Cement-Carbon Nanotubes based Composite

Giuseppe Ferro[1, a], Jean-Marc Tulliani[2,b], Simone Musso[3,c], Alberto Tagliaferro[3,d]

Politecnico di Torino, Corso Duca degli Abruzzi, 24, 10129 Turin, Italy

[1]Structural Engineering department

[2]Materials Science and Chemical Engineering department

[3]Physics department

[a]giuseppe.ferro@polito.it, [b]jeanmarc.tulliani@polito.it, [c]simone.musso@polito.it,
[d]alberto.tagliaferro@polito.it

Keywords: Cement, concrete, composite, CNTs, nanotube, functionalized

Abstract. In order to create new cement matrix composites, functionalized multi-walled carbon nanotubes (f-MWCNTs) were added to cement. f-MWCNTs differ from pristine CNTs for the presence of carboxylic groups (-COOH) inserted on the graphitic lattice by oxidative treatments.

Different composite samples with f-CNTs were prepared and then compared with plain concrete samples. The mechanical properties of the newly formulated composites were analyzed, as the chemical and surface properties of the materials.

Even though it was expected that the addition of f-CNTs could reduce the pore size distribution and decrease porosity, hence increasing mechanical properties of the composite, the f-CNT containing samples exhibited a significant reduction both in flexural and compressive strength. We suggest that the worsening in mechanical properties is due to the high degree of functionalization and defectiveness of CNTs. In fact the f-CNTs worked as water absorbers, hence lowering the level of hydration of the cement.

The phase composition was characterized by means of thermogravimetric analysis coupled with mass spectroscopy and it was found that there were poor interfacial interactions between carbon nanotubes and the cement; the concrete as such showed a higher hydration (such as CSH, calcium silicate hydrates and calcium hydroxide). The mineralogy and microstructure of samples were analyzed by means of an X-Ray diffractometer and scanning electron microscope. Carbon nanotubes samples showed an heterogeneous distribution of the degree of hydration. It was demonstrated that composite samples need a longer time of ageing, in order to join similar mechanical properties as concrete as such.

Introduction

Carbon nanotubes (CNTs) have received an ever increasing scientific and industrial interest during these last years due to their exceptional physical and chemical properties that render them suitable for numerous potential applications ranging from living matter structure manipulation to nanometer-sized computer circuits and composites materials [1]. In particular, CNTs have been used to reinforce polymers [2-3], metals [4-5] and ceramics [6-7]. CNTs are hollow tubular channels formed either by one wall (SWCNTs) [8,9] or several walls (MWCNTs) [1] of rolled graphene sheets. The diameter can vary from few nanometers to several dozen depending on the deposition parameters and the nature of the synthesis method, i.e., arc-discharge, laser ablation, or catalytic chemical vapor deposition (CCVD) and usually exhibit an extremely high aspect ratio (length-to-diameter ratio) ranging from 30 to more than many thousands [10].

Pristine CNTs can be either opened at the end or closed with hemi-sphere of fullerene, with catalyst particles trapped inside the hollow cavity. It has to be underlined that most of the CNTs outstanding properties, such as mechanical properties, are related to lattice defect free material
Recently [11], carboxylic groups functionalized CNTs (f-CNTs) were employed in concrete and allowed an increase of the compressive and flexural strength. In that case, a decreasing in CNTs mechanical properties resulting from the functionalization of the graphitic lattice was compensated by a stronger connection between f-CNTs and cementitious matrix originated by chemical bonds between the two phases.

The aim of our work was to achieve the manufacture of a more versatile product by preparing a self-compacting concrete (SCC) with improved mechanical properties at a microscopic level by means of f-CNTs addition. In particular, as we noticed in the preliminary tests, the use of a SCC avoided the compacting phase of the fresh concrete cast preventing that f-CNTs could come up during the procedure. As a result, a more homogeneous composite was obtained.

As proved by flexural and compressive tests, the composite exhibited poor properties suggesting a non ideal hydration of the cement. As we propose, this result can be related to an unlike absorption of water by the f-CNTs. Several techniques were used to characterize the functionalized MWCNTs in order to explain their behavior.

Experimental

Two different samples were prepared containing no fibres and 0.5 wt. % of f-CNTs with respect to cement. For the preparation of SCC two commercial additives were employed: a dispersant, Dynamon SP1, an acrylic dispersion into water and a viscosity modifier, Viscofluid SCC/10 to increase cohesion and homogeneity of concrete mixture and to avoid segregation and bleeding phenomena.

Nanocyl® 3101 series, multiwall carbon nanotubes (MWCNT) produced via CCVD process, purified and functionalized with carboxylic groups were used [12] and their features are reported in table 1.

Table 1 - Nanocyl® 3101 serie features [12]

Property	Value	Unit
Average diameter	10	[nm]
Length (average)	0.1 - 10	[μm]
Carbon Purity	> 95	[%]
Metal Oxide (impurity)	< 5	[%]
-COOH functionalization	< 4	[%]

The aggregates were sieved through a 1.6 mm sieve and CEM II/A-S 42.5 R was used **[13]**; the composition of the samples are reported in table 2.

Table 2 – Composition of the prepared samples

Component	Quantitative
Cement	400 kg/m^3
Water	w/c=0.45 (180 kg/m^3)
Sand	1720 kg/m^3
Dispersant	1.1 wt.% w respect to cement
Viscosity modifier	0,5% wt.% w respect to cement
f-MWCNT (when added)	0,5% wt.% w respect to cement

Two series of samples were prepared. In a first time, the nanotubes were dispersed into water and sonicated by means of an ultrasonic probe during two hours, while in a second time the CNTs were dry mixed with cement and sand. After casting, the samples were maintained 24 h in a water vapour saturated atmosphere. Subsequently the samples were demolded and put for 27 days in 20°C water until tests, leading to a total curing time of 28 days. Flexural and compressive tests were performed onto prisms (40 × 40 × 160 mm^3), while the cubic ones (10 cm in side) were submitted to compressive tests. Prisms were submitted to flexural tests after 28 days, according to UNI-EN standards [14] and, onto the fragments obtained, compressive tests were also performed. The load was then applied vertically at a crossarm rate of 0.1 mm/min. Cubes were also cured for 20 days under air, after the initial 28 days of curing under water.

After the mechanical tests, the samples were roughly crushed to separate the aggregates from the binder, which was then finely ground with a concrete and a pestle. The powder obtained by grinding the binder was finally sieved with a sieve having apertures of 40 μm. These samples were characterized by means of TG (TGA, Mettler Toledo, TGA/SDTA 851°) - MS (Balzer QuadstarTM 422 V60) from 20° to 1000°C and an heating rate of 15°C/min and XRD (XRD, X'Pert Philips).

An extensive characterization of the functionalized CNTs has been performed in order to clarify the behavior of the material during the composite preparation.

The morphology of functionalized CNT samples was characterized by scanning and transmission electron microscopy (FE-SEM, TEM). Evaluation of lattice defect degree was performed by Raman spectroscopy (MicroRaman Renishaw Ramascope, Ar+ laser 514.5 nm excitation). Fourier transformed infrared spectroscopy (FT-IR) and EDX (Energy Dispersive X-Ray) analysis were used to estimate the presence of reactive groups on the CNTs surface.

Thermal oxidation of CNTs was investigated by means of a thermogravimetric analysis (TGA) 2050 balance (TA inc.). About 10 mg of the samples were placed in an alumina sample pan, and the TGA experiments were performed with a 60 cm3/min air flow (99,999 % purity) and with a 10 °C/min heating ramp.

Results and discussion

Samples made by dispersing CNTs into the water

From the results of flexural tests (Fig. 1a), it can be observed that, in the case of f-MWCNT additions, the mechanical strength was decreased by a factor of 2.6, respect to reference samples: 10.08 ± 0.22 MPa and 3.85 ± 0.23 MPa, for the concrete as such and with nanotubes, respectively. The compressive resistance of the prisms (Fig. 1b) was even 6 times lower respect to the concrete with no f-CNTs: 93.02 ± 2.18 kN and 15.53 ± 3.04 kN, respectively. These results were obviously confirmed by the compressive tests performed onto the cubes: 44.6 MPa, for the concrete as such, and 12.2 MPa, for the material containing nanotubes. However, in this case, the ratio between the compressive strength of the two series of samples was lower, respect to the previous compressive tests, and was equal to 3.7.

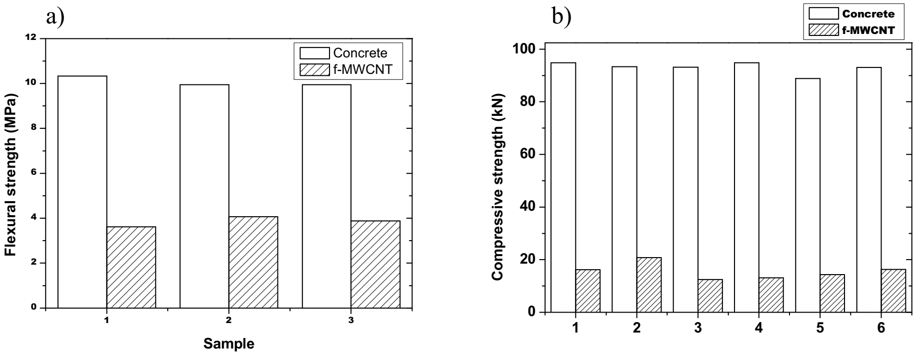

Figure 1 – Flexural (a) and compressive (b) strength of concrete w and w/o f-MWCNTs

The bad mechanical properties observed after nanotubes additions were related to a poor cement paste hydration, as illustrated by TGA (Fig. 3), where the quantitative of tobermorite formed in the absence of f-MWCNTs is higher (peak at 102° and 116°C, respectively for the concrete as such and for the sample with nanotubes) [15]. Tobermorite ($3CaO.2SiO_2.xH_2O$) is formed during hydration of the calcium silicate phases, which are C_3S ($3CaO.SiO_2$) and C_2S ($2CaO.SiO_2$). For the two hydrated samples, the slight peaks at around 160°C are due to ettringite thermal decomposition, while the peaks at around 450°-460°C are due to calcium hydroxide decomposition, other hydrated phases formed during hydration of Portland cement [15]. In all the samples, calcium carbonate is present and leads to the peaks above 700°C. In the case of the anhydrous cement, the peak at 131°C is attributed to gypsum dehydration. Gypsum is added to the clinker to form Portland cement.

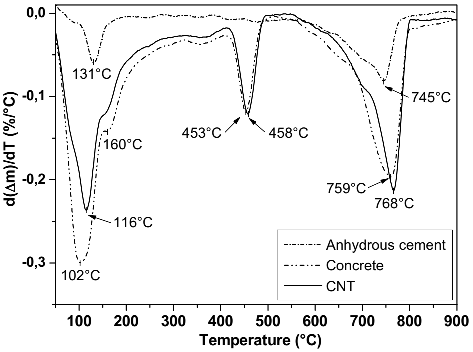

Figure 3 – TGA onto anhydrous cement and concrete w and w/o f-MWCNTs powders

XRD onto the sieved powder coming from the samples containing the f-MWCNTs after hydration evidenced the presence of aragonite together with calcite. While the latter one is common, aragonite crystals are not so common and are probably favoured by the carboxylic groups onto the nanotubes [16].

Samples made by dispersing CNTs with cement and sand

A second series of samples were then prepared, where the f-MWCNTs were dry mixed with cement and sand, before water addition. Due to the fact that the mixture's workability was limited, according to the recipe described in table 2, the water/cement ratio was raised to 0.56. After 28 days of curing, the flexural strength of the prisms was equal to 8.2 ± 0.38 MPa and 7.52 ± 0.45 MPa, respectively for the concrete as such and containing nanotubes (3 samples of each). Obviously, due to a higher water/cement ratio, the flexural strength of concrete as such is lower for these samples, respect to the previous one, but, in this case, the nanotubes addition led only to a loss of mechanical resistance of 8.3%. Similar results were obtained with the compressive tests onto the fragments coming from flexural tests: 80.3 kN and 59.2 kN, respectively for the concrete as such and with nanotubes

Characterization of MWCNT

As shown by TEM images (Fig. 4a), MWCNTs have an average diameter of 15-20 nm. SEM analysis (Fig. 4b) revealed a not meaningful amount of carbonaceous by products.

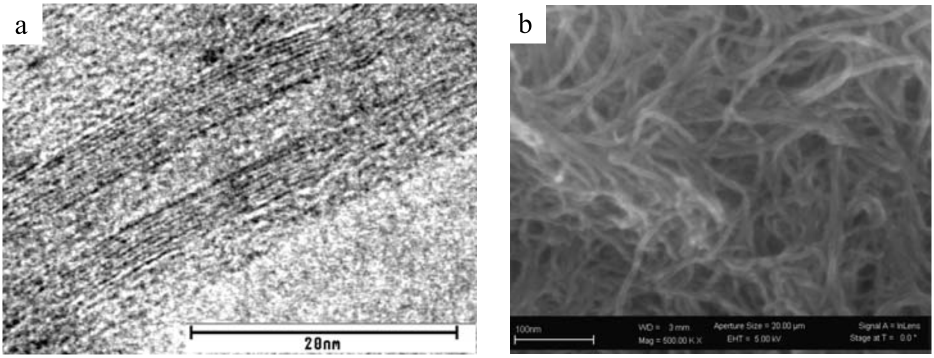

Figure 4 - Electron microscope analysis showing functionalized MWCNTs. (a) TEM image and (b) low resolution SEM image.

FT-IR spectra of pristine MWCNTs do not generally show strong features, thus, modifications in some characteristic peaks allows the confirmation of the presence of carboxylic groups in oxidized/functionalized material [17]. The 1721 cm^{-1} peak in Figure 5a may correspond to the stretching vibration mode of C=O (carboxylic group); the 1584 cm^{-1} peak to the asymmetric stretching vibration of anion carboxylate ($-COO^-$) and stretching of the C=C bonds placed by the functional group; the 1405 cm^{-1} peak to the symmetric stretching vibration of the anion carboxylate ($-COO^-$), probably overlapped with the aromatic C=C signal. The features at approximately 900 cm^{-1} are assumed to be not relevant, since they are likely due to some contamination during the sample preparation steps, while peak at circa 1580 cm^{-1} is related to the C=C stretching of the aromatic structure.

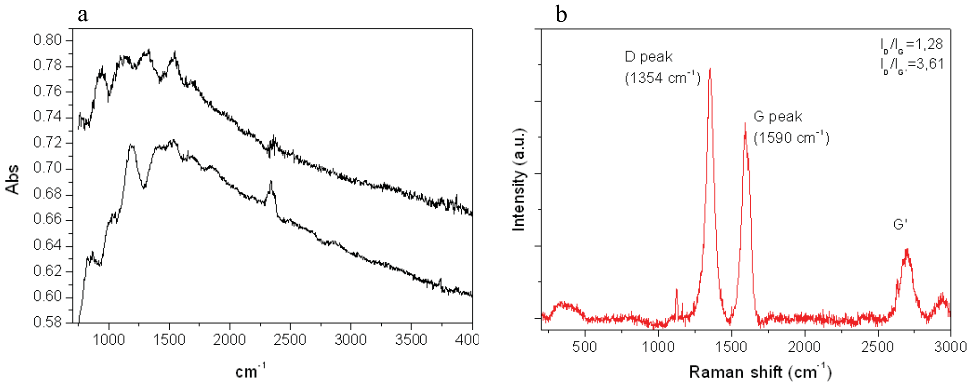

Figure 5 - FT-IR (a) and Raman spectra (b) of functionalized MWCNTs.

Presence of oxygen, likely bonded in carboxylic groups, was found with EDX investigation (Fig. 6). Also chlorine was revealed, although is presence can be ascribed either as an impurity or as part of acyl chloride groups resulting from the functionalization process. The lack of signals attributable to metal particles suggests that functionalization treatment caused the removal of the catalyst particles indispensable for the CNT growth.

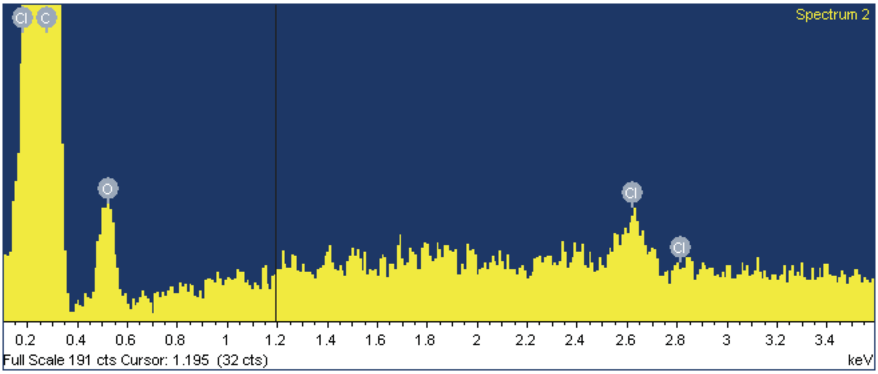

Figure 6 - EDX analysis on functionalized MWCNTs

In general, the Raman spectra of pristine and treated CNT samples are composed of two characteristic peaks for the nanotubes: the G band near 1590 cm^{-1} and the D band at 1360 cm^{-1}. The G band is related to the graphite E_{2g} symmetry of the interlayer mode, which reflects the structural intensity of the sp^2-hybridized carbon atoms of the nanotubes. Since the D band (breathing mode, A_{1g}-band) as a result of the disordered carbon atoms increases with the lattice disorder, while the G band does not have dependence on the amount of disorder, the extent of the defects in carbon nanotubes can be evaluated by the ratio of the D and G band intensities (I_D/I_G) [18]. The result of the Raman analysis reported in Figure 5b showed a I_D/I_G ratio of 1.2. thus confirming the presence of a high degree of lattice disorder resulting from the oxidative process.

Thermo-gravimeter analysis in air (Fig. 7), gave information about the thermal stability of functionalized CNTs in oxidative environment. The weight loss starting nearby room temperature corroborated the presence of a significant amount of volatile groups, hence carboxylic groups. Moreover, in agreement with EDX investigation, thermo oxidative analysis showed a negligible amount of residue (less than 1.6 % in weight) confirming the absence of catalyst particles.

The position and narrow shape of the peak in the weight derivative curve reveals an uniform material with high quantity of reactive spots (lattice defects).

The investigation confirmed that the f-CNTs have a high degree of defects and oxidized groups which can strongly improve the interaction of the material with the water used during preparation of composite.

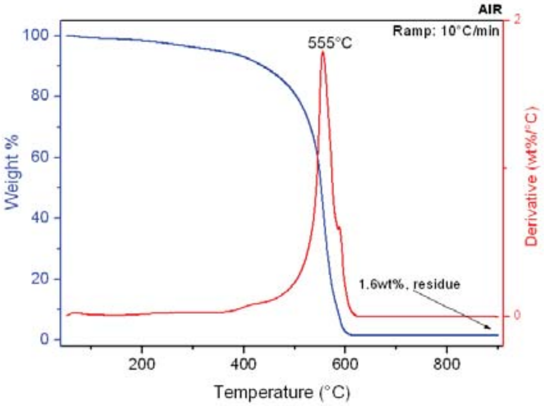

Figure 7 - Thermo-gravimeter analysis in air flow on functionalized MWCNTs (heating ramp 10°C/min)

Conclusions

Interaction of CNTs with several solvents, and in particular with water has been studied extensively, both at the microscopic level [19,20] and macroscopic level [21]. In fact, since pristine material shows non-reactive and very hydrophobic nature, tailoring of wettability properties by acid oxidative treatments [22,23] can play a key role in CNTs dispersion in liquid and in their subsequent performance as reinforcements in composites. As has been described into the literature [8], oxidative acid treatment can strongly increase the CNTs wettability. As a consequence, depending also on the diameter of the hollow cavity, functionalized CNTs can strongly suck inside aqueous solutions by means of capillarity behaviour favoured by hydrophilic character.

As confirmed by the analysis performed on f-CNTs used to produce concrete-composite, the high amount of lattice defects and carboxylic groups can justify a strong hydrophilic behaviour that is probably responsible for the incomplete hydration of cement paste added with nanotubes which initially retained the water during concrete preparation and then released it progressively during air curing (for the cubic samples).

Work is now in progress with non functionalized CNTs, to avoid such drawbacks.

References

[1] S. Iijima: Nature Vol. 354 (7) (1991), p. 56

[2] H.D. Wagner, O. Lourie, Y. Feldman and R. Tenne: Appl. Phys. Lett. Vol. 72 (2) (1998), p.188

[3] D. Qian, E.C. Dickey, R. Andrews and T.Rantell: Appl. Phys. Lett. Vol. 76 (20) (2000), p.2868

[4] S.R. Dong, J.P. Tu and X.B. Zhang: Mater. Sci. Eng. A Vol. 313 (2001) p.83

[5] T. Kuzumaki, K. Miyazawa, H. Ichinose and K. Ito: J. Mat. Res. Vol. 13 (1998), p.2445

[6] A. Peigney, C. Laurent, E. Flahaut, A. Rousset: Cer. Int. Vol. 26 (2000), p.677

[7] R.Z. Ma, J. Wu, B.Q. Wei, .J Liang and D.H. Wu: J. Mat. Sci. Vol. 33 (1998), p.5243

[8] S. Iijima and T. Ichihashi: Nature Vol. 363 (1993), p. 603

[9] D.S. Bethune, C.H. Kiang, M.S. De Vries, G. Gorman, R. Savoy, J. Vazquez and R. Beyers: Nature Vol. 363 (1993), p. 605

[10] O. Ersen, J. Werckmann, M. Houlle, M.J. Ledoux and C. Pham-Huu: Nano Lett., Vol. 7 (7) (2007), p. 1898

[11] G.Y. Li, W. P. Ming and X. Zhao: Carbon Vol. 43 (2005), p. 1239

[12] Information on http://www.nanocyl.be

[13] UNI-EN 197/1 standard

[14] UNI-EN 196-1 standard

[15] J. Dweck, P. F. Ferreira da Silva, P.M. Büchler and F. K. Cartledge: J. Therm. Anal. & Cal. Vol. 69 (2002), p. 179

[16] N. Wada, K. Yamashita and T. Umegaki: J. Col. & Interf. Sci. Vol. 212 (1999), p. 357

[17] Y. Wang, Z. Iqbal and S.V. Malhotra: Chem. Phys. Lett. Vol. 402 (2005), p. 96

[18] S. Musso, S. Porro, M. Vinante, L. Vanzetti, R. Ploeger, M. Giorcelli, B. Possetti, F. Trotta, C. Pederzolli and A. Tagliaferro, Diam. Rel. Mater. Vol. 16 (2007), p. 1183

[19] E. Dujardin, T. W. Ebbesen, A. Krishnan and M. M. J. Treacy: Adv. Mater. Vol. 10 (17) (1998), p. 1472

[20] T. Kanyo, Z. Konya, A. Kukovecz, F. Berger, I. Dekany and Kiricsi I.: Langmuir Vol. 20 (2004), p. 1656

[21] M Pavese, S Musso, S Bianco, M Giorcelli and N. Pugno: J. Phys. Cond. Matter. (submitted)

[22] S. Porro, S. Musso, M. Vinante, L. Vanzetti, M. Anderle, F. Trotta, A and Tagliaferro: Physica E Vol. 37 (2007), p. 58

[23] S. Musso, S. Porro, M. Vinante, L. Vanzetti, R. Ploeger, M. Giorcelli, B. Possetti, F. Trotta, C. Pederzolli and A. Tagliaferro: Diam. Rel. Mat. Vol.16 (2007), p. 1183