Influence of carbon nanotubes structure on the mechanical behavior of cement composites

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ABSTRACT

Cement matrix composites have been prepared by adding 0.5% in weight of multi wall carbon nanotubes (MWCNTs) to plain cement paste. In order to study how the chemical–physical properties of the nanotubes can affect the mechanical behavior of the composite, we compared the specimen obtained by mixing the same cement paste with three different kinds of MWCNTs. In particular, as-grown, annealed and carboxyl functionalized MWCNTs have been used. In fact, while high temperature annealing treatments remove lattice defects from the walls of CNTs, hence improving their mechanical strength, acid oxidative treatments increase chemical reactivity of pristine material, consequently chemical bonds between the reinforcement and the cement matrix are supposed to enhance the mechanical strength.

Flexural and compressive tests showed a worsening in mechanical properties with functionalized MWCNTs, while a significant improvement is obtained with both as-grown and annealed MWCNTs.

The phase composition of the composites was characterized by means of thermo gravimetric analysis coupled with mass spectroscopy, while the mineralogy and microstructure were analyzed by means of an X-ray diffractometer and scanning electron microscope. The results are interpreted and discussed taking into account the chemical and physical properties of the MWCNTs by means of EDX, TGA, SEM and Raman analysis.

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1. Introduction

Carbon nanotubes (CNTs) are hollow tubular channels, formed either by one wall (SWCNTs) or several walls (MWCNTs), of rolled graphene sheets [1]. They have received an ever increasing scientific and industrial interest 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 [2,3]. Since CNTs exhibit great mechanical properties along with extremely high aspect ratios (length-to-diameter ratio) ranging from 30 to more than many thousands, they are expected to produce significantly stronger and tougher cement composites than traditional reinforcing materials (e.g. glass fibers or carbon fibers). In fact, because of their size (ranging from 1 nm to tens of nm) and aspect ratios, CNTs can be distributed in a much finer scale than common fibers, giving as a result a more efficient crack bridging at the very preliminary stage of crack propagation within composites.

However, properties and dimensions of CNTs strongly depend on the deposition parameters and the nature of the synthesis method, i.e., arc-discharge [4], laser ablation [5], or chemical vapor deposition (CVD) [6]. In view of a commercial application the CVD technique is the only one that can offer a path towards low-cost and large scale production [7,8], albeit it must be highlighted that CVD can produce nanotubes that have non-negligible amount of lattice defects along the graphene walls and often these tubes are curled and aggregated to form bundles and ropes that have a lower strength and are very difficult to disperse [9].

The amount of defects can play a key role for cement reinforcement application. In fact, defect free CNTs, obtained with a complete graphitization process achieved by heat-treatment at high temperature [10], either in vacuum or inert environment, show outstanding mechanical properties [11], although they are incapable to form proper adhesion with the matrix, causing what it is called sliding [12]. If the nanotubes are assembled in bundles there is an additional sliding inside the bundle that prevents a satisfactory load transfer.

On the other hand, while lattice defects limit mechanical strength, they are reactive spots that can be used to produce functional groups on the outer walls by chemical treatments with acid solutions. These superficial chemical groups, such as carboxylic (–COOH) groups, can originate strong chemical bonds between CNTs and cementitious matrix, thus enhancing the reinforcement

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Table 1
Features of the three different MWCNTs dispersed in the cement.

Property	p-CNTs [15]	a-CNTs [16]	f-CNTs[1]
Deposition technique	CVD	CVD	CVD
Average diameter (nm)	40–80	40–80	10–20
Length (average) (μm)	400–1000	200–400	0.1–10
Carbon Purity (wt.%)	>92	>99	>95
Metal Oxide (impurity) (wt.%)	<6	<1	<5
–COOH functionalization (wt.%)	0	0	<4

Table 2
Composition of the prepared samples. For each composition three samples have been cast in order to perform mechanical tests a 1, 7 and 28 days.

Components	Cement-additive	Cement-CNTs-additive
Cement CEM II A/S R, according to EN 197/1 standard	450 kg/m^3	450 kg/m^3
Water	w/c = 0.40 (180 kg/m^3)	w/c = 0.40 (180 kg/m^3)
Sand (standard [17])	1720 kg/m^3	1720 kg/m^3
Superplasticizer (wt.% with respect to cement)	1.1	1.1
Viscosity modifying agent (wt.% with respect to cement)	0.5	0.5
MWCNT (wt.% with respect to cement)	0	0.5

efficiency even though to the detriment of graphitization degree [13,14].

Furthermore, chemical treatments can help to disentangle the bundles, hence facilitating a uniform dispersion at the single tube level, above all in aqueous media such as that for cement composites.

Proper dispersion and adequate load transfer are the main challenges in the search for efficient carbon nanotube reinforced cement composites.

The present work compares the results obtained with flexural and compressive measurements performed on unreinforced cement and three different cement-based composites containing as-grown, annealed and functionalized MWCNTs, respectively. Furthermore, the phase composition of the composites is characterized by means of thermo gravimetric analysis (TGA) coupled with mass spectroscopy (MS), while the mineralogy and microstructure are analyzed by means of an X-ray diffractometer (XRD) and scanning electron microscope (SEM).

The results are discussed with regard MWCNTs properties, which have been characterized with several techniques.

2. Experimental

Pristine MWCNTs (labeled p-CNTs from now on for brevity purposes) have been synthesized in Physics Department at Politecnico di Torino (Italy) [15], while annealed MWCNTs (labeled a-CNTs from now on) have been provided by Nano Carbon Technologies Co., Ltd., Akishima-shi, Tokyo (Japan) [16] and carboxyl-group functionalized MWCNTs (Nanocyl 3101, labeled f-CNTs from now on) have been purchased to Nanocyl S.A.[1] Nanotubes features are reported in Table 1.

In order to minimize the size of aggregated MWCNTs, they were all dispersed in acetone by means of an ultrasonic probe (vibration by ultrasound). After 4 h, the sonication was stopped and the acetone was allowed to evaporate.

The cement composite samples were prepared in rotary mixer by adding cement, water, sand and 0.5 wt.% of CNTs powder with respect to cement. Moreover, superplasticizer (Mapei, Dynamon SP1,[2] an admixture based on modified acrylic polymer for precast concrete) and viscosity modifying agent (Mapei, Viscofluid SCC/10[3]) have been added to the mixture during the stirring stage, to help increasing cohesion and homogeneity of concrete mixture and also to avoid segregation and bleeding phenomena. All the composition details are reported in Table 2.

After pouring each mixture in a stainless steel prism shaped mold, an electric vibrator was used to ensure good compaction, by letting the samples falling down from height of 15 mm for 60 times [17]. The samples were then maintained 24 h in a water vapor saturated atmosphere. Subsequently they were de-molded and put for 27 days in 20 °C water until tests, leading to a total curing time of 28 days.

Three-points bend tests (span = 100 mm) were performed onto the 28 days cured prism shaped samples ($40 \times 40 \times 160$ mm^3), according to UNI-EN standards [17]. The modulus-of-rupture (MOR) is the surface stress at failure in bending and is equal to:

$$\sigma_{max} = \frac{3}{2} \frac{F^2_{max} \cdot l}{bt^2} \tag{1}$$

where b is the beam width, t the height, l the span and F_{max} is the maximum force in a bent beam at the instant of failure.

Then, onto the two fragments obtained by each prism, compressive tests were also performed on a 40×40 mm^2 surface, by means of self-aligning squared seating platens. The compression resistance (R_c) is the maximum force at the instant of rupture. The load was then applied vertically at a crossarm rate of 0.1 mm/min, for both tests.

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 TGA (Mettler Toledo, TGA/SDTA 851°)-MS (Balzer QuadstarTM 422 V60) from 20 °C to 1000 °C and an heating rate of 15 °C/min, XRD (XRD, X'Pert Philips), SEM.

An extensive characterization of the three typologies of MWCNTs (p-CNTs, f-CNTs and a-CNTs) has been performed in order to comprehend how their different properties affected the behavior of the final composite.

The morphology were 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 thermo gravimetric 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 cm^3/min air flow (99.999% purity) and with a 10 °C/min heating ramp.

3. Results and discussion

3.1. Characterization of MWCNTs

The diameter of the used CNTs (reported in Table 1) and the negligible amount of carbonaceous by products was revealed by SEM and TEM analyses (Fig. 1). TEM images of a-CNTs are reported elsewhere [16,18]. Moreover, the SEM images showed that p-CNTs are much more curled and entangled than a-CNT. This different
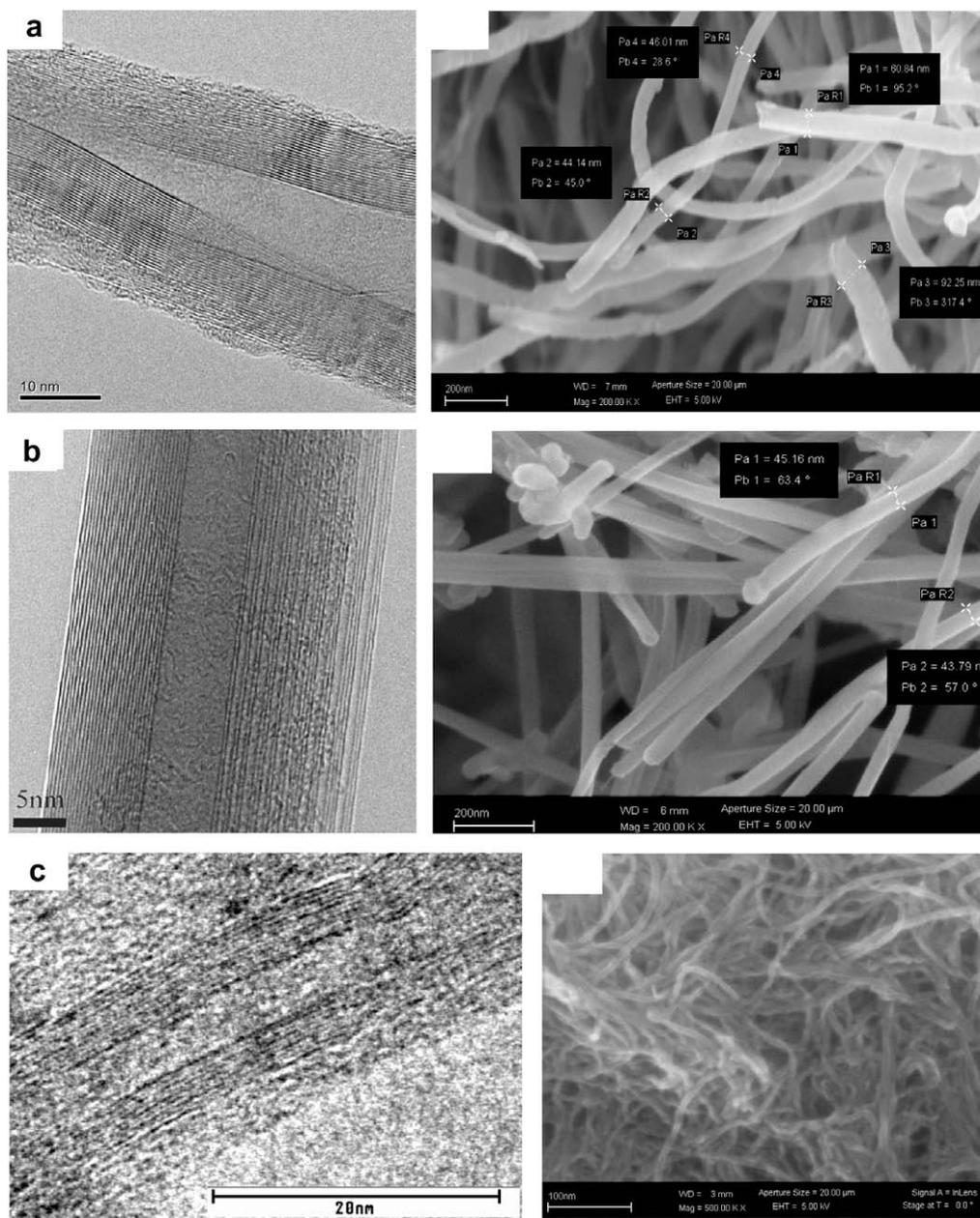

Fig. 1. Electron microscope analysis showing p-CNTs (a), a-CNTs (b) and f-CNTs (c). TEM images are reported on the left while SEM image are on the right. The TEM image of a-CNTs (b-right) is reprinted with permission from Ref. [16]; copyright of Elsevier.

morphology is probably caused by the not-negligible amount of lattice defects produced during the deposition of p-CNTs. As a result of the functionalization process also the f-CNTs are kinked and curled.

FT-IR spectra of p-CNTs and a-CNTs (not reported here) did not show strong features, thus, the presence of carboxylic groups in oxidized/functionalized f-CNTs was confirmed by some FT-IR (Fig. 2) characteristic peaks [19]. The 1721 cm^{-1} peak in Fig. 2 may corresponds 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 ca. 1580 cm^{-1} is related to the C=C stretching of the aromatic structure.

EDX investigation proved the presence of significant amount of oxygen bonded on the side walls of f-CNTs (Fig. 3). However, contrary to what was expected, probably oxygen is not only due to the presence of carboxylic groups. In fact, also chlorine was revealed, and its 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.

At last, the degree of graphitization of the nanotubes was verified by Raman spectroscopy [20] and thermo gravimetric analysis (TGA) [14].
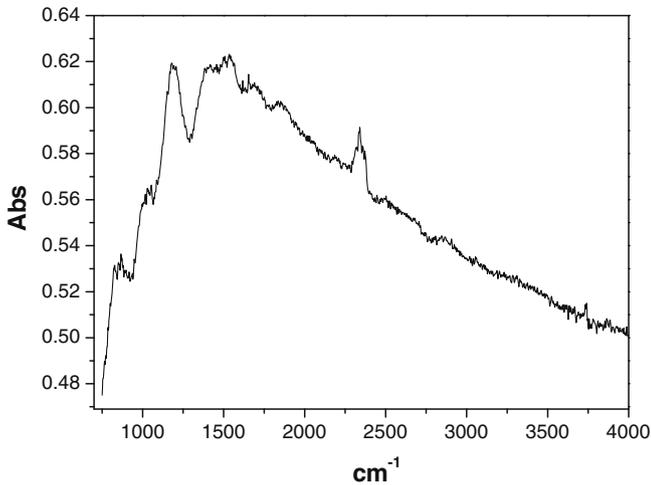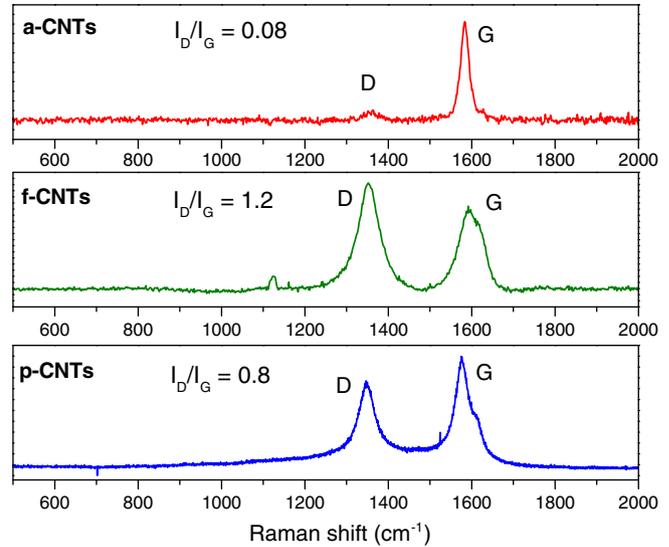
Fig. 2. FT-IR spectrum of f-CNTs.

Fig. 4. Raman spectra of p-CNTs, a-CNTs and f-CNTs.

In Fig. 4 the Raman spectra of the three species of nanotubes are compared. CNTs spectra are composed of two characteristic peaks: the $1344\ cm^{-1}$ peak (the so called D band) due to the disorder-induced phonon mode (breathing mode, A_{1g}-band) and the $1591\ cm^{-1}$ peak (the so called G band) assigned to the Raman-allowed phonon mode (E_{2g}-band). In order to estimate the structural ordering, of particular interest is the evaluation of the G band narrowing and of the I_D/I_G ratio [20,14]. In fact, whereas the intensity of the G-band (I_G) does not depend on the lattice defect density, the D-band intensity (I_D) decreases as defect density decreases.

The high crystalline quality of the annealed CNTs with respect with p-CNTs and f-CNTs was confirmed both by the noteworthy decreasing in the bandwidth of the G peak and also by the decreasing of the I_D/I_G ratio. On the other hand, Raman analysis proved that the oxidative process highly increased the lattice disorder for the f-CNTs.

These results are confirmed by the TGA reported in Fig. 5. In fact, due to the absence of lattice defects, hence oxygen reactive sites, the a-CNTs were thermally the most stable towards oxidative degradation. The functionalized CNTs exhibited a not-negligible weight loss in a temperature range (180–400 °C) where both p-CNTs and a-CNTs were extremely stable. This can be explained with the fact that the functional groups tend to be significantly desorbed by the CNT surface. Moreover the overall thermal stability of f-CNTs is lower than p-CNTs and a-CNTs due to the high amount of lattice defects.
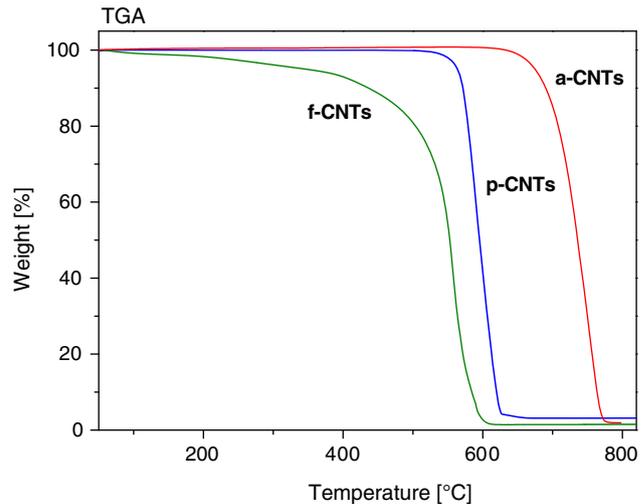

Fig. 5. Thermo-gravimeter analysis in air flow on p-CNTs, a-CNTs and f-CNTs (heating ramp 10 °C/min).

3.2. Characterization of composites

From flexural tests results (Fig. 6a), it can be observed that, while the addition of carboxyl functionalized MWCNTs decreased
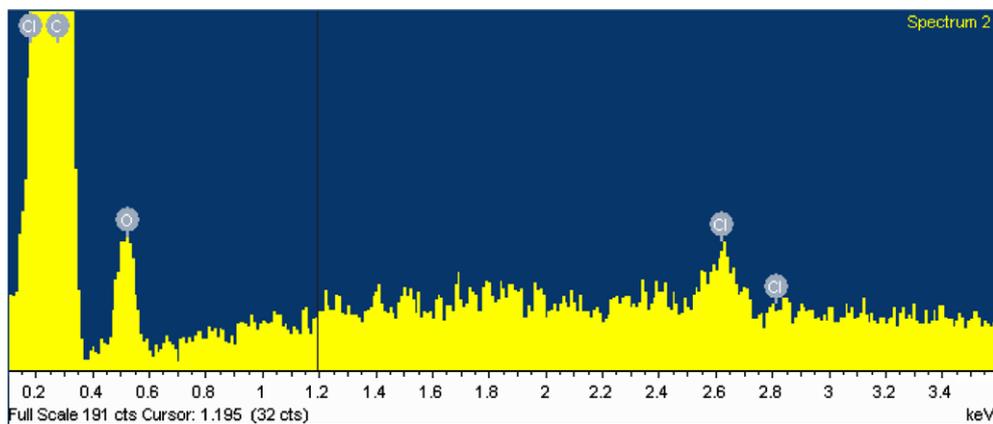

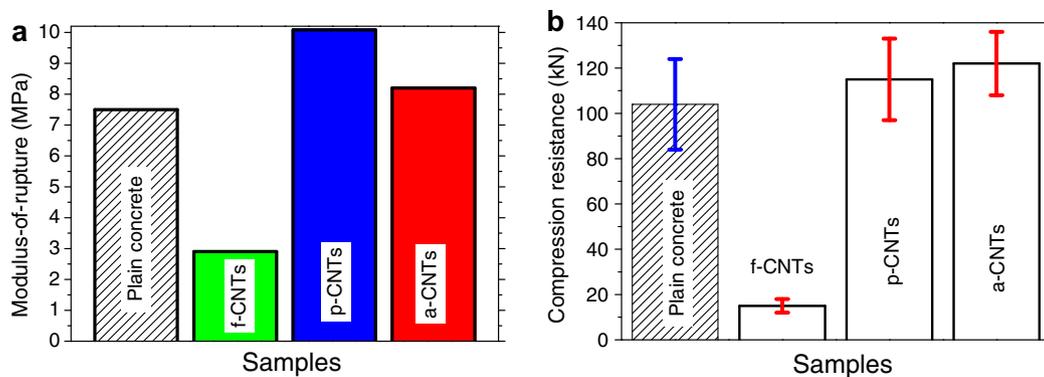**Fig. 3.** EDX analysis on f-CNTs.

Fig. 6. Modulus-of-rupture (a) and compression resistance (b) of concrete. With and without MWCNTs.

mechanical strength by a factor of 2.5 with respect to the plain cement, the presence of pristine CNTs produce an enhancement of approximately 34%. Annealed CNTs-cement composite showed a negligible improvement of approximately 9%.

The average compression resistance of the two half of the prism made with f-CNTs (Fig. 6b) was even six times lower with respect to the concrete with no CNTs: 104 ± 20 kN and 15.53 ± 3.04 kN, respectively. On the other hand, a-CNTs and p-CNTs produced an improvement of 10–20% with respect to plain cement. All the results arising from the mechanical tests are reported in Table 3.

The poor mechanical properties observed after addition of carboxyl functionalized MWCNTs (f-CNTs) were related to a reduced amount of Tobermorite gel as a consequence of a low cement paste hydration. As confirmed by TGA shown in Fig. 7, the quantitative of tobermorite gel ($3CaO \cdot 2SiO_2 \cdot xH_2O$) formed in presence of f-CNTs (peak at 116 °C) is notably lower than that obtained (peak at 102 °C) for the plain concrete. Tobermorite gel, which is formed during hydration of the calcium silicate phases such as C_3S ($3CaO \cdot SiO_2$) and C_2S ($2CaO \cdot SiO_2$), exerts a significant influence on cement strength as demonstrated in literature [21]. We assume that, due to the presence of hydrophilic groups on the f-CNT surface, the nanotubes absorb a not-negligible amount of water hampering the cement paste hydration. For the two hydrated samples, the slight peaks at around 160 °C are due to ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) 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 [21]. 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.

XRD onto the sieved powder coming from the samples containing the f-CNTs 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 [22].
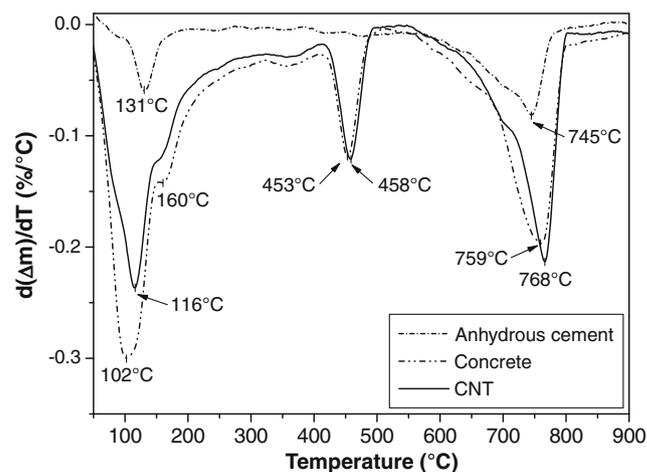

Fig. 7. DTG curves of anhydrous cement and of concrete w and w/o f-MWCNTs powders.

In order to confirm whether the cement hydration was actually hampered by the presence of carboxyl functionalized CNTs, we prepared two new mixtures of cement, with and without f-CNTs, increasing the water/cement ratio up to 0.56. Following the same receipt explained before, after 28 days of curing, the modulus-of-rupture of the prisms was equal to 6.2 MPa and 6.0 MPa, respectively for the concrete as such and containing f-CNTs (three samples 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 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 f-CNTs. It is plausible that since f-CNTs can only absorb water up to a certain limit, the excess of water is available to hydrate the cement paste producing a composite with mechanical properties slightly worse than those of plain cement.

4. Conclusions

The mechanical strength of cement composite was strongly affected by the defectiveness and chemical properties of the multi wall carbon nanotubes (MWCNTs) utilized. Flexural and compressive tests performed on cement composite containing functionalized CNTs (f-CNTs), showed a significant reduction of the performances compared to pristine cement. This behavior was justified taking into account that f-CNTs were so hydrophilic to absorb

Table 3
Modulus-of-rupture and compression resistance of the cement with and without addition of MWCNTs.

Sample	Modulus-of-rupture, σ_{max} (MPa)	Compression resistance, R_c (kN)
Plain cement	7.5	104 ± 20
Cement w 0.5 wt.% of p-CNTs	10.1	115 ± 18
Cement w 0.5 wt.% of a-CNTs	8.2	122 ± 14
Cement w 0.5 wt.% of f-CNTs	2.9	15 ± 3

most of the water contained in the cement mixture, hence hampering the proper hydration of the cement paste. This hypothesis was confirmed by low amount of tobermorite gel produced during hydration process as showed in the TGA. Moreover, we proved that a suitable hydration of the cement paste was obtained only increasing the water/cement ratio from 0.4 up to 0.56.

On the other hand, both pristine and annealed MWCNTs induced an improvement in the mechanical properties of the composite. This result suggested that, even if a significant number of defects in the CNT atomic network can produce curved CNTs with deteriorated mechanical properties [9,23], the ultimate strength of the nanocomposite can be enhanced. However, we must emphasize that a more favourable CNTs dispersion within the matrix is obtainable with a lower degree of entanglement between adjacent CNTs.

Acknowledgements

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