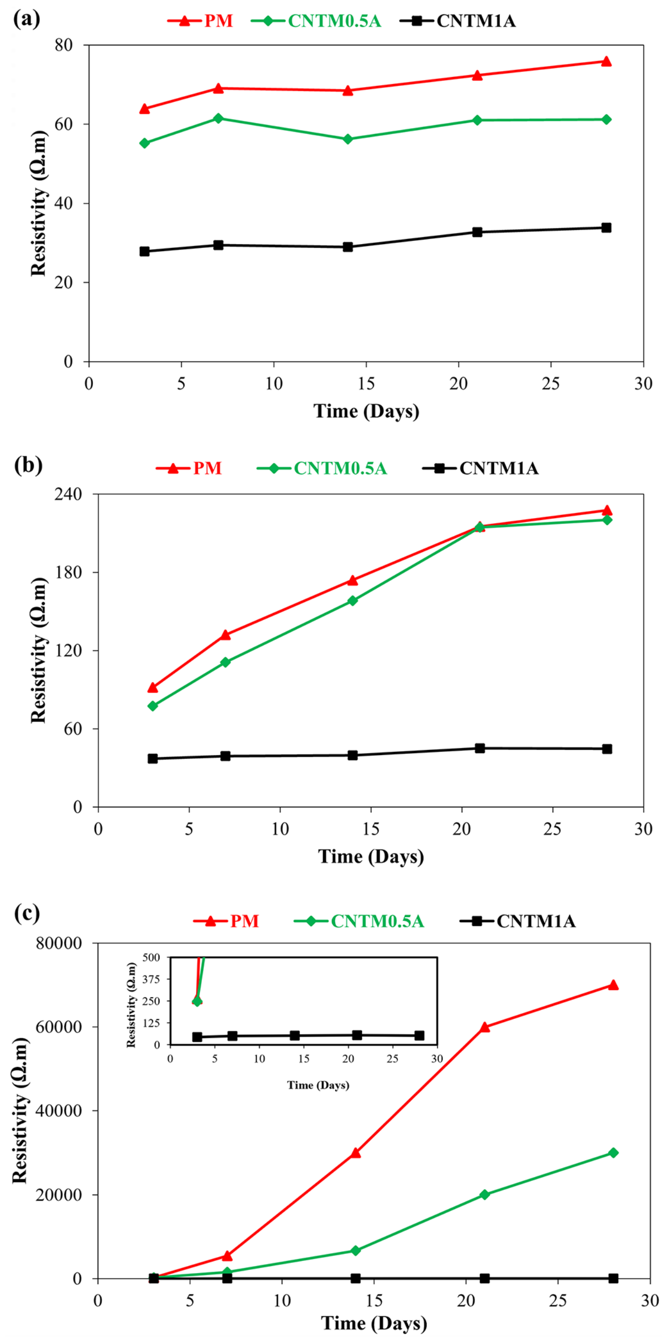

Fig. 12. Resistivity of specimens under (a) saturated surface dry (SSD) conditions, (b) room conditions (RC) and (c) oven dried (OD) conditions.

The above results reveal the significant variation in resistivity values for plain mortar and 0.5% CNT mortar under different conditions of conservation. However, with 1% CNT content, the variation in the resistivity values under different conditions of conservation is negligible. Moisture content has no significant effect on the electrical properties of mortar specimens prepared with 1% A-CNT content.

Furthermore, the resistivity of each specimen was determined by placing the specimens in an oven at different temperatures resulting in different degree of saturation to

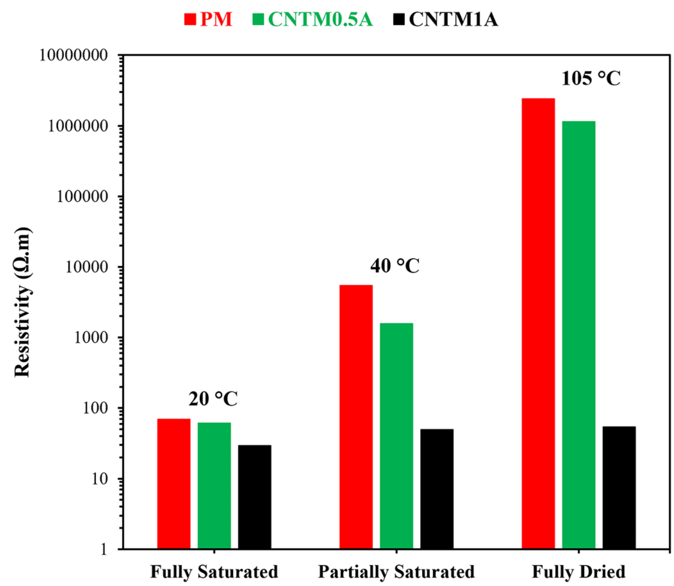

Fig. 13. Resistivity of specimens at different degree of saturation.

evaluate the response of the material under different moisture content and compared with the resistivity of specimens placed in water at 20 °C, as shown in Figure 13. An analysis of Figure 13 indicates that the resistivity of mortar with higher CNT content is insensitive to the degree of saturation. However, at lower CNT contents, the resistivity of the material increases with the decrease in the degree of saturation as the water content available for ionic conduction at lower temperatures vanishes. Therefore, 1% dosage of annealed CNT will be adopted in the following to study the piezo-resistive behavior of the material under mechanical loading.

4.2 Mechanical properties

Compressive and flexural tests were conducted after 28-days of curing to evaluate the mechanical properties of cementitious materials. Figures 14 and 15 show the compressive and flexural strength for composites containing 0.5 and 1% content of P-CNT, D-CNT and A-CNT. Compressive and flexural strength of all the composites containing CNT are less as compare to plain mortar in agreement with results available in the literature [46]. Compressive and flexural strengths of the composites containing dispersing agent are reduced to around 60 and 65 to 75% with respect to the control one indicating the generation of foam, resulting in increase of hollow structure within the cementitious matrix [27,28]. However, 10 to 20% reduction in compressive strength and 30 to 40% reduction in flexural strength are observed with the addition of P-CNTs while, 15 to 20% reduction in compressive, and flexural strength is observed with the addition of A-CNTs as compared to the mortar without CNTs. It can also be observed that the flexural strength of composites containing P-CNTs is less than the one containing A-CNTs as well as the compressive strength with higher content of P-CNT is less due to the poor

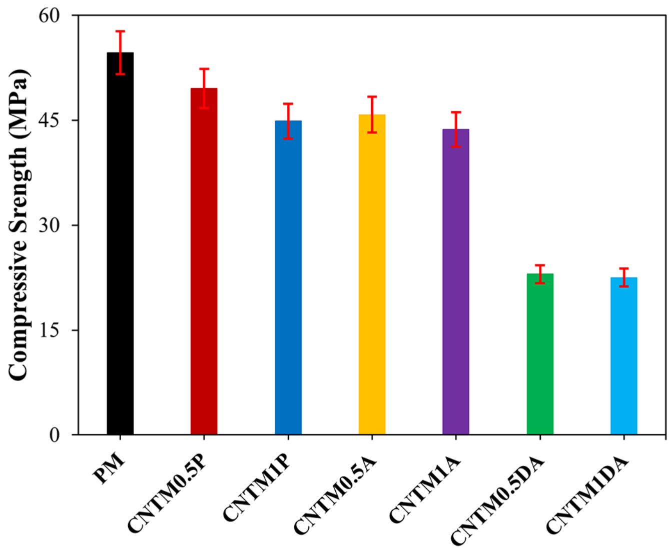

Fig. 14. Compressive strength of cementitious composites after 28-days.

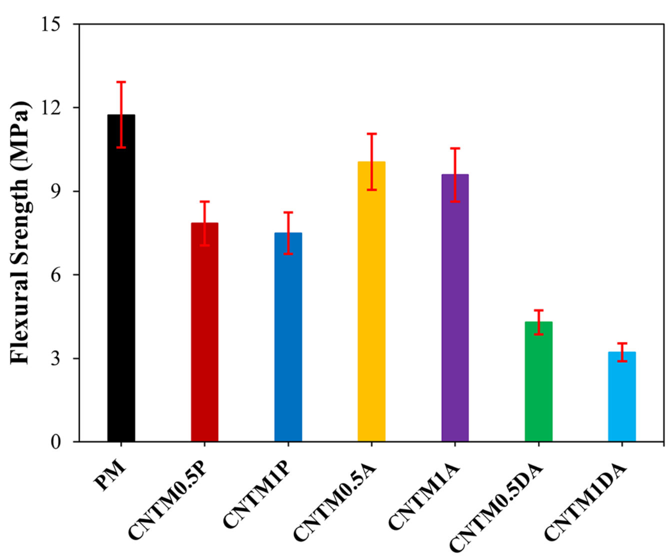

Fig. 15. Flexural strength of cementitious composites after 28-days.

dispersion and formation by large agglomeration of P-CNTs. It is reported [46] that with lower content of CNT (0.05%), mechanical properties of mortar improved. In the same study, with the higher content (0.5%), depreciation in the mechanical properties was observed. It is reported that this decrease in mechanical properties was due to the increase in the porosity of composite with the increase in CNTs content. As CNTs are nanoparticles, they tend to fill the micro-pores thus increasing the density of the matrix, ideally. However, CNTs tend to agglomerate due to strong attractive forces and with the increase in content of CNTs, formation of large agglomeration is possible leading towards the weakening of the matrix under compression or flexure.

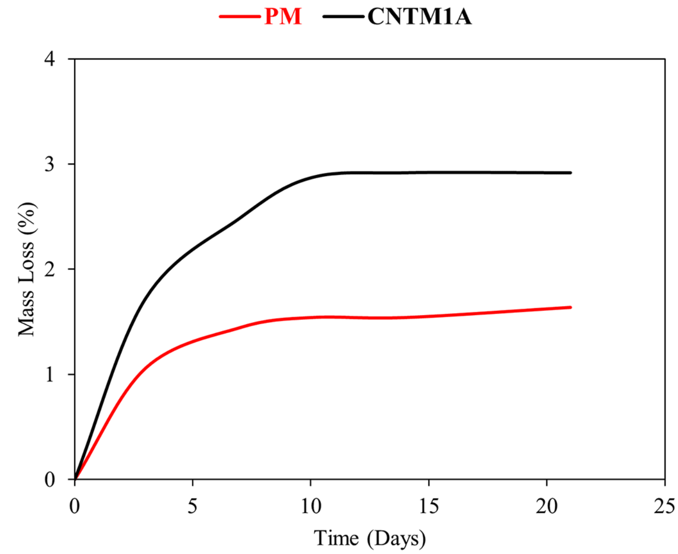

Fig. 16. Mass loss versus time under controlled atmosphere (20 °C and RH 50%).

4.3 Self-sensing test

From the resistivity test, it is observed that mortar specimens prepared with annealed CNTs (1% content) show stable resistivity response irrespective of the degree of saturation. Therefore, cyclic compressive test was carried out on the specimens containing 1% of CNTs and with no CNTs to compare the results. Before self-sensing test, samples were kept in controlled atmosphere (20 °C and RH of 50%) for 3 weeks till no further appreciable loss in mass is observed. Loss of water from each specimen is shown in Figure 16. Self-sensing response of the material under cyclic is observed by measuring the fractional change in voltage (FCV) at WSB circuit. FCV is calculated using the following relation.

$$FCV = \frac{V - V_o}{V_o} \times 100, \qquad (3)$$

where V is the voltage measured by digital multimeter (DMM) during the test and V_o is the voltage at balanced condition at the stress level 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 balanced condition) Resistance for three potentiometers and corresponding so called balanced voltage (V_o) for each material are presented in Table 5. Figure 17 shows the piezoresistive response of each material under cyclic loading (from 0.6 MPa as minimum stress to 10 MPa of stress as peak). All the specimens were partially saturated as shown in Figure 16 during the test. Upon loading, strain varies linearly and on un-loading it goes to initial value linearly indicating the elastic loading regime. It is observed that each material shows piezo-resistive response under cyclic loading as FCV increases during the loading and

Table 5. Voltage and resistance at the balanced condition of WSB circuit.

Specimen name	Number	V_o	Resistance of potentiometer
	–	mV	kΩ
PM	1	123.3	440
	2	175.5	650
	3	163.5	600
CNTM1A	1	11.75	1.42
	2	14.87	1.42
	3	15.80	1.51

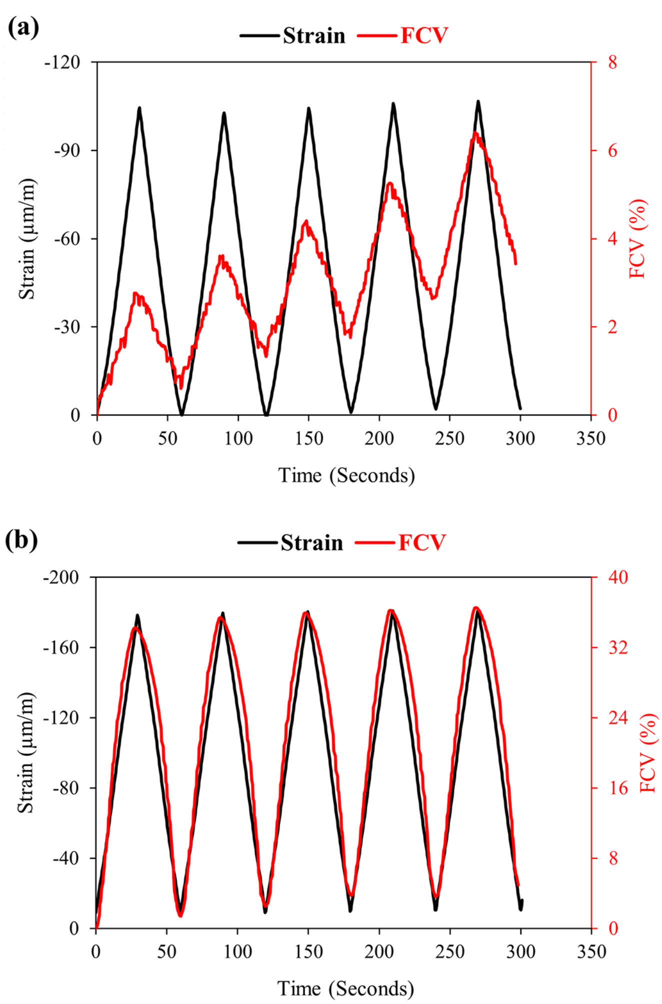

Fig. 17. Piezo-resistive response of (a) PM and (b) CNTM1A under cyclic loading.

decreases during unloading cycle. However, the variation of FCV is not in line with strain in each cycle of loading for plain mortar, while the variation of FCV is in line with strain in each loading cycle for mortar containing 1% of A-CNT (CNTM1A). As explained in Section 4.1.2, the conduction in plain mortar is mainly due to the movement of ions through free water. Plain mortar offers high resistance to the current as shown in Table 5, due to the partial saturation resulting in the poor sensitivity of the piezoresistive response. However, due to the stable resistivity of the specimen with 1% CNT (CNTM1A), sensitivity of the piezoresistive response is very high. The maximum variation in FCV shown by plain mortar is 6.3% indicating high resistance offered by plain mortar, while in case of CNTM1A, variation in FCV is 35% indicating the high sensitivity of the material.

5 Conclusion

In this contribution, a detailed study has been conducted to point out the effect of dispersion of carbon nanotubes, functionalized using different methods, on electrical and mechanical properties of cementitious composites. Dispersion of these nanoparticles was assessed through visual observations on solutions and a resistivity test on cementitious composites. Resistivity measurements were made after different curing periods and under different saturation conditions. The percolation threshold was observed by measuring the resistivity in order to determine the optimum content of nanoparticles needed to obtain self-sensing capability of composites for structural health monitoring. The following conclusions can be drawn:

- According to the visual observations, dispersive agent is efficient for CNT dispersion in water, notably in comparison to the dispersion of pristine CNT;
- Electrical resistivity measurements on the specimens with Pristine CNT (0.5 and 1% content) dispersed with sonication show an increase in the resistivity over time, indicating the poor dispersion of CNT within the matrix;
- Electrical resistivity measurements on the specimens with different contents of CNT (0.5 and 1%) dispersed with the dispersive agent followed by sonication reveal that the resistivity values are higher than that of plain mortar regardless of the dose of CNT. This is an indication of the negative effect of the dispersive agent used in this study on the conductivity of material;
- Regarding the influence of the different conditions of conservation, specimens prepared with different dispersion methods (sonication and dispersive agent) indicate an increase in the resistivity with decreasing saturation degree. This indicates that conduction in these specimens is mainly ionic conduction. With the evaporation of water, ionic conduction is affected;
- Electrical resistivity of the specimens prepared with annealed CNT indicates that with 1% CNT content, resistivity remains stable regardless of the age of the material. This is the indication of formation of direct

conductive paths at content close to 1% of annealed CNT;
- At different moisture contents, specimens with 1% annealed CNT show negligible differences in resistivity;
- Mechanical test results show a detrimental effect of the used dispersive agent on the material's properties irrespective of the content of CNTs. However, with addition of pristine and annealed CNTs, the impact on the reduction of mechanical properties is less;
- Under cyclic compressive loading, piezoresistive response of the specimen containing 1% of annealed CNT indicates good sensitivity and linearity with each loading cycle. The improvement of sensitivity by annealed CNT is well appreciated when comparing it with the one of plain mortar that exhibits poor piezoresistive response during each cycle of loading.

Conflict of interest

The authors report no potential conflict of interest regarding the publication of this paper.

Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article.

Acknowledgements. The authors are grateful to Dr Emmanuel Flahaut of the Centre Inter universitaire de Recherche et d'Ingénierie des Matériaux (CIRIMAT) Toulouse, France for providing technical assistance. The authors are also thankful to the Higher Education Commission (HEC) of Pakistan and the Laboratoire Matériaux et Durabilité des Constructions (LMDC) Toulouse for finanical support of the thesis that is the source of this work.

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Cite this article as: Shaban Shahzad, Ahmed Toumi, Jean-Paul Balayssac, Anaclet Turatsinze, Vanessa Mazars, Cementitious composites incorporating Multi-Walled Carbon Nanotubes (MWCNTs): effects of annealing and other dispersion methods on the electrical and mechanical properties, Matériaux & Techniques **110**, 104 (2022)