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Oxidation of Carbon Nanotubes for Improving the Mechanical and Electrical Properties of Oil-Well Cement-Based Composites / Lavagna, L.; Bartoli, M.; Suarez-Riera Daniel, David.; Cagliero, D.; Musso, S.; Pavese, M.. - In: ACS APPLIED NANO MATERIALS. - ISSN 2574-0970. - ELETTRONICO. - 5:5(2022), pp. 6671-6678. [10.1021/acsanm.2c00706]

Publisher:
American Chemical Society

Published
DOI:10.1021/acsanm.2c00706

ACS APPLIED NANO MATERIALS

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Article

Oxidation of Carbon Nanotubes for Improving the Mechanical and Electrical Properties of Oil-Well Cement-Based Composites

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Cite This: *ACS Appl. Nano Mater.* 2022, 5, 6671−6678

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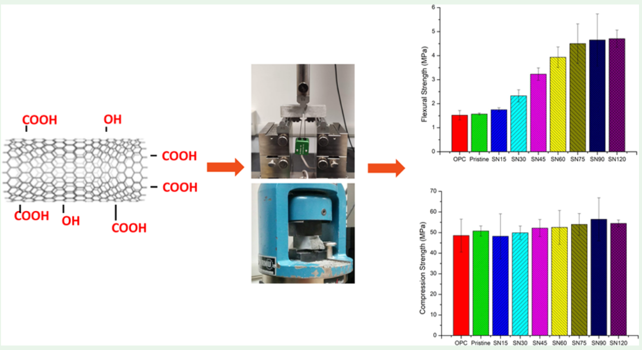


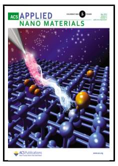
ABSTRACT: Carbon nanotubes are used to improve both the mechanical properties and electrical conductivity of cement, allowing the preparation of a strengthened and toughened cement that can be used for self-monitoring applications. Functionalization by reaction with acid is necessary to guarantee both a good dispersion in water and a strong interaction with cement. Sulfonitric acid (a solution of sulfuric acid and nitric acid) is the best oxidation treatment to decorate the surface of carbon nanotubes with polar groups. The time of treatment influences the mechanical and electrical properties of the composites, and in this work, the effect of the length of the treatment on both CNTs and composites was thoroughly analyzed. It was shown that a long-time oxidation treatment (90 min) was very effective to obtain well-dispersed carbon nanotubes that allow us to obtain cement-based composites with a large improvement of mechanical properties with respect to plain cement: 213% for flexural strength, 90% for fracture energy, and 20% for compressive strength. Furthermore, the electrical resistivity of cement-based composites was reduced to only 3% of the value of plain cement.

KEYWORDS: *carbon nanotubes, cement-based composites, oxidation, mechanical properties, electrical properties*

■ INTRODUCTION

The scientific community started to seriously focus its attention on carbon nanotubes (CNT) structures only after the observation of multiwalled carbon nanotubes (MWCNTs) in 1991[1] and of single-walled CNTs (SWCNTs) in 1993.[2,3] Indeed, CNTs have a strong industrial interest due to their unique physical and chemical properties.[4] They can be used for numerous applications, from composites[5−8] to new biomaterials like biosensors[9] and in medicine.[10] The use of CNTs in cement and concrete-based applications started to attract considerable research interest only in the last decade.[11,12] In fact, recently it was shown that several different nanofillers can be used to prevent crack initiation and propagation in cement-based materials,[13] thus improving the fracture toughness; therefore, nano-modified cements could be applied to reduce the risks caused by earthquakes, defects of construction, or pressure stresses.[14] Moreover, when a conducting reinforcement is inserted in a cement matrix, if the reinforcement content is lower than the percolation threshold, electrical resistance is observed to be subject to the applied stress; this behavior allows the real-time mechanical monitoring of structures.[15] Carbon nanotubes seem an obvious choice for such an application since they can allow both nano-reinforcement and piezoresistance.[16] However, to obtain good performances, two aspects are dominant: the dispersion of CNTs in the cement (i.e., in the water used for the cement preparation) and the interaction with the cement matrix.[17,18] In the literature, there are several examples of how to disperse CNTs in water, either by sonication[19] or by using a dispersant.[20] However, sonication allows the fragmentation of CNTs bundles, but it is not sufficient to guarantee the stability of the CNTs dispersion in water.[21] Dispersants are efficient in keeping the CNTs separated in solution; however, the interposition of a layer of molecules between CNTs and cement is not guaranteeing a good interaction between reinforcement and matrix, and as a consequence neither the strengthening effect nor the improvement of conductivity or sensing ability.[22,23] An alternative way of guaranteeing at the same time good interaction with cement and good dispersion in water is the functionalization of carbon nanotubes. Although many functionalization methods can be found in the literature, wet functionalization via acidic oxidation is the most common.[24−33] In fact, an acid treatment can assure the formation of polar groups on the surface of CNTs, which improve both the interaction with the cement and the

Received: February 15, 2022
Accepted: April 14, 2022
Published: April 27, 2022



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dispersion in water.[18] The drawback of such treatments is the creation of defects in the graphitic lattice of nanotubes, which can degrade the performance of the CNTs if the functionalization is excessive.[26] Another issue is that an extremely large number of hydrophilic groups on the surface of CNTs can cause excessive absorption of water that is consequently no more available for the complete hydration of cement.[34] Lavagna et al., in two studies,[35,36] suggest that in the case of carbon fibers and graphene the best solution can be found with a limited oxidation of carbon, guaranteeing the required degree of oxygen-containing groups on the surface, without negatively affecting the reinforcement structure and thus the cementitious composite performance.

It is currently unclear in the literature which is the best oxidation reaction time to guarantee the best mechanical and electrical properties of cement-based composites containing carbon nanotubes. In this work, we seek to understand and adjust the effect of acidic treatment on CNTs to obtain both a good dispersion in water and a good interaction with cement, with the aim to find the conditions that maximized the mechanical and electrical properties of cement-based composites containing CNTs.

MATERIALS AND METHODS

Commercial Nanocyl 7000 carbon nanotubes (average diameter 9.5 nm, average length 1.5 μm, carbon purity 90%) were chemically oxidized by reaction with mixtures of different chemicals: sulfuric acid 98% (H_2SO_4), nitric acid 65% (HNO_3), hydrochloric acid 67% (HCl), and hydrogen peroxide 30% (H_2O_2), all by Sigma-Aldrich. For stopping the reaction at the required time, sodium hydroxide (NaOH, Merk 97%) was used to neutralize the pH at the end of the treatment. The cement-based powder used in this study is an API (American Petroleum Institute) oil-well cement Class G (Lafarge North America). Table 1 shows the composition of the cement used.

Table 1. Composition and Properties of Class G Cement

oxide	(wt %)	phase	(wt %)
SiO_2	21.7	C3S	66
CaO	62.9	C2S	18
Al_2O_3	3.2	C3A	7
Fe_2O_3	2.7	C4AF	9
MgO	4.3		
SO_3	2.2		
Na_2O	0.54		
loss on ignition	0.74		
insoluble residue	0.14		

Thermogravimetric analysis was conducted in a TGA instrument Mettler Toledo 1600, in flowing 50 mL·min^{-1} air. Samples were heated from 25 to 1000 °C with a constant heating ramp of 10 °C·min^{-1}. The air was supplied with a constant flow rate (50 mL·min^{-1}).

Raman spectroscopy was performed using a Renishaw inVia (H43662 model, Gloucestershire, U.K.) equipped with a green laser line (514 nm) with a 50× objective. Raman spectra were recorded in the range of 250−3500 cm^{-1}.

Electrical resistivity was measured through a methodology reported in Giorcelli et al.[37] The experimental setup was composed of two solid copper cylinders, 30 mm in diameter and 5 cm in length. The sample was positioned between the aligned copper cylinders, and a tight contact between cylinders and sample surface was achieved using a hydraulic press (Specac Atlas Manual Hydraulic Press 15T) and a thin copper foil. Electrically insulating sheets were placed between the conductive cylinders and the load surfaces to ensure that the electrical signal passed only through the sample. The resistance of the composite samples was measured using an Agilent 34401A multimeter.

A scanning electron microscope (SEM) FEG ASSING SUPRA 25 was used to observe the aspect of nanotubes before and after acid treatment and to evaluate their dispersion and interaction with cement.

The mechanical properties of the cement composites were measured with a three-point bending test (ASTM C348) controlled by crack mouth opening displacement (CMOD) following the standard JCI-S-001-2003. The specimens were tested with a single-column ZwickLine z050 flexural testing machine having 50 kN maximum load capacity and a 1 kN load cell. As described in the literature,[38] this measurement requires the samples to be notched in the middle (notch having a depth of 5 mm and a width of 2 mm). CMOD was controlled at the fixed rate of 0.005 mm/min by placing an extensometer on the two sides of the notch; the used span was 65 mm. After the flexural test was complete, one of the two halves of each sample was used to evaluate the compressive strength. Compressive tests were performed using the same machine but using a 50 kN load cell, a pre-load of 20 N, and a test speed of 600 N/s. Each result of compressive and flexural strength was the average of at least four specimens.

Geometrical density was evaluated on specimens polished to obtain flat, perpendicular surfaces. A caliper was used for estimating the width, length, and height, and the samples were weighed on a RADWAG PS 510/C/1 analytical balance (Figure 1).

EXPERIMENTAL SECTION

The first step of this work was to select the best acid mixture to guarantee a stable dispersion of oxidized carbon nanotubes in water. Four oxidative acid mixtures were compared: (a) 1 HNO_3: 3 HCl (aqua regia); (b) HNO_3 (nitric acid); (c) 3 H_2SO_4: 1 H_2O_2 (piranha solution); (d) 1 HNO_3: 3 H_2SO_4 (sulfonitric acid). A small amount (0.1 g) of pristine CNTs was soaked in 100 mL of each acid at 30 °C for 30 min. During the reaction, the CNTs suspension was continuously mixed by sonication, using an ultrasonic bath (SONICA 2400 MH series). At the end of the treatment, the acid solutions were neutralized with a basic solution of NaOH 1 M up to pH 7. The functionalized CNTs were then recovered via filtration with a fritted glass filter (G4 class Pyrex). The CNTs were then washed several times with ultrapure water and dried overnight at 80 °C. The dried CNTs were dispersed in water with an ultrasonic tip (Vibra-cell, power 100 W for 15 min) and poured into a test tube for observing the possible sedimentation of badly dispersed specimens. As shown in Figure 2, the evaluation of the dispersion was made by comparing the behavior of the CNTs suspension in each test tube after different periods of time (in Figure 2 are shown the images after 1 and 24 h from the insertion of the solution in the test tube). Badly dispersed carbon nanotubes (cases a, b, and c in Figure 2, corresponding to oxidation with aqua regia, nitric acid, and piranha solution) form large agglomerates that start to precipitate after only 1 h. The CNTs are then fully precipitated at the bottom of the test tube within 24 h. On the other hand, in the test tube containing CNTs treated with sulfonitric acid (case d in Figure 2), a significant amount of the material remains suspended in the solution after 24 h. To determine the real extent of dispersion, it is however necessary to observe a very dilute suspension; otherwise, the dark color of the concentrated suspension will not allow us to discriminate between nanotubes completely dispersed and small bundles of agglomerated nanotubes remaining in the water due to the small size. After 1:9 dilution of the supernatant, it is possible to observe a uniform, light gray color that guarantees a suspension made of individual nanotubes and stable over time.[39]

Once determined that aqua regia, nitric acid, and piranha solution were not effective in the oxidation and dispersion of carbon nanotubes, and thus that only sulfonitric acid could give a suspension suitable for the preparation of cement-CNT composites, the effect of the duration of the treatment with sulfonitric acid on carbon nanotubes was assessed, by preparing multiple samples, considering

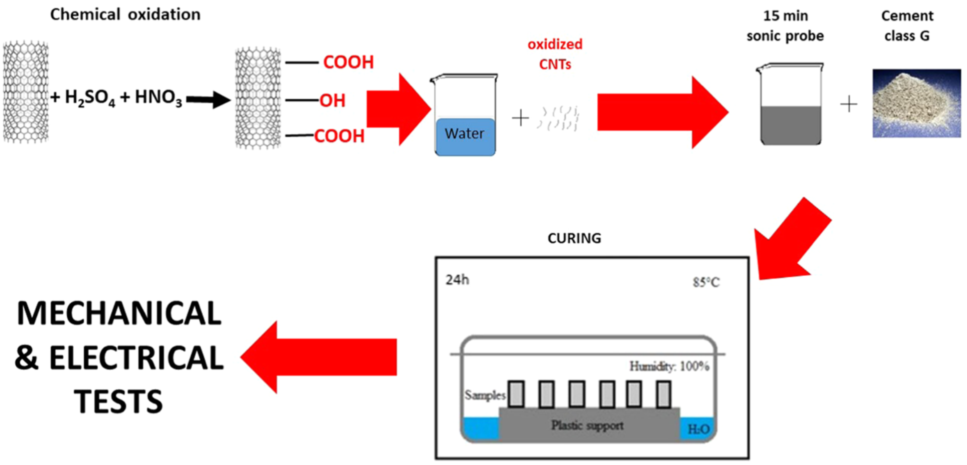

Figure 1. Preparation route of the samples.

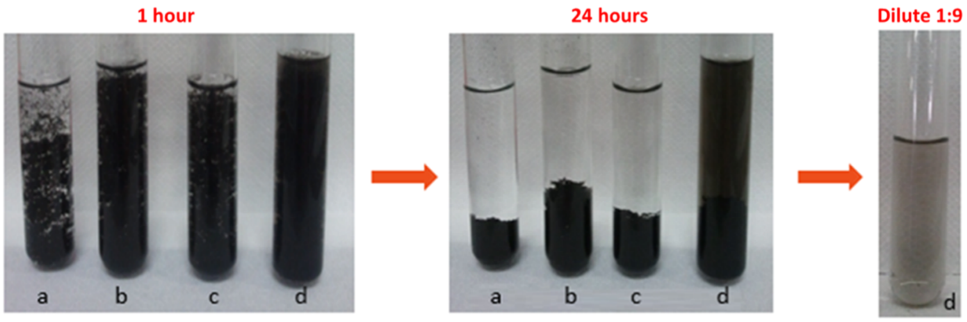

Figure 2. Test tubes used to evaluate the dispersion in water of CNTs treated with: (a) aqua regia, (b) nitric acid, (c) piranha solution, and (d) sulfonitric acid.

Table 2. Sample Name (Treatment/Time), Time of Acid Treatment, Density of the Specimens, and the Mechanical and Electrical Performances of the Cement Composites Containing 0.1% bwoc of the Pristine and Oxidized CNTs Resulting from Each Test

sample name	time [min]	density of the sample (g/cm^3)	flexural strength (MPa)	fracture energy (J)	compression strength (MPa)	electrical resistivity (10^6 Ω m)
OPC		1.63	1.5 ± 0.2	1.3 ± 0.5	48.6 ± 7.9	3.7
Pristine		1.61	1.6 ± 0.04	1.4 ± 0.3	50.8 ± 2.5	3.6
SN15	15	1.70	1.7 ± 0.1	1.6 ± 0.1	51.7 ± 10.2	3.0
SN30	30	1.76	2.3 ± 0.3	1.5 ± 0.2	49.9 ± 3.3	3.3
SN45	45	1.72	3.2 ± 0.3	1.6 ± 0.5	52.2 ± 4.1	1.9
SN60	60	1.74	3.9 ± 0.4	1.7 ± 0.1	52.5 ± 8.2	1.1
SN75	75	1.79	4.5 ± 0.8	2.1 ± 0.4	54.0 ± 5.3	0.5
SN90	90	1.88	4.7 ± 1.1	2.4 ± 0.7	56.4 ± 10.5	0.09
SN120	120	1.80	4.7 ± 0.4	2.2 ± 0.1	54.5 ± 1.6	1.3

oxidation times of 15, 30, 45, 60, 75, 90, and 120 min. The oxidized carbon nanotubes obtained with these treatments were used to prepare cement-based composites, containing 0.1% bwoc (by weight of cement) CNTs. This value was chosen to remain under the CNTs percolation threshold, as suggested in the literature for applications that involve sensing.[35,36,40,41] Also, samples of cement, both with and without pristine CNTs, were used for comparison.

The procedure to prepare cement involves redispersion of the carbon nanotubes in water with an ultrasonic tip for 15 min at a 100 W power. The slurry of CNTs and water was then stirred mechanically for several minutes, while cement powder was slowly added. The slurry, prepared at a water-to-cement (w/c) ratio of 0.45, and containing 0.1% bwoc of CNTs, was then poured into apposite molds and cured for 24 h at 85 °C in a controlled environment, at 100% of relative humidity. Prismatic molds of size 20 × 20 × 80 mm were used for the cement composites that were then mechanically tested to obtain flexural strength, fracture energy, and compression strength. The results of the tests are shown in Table 2.

■ RESULTS

TGA analyses (Figure 3A) show that the weight loss curves of pristine (black) and sulfonitric treated samples (red and blue curves) are very different. Lower thermal stability was detected for oxidized CNTs, with complete oxidation starting below 400 °C. This kind of behavior is due to the acidic treatment. A greater amount of reactive and temperature-sensitive chemical groups were introduced by the sulfonitric treatment as shown in the literature.[42] The degradation curve (red) after 30 min of sulfonitric treatment is composed of two stages: the first from 150 to 300 °C is due to decarboxylation of carboxylic functional groups present on the surface of the oxidized

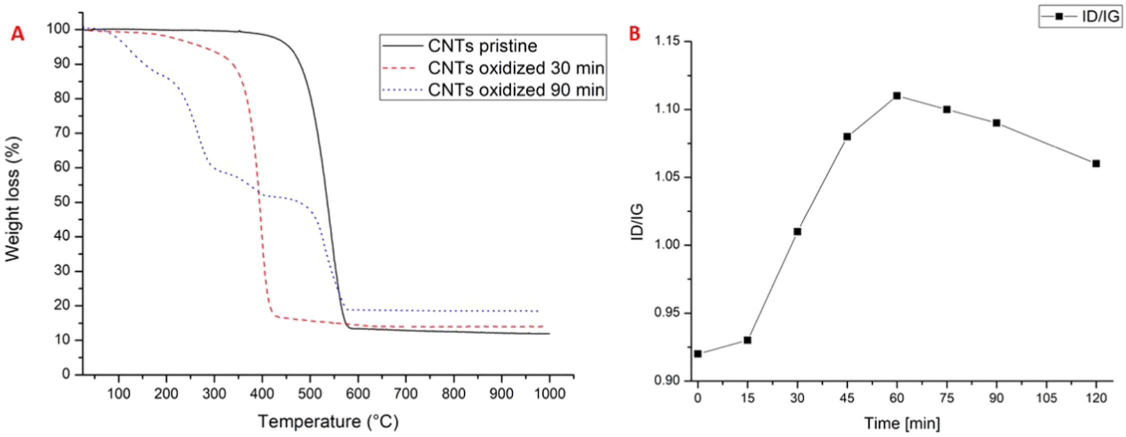

Figure 3. Thermogravimetric analysis (A) of pristine CNTs pristine (black line) and after oxidation with sulfonitric acid for 30 min (red line) and 90 min (blue line). Raman ID/IG ratio vs oxidation time (B).

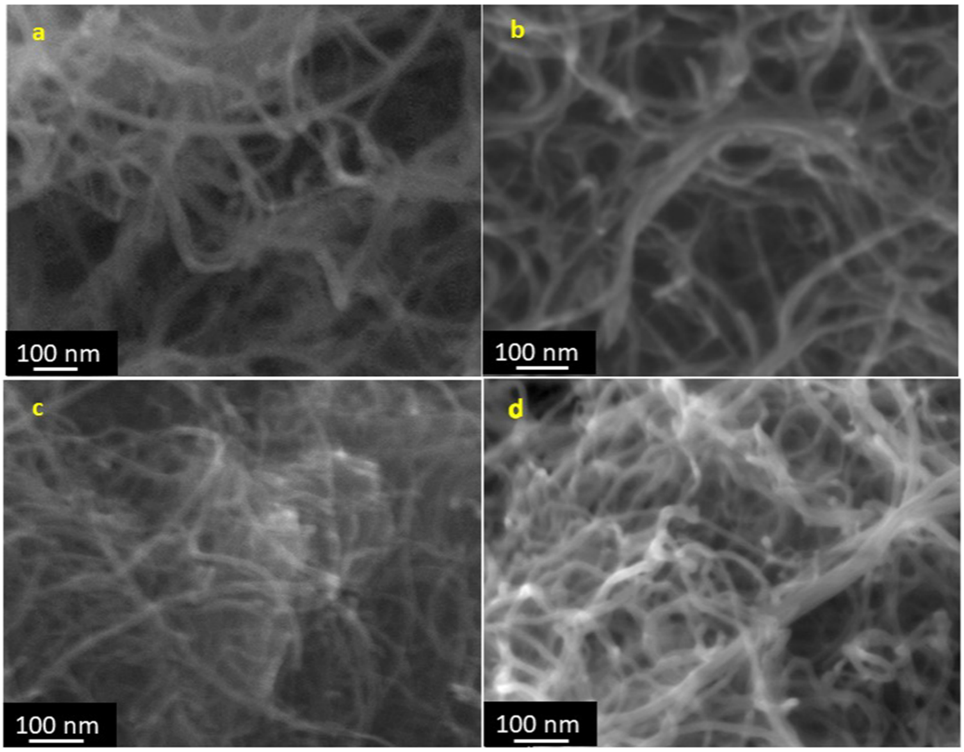

Figure 4. SEM images of pristine CNTs (a), CNTs oxidized with sulfonitric acid for 30 min (b), 90 min (c), and 120 min (d).

CNTs.[43] The second step near 400 °C corresponds to the thermal oxidation and degradation of remaining carbon.[44] The degradation curve of CNTs oxidized for 90 min is more complex. The first weight loss around 150 °C corresponds to the evaporation of the adsorbed water.[24] The decarboxylation of the carboxylic groups present on the walls starts from 150 to 300 °C.[43] Thermal degradation in the range between 300 and 400 °C may be explained by the elimination of hydroxyl functionalities, attached to the MWCNT walls.[44] Finally, the thermal oxidation of the remaining carbon occurs at temperatures higher than 400 °C, as explained before.

The acidic treatment tends to damage the external graphitic lattice structure of CNTs. This effect is confirmed by Raman analysis (Figure 3B). The trend of the ratio between peak I_D and I_G peaks (I_D/I_G), which indicated the extension of the graphitic defects[45] shows an increment that starts to decrease after 60 min. This behavior indicates that the longer is the treatment time, the greater is the amount of defects on the graphitic lattice of the CNTs. The reduction after 60 min of acidic treatment is probably due to two phenomena: the recombination of the carbon structure has already been shown in SWCNTs where rope-shaped cross-linked aggregates were observed after prolonged oxidative treatments as reported by Zhang et al.[46] Furthermore, the strong oxidative treatment could lead to the removal of small oxidized carbon fragments and to a partial exposure of the inner layers of CNTs as mentioned by Yu et al.[47]

Scanning electron microscopy was used to investigate the possible CNTs fragmentation occurring during the acid oxidation treatment. Figure 4 shows the SEM images of pristine CNTs and of CNTs after 30, 90, and 120 min of oxidation treatment. The samples treated for 30 and 90 min

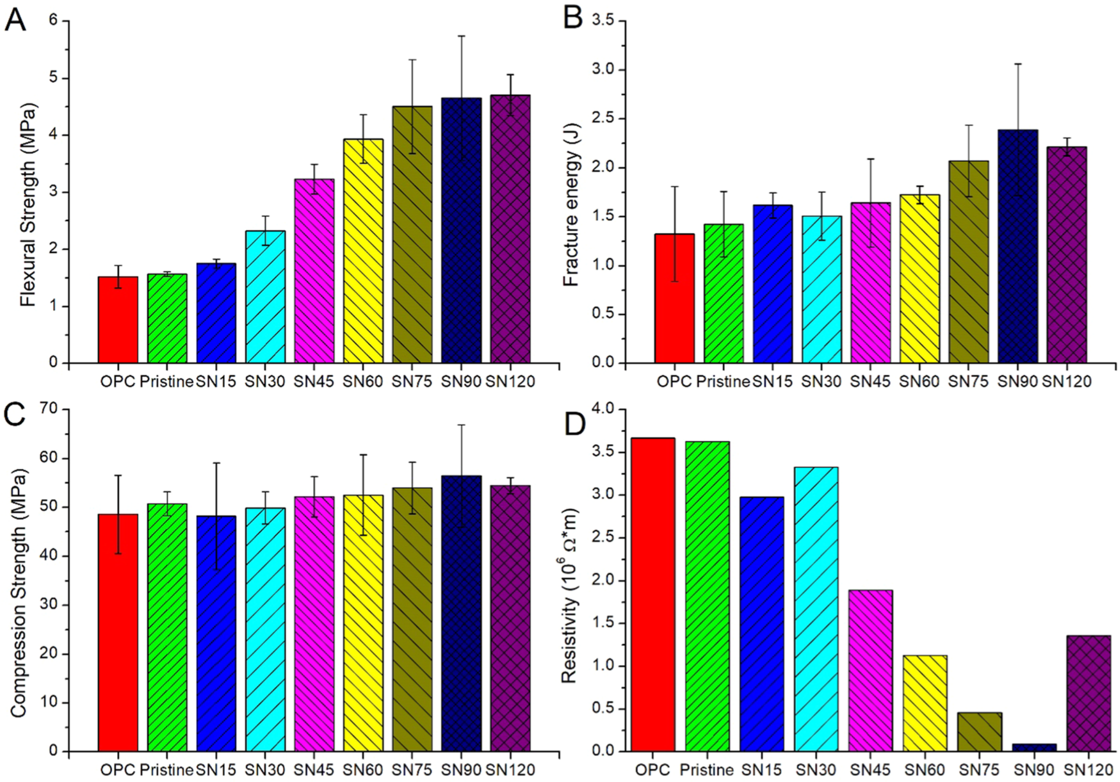

Figure 5. (A) Flexural strength, (B) fracture energy, (C) compression strength, and (D) electrical resistivity of bare cement and cement containing pristine and oxidized CNTs.

present no significant damage, the appearance of CNTs being similar in both cases. Instead, the CNTs treated for 120 min exhibit a certain degree of damage, in particular shortening and unzipping phenomena, with also the presence of carbon particles of different shapes.

From the mechanical point of view, the enhancement of mechanical properties depends on treatment time. Figure 5A presents the flexural strength of cement paste without CNTs, with pristine CNTs, and with CNTs oxidized at different times (from 15 up to 120 min). Flexural strength significantly improved with the increase of oxidation time. Pristine, SN15, and SN30 have flexural strengths 6%, 15%, and more than 50% higher than plain cement (1.5 MPa). Additionally, functionalized specimens 45, 60, 75, and 90 min presented the highest flexural strength improvements: 3.2, 3.9, 4.5, and 4.7 MPa respectively, which are higher by approximately 115, 160, 200, and 213% in comparison to plain specimens. Samples functionalized for 120 min had the same performance as the 90 min ones. Fracture energy (Figure 5B) exhibits a trend similar to flexural strength. The fracture energy of those specimens with higher functionalization times, from 60 to 90 min (SN60, SN75, and SN90), increased considerably with respect to the cement paste, of over 30, 60, and almost 90%, respectively. On the other hand, SN15 to SN45 specimens show a small improvement in relation to the simple cementitious paste. The samples functionalized for 120 min presented a value slightly smaller than 90 min. For compressive strength (Figure 5C), there is an increasing trend, too, even if less evident than in the previous cases. Cement containing CNTs with high functionalization times, 75 (SN75) and 90 (SN90) minutes, showed an increasing trend, with strength higher more than 10% and almost 20%, respectively, compared to OPC. After 120 min, as before, the strength did not increase further but slightly reduced. On the other hand, short functionalization times generate low improvements, and even functionalization times of 45 or 60 min did not significantly influence the compressive strength, which increased only around 8%.

The addition of CNTs and functionalized CNTs modifies also the resistivity of cement paste. The electrical resistivity follows an inversely proportional trend with respect to flexural strength and fracture energy. It can be observed that resistivity shows a decreasing trend with increasing CNTs functionalization time from 15 to 90 min. Specimens from SN45 to SN90 show much lower values compared to control, specifically, a resistivity reduction by nearly a fifth, almost 70% and 90% when CNTs were functionalized for 45, 60, and 75 min respectively, while 90 min functionalization results in the very significant 97% decrease compared to control. A longer functionalization time, 120 min, brings instead to the worsening of electrical properties. Short functionalization times, from 0 to 30 min, did not lead to a significant reduction of electrical resistivity. To evaluate which parameters have the most influence on the improvement of mechanical and electrical properties, a statistical analysis was performed. The Spearman correlation coefficient is a nonparametric statistical measure of correlation. It measures the degree of relationship between two variables.[48] Unlike Pearson's linear correlation coefficient, the Spearman coefficient does not measure a linear relationship even when interval measures are used. In fact, it allows us to establish how well a relationship between two variables can be described using a monotone function. The more the value in absolute terms approaches 1, the more there is correlation between the parameters, the more the value approaches 0, and the less there is correlation between the parameters. Data correlations have been evaluated using a nonparametric statically coefficient[49] (Spearman), as shown in Table 3.

Table 3. Spearman Correlation Coefficients Setting Oxidation Time or Sample Density as an Independent Variable

	time [min]	density of the sample (g/cm^3)
time [min]	1	
density of the sample (g/cm^3)	0.894	1
flexural strength (MPa)	0.999	0.905
fracture energy (J)	0.938	0.850
compression strength (MPa)	0.905	0.761
electrical resistivity (10^6 Ω m)	−0.833	−0.762

Spearman coefficients showed a strong positive correlation with all of the mechanical properties investigated and a negative one with electrical resistivity. Accordingly, it is possible to assume a dependency of all of the properties on the oxidation degree of CNTs. Density was poorly correlated with compression strength and only moderately correlated with both fracture energy and electrical conductivity positively and negatively, respectively. Nevertheless, density had a good positive correlation with flexural strength, even if general Spearmen coefficients were sensibly lower compared with those achieved considering oxidation time. Spearman coefficients remain stable even if the CNT functionalization for 120 min altered the trend, in particular for resistivity, due to the inferior performance of the specimens.

DISCUSSION

Thanks to the presence of polar groups on their surface (Figure S1), oxidized CNTs exhibit greater water wettability than pristine CNTs.[29] In fact, carboxylic and hydroxyl groups are principally grafted on the surface after sulfonitric treatment.[50] These polar groups increase the ease of dispersion of CNTs in the water used for the preparation of cement, thus also improving the dispersion of the reinforcement in the matrix. Furthermore, the carboxyl groups introduced on the surface of the CNTs can react with the hydrated products of cement ($Ca(OH)_2$ and C−S−H),[51,52] thus enabling the interaction of the reinforcement with the matrix via the formation of primary or secondary bonds.[53]

The improvement of flexural strength and fracture energy is probably related to the well-known bridging effect of CNTs when they have good interaction with the cement paste.[40,54] Furthermore, the presence of carbon nanotubes functionalized with carboxyl and hydroxyl groups could promote the nucleation of cement hydrate products, thus improving the C−S−H gel structure.[55,56] This is also shown in Figure S2, where hydrated cement grains can be observed to grow over the oxidized carbon nanotubes. Regarding the slight improvement of compressive strength, the Spearman correlation coefficient suggests that this trend is correlated with the functionalization time rather than with the density of the samples, as reported in the literature.[57] It must be noted that, even though the long-time sulfonitric treatment (up to 90 min) can certainly damage the graphitic lattice, the final mechanical properties still increase due to the improved dispersion and adhesion between nanotubes and matrix. However, when CNTs are oxidized over a certain threshold, the nanotubes start to break, and thus their reinforcing effect is reduced. In this case, we noticed that the mechanical properties decline after 120 min of oxidation, suggesting that the damage to the graphitic structure of the nanotube starts to prevail.

When CNTs are not optimally dispersed, only a minor improvement of electrical properties is recorded, as reported by Wansom et al.[58] In fact, an efficient dispersion is probably the key factor for improving electrical properties, even if due to the presence of carboxylic and hydroxyl groups, the dispersion is accompanied by the strengthening of the interaction of CNTs with the cement paste. The conductivity of the composites increases with oxidation time and confirms the good dispersion of the CNTs in the cement matrix.

In Table 4, the values of flexural strength obtained in this work are compared with the results of several literature papers.

Table 4. Comparison of Flexural Strength Increase in Cementitious Nanocomposites Reinforced with CNTs

researcher	nanocomposite	amount of CNTs (wt % of cement)	flexural strength increase (%)	refs
Li et al.	mortars	0.50	25	51
Cwirzen et al.	cement paste	0.042	10	60
Konsta-Gdoutos et al.	cement paste	0.08 and 0.048	25	61
Zou et al.	cement paste	0.038 and 0.075	50	62
Gdoutos et al.	mortar	0.1	18.6	63
Konsta-Gdoutos et al.	mortars	0.1	81	59
Lavagna et al. (this work)	cement paste	0.1	210	

The comparison is limited to works where the flexural test methodology is the same with respect to this work. Particularly interesting is the paper of Konsta-Gdoutos,[59] which shows how the chemical functionalization of carbon nanotubes brings a strong beneficial effect to flexural strength. An overall view on the improvement of mechanical properties achieved using CNTs is presented in the review of Reales et al.,[11] where several other test methods are considered.

CONCLUSIONS

In this work, it was shown how the oxidation time of CNTs reinforcement is closely correlated with the mechanical and electrical properties of cement-based composites. CNTs oxidized with sulfonitric acid for a sufficient time are more easily dispersed in water and contain a greater number of functional groups on their surface that ensure good dispersion in cement-based matrix and a strong interaction with the hydrated cement phases. It was found that 90 min oxidation brings the best results in terms of mechanical performance (flexural strength, fracture energy, compression strength) and electrical resistivity. However, an excessively long acid treatment can invert the positive trend since the damage to the nanotubes becomes prevalent with respect to the oxidation positive effects. The characterization of the oxidized carbon nanotubes demonstrates that the graphitic surface of the nanotubes is progressively damaged during the oxidation; however, upon 90 min oxidation, the damage is not sufficient to break the nanotubes and limit their strengthening effect. The oxidized CNTs therefore guarantee a conductive and mechanically performing nanocomposite useful for future developments in the online monitoring of structures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.2c00706.

Characterization methods, FT-IR characterization, and SEM photograph (PDF)

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Notes

The authors declare no competing financial interest.

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