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EFFECT OF GO NANOSHEETS ON MICROSTRUCTURE, MECHANICAL AND FRACTURE PROPERTIES OF CEMENT COMPOSITES

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ABSTRACT

The aim of the present paper is to investigate the effects of graphene oxide (GO) nanosheets addition in a cement-based material from both a microstructural and a mechanical point of view. In particular, an experimental campaign is performed on both plain mortar and mortar reinforced with 0.03% GO nanosheets, obtained through the Brodie's method. The chemical and microstructural characterisation of the above materials is carried out by employing X-ray powder diffraction and SEM-EDS analysis, whereas the mechanical properties and fracture toughness are determined through flexural, compressive and fracture tests.

KEYWORDS

cement composite; fracture toughness; GO nanosheets; nanomaterial addition

1. INTRODUCTION

Cement-based materials (cement paste, mortar and concrete) belong to the category of the most used building materials in civil engineering **[1,2]**, due to their wide availability, long durability and relatively low cost **[3,4]**. However, during the hardening stage of cementitious composites, cracks and voids easily appear in structures, besides the fact that during service life of cement-based structures cracks easily form due to low fracture toughness and tensile strength of cement paste **[5,6]**. These defects both reduce the load bearing capacity and accelerate the effect of corrosive media.

In such a context, a great effort has been devoted to improve the mechanical properties of cementitious materials, by adjusting the cement/mortar ratio, optimising the aggregate gradation and incorporating reinforcing fibres into composite **[7-9]**. Relatively to reinforcing, typical applications include steel fibres **[10-13]**, carbon fibres **[14-16]**, polymer fibres **[11,17-19]** and hybrid fibres **[11,20-22]**, used to reduce cracks nucleation, thus giving increased tensile strength and fracture toughness to fibre-reinforced cementitious composites.

Regarding the use of such fibres, the mechanical reinforcing effect mainly depends on the bonding properties at the interface between fibres and surrounding matrix **[23-25]**. However, it is worth noticing that the addition of fibres tends to introduce air voids in the matrix during casting process, reducing the compressive strength of Fibre-Reinforced Cement Composites (FRCCs) **[26]**.

In such a context, the addition of nanostructures can represent a promising solution for enhancing the cement-based materials

performance **[27-31]**. As a matter of fact, from experimental evidences, significant improvements of both flexural and compressive strengths, fracture behaviour and durability has been obtained even for very low amounts of carbon-based nano-reinforcers **[27]**. For instance, the beneficial effect of multi-walled carbon nanotubes (MWCNTs) on both impact strength and fracture toughness of a two-stage fibrous concrete was investigated by Murali et al. **[28]**, whereas Gengying et al. **[29]** focused their study on the enhanced mechanical and fracture properties of a cement mortar, incorporating a polyvinyl alcohol latex nano-engineered with MWCNTs. Liu et al. **[30]** investigated the effect of MWCNTs addition on the mechanical and microstructure properties of a reactive powder concrete during dry-wet cycles with the high concentration of sulfate, showing an increment of material durability. Moreover, an attempt to use nanostructures, such as CNTs, in order to improve the compressive fatigue performance of cementitious composites can be found in the work of Li et al. **[31]**, showing a great potential of such nanostructures for extending service life of concrete structures.

Among nanostructures, graphite/graphene-related nanosheets (such as, for example, *graphite oxide* and *graphene oxide*) are able to improve the macroscopic properties of cement composites both due to their outstanding physical, chemical and mechanical properties, and by regulating the crystalline morphology of cement hydration products **[32]**.

In particular, *graphite oxide* is an oxidised version of graphite functionalised with groups containing oxygen, like hydroxyl,

epoxide, carboxyl and carbonyl groups **[33,34].** It is made of layers of sp^2 and sp^3 hybridised carbon atoms arranged in a hexagonal lattice structure. In case of few layers (usually less than 10), it is referred as *graphene oxide* (GO).

Graphite oxide is synthetized by using typically four basic methods: Staudenmaier, Hofmann, Brodie and Hummers. Many variations of such methods exist, with improvements constantly being explored to achieve better results and cheaper processes **[35].** The effectiveness of an oxidation process is generally evaluated by means of the carbon/oxygen ratio of the *graphite oxide*.

According to the current literature, it has been observed that the addition of *graphene oxide* (GO) in cement-based materials provides the following advantages:

(i) the functional groups (epoxide, hydroxyl, carboxyl and carbonyl), present on the planes and at the edges of GO, facilitate solubility both in water and in protic solvents **[36];**

(ii) the above functional groups of GO, combined with its specific surface area, facilitate the nucleation of calcium silicate hydrate (C-S-H) and allow the formation of chemical bonding networks that increase the mechanical strength of GO-reinforced cementitious composites (GRCCs) **[36];**

(iii) the nanoscale 2D size allows to fill in tiny cracks and voids between hydration products of cement, decreasing the porosity and improving the compactness of GRCC **[32];**

(iv) GO nanosheets provide toughening mechanisms, triggering crack deflection, branching and bridging, leading to an increasing of failure tolerance of GRCC **[36]**;

(v) GO nanosheets can regulate, during cement hydration reaction, the microstructure of hydration crystals, that are therefore characterised by both regular shapes and a uniform distribution in cement paste, leading to an increase of the mechanical strength and fracture toughness of GRCC **[37,38]**.

Many studies available in the literature are dedicated to investigate the improvement in terms of both physical/chemical properties and compressive, tensile and flexural strengths of cement-based composites when GO is used as a reinforcement (see the reviews reported in Refs. **[39-41]**).

However, only few works are dedicated to measure fracture toughness **[42,43]**. In such a context, Luo et al. **[42]** included GO nanoplatelets (GNPs) in mortar, prepared by using both natural and recycled sand, where the nanoplatelets were characterised by a flake diameter <500 mm. Different amounts of GNPs were considered, that is, 0.025 and 0.05% by weight of cement; such nanoplatelets were mixed into water with the superplasticizer, and ultrasonically dispersed for 1 hour. Fracture toughness testing, by using a SENB configuration, was performed. Fracture toughness ranged from 0.7298 to 0.7671 $MPa\sqrt{m}$ for an amount of GNPs equal to 0.025 and 0.05%, respectively, when natural sand was used, whereas from 0.6019 to 0.7139 $MPa\sqrt{m}$, when recycled sand was used.

Akono et al. **[43]** included GNPs in mortar, where the nanoplatelets were characterised by a thickness of 8-15 nm and a specific surface of 500-700 m^2/g. Different amounts of GNPs were considered, ranging from 0.1 to 0.5% by mass of cement; a novel synthesis protocol was employed, consisting in the four steps detailed in Ref. **[43]**. Fracture toughness ranged from 0.706 to 0.721 $MPa\sqrt{m}$ for an amount of GNPs varying from 0.1 to 0.5% by mass of cement, respectively.

The topic of the present study falls within the measurement of fracture toughness of cement-based materials reinforced with GO. In particular, the fracture toughness is determined by means of a method, proposed by some of the present authors **[11,21,44,45]**, which is able to take into account the possible crack deflection (or kinked crack), typically observed during the stable crack propagation in quasi-brittle materials. To the best knowledge of the authors, other methods with such a peculiar feature are not available in the literature. Moreover, for the above materials, both a microstructural, flexural, and compressive characterisation is performed.

The paper is structured as follows. In **Section 2**, the experimental campaign carried out on a cement-based composite reinforced by 0.03% GO nanosheets is described. **Section 3** is dedicated to present the results obtained in terms of: structural characterisation of the GO nanosheets; chemical and microstructural characterisation of the cement composite; mechanical properties and fracture toughness of the cement composite. **Section 4** is devoted

to the discussion of the effects of GO nanosheets on both microstructure and mechanical and fracture properties of cement composite, whereas conclusions are summarised in **Section 5.**

2. EXPERIMENTAL CAMPAIGN

2.1 Raw materials

The raw materials employ for the preparation of cement-based composite specimens are: graphite, cement, aggregates and a superplasticizer.

2.1.1 Graphite

A highly pure graphite powder is purchased from SGL Carbon group (RW-A grade) and is characterised by an average size of 66 μm.

2.1.2 Cement

The cement is a limestone Portland cement (42.5R CEM II/A-LL type) complying with the UNI 9156:2015 and UNI EN 197 European Recommendations **[46,47].** Such a cement contains a percentage of Portland Clinker between 80 and 94% and a percentage of limestone (LL) between 6 and 20%, whereas secondary constituents are present in quantities not exceeding 5%. In particular, the sulphates and chlorides amounts are lower than 3% and 0.1%, respectively **[46].**

2.1.3 Aggregates

The aggregates consist of a commercial silica sand with a grain size distribution (from 0.08mm to 2mm) determined according to the UNI EN 196-1:2005 European Recommendation **[48].**

2.1.4 Superplasticizer

A polycarboxylate superplasticizer (PC) with 40% solid content is supplied by BASF Construction Chemicals Italia S.p.a., Treviso, Italy **[49]**. Such an additive belongs to the category of amphipathic surfactants (that is, their molecules have both hydrophobic and hydrophilic parts); they are used to reduce surface tension and play an important role in particles dispersion and as wetting agents and stabilisers. Among the available surfactants, PC is chosen also due to its capacity to improve the workability of the cement paste.

2.2 Preparation methods

2.2.1 Preparation of GO nanosheets

Graphite is oxidized following Brodie's method **[50-52]**. This synthetic approach, compared to the classic Hummers' method widely used in literature, allows to obtain a "greener" product avoiding the use of potassium permanganate ($KMnO_4$) which can easily pollute the obtained graphite oxide. In details, 5g of graphite powder are mixed with 40g of sodium chlorate ($NaClO_3$) powder (1:8 wt ratio) inside a three-necked round-bottomed flask placed in an ice bath (~0°C). By keeping the mixture under continuous stirring, 50 ml of concentrated HNO_3 are slowly added to the reagents.

Then, the suspension is:

(1) heated at 60°C for 8h with a slow thermal ramp (20°C/h) and then cooled to room temperature (with a rate of 30°C/h);

(2) diluted in type-1 purified water and filtered using a Büchner funnel;

(3) suspended in a 3M solution of HCl 37%, filtered, and carefully washed on the filter until the pH of the liquid phase increased to 7;

(4) dried in an oven at 60°C overnight.

At the end of the above procedure, graphite oxide is obtained. Such a graphite oxide is a molecule with a not well-defined chemical structure; however, its chemical composition usually consists of approximately 75% of carbon and 25% of oxygen by weight.

In order to produce the aqueous solution for the preparation of cement-based composite, 42% (by weight of cement) of deionized water and 0.3% (by weight of cement) of PC are added to 0.03% (by weight of cement) of graphite oxide. Subsequently, the solution is stirred for 30 minutes at 60°C and dispersed by a High intensity Ultrasonic Processor at 200W for 30 minutes using a pulsed mode (pulse duration of 2 seconds). Finally, a stable graphene oxide (GO) nanosheets dispersion in aqueous solution is obtained.

2.2.2 Preparation of cement composite

For the preparation of the specimens, the dry mixture proportions adopted for both plain mortar (PM) and mortar reinforced with 0.03% GO nanosheets (GO-B) are: cement:water:sand (by weight) = $1{:}0.42{:}3$. For the PM specimens, a certain amount of PC (about 0.003 by weight of cement) is added to the water. Moreover, for GO-B specimens, the water is replaced by the aqueous solution, containing both GO and PC, which preparation is described in Section 2.2.1. Such an aqueous

solution is slowly added to the dry mixture and the fresh slurry is continuously mixed for 3-5minutes (**Figure 1(a)**).

The fresh slurry workability is measured by means of the flow table test according to the UNI EN 1015-3:2007 European Recommendation **[53]**. In particular, the obtained flow is equal to about 57.47% after jolting the flow table 15 times in approximately 15s (**Figure 1(b)**). The workability of GO-B fresh slurry is taken as reference to determine the appropriate PC content in the PM mixture in order to achieve the same self-compacting properties.

The fresh slurry is hence placed in moulds and compacted in two steps: the half-filled moulds are placed on the flow table and jolted 60 times in approximately 60s; then, they are completely filled and compacted again on the flow table with 60 jolts (**Figure 1(c)**).

Each mould consists of a prismatic shape beam, whose sizes depend on the test type being performed (further details can be found in the following Section).

Figure 1

Finally, the specimens are cured in laboratory for 24 hours under normal climatic conditions (temperature equal to 21°C and relative humidity of 50%) and, after demoulding, are submerged in water at room temperature for 28 days of curing.

2.3 Testing methods

2.3.1 Method for structural characterisation of GO

The X-ray powder diffraction (XRD) is performed using a Bruker D8 DISCOVER diffractometer, operating in Debye-Scherrer geometry, equipped with copper anode and a Rayonix MX225 2D area detector (analysis with Fit2D software), in order to evaluate the effective oxidation of graphite. As a matter of fact, XRD spectra of both pure graphite powder and GO powder are obtained.

The XRD spectra are acquired by using an accelerating voltage of 40kV and a beam current of 40mA with a CuKa radiation (lambda = 1.54178 Å), with a 2θ angle variation between $5°$ and $50°$.

2.3.2 Methods for chemical and microstructural characterisation of cement composite

The X-ray powder diffraction is performed by using a Bruker D2 PHASER diffractometer (Bruker, Karlsruhe, Germany), equipped with an Si(Li) solid state detector, in order to determine the mineralogical composition of both the mix constituents (aggregates and cement) and the cement-based specimens. In particular, such an analysis is performed on both PM and GO-B specimens. Note that, specimens are ground into a fine powder and sieved in order to remove as much aggregates as possible.

Qualitative analyses of the main mineralogical phases are done with the EVA software (Bruker) and COD database (Crystallography Open Database). The X-ray patterns are obtained by using a CuKa radiation (lambda = 1.54178 Å) with a voltage of 30kV and a current of 10mA. Moreover, the 2θ angle varies between $6°$ and $70°$, with a step of $0.02°$ and a counting time of $2\,s$ per step. Note that, XRD

measurements have a detection limit of approximately 3–5 wt% and, consequently, minority phases may not be properly captured.

The SEM observations are performed by using a SEM–EDS Jeol 6400 Scanning Electron Microscope equipped with an Oxford EDS (Energy Dispersive System) microprobe, in order to examine the microstructure of both PM and GO-B specimens. In particular, a BSE mode (backscattered electrons detector) is employed.

The specimens for the SEM observations are cubes with sizes of 10x10x10mm, covered with a high-conductance thin graphite film in order to avoid electric charging effects. During the observations, about 15 analytical points per specimens are taken.

The SEM images are obtained by using 20 kV and 1.2 mA current, 1 mm beam diameter and 75 s counting time.

2.3.3 Methods for mechanical characterisation of cement composite

Three mechanical properties (flexural and compressive strengths and fracture toughness) of both plain mortar (PM) and GO-reinforced mortar (GO-B) specimens are investigated in the present experimental campaign. In particular, the experimental campaign consists of:

(i) three-point bending tests performed on unnotched specimens (named PM_f and GO-B_f, where f stands for flexural), to determine the flexural strength;

(ii) compression tests performed on halves (named PM_c and GO-B_c, where c stands for compression) of the specimens broken during the flexural tests, to determine the compressive strength;

(iii) three-point bending tests performed on notched specimens (named PM_k and GO-B_k, where k stands for fracture), to determine the fracture toughness.

The three-point bending tests are carried out by means of the universal testing machine Instron 8862 (load cell up to 100kN with an accuracy of 0.02%), whereas the compression tests through a standard compression testing machine (load cell up to 300kN).

The following Sub-Sections briefly summarise the specimen geometries and the experimental set-up related to the above tests.

2.3.3.1 Flexural and compression tests

The UNI EN 196-1:2006 European Recommendation **[48]** is employed in order to perform both the flexural and compression tests.

Regarding three-point bending tests, three unnotched specimens are employed, having a prismatic shape with the following geometrical sizes: width (B) × depth (W) × length (L) = $40\,\text{mm}$ x $40\,\text{mm}$ x $160\,\text{mm}$, and support span (S) = $120\,\text{mm}$. The tests are performed under load control with a rate equal to $45\,\text{Ns}^{-1}$, following the suggestion of the ASTM C348-14 Standard **[54]**, and each specimen is monotonically loaded up to failure. By employing the experimental value of the peak load, P_f, the flexural strength, R_f, is computed according to the following equation **[48]**:

$$R_f = \frac{1.5 \cdot P_f \cdot S}{W^3} \qquad (1)$$

As far as compression tests are concerned, the six halves prismatic specimens, resulting after performing the flexural tests, are employed. The tests are carried out under load control with a rate equal to $2400 \pm 200\,\mathrm{Ns^{-1}}$ until specimen failure. By employing the experimental value of the peak load, P_c, the compressive strength, R_c, is computed according to the following equation **[48]**:

$$R_c = \frac{P_c}{1600} \tag{2}$$

2.3.3.2 Fracture tests

The Two Parameter Model (TPM) **[55]** and the RILEM Recommendations **[56,57]** are employed in order to perform the fracture tests. In particular, at least four prismatic specimens (with geometrical size: $B \times W \times L = 30\,\mathrm{mm} \times 60\,\mathrm{mm} \times 300\,\mathrm{mm}$, and $S = 240\,\mathrm{mm}$) are employed, presenting a notch (with length $a_0 = 20\,\mathrm{mm}$) in the lower part of the middle cross-section. Such a notch is realized by using a circular saw, thus obtaining a blunt notch. The tests are performed under Crack Mouth Opening Displacement (CMOD) control, employing a clip gauge (characterised by a maximum travel of 4 mm with an accuracy of ±0.05%) at an average rate equal to 0.15 $\mathrm{mmh^{-1}}$. More precisely, each specimen is monotonically loaded up to peak load, $P_{\max}$; then, the post-peak stage follows and, when the load is equal to about 95% of $P_{\max}$, the specimen is fully unloaded by proceeding under load control. Finally, the specimen is reloaded up to failure under CMOD control with the same initial average rate.

After the failure of each tested specimen, a visual inspection of the crack path is performed in order to take into account if cracks starting from the notch tip deflect (kinked cracks), as is generally observed for quasi-brittle materials **[11,21,44,45]**. In particular, the kinking angle, α, formed by the crack path with respect to the loading direction is measured for both PM_k and GO-B_k specimens. Note that, when a kinked crack is visually observed and the kinking angle is not constant along the crack path, it is assumed that the crack, at the peak load $P_{\max}$, is characterised by two branches. The following procedure is used to compute α:

- when the length of the first crack branch is less than the second one, the angle is assumed to be equal to the orientation of the second branch;
- whereas, when the length of the second crack branch is less than the first one, the angle is assumed to be equal to the orientation of the first branch.

Moreover, when the fracture surface is not plane, the mean value of α θ is computed by averaging the values related to front- and back-side of the specimen.

By exploiting the experimental results in terms of α, $P_{\max}$, initial, C_i, and unloading, C_u, linear elastic compliances, both the elastic modulus, E, and the fracture toughness, $K^S_{(I+II)C}$, are computed according to the Modified Two-Parameter Model (MTPM) **[11,21,44,45]**.

3. RESULTS

3.1 Structural properties of GO

In order to evaluate the effective oxidation of graphite, **Figure 2** shows the X-ray diffraction (XRD) spectra of both pure graphite (see black line in **Figure 2**) and GO (red line in **Figure 2**).

Figure 2

From **Figure 2**, it can be observed that the interlayer distance of GO is expanded to 0.6-0.7nm with respect to that of pure graphite equal to 0.33nm, while typical AB stacking of graphite is preserved. Moreover, the characteristic diffraction peak (0 0 2) of pure graphite at $2\theta = 26.5°$ is shifted at about $15°$ in the GO spectrum. At the same time, an increase of full width half maximum (FWHM) of the peak is observed, revealing a sizeable reduction of the crystallite size in GO, estimated to be about 100 nm. These results confirm that both carboxyl and hydroxyl groups are penetrated into the graphite interlayers, thus weakening the interaction between such layers.

3.2 Chemical and microstructural properties of cement composite

Figure 3 shows the X-ray diffraction (XRD) patterns of: aggregates (**Figure 3(a)**), cement (**Figure 3(b)**), PM specimen (black line in **Figure 3(c)**) and GO-B specimen (grey line in **Figure 3(c)**).

Figure 3

As far as aggregates are concerned (**Figure 3(a)**), the XRD pattern shows that only quartz (SiO_2), without any impurities, is present.

Relatively to the cement (**Figure 3(b)**), the main mineralogical phases are hereafter reported in abundance order: tricalcium silicate C_3S (Ca_3SiO_5), dicalcium silicate C_2S (Ca_2SiO_4), calcite ($CaCO_3$), tricalcium aluminate C_3A ($Ca_3Al_2O_6$), gypsum ($Ca_2SO_4 \cdot 2H_2O$) and tetracalcium aluminoferrite C_4AF($FeCa_2AlO_5$).

From **Figure 3(c)**, no substantial differences between PM (black line) and GO-B (grey line) specimen patterns can be noticed. In particular, the following cement hydration products are found in both specimens, that is (in abundance order): calcium hydroxide CH ($Ca(OH)_2$) (portlandite) and ettringite AFt ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26(H_2O)$). Monosulfonate AFm ($Ca_4Al_2O_7 \cdot nH_2O$) seems to be present in small quantities (see the small peaks at $2\theta = 10.9°$ and $22.1°$ in **Figure 3(c)**); however, a reliable identification cannot be done due to the poorness of this phase. Moreover, tricalcium silicate C_3S, dicalcium silicate C_2S, calcite and gypsum are also present. Finally, the peaks of quartz (SiO_2) are still present in the XRD patterns (see **Figure 3(c)**), although an attempt to remove the presence of the aggregates has been done.

Figures 4 and **5** show the microstructure images of both PM and GO-B specimens, respectively.

Figure 4

Figure 5

As far as PM specimen is concerned, quartz (see dark grey regions) and Ca-rich phases (see light grey regions) can be seen in **Figure 4(a)**. In **Figure 4(b)**, it can be noted that the Ca-rich phases are formed by smaller crystals with respect to those of quartz. Moreover, the actual dimension of these crystals cannot be easily measured since they are mainly crystalline aggregates. **Figure 4(c)** shows a specific area of the PM specimen containing elongated Ca-rich silicate crystals with a dimension of few microns. Note that, such crystals primarily growth in correspondence of pores, cracks and loose structure of the material.

From **Figure 5**, it can be observed that the GO-B specimen morphology is similar to that of PM one (that is, quartz and Ca-rich phases are present), especially for large magnifications. However, Ca-rich silicate crystals are characterized by a different shape with respect to those observed in PM specimen, as shown in **Figure 5(c)** for a specific area of the examined GO-B sample. In particular, tabular shaped crystals with micrometric sizes are homogeneously detected in such an area. Moreover, the addition of GO nanosheets in the present material promotes the development of hydration crystals arranged close to each other in an orderly manner (**Figure 5(c)**), whereas such crystals are configured in a more disordered cluster in PM specimen (**Figure 4 (c)**).

3.3 Mechanical properties of cement composite

The flexural and compressive strengths are determined according to the test methods presented in Sub-Section 2.3.3.1.

As far as flexural tests are concerned, the mean value, μ, and the standard deviation, σ, of peak load, P_f, and flexural strength, R_f, for each specimen type are listed in **Table 1**. It can be observed that only a modest increment (about 4%) of the flexural strength is achieved for GO-reinforced (GO-B_f) specimens with respect to plain mortar (PM_f) ones. Moreover, a careful examination of R_f results suggests that the difference between mean values should be a consequence of aleatory variability and/or measurement errors, that is, the addition of GO seems not to improve the flexural strength of mortar. As matter of fact, by subtracting one standard deviation from the mean value of R_f related to GO-B_f specimens, the result obtained is almost equal to the mean value of R_f related to PM_f specimens.

Table 1

Regarding the compression tests, the mean value, μ, and the standard deviation, σ, of peak load, P_c, and compressive strength, R_c, for each specimen type are listed in **Table 1**. A trend similar to that observed for flexural strengths can be remarked for compressive ones, with an increment of about 3% when GO nanosheets are added to the cement-based material.

3.4 Fracture toughness of cement composite

The fracture toughness is determined according to the test method presented in Sub-Section 2.3.3.2. In order to achieve more reliable results, five PM specimens and five GO-B specimens are tested.

Figures 6 and **7** show the experimental load-CMOD curves for PM_k and GO-B_k specimens, respectively. A significant increase of the peak load can be noticed for GO-B_k specimens in comparison to PM_k ones. Moreover, by considering the post peak stage in the above curves, no remarkable differences in terms of load bearing capacity are observed between the specimen types. As a matter of fact, in correspondence of a CMOD of 0.15mm, the load is equal to about 0.2 kN for all the specimens.

Figure 6

Figure 7

The crack paths for PM_k and GO-B_k specimens are shown in **Figures 8** and **9**, respectively. Starting from the notch tip, a crack characterized by a deflected path is generally observed for both PM_k and GO-B_k specimens. Such a deflection is probably due to the inhomogeneities (i.e. aggregates) embedded in the cementitious matrix. Consequently, a mixed-mode regime occurs at crack tip, even if a remote pure Mode I loading is applied during the test. Note that the use of the above kinking angle in the MTPM formulation prevents the overestimation of the fracture toughness determined by considering crack propagation under pure Mode I loading.

Figure 8

Figure 9

The mean value, μ, and standard deviation, σ, of peak load, P_{max}, kinking angle, α, elastic modulus, E, and fracture toughness, $K^{S}_{(I+II)c}$ are listed in **Table 2** for each specimen type. It can be observed an increase of about 23% of P_{max} for GO-B_k specimens with respect to PM_k ones, whereas the elastic modulus is almost constant, with an increment of about 5%. As matter of fact, by subtracting one standard deviation from the mean value of E related to GO-B_k specimens, the result obtained is almost equal to the corresponding one related to PM_k specimens. Moreover, also the kinking angle, α, seems to be not affected by the GO addition, since α mean values are quite similar.

According to **Table 2**, the best performance in terms of fracture toughness is observed when GO nanosheets are used as reinforcement materials, with an increase of the mean value of $K^{S}_{(I+II)c}$ equal to about 26% with respect to that computed for PM_k specimens.

Table 2

4. GO EFFECTS ON MICROSTRUCTURE, MECHANICAL AND FRACTURE PROPERTIES OF THE CEMENT COMPOSITE

As previously introduced in Sub-Section 3.2, the cement in an anhydrous state mainly consists of the following four mineral phases:

tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tricalcium aluminoferrite (C_4AF). The surface of GO has many oxygen functional groups, and the main ones are –OH (hydroxyl) and -COOH (carboxyl). As pointed out in Ref. **[48]**, during the hydration process, such groups react preferentially with three of the aforementioned mineral phases, that is C_3S, C_2S and C_3A, to form the growth points of the hydration products, consisting in: (i) a gel (C-S-H) and (ii) three crystals (that is, calcium hydroxide CH, ettringite AF_t, monosulfonate AF_m).

According to the experimental outcomes reported in **Section 3**, it can be stated that the addition of GO nanosheets in the present material promotes the development of hydration crystals characterised by a tabular shape and arranged close to each other in an orderly manner. On the other hand, the hydration crystals related to the cement-based material without GO are configured in a more disordered cluster with an elongated shape.

As far as the GO effects on mechanical properties are concerned, the slight increase in terms of both flexural and compressive strengths is due to the tabular shape of the hydration crystals. As a matter of fact, such crystals, which form a compact structure, allow the GO_B specimens to withstand higher loads with respect to the PM specimens, where elongated crystals are present.

Moreover, the significant improvement of the fracture behaviour observed for GO_B specimens with respect to PM ones is mainly due to the fact that the tabular crystals are able to fill the area in correspondence of pores, cracks and loose structure in an ordered

manner, thus reducing the typical brittleness of cement-based materials.

5. CONCLUSIONS

The aim of the present paper is to investigate the effects of GO nanosheets addition in a cement-based material from a microstructural and mechanical point of view. In particular, the main novelties of the paper lie in:

- the oxidation of graphite by using the Brodie's method, which allows to obtain a "greener" GO with respect to that of the classic Hummers' method widely used in the literature;
- the determination of the fracture toughness of the present cement composite, being such a material property lacking in many research works available in the literature.

First of all, an experimental campaign has been performed on both plain mortar and mortar reinforced with 0.03% GO nanosheets. In particular, a chemical and microstructural characterisation of the above materials has been carried out by employing X-ray powder diffraction patterns and SEM images, whereas the mechanical properties and fracture toughness have been determined through flexural, compressive and fracture tests.

According to the experimental data, it has been observed that the GO-B specimen morphology is similar to that of PM one, that is, quartz and Ca-rich phases have been found in both specimen types. Moreover, the Ca-rich phases are formed by smaller crystals with respect to those of quartz. However, in GO-B specimens, Ca-rich

silicate crystals are present with a different shape respect to those observed in PM specimens. As a matter of fact, hydration crystals with a compact polyhedron-like shape and arranged close to each other in an orderly manner have been observed in presence of GO, whereas disordered and elongated crystals have been found in plain mortar.

In conclusions, it can be observed that the tabular shape of the hydration crystals of GO reinforced mortar produced:

(a) a flexural strength increasing of about 4%;

(b) a compressive strength increasing of about 3%;

(c) a fracture toughness increasing of about 26%, by filling in an ordered manner the area in correspondence of pores, cracks and loose structure;

with respect to the properties characterising the plain mortar.

Based on such encouraging results, more work needs to be done in terms of a deep investigation on the effects of GO reinforcement in cement-based material in order to spread the use of such a material in the construction field. In particular, different GO percentages will be considered, together with the addition of metallic/synthetic/natural fibres into the mixture, in order to further increase the composite mechanical behaviour.

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NOMENCLATURE

a_0	notch length
B	specimen width
C_i	initial linear elastic compliance
C_u	unloading linear elastic compliance
E	elastic modulus
$K^S_{(I+II)C}$	critical mixed mode stress-intensity factor
L	specimen length
P_c	peak load related to compression tests
P_f	peak load related to flexural tests
$P_{\max}$	peak load related to fracture tests
R_c	compressive strength
R_f	flexural strength
S	support span
W	specimen depth
μ	mean value
σ	standard deviation