Influence of carbon nanotubes addition onto the mechanical properties of restoration mortars

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ABSTRACT. For the first time, carbon nanotubes (CNTs) have been added to a grout. The samples were prepared with up to 0.8 wt% of CNTs, with respect to the binder, and were characterized by three-point bending and compressive tests. The results showed that these additions continuously increased the flexural and the compressive strength, as well as the fracture energy, for a CNTs content up to 0.12 wt% with respect to the binder.

SOMMARIO. E' stata valutata per la prima volta l'influenza dell'aggiunta di nanotubi di carbonio (CNTs) a delle malte per iniezioni. Sono stati preparati campioni aventi fino a 0,8% in peso di CNTs, rispetto al legante, e caratterizzati tramite prove di flessione a tre punti e di compressione. I risultati hanno dimostrato che tali addizioni aumentano la resistenza a flessione ed a compressione, così come l'energia di frattura, per aggiunte di CNTs fino a 0,12% rispetto al legante.

KEYWORDS. Grouting; Carbon nanotubes.

INTRODUCTION

Masonry is a composite material, made of stones and mortar, bricks and mortar, or stones. Not only the nature of mortar and stones can account for the type of deterioration of the masonry, also the structural built up plays an important role. The deterioration in regular brickwork masonry differs from that in a wall, composed of an inner and outer layer of natural stone, with a rubble masonry core in between [1].
Grout injection is one of the techniques most widely used in the consolidation of masonry aiming at increasing its compactness. At the same time, it enables the establishment of links between the internal and external layer, therefore increasing its resistance and the monolithic behaviour. The grouts to be used for the injection should be correctly designed to achieve the maximum performance. This means that, besides strength, principles such as masonry ductility and durability should be taken into consideration, since a bad choice of grout composition may jeopardize the performance of old masonries [2]. The improvement of the mechanical behaviour of a structure requires the design of a grout with very good injectability and bonding properties, in order to allow the injection of small cracks and voids, and to assure continuity to the masonry [1]. The desired mechanical properties of the grout depend of the structure level of damage and of its structural improvement requirements. It also depends on the time span within which the required mechanical properties must be achieved, since the strength development rate is a controlling factor. For slowly hydration

binders it is impossible to achieve acceptable levels of strength within a reasonably short time dictated by structural necessities.
Tab. 1, adapted from ref. [3], presents a brief summary of the grout design requirements concerning the mechanical behaviour of the injected structure.

Requirement	Description
Injectability	- low yield value and viscosity, - penetrability: in voids with diameter smaller than 0.3 mm, - stability: no substantial density gradients along the height of the stored grout - low bleeding: lower than 5% after 120 min rest.
Bonding with existing materials	- relatively low shrinkage (although autogeneous shrinkage is unavoidable), - minimal heat of hydration, - setting and hardening in dry as well as in wet environment.
Sufficient mechanical properties within a defined time span	- development of the required mechanical properties in 90 days, - compressive and flexural strength dictated from the structural analysis.

Table 1: Requirements of grouts related to the mechanical behaviour of the injected structure [3].

Durability requires the development of a microstructure as close as possible to the microstructure of the existing materials. This can be achieved partly with the use of raw materials similar to the existing ones. However, the expected mechanical properties may be insufficient. A compromise is possible within the use of a limited Portland cement content, as it is used in the binary and ternary grouts [3]. The bonding is also a key factor for the durability requirement, since it limits the intrusion of detrimental agents and the subsequent undesirable chemical reactions [3]. A concise summary of the durability requirements is presented in Tab. 2.

Requirement	Description
Compatible microstructure	- compatible porosity and pore size distribution: they depend on the porosity of the existing materials as well as on the required strength of the new materials - type of the hydration products: similar (though not necessarily identical) to the existing
Bonding with existing materials	- limitation of diffusion of SO_2, chlorides… - resistance against deterioration due to environmental factors
Raw materials properties	-minimal gypsum and soluble salts content, in particular alkali

Table 2: Requirements of grouts related to the durability of the injected structure [3]

Deterioration phenomena appear in mortars as well as in stones. As a result, the quality of both, and the quality of the bond between stones and mortar diminish. The mechanical action on the masonry walls normally causes distributed vertical compressive stresses in the masonry, but at every discontinuity such as cracks, holes and pores, interfaces between stones and mortar, also tensile stresses will appear [1]. Their magnitude is of the same order as the compressive stresses. The tensile stresses can cause cracking or micro-cracking in stones, mortar or in the bond between them. This cracking can be intensified by vibrations, earthquakes, shocks, wind loads etc. It must be stressed that compressive stresses are mostly not harmful to masonry, except in some rare. Having in mind that tensile stresses are causing masonry failure, it is evident that every strengthening method must introduce elements or systems, capable of withstanding these tensile stresses [1]. To this aim, in this work, we propose to add carbon nanotubes (CNTs) to a commercial injection mortar (Mapei, Mape Antique I), as, to the best of our knowledge, this has never been done before. On the contrary, carbon nanotubes used as reinforcing fibers to cement has been explored since many years [4-6]. The functional effect of their addition in a concrete equates to the one obtained with the addition of fibers. Microfibers can interact with the fracture evolution by arresting the growth of microcracks and can delay the propagation of microcracks, thus impeding their coalesce to form the first macrocrack. The addition of Carbon Nano Tubes (CNTs) also provides a better ductility, an increase of the fracture energy, a decrease in the amount of reinforcement and an increased durability.

EXPERIMENTAL

Mapei Mape Antique I is a ready to use, cement-free fillerized hydraulic binder formulated in a fine powder (< 100 micron). When mixed with approximately 35% water it produces a fluid, stable slurry able to fill cavities in structures to be consolidated [7]. Mape Antique I contains about 50% of filler, therefore CNTs were added as a percentage by weight of the binder (Tab. 3). In order to fill the standard metallic formworks (40 × 40 × 160 mm³) for the production of three samples of each composition, a quantity of 1.2 kg of dry mortar was used. In the present work, commercial multi-walled CNTs (MWCNTs, Nanocyl 7000 series, Tab. 4) were first added and mechanically dispersed in the water required for the mixing of the grout and then, sonicated for three hours before mixing with Mape Antique powder. Surfactants were also used to this aim. In our case, Mapei Dynamon SP2 was added to the water in an amount of 1 g, after preliminary tests.

Material	Quantity	Sample
Mape Antique I (g)	1200	
Water (g)	420	
CNTs (% w respect to binder)	0.000	A1
	0.025	B1
	0.050	B2
	0.080	B3
	0.120	B4
	0.250	A2
	0.500	A3
	0.800	A4

Table 3: Typical injection mortar compositions investigated in this work.

Property	CNTs
Average diameter (nm)	40-80
Length (average) (μm)	400-1000
Carbon purity (wt%)	> 92
Metal oxide (impurity) (wt%)	< 6

Table 4: Features of the MWCNTs dispersed in the cement.

Mape Antique was slowly added to the mix water-dispersed CNTs by means of a mixer (Hobard Model N-50) at low speed. Once a homogeneous paste was obtained, the last step of mixing was carried out for five minutes at medium speed. The grout was then cast into the molds and kept for 5 days in the formworks in a humid atmosphere at room temperature. Then, the samples were demolded and cured for 21 days in the same conditions.
The notches were made using a Remet Type TR100S saw, with a 2 mm thickness diamond cut-off wheel. Notches were cut on a single specimen at the time. Notch depth was equal to 12 mm.
Three-points bend tests (span = 150 mm) were performed onto the 28 days cured prisms. The test equipment used for mechanical characterization was manufactured by MTS Systems Corporation. The measurement of crack propagation was performed in the Crack Mouth Opening Displacement mode (CMOD, Fig. 1). In our case, a clip-on gauge was used to control the displacement at gap level during loading in order to determine the fracture energy. Specifically, the clip-on gauge MTS Model 632.03F-030 was employed. It has an operating range between -100 and +150°C and the displacement

range between 6+12 mm, i.e. 12 mm useful for test measurement. Installation of the Clip-on gauge was done by means of two knives bolted on two intermediate bases glued on the specimen itself at the two sides of the notch. The gap between the knives was equal to 6 mm. Data sampling was adjustable and data were recorded at 10 Hz into a specific database by the MTS test machine PC. Complementary to the MTS machine data, a back-up data base was recorded at 1 Hz by CatMan system which provided a real time graphics interface for the test operator.

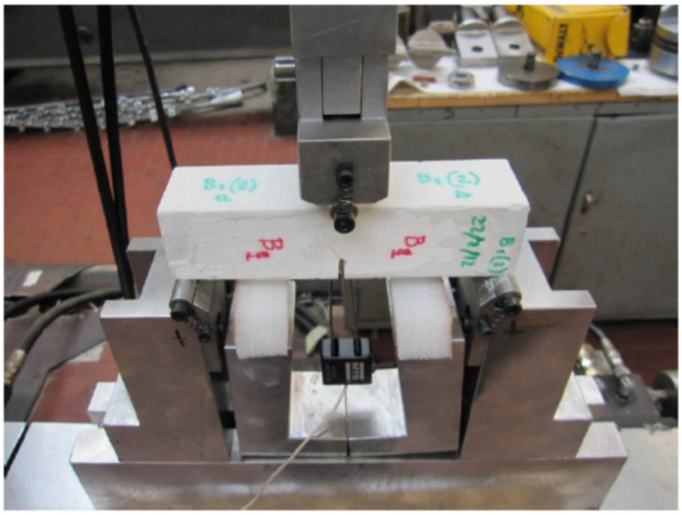

Figure 1: Three-point flexural test configuration.

The fracture energy is defined as the post-crack energy absorption ability of the material and it represents the energy that the structure absorbs during failure. The specific fracture energy, G_f (J/m^2 or N/m), was calculated as the area under the force–displacement curve up to a defined displacement of 1.5 mm divided by the area of the fracture plain [8].
Compressive strength was also determined on 40 × 40 × 80 mm^3, by-products of the previous flexural tests, in accordance to STM C 348 compressive strength standard. The testing machine was equipped with two steel bearing blocks with hardened faces. One bearing block was spherically seated and the other rigidly mounted (Fig. 2). The testing machine was accurate with a tolerance of ± 1.0% of the compressive strength of the specimen. The load was applied at a cross arm rate of 500 N/s.

Figure 2: Compression test configuration.

Finally, mercury intrusion porosimetry was also used on fragments of the broken samples, to evaluate the influence of CNTs on the opened porosity. The samples were kept in an oven overnight, prior to each measurement.

RESULTS AND DISCUSSION

Average mortar density after curing time was 1.69 ± 0.05 g/cm³. Three-point bending test results are summarized in Tab. 5 and a typical load-CMOD opening curve is illustrated for each studied composition (Fig. 3-10). The modulus-of-rupture (MOR) is the surface stress at failure in bending and is equal to:

$$MOR = \frac{3.F.S}{2.w.h^2} \qquad (1)$$

where, *w* is the beam width, *h* the height, *s* the span and *F* is the maximum force in a bent beam at the instant of failure. Therefore using the maximum load and knowing the specimens dimensions the MOR was calculated, Tab. 5 refers. Height h was considered to be the theoretical median fracture area, i.e. the median area less the area generated by the notch of 12 mm.
From 0.25 wt% addition of CNTs to the grout, some agglomerates of CNTs are clearly visible in the matrix, indicating a not perfect dispersion, even after a three hours sonication time. Some macropores, due to entrained air bubbles during mixing, are also evident.
Within the context of this work, results of the tests carried out indicate that CNTs addition to injection Mortar Mapei Mape Antique I increases the fracture energy significantly, up to a ratio greater than 2.0 for a CNTs weight of addition of 0.25 % (Fig. 11). Exceeding this amount of CNTs addition, the *Gf* value, tends to decrease.

Sample	CNTs content	Max load (N)	G_f ($\times 10^{-3}$. N/m)	MOR (MPa)
A1	0.000	60.90	20.37	0.44
B1	0.025	110.21	26.62	0.81
B2	0.050	100.96	23.01	0.74
B3	0.080	102.67	27.10	0.72
B4	0.120	106.37	38.37	0.82
A2	0.250	85.22	42.75	0.62
A3	0.500	63.17	19.27	0.66
A4	0.800	97.12	38.42	0.71

Table 5: Average maximum load and fracture energy of the studied compositions

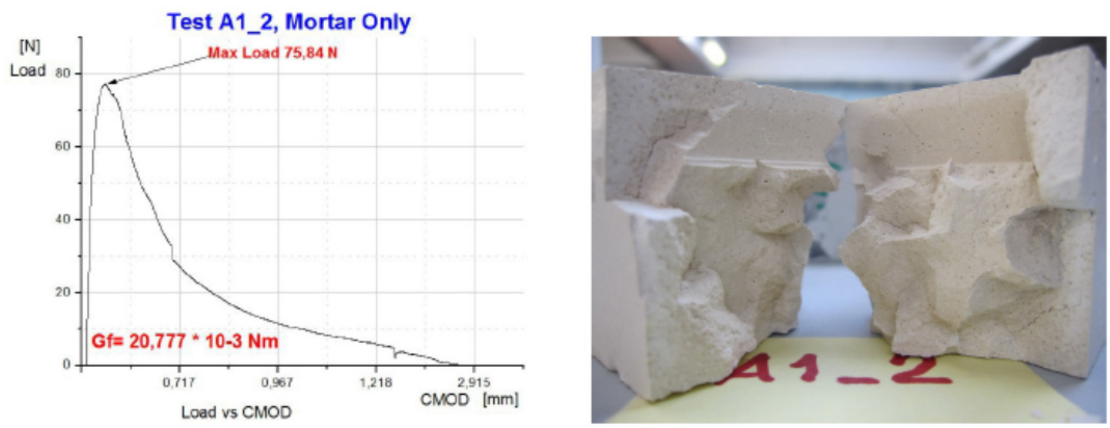

Figure 3: Load-CMOD opening curve for pure Mape Antique I sample.

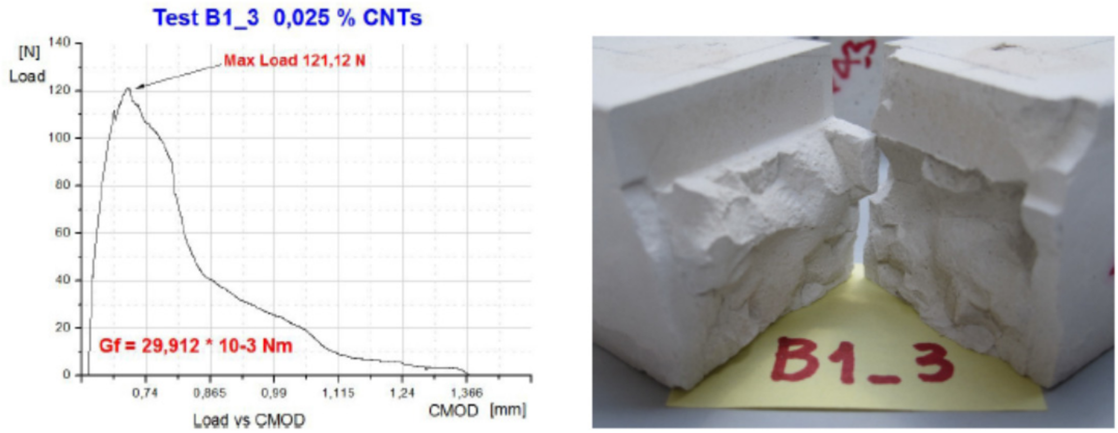

Figure 4: Load-CMOD opening curve for Mape Antique I + 0.025 wt% of CNTs sample.

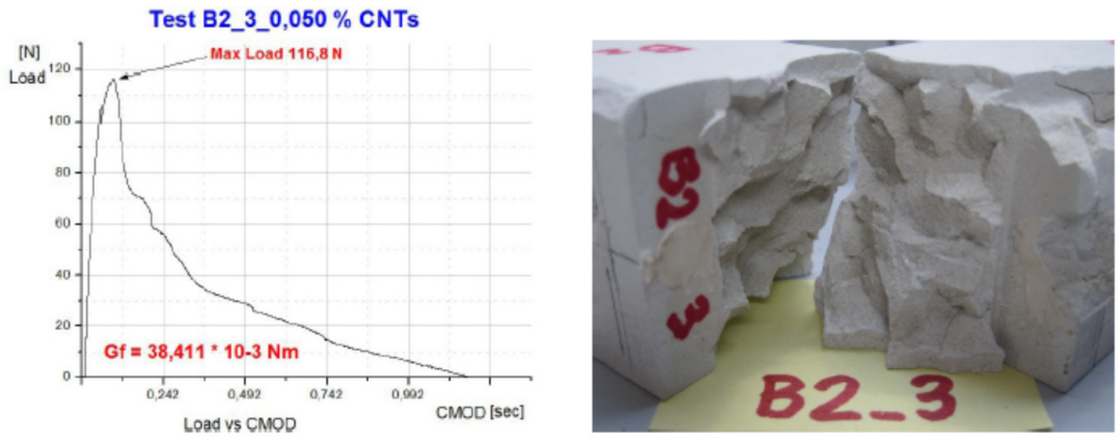

Figure 5: Load-CMOD opening curve for Mape Antique I + 0.05 wt% of CNTs sample.

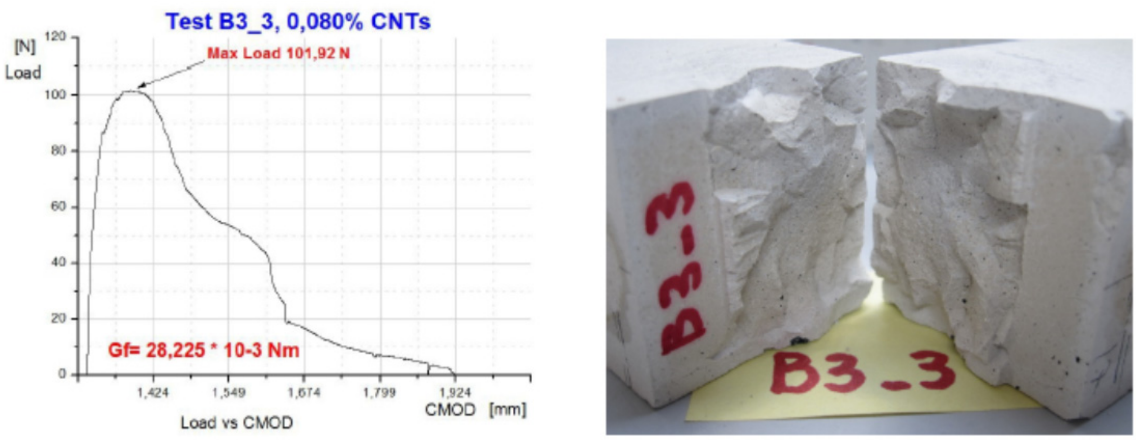

Figure 6: Load-CMOD opening curve for Mape Antique I + 0.08 wt% of CNTs sample.

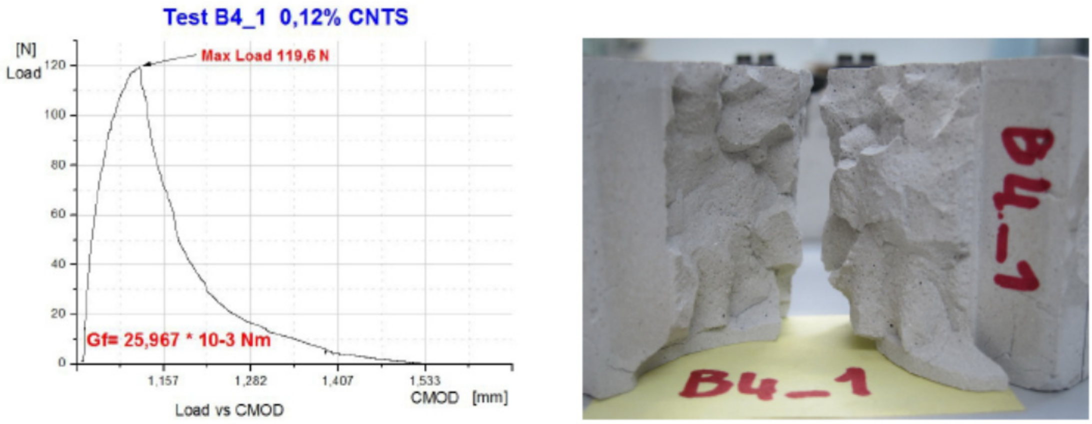

Figure 7: Load-CMOD opening curve for Mape Antique I + 0.12 wt% of CNTs sample.

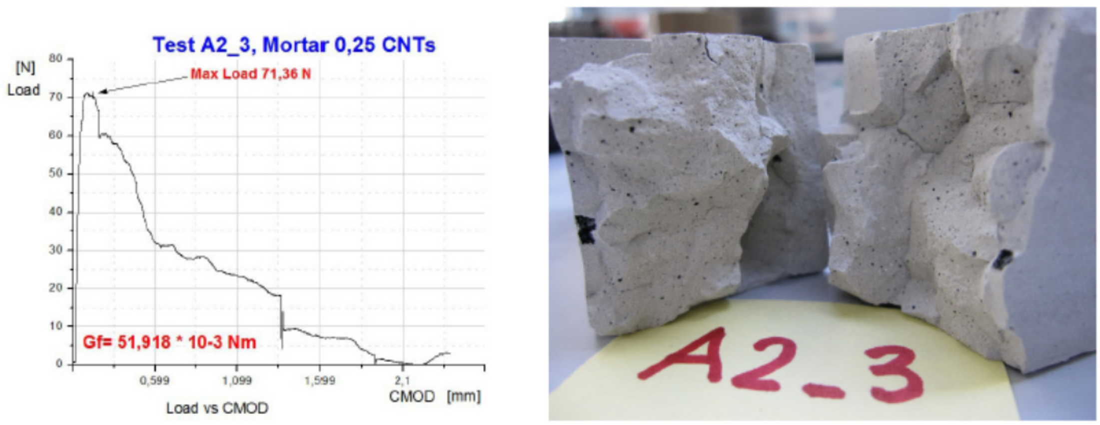

Figure 8: Load-CMOD opening curve for Mape Antique I + 0.25 wt% of CNTs sample.

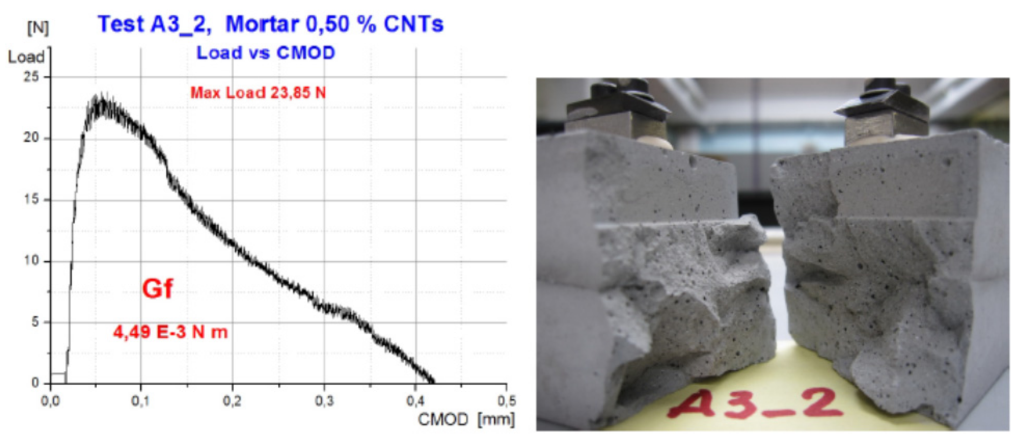

Figure 9: Load-CMOD opening curve for Mape Antique I + 0.5 wt% of CNTs sample.

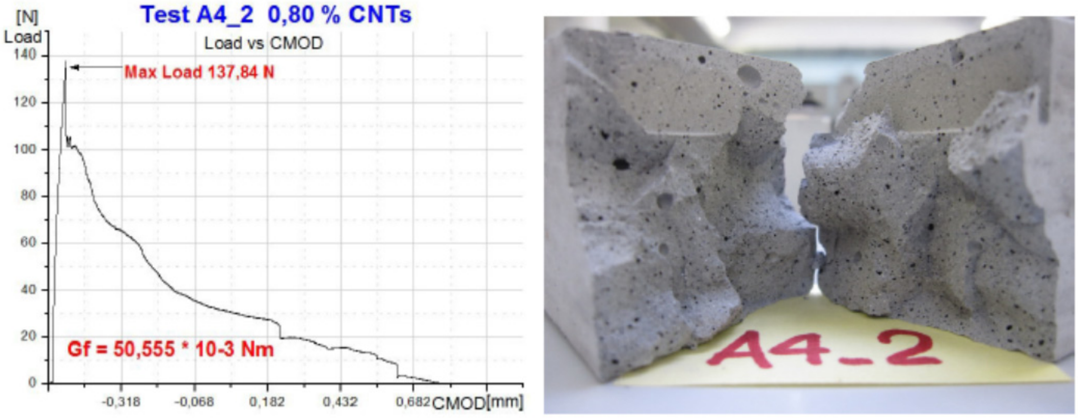

Figure 10: Load-CMOD opening curve for Mape Antique I + 0.8 wt% of CNTs sample.

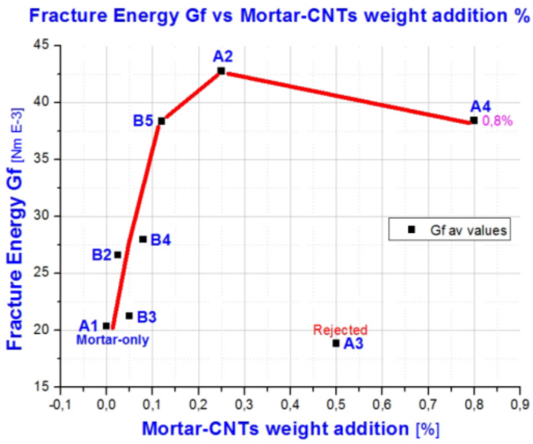

Figure 11: Influence of CNTs content on fracture energy for the investigated grout.

Compression tests also confirmed the beneficial effect of CNTs addition to the grout (Tab. 6).

Sample	CNTs content	Max load (kN)
A1	0.000	22.78
B1	0.025	29.52
B2	0.050	28.01
B3	0.080	29.99
B4	0.120	30.95
A2	0.250	20.96
A3	0.500	28.63
A4	0.800	30.00

Table 6: Average maximum load in compression.

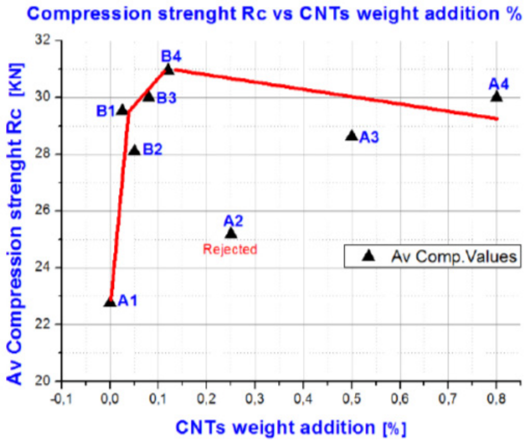

Figure 12: Influence of CNTs content on the compressive strength for the investigated grout.

Mercury intrusion porosimetry (MIP) evidenced that the increasing CNTs content in the grout slightly lowered the average pore size and the porosity for additions up to 0.25 wt% (Tab. 7).

Sample	CNTs content	Average porosity (%)	Average pore size (radius)(micron)
A1	0.00	37.1	0.038
B4	0.12	35.2	0.027
A2	0.25	36.3	0.030
A4	0.80	38.6	0.027

Table 7: Mercury intrusion porosimetry results (average of two measurements).

It is evident from these results that CNTs can interact with the fracture evolution by arresting the growth of microcracks and can delay the propagation of microcracks, thus impeding their coalesce to form the first macrocrack, as observed in cement pastes. Moreover, the addition of CNTs also provides an increase of the fracture energy.

CONCLUSIONS

For the first time, carbon nanotubes have been added to a grout. The results showed that these additions continuously increased the flexural and the compressive strength, as well as the fracture energy for a CNTs content up to 0.12 wt% with respect to the binder. This work must now be completed with rheological studies, in order to evaluate the influence of CNTS incorporation into the grout on the viscosity of the mix.

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