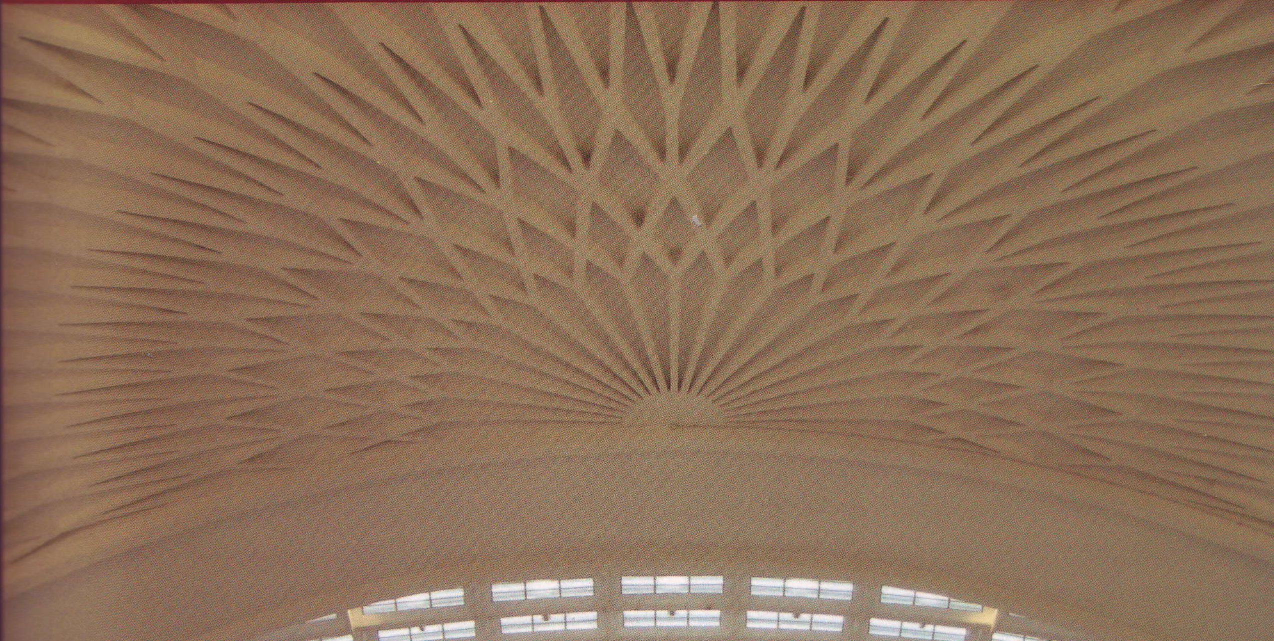
2nd Workshop on

The new boundaries of structural concrete

Università Politecnica delle Marche - ACI Italy Chapter
Ancona, Italy, September 15 - 16, 2011

Papers, Invited lectures

Editors
Luigino Dezi, Giacomo Moriconi and Roberto Realfonso



EDIZIONI

The New Boundaries of Structural Concrete
Università Politecnica delle Marche – ACI Italy Chapter, Ancona, Italy, September 15-16, 2011

The influence of carbon nanotubes dispersion on stress sensitivity of cementitious composites materials

L. Coppola[1], A. Buoso[2] and F. Corazza[3]

ABSTRACT: Adding carbon nanotubes to the cement matrix, the electrical resistivity of cementitious composites changes with the stress conditions under static and dynamic loads. This particular behaviour can be used to evaluate the stress level in reinforced concrete structures, to monitor the traffic flow, to weigh vehicles. In this paper data on pressure-sensitive behaviour under compressive stress of cement pastes and mortars containing different percentages (from 0.1% to 1.0% vs cement mass) of MWNTs are presented. In order to form a conductive network and enhance the piezoresistive properties of cementitious mixtures, Carbon NanoTubes (CNTs) need to be efficiently dispersed in the cement matrix. Two different methods to disperse CNTs in the cement matrix were used: the first one schedules a 10 minutes sonication by an ultrasonic generator of a solution containing CNTs and about 50% of the mixing water and the second one uses a surfactant. The piezoresistivity properties of the cementitious mixtures manufactured with the two CNTs dispersing methods will be compared. Experimental results show that the piezoresistive response is better for cementitious composites manufactured by using the surfactant agent to disperse CNTs. Data indicate that – thanks to the better dispersion of nanotubes promoted by the surfactant - the pressure-sensitivity properties of cement pastes can be achieved even by using a very low percentage of CNTS (0.1% vs cement mass). These findings seem to indicate that self-sensing CNTs/cement composite can be produced. These smart materials have great potential and they could be used in the next future in concrete field for practical applications.

1 INTRODUCTION

In 1991, Sumio Iijima (Iijima, 1991) used a high resolution transmission electron microscope (TEM) in order to study the particulate created in an electric discharge between two carbon electrodes. He discovered that this particulate contained structures consisting of a lot concentric microtubules of graphitic carbon with outer diameters of 4-30 nm and a length of up to1 μm, the carbon nanotubes. CNTs are formed from a graphite sheet (that is hexagonal networks of carbon atoms) rolled up to pipe form, with the two closed extremities by hemispherical caps. Single Wall carbon NanoTubes (SWNT) are constituted by only one graphite sheet and Multi Wall carbon NanoTubes (MWNT) are formed by sheets positioned as concentric cylinders inserted one inside the other. The diameter of a SWNT ranges from 0.4 nm to 10 nm and their length is usually of the micrometer order. The diameter of the MWNTs is greater than the SWNTs, reaching tens of nanometers (Wagner, 1998). CNTs have a high tensile strength up to about 100 times than steel, despite their specific mass is six times lower. CNTs possess exceptional electrical and thermal conductivity (Li, 2005). Therefore addition of carbon nanotubes in electrical insulating polymeric or cementitious matrix can change dramati-

---

[1] *Professor, Faculty of Engineering, University of Bergamo, Italy, luigi.coppola@unibg.it*
[2] *Assistant researcher, Faculty of Engineering, University of Bergamo, Italy, alessandra.buoso@unibg.it*
[3] *Manager R&S CTG – Italcementi Group S.p.A., f.corazza@itcgr.net*

cally electrical conductivity. It was evidenced that the electrical conductivity of polymer would increase about 108 times when carbon nanotubes were added in the amount of 7-11% (by polymer mass). In the same way addition of carbon nanotubes in cementitious mixtures determines a decrease in the electrical resistivity. Moreover electrical resistivity of cementitious mixtures containing carbon nanotubes changes with stress level in the composite (Li, 2007). Variation in the electric resistivity can be ascribed to the increase in the number of contact points of CNTs by enhancing loading: the higher the compressive stress, the higher the contact points, the lower the resistivity. In the present paper rheological properties, electrical resistivity and pressure-sensitive behaviour under cyclic compressive loading of cement composites containing multi-walled carbon nanotubes were investigated.

2 EXPERIMENTAL PROCEDURES

2.1 Materials

The experimental program was carried out on cement pastes and mortars containing different amount of MWNTs. Rheological properties of cementitious mixtures were evaluated. Electrical resistivity on unloaded and loaded cement paste and mortar specimens was measured. An Ordinary Portland Cement (CE I 52.5R - according to EN 197/1) was used. Multi-Wall CNTs provided by Shenzhen NANO Tech. Port. Co. Ltd. (China) with average diameters about 10–30 nm were added in cement pastes and mortars. For mortars, CEN Standard sand (ISO standard sand) was used.

2.2 Mixing procedure

In order to form a conductive network and investigate their rheological and electrical properties, CNTs need to be fully dispersed in the cement matrix. In fact, CNTs tend to aggregate together and form nanotube clusters and bundles. In this research, two different methods to disperse CNTs for the fabrication of CNT/cement composites were used.
Method #1. Carbon nanotubes were weighed and mixed with about 50% of mixing water in a beaker by means of a glass wand. Then, the solution was sonicated by an ultrasonic generator (Sonica ultrasonic cleaner) for 10 minutes. The remaining water and the cement (and the sand for the mortars) was finally added into the bowl and hand mixed for 3 minutes. Then, the bowl was positioned into the mixer. The mixing procedure adopted was that according to UNI EN 196–1:2005 (Coppola, 2010).
Method #2. An alternative method of dispersing CNTs in cement matrices is to use a non-covalent surface modification for CNTs surface. With a non-covalent interaction, surfactants can be wrapped around the nanotubes, favouring a better dispersion of CNTs in the aqueous solution. In this research, the critical micelle concentration of $1.4 \cdot 10^{-2}$ mol/l of Sodium Linear Alkylbenzene Sulfonate (LAS) was used. The surfactant was firstly mixed with water using a magnetism stirred for 10min. Then, MWNTs were added into the aqueous solution and sonicated with an ultrasonic generator for 2 hours to make a uniformly dispersed suspension. Then a mortar mixer was used to mix this suspension and the cement (and the sand for the mortar) for 3 minutes. Finally a defoamer, tributyl phosphate (0.5% by cement volume), was added into the mixture and mixed for another 3 minutes (Yu, 2009). Four cement pastes and four cementitious mortars with the same w/c ratio (0.60) were prepared. The composition of cement pastes and mortars are summarized in Table 1 and Table 2, respectively.

2.3 Preparation of cement composites specimens

Fresh cement composites were poured into steel moulds immediately after the mixing. The mixtures was placed into the moulds (40x40x160mm) in three layers and compacted by several jolts. Afterward, the material in excess was eliminated by means of a scraper. Stainless steel (diameter 1.0mm) gauzes with openings of 1.25x1.25mm^2 were used as electrodes as shown in Figure 1. The two probes were positioned symmetrically at a distance of 40mm from each other (Baoguo, 2010).

Table 1- Composition of cement pastes

COMPOSITION		PM1_0.1	PM2_0.1	PM1_1.0	PM2_1.0
CE I 52.5R (Kg/m^3)		1084	1080	1034	1030
Water (Kg/m^3)		650	641	620	611
w/c ratio		0.60	0.60	0.60	0.60
CNTs	(%)	0.1	0.1	1.0	1.0
	(Kg/m^3)	1	1	10	10
LAS (Kg/m^3)		-	10	-	10
Tributyl phosphate (Kg/m^3)		-	2	-	2

Table 2- Composition of mortars

COMPOSITION		MM1_0.1	MM2_0.1	MM1_0.5	MM2_0.5
CE I 52.5R (Kg/m^3)		490	490	480	480
Water (Kg/m^3)		290	285	290	285
w/c ratio		0.60	0.60	0.60	0.60
Sand (Kg/m^3)		1460	1460	1445	1445
s:c ratio		1:3	1:3	1:3	1:3
CNTs	(%)	0.1	0.1	0.5	0.5
	(Kg/m^3)	0.5	0.5	2.4	2.4
LAS (Kg/m^3)		-	5	-	5
Tributyl phosphate (Kg/m^3)		-	1	-	1

2.4 Curing conditions

Moulds were stored in a room at 20±2°C. All the specimens were demoulded the day after the mixing, then marked, soaked into water at (20.0±1.0) °C for 7 days and finally dried for 24 hours in oven at 40±2°C.

2.5 Testing procedure and evaluation techniques

Electrical resistance measurements were made by a two-probe method using a digital multimeter (Keithley 2001, Keithley Instruments Inc., USA) on the unloaded specimen. Then the specimen was vertically positioned under the test machine and the electrodes were connected to the clamps of a multimeter. The resistance was measured increasing load, gradually applied through a force rate fixed at 0.02KN/sec. Three different load cycles were used to test the electrical responses of the specimens:

1. Seven load/unload cycles up to 12% of the compressive strength of the cementitious material;
2. load/unload cycles in the elastic range (compressive stress equal to 4%, 8% and 12% of compressive strength);
3. load/unload cycles in the inelastic range (compressive stress equal to 12%, 20% and 30% of compressive strength).

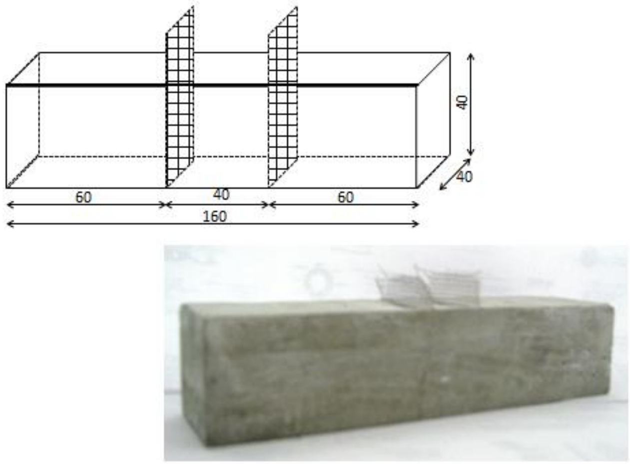


Figure 1 - Electrodes configuration in the specimen (size in mm).

3 RESULTS AND DISCUSSIONS

Table 3 shows the density of cement pastes and mortars. Pastes prepared with *Method #2* have a specific mass substantially equal to that of mixtures produced by using *Method #1*. Mortars manufactured by *Method #2*, on the contrary, showed a specific mass significantly lower than that detected for mortars produced by Method #1 (8.0% and 3.6%, for 0.1% and 0.5% CNTs addition, respectively). The decrease in the specific mass of mortars produced with method #2 should be ascribed to the defoamer not able to remove completely the air entrapped by the surfactant.

Table 3- Density of cement pastes and mortars.

	Specimen	Density (kg/m^3)	Density (*Method #2* vs. *Method #1*)	
			(kg/m^3)	%
Pastes	PM1_0.1	1739	-	-
	PM2_0.1	1723	-16	-0.9%
	PM1_1.0	1751	-	-
	PM2_1.0	1754	3	0.2%
Mortars	MM1_0.1	2201	-	-
	MM2_0.1	2024	-177	-8.0%
	MM1_0.5	2182	-	-
	MM2_0.5	2103	-79	-3.6%

Figure 2 concerns electrical resistance values in unloaded condition of cement pastes manufactured with both dispersion *Method #1* and *#2* at different CNTs percentages. The addition of carbon nanotubes dispersed by *Method #2* produces a marked decrease in the electrical resistance independently of the CNTs dosage. This means that *Method #2* permits to obtain a better dispersion of carbon nanotubes in the cement matrix. On the contrary, electrical resistance values on unloaded condition of cement mortars are lower for composites manufactured with dispersion *Method #1* compared to that obtained by using *Method #2*, independently of CNTs percentage (Figure 3). Probably, the air entrapped on mortar specimens manufactured with dispersion *Method #2* (Table 2) causes a significant increase in the electrical resistance. Consequently, the current flow was slowed by the high air void percentages and, hence, the conductivity is lower with respect that of specimens made using dispersion *Method #1*.

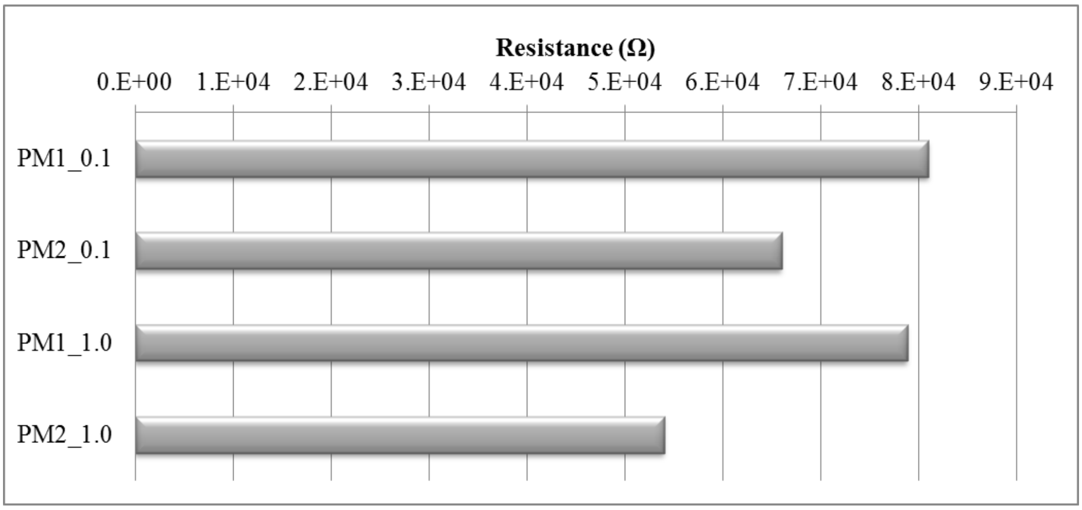


Figure 2 - Electrical resistance of cement pastes in unloaded condition.

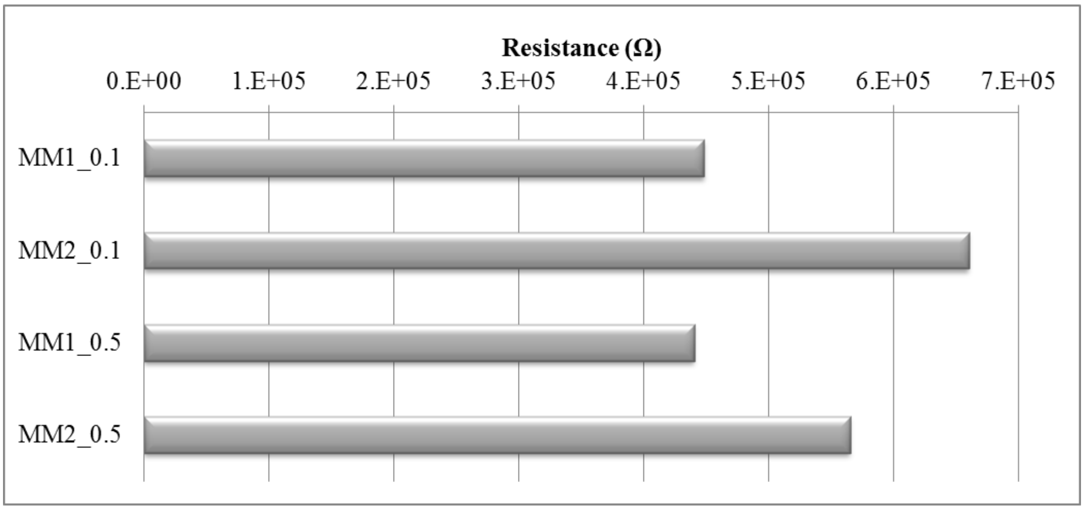


Figure 3 – Electrical resistance of cement mortars in unloaded condition

Figure 4 presents the variation of the electrical resistance of CNTs reinforced cement pastes under different compressive stress level (from 0% to 30% of the compressive strength). In the elastic range (stress up to 12%), the electrical resistance remarkably changed only for the cement pastes containing 0.1% of CNTs dispersed by *Method #2*. On the contrary, negligible changes in the electrical properties were noticed for cement pastes manufactured with *Method #1*, independently of the percentages of CNTs embedded in the cement matrix. Results highlight that an evident pressure sensitivity is achievable by means of an efficient dispersion (by using *Method #2*) of 0.1% CNTs. Increasing the dosage of CNTs up to 1.0% the stress sensitivity behaviour is less evident because the difference in the number of contact points between the unloaded and loaded condition is lower. As stated in the percolation theory, the magnitude of the electrical conductivity increases with the CNTs content. However, independently of the stress level applied, a critical percentage exists and above this value further fibers addition will not produce any significantly variation in conductivity (Chiarello, 2005).

In the inelastic range (stress from 12% to 30% of the compressive strength), a remarkably decrease of the electrical resistance was detected for the cement paste containing 0.1% of CNTs dispersed by *Method #2*. A lower change in the electrical resistivity was measured for the cement paste with the same percentage of CNTs added by using *Meth-*

od #1. Moreover, independently of the CNTs dispersion method, the higher the stress applied the lower the electrical resistance of the composite materials. Again, as for stress in the elastic range, cement pastes with 1% of CNTs added by means of *Method #2* show a lower change in the electrical resistivity with respect variations of the same properties measured for the paste with 0.1% manufactured with the same dispersion method. Data seem to indicate excellent piezoresistive properties when CNTs are added to the cement matrix by means of the more effective dispersion *Method #2*. Moreover the lower dosage (0.1%) is more sensitive to the variation of the stress applied.

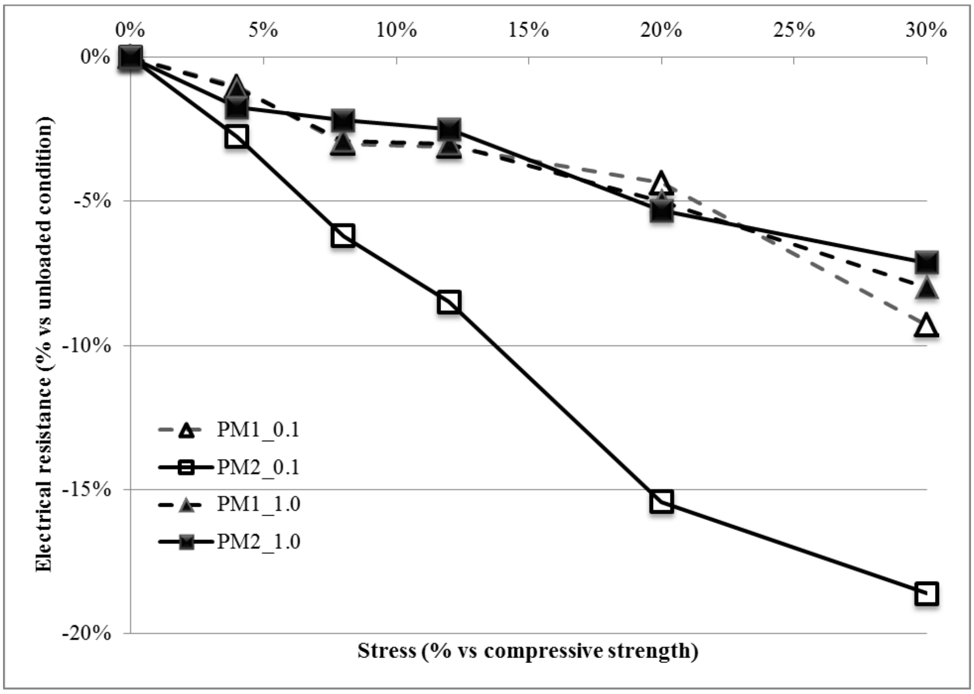


Figure 4 – Cement paste electrical resistance change under load up to 30% of the compressive strength

Figure 5 shows the variation of the electrical resistance of CNTs reinforced mortars. The electrical resistance under compressive loading changes less compared to cement pastes. Data indicate that mortars are less pressure-sensible than cement pastes. Probably the CNTs percentage added in the mortars was too low to create a carbon nanotubes network inside the specimens when the stress applied was less than 10% of the compressive strength. Changes of the electrical resistance of mortars by increasing compressive stress up to 30% of the compressive strength are significant only for mortars containing 0.5%CNTs produced by dispersion *Method #2*. However the decrease of the electrical resistance was less evident if compared to the same value obtained for cement pastes. This different behaviour between mortars and pastes could be ascribed to the low CNTs dosage used with respect the high air void present in the cementitious matrix of the mortars.

4 CONCLUSION

Electrical resistivity of cement composites containing carbon nanotubes were investigated as a function of the percentage of CNTs, the dispersion method of CNTs in the cement matrix and the level of compressive stress acting on the cementitious material. In the absence of load the addition of carbon nanotubes dispersed by using a surfactant (*Method #2*) produces a marked decrease in the electrical resistance of cement pastes.

Method #2 permits to obtain a better dispersion of carbon nanotubes in the cement matrix with respect *Method #1* based on a mere sonication of the aqueous solution containing CNTs. On the contrary, on unloaded condition electrical resistance measured on cement mortars manufactured with dispersion *Method #1* is lower, independently of CNTs percentage. Probably the higher air entrapped (as a consequence of the use of surfactant to better disperse CNTs) reduces the conductivity of specimens made by *Method #2*.

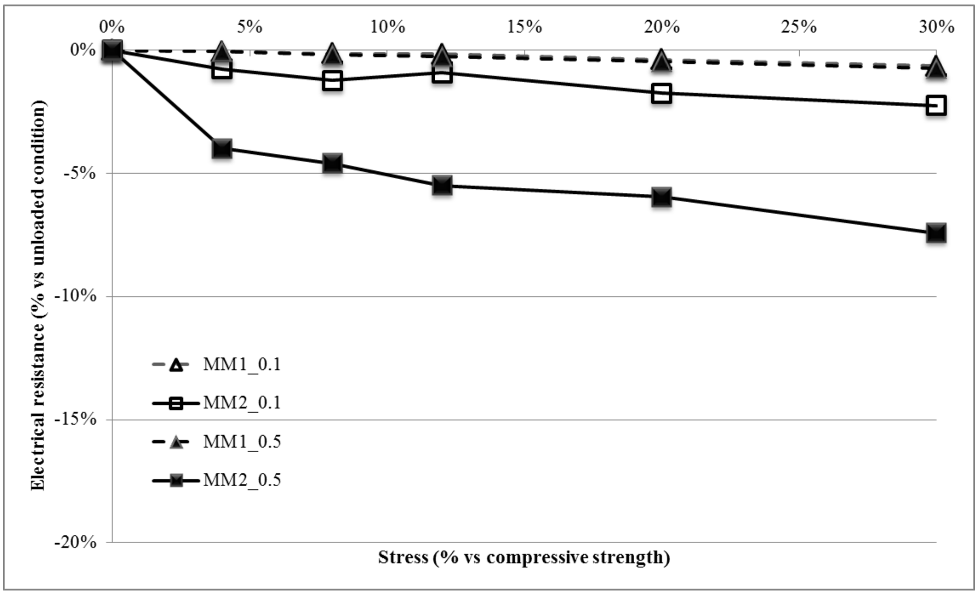


Figure 5 – Cement mortar electrical resistance change under load up to 30% of the compressive strength

Excellent piezoresistive properties were achieved when CNTs are added to the cement pastes by means of the more effective dispersion *Method #2*, independently of the percentage of CNTs used, even if the lower dosage (0.1%) is more sensitive to the variation of the stress applied.

Data indicate that mortars are less pressure-sensible with respect cement pastes. Probably the CNTs percentages used were too low to create a carbon nanotubes network inside the specimens. When the compressive stress is as high as 30% of the compressive strength, significant variations of electrical resistance were noticed only for mortars containing 0.5%CNTs produced by dispersion *Method #2*.

Based on the results of the present experimental research CNTs cement composites have great potential and they could be used in the next future in concrete field for practical applications to monitor the stress level of reinforced concrete elements subjected to compressive loads. In particular, information on actual stress existing in reinforced concrete elements could be improve the design procedures of structures.

REFERENCES

Chiarello M., Zinno R. (2005), *Cement& Concrete Composites 27*, 463 - 469;

Coppola L., Borgarello E., Buoso A., Corazza F., Crippa E. (2010), *Proceedings of the 1st Workshop "Le nuove frontiere del calcestruzzo strutturale – The new boundaries of structural concrete"*, ACI ItalyChapter (Salerno), 299 - 306;

Iijima S. (1991), *Nature 354*, 56 - 58;

Li G. Y., Wang P. M., Zhao X. (2005), *Carbon 43*, 1239 - 1245.

Baoguo H., Xun Y., Jinping O., "*Effect of water content on the piezoresistivity of MWNT/cement composites",* J Mater Sci (2010) 45, 3714–3719

Wagner, H.D. et al. (1998), *Stress-induced fragmentation of multi-walled carbon nanotubes in a polymer matrix,* ApplPhysLett 72(2), 188 – 190;

Yu X., Kwon E. (2009), *Smart Mater. Struct. 18*, 5pp.

The Workshop “The New Boundaries of Structural Concrete”, organized at the Università Politecnica delle Marche (Italy) in September 2011, arises from a joined initiative between this University and the American Concrete Institute (ACI) Italy Chapter.

The workshop has been articulated by organizing over 30 lectures in four different sessions. These sessions are listed below by following the chronological order scheduled by the workshop program:

Session A - Performance and life-cycle costs of new concrete structures.
Session B – Controlled-performance concrete
Session C - New scenarios for concrete
Session D - Concrete quality control on site

The proceedings volume collects the latest advances of the research in the above mentioned topics and so, is addressed not only to members of the scientific community but also to representatives of the industry and to professionals directly involved in the design and construction of the new structures and in the retrofitting of existing ones.

ISBN 978-88-904292-2-4

9 788890 429224