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GRAPHENE OXIDE AS ADDITIVE FOR INCREASING THE STRENGTH AND DURABILITY PERFORMANCE OF EXISTING CONCRETE STRUCTURES

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ABSTRACT

Graphene and graphene-based nanosheets (GNS) have valid mechanical, thermal and electrical properties, enabling interesting applications for improving structural strength and durability. If combined with the Ordinary Portland Concrete (OPC), they can enhance its mechanical behaviour, an analogous improvement in terms of strength can also be seen in Ultra-High-Performance Concrete (UHPC). These features appear very useful in case of the restoration of existing concrete structures, thanks to the durability properties due to the GNS. Providing a wide state of the art about the use of GNS in concrete structures, this paper shows the strength improvements achievable in term of strength and durability. The benefits are finally discussed in relation to the restoration of existent concrete buildings.

KEYWORDS: Graphene; Graphene-based nanosheets; Concrete Building Restoration

1. INTRODUCTION

The addition of reinforcing materials in the concrete has become a common practice to improve its mechanical performance. It is valid both for new and existing concrete buildings often afflicted by conservation problems, interesting the external surfaces of the concrete elements (exposed to wet conditions, pollutions and inadequate maintenance over time) and the steel reinforcements (corrosion due to carbonation or chloride ions). For existing buildings, a better structural response is demanded using materials able to contain the thickness of the reinforcements and to guarantee the workability; moreover, the durability issues related to the new concrete parts and the existent ones represent a fundamental aspect to guarantee . Therefore, fibers such as steel, glass, polymers, and carbon have been extensively studied, over the past decades, for developing fiber-reinforced composites. Although microfibers enhance the ductility and toughness of the concrete matrix, their influences on compressive strength and durability are limited. The functionalization of carbon and polymer fibers enables them to form covalent bonds with the cement matrix; however, their small specific surface area limits their contribution to the interfacial strength [1]. Therefore, nanomaterials can provide a better solution than traditional fibers for reinforcing at the nanoscale and for allocating a much higher specific surface area for cement matrix interaction. Some nanomaterials can improve the interfacial structure and internal matrix properties. The paper is focused on the use of graphene and its products to improve the mechanical performance of the cement composites. Graphene is the basic structural unit for graphitic materials of any dimension. It is composed of a single-layer sheet of carbon atoms closely packed into a two-dimensional (2D) (0.335 nm thickness) honeycomb framework [2]. It can be wrapped up into 0D fullerenes, rolled into 1D nanotubes or stacked into 3D graphite [3].The most popular graphene nanosheets (GNS), as material used for improving the mechanical performance of the cementitious material, are: (a) graphene oxide (GO), (b) Graphene nanoplates (GNPs) and (c) reduced graphene (rGO). Graphene oxide (GO) [4] is the most studied GNS in cement composites, it consists of a mono-layer sheet with a hexagonal carbon network. GO is a single-atomic layered material, made by the powerful oxidation of graphite. It is an oxidized form of graphene, laced with oxygen-containing groups.

It is considered easy to process since it is dispersible in water (and other solvents). The main differences with respect to the pure graphene are: (i) it bears hydroxyl, epoxide, carboxyl, and carbonyl functional groups on its surface, (ii) it exhibits higher reactivity with cement and superior dispersion in the matrix, being useful for cementitious composites, (iii) it is cheaper to produce in comparison to graphene. Reduced graphene oxide (rGO) has less functional groups in its structure in comparison to GO, presenting intermediate properties between GO and pure graphene. However, the superior properties of graphene can be partly restored by reducing simultaneously the oxygen functional groups of GO. Graphene nanoplatelets (GNPs) are compressed layers of graphene sheets with thickness less than 100 nm and diameter of several micrometers, due to their increased thickness, GNPs are a cheaper alternative to graphene [5], representing the preferred form of GNS for structural composites[6]. Procedures used for producing GNS are widely discussed in [7],[8],[9],[10],[11]. The present paper refers about GO and GNPs because their use in constructions applications is widely studied. In the following, the strength improvements obtained by the introduction of graphene products are discussed in several respects in Section 2 and the durability enhancements are underlined in Section 3.

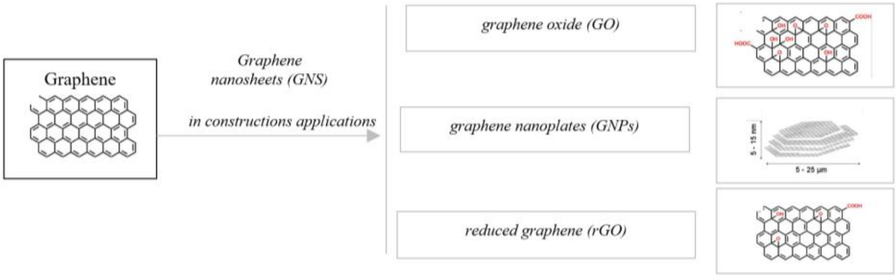

Figure 1: Graphene in construction application, adapted from [10]

2. STRENGHT IMPROVEMENTS IN THE CEMENT-BASED COMPOSITES BY GRAPHENE

2.1. The importance of the nano-reinforcements in cementitious matrix materials

The graphene-based microfibers can be used to reinforce cementitious materials. Many attempts have been directed to enhance the performance of cement-based materials by fly ash [12], silica fume, macro reinforcements and micro reinforcement such as fibers (Fiber Reinforced Concrete). In the last years, the research is moving toward the nano reinforcements that would delay the nucleation and growth of cracks at the nanoscale. The most common cement in the production of mortar and concrete is the Ordinary Portland Cement (OPC). It is mainly constituted of silicates and aluminates. The latters are (i) relevant for the setting and hardening processes, (ii) hydrate faster respect to the silicates but (iii) do not contribute to the mechanical resistance, [13]. About the hydration of silicate, two products are given: hexagonal crystals of calcium hydroxide (Portlandite) and a variety of calcium hydrate product (called gel C-S-H or cement gel). The Portlandite is subjected to fracture for the weak~~er~~ bond between the layers of its crystals. On the other hand, the C-S-H structure is responsible for the mechanical resistance representing the 80% of the final volume and the 50% of the hardened mass. In the concrete of the existent buildings the mechanical property depends on the intrinsic porous microstructure of the hydrated cement paste and on the formation of an Interfacial Transition Zone (ITZ) between the paste and the coarse aggregates. Cement paste behavior by its porous permeable properties. Instead, the ITZ represents a sort of “weak-link in the chain”, and it is considered as the strength-limiting phase in concrete. Moreover, the mechanical properties of concrete are influenced not only by the properties of the individual constituents (cement paste and aggregate) but also by their contents, their mutual interactions and their spatial configuration,[14]. Individually cement paste and aggregates both show brittle nearly linear elastic behavior and sudden failure. In contrast, concrete shows significant quasi-ductile behavior until reaching the fracture due to the development of multiple micro-cracking in the ITZ, [15][16].The adhesion between aggregate and cement paste within the transition zone is one of the factors that govern the concrete final strength. The most important limitation of concrete is its inherent quasi-brittle nature, also the exposure to the environmental conditions unfavorably affects the durability of concrete structures. Various types of, the already mentioned reinforcements are applied to concrete to ensure the required mechanical resistance by controlling the initiation and propagation of cracks. Nevertheless, these kinds of reinforcements do not affect cement hydration products, thus the brittleness and cracking still occur at the nanoscale. The incorporation of nanomaterials, as the graphene derivatives can offer suitable improvements. Nano-reinforcements in cementitious matrix materials could be much effective than the conventional steel bar/fiber reinforcements (at millimeter-scale) because they can control nano-size cracks (at the initiation stage) before they develop into micro-size cracks,[17].

2.2. General specifications Graphene Oxide (GO) in Ordinary Portland Cement (OPC)

The influence of Graphene Oxide (GO) on the Ordinary Portland Cement (OPC) is mainly studied in terms of strength and workability of the composite. In [18] the compressive and flexural strength improvement is in the range 15–33% and 41–59%with only 0.05 %wt of GO nanosheets in OPC matrix is reported (0.05% of GO with respect to the water contenent called wt). The reinforcement of the matrix by the GO nanosheets was attributed to the strong interfacial adhesion between GO and cement matrix, [19] and [20]. Thanks to the use of GO, the cracks in a graphene-cement composite, usually transversally directed in the plain matrix, are arrested since they cannot pass through the graphene sheets, consequently there is a reduction of the micro-crack. In [21] the impact of GO nanosheets (with size ranging from 5 nm to 1500 nm) on the properties of OPC paste is compared to other nanomaterials widely used as the aluminum oxide nano-powder (n-Al2O3; mean size <50 nm) and colloidal silicon dioxide nanoparticles (n-SiO2; average size 12 nm). The overall results suggest-the performance of GO is better in comparison to n-Al2O3 and n-SiO2, see Table 1. Even at small concentrations (0.02% by weight) GO shows efficiency in comparison to the 3-dimensional nanomaterials such as n-Al2O3 and n-SiO2. The good performance of GO can be attributed to its quality of better dispersion in a polar solvent, like water, to shape and size factors, and to the presence of functional groups such as carboxyl and hydroxyl on the structure of the graphene sheets. In [22] it is also present a comparison between the mechanical properties obtained in OPC by functionalized carbon nanotubes (FCNTs) and GO cement (ranging between 0.125%wt and 1.00%wt). GO shows more uniform dispersion and higher possibility of interfacial adhesion with the hydration products in comparison to FCNTs. In terms of compressive strength: an improvement of the 77% was obtained by GO (at 1%wt) and of the 58% for FCNT composites (at 0.5%wt). In terms of tensile strength, FCNTs have showed a slightly higher enhancement (40%) in comparison to GO (37.5%) composites with the same 0.25%wt. A note about the workability, a mini slump tests were analyzed in [23]; the addition of GO sheets leads to a slight reduction in workability, when 0.05% GO is added, the slump diameter is reduced about 6.5%. This result could be due to the large surface area of GO sheets which reduce the available water in the fresh mix. Nevertheless, the workability of GO/cement composite is still comparable to that one of the plain cement paste, [23].

Table 1: Performance in pastes with nanomaterials (expressed % of control paste), adapted from [21]

n	Paste mixes	% by wt of cement	Percent increment or decrement		
			Compressive strength 7/28 days	Flexural strength 7/28 days	Slump spread
1	control	-	100/100	100/100	100
2	GO	0.02	120/122	170/123	87
3	n-Al2O3	0.20	132/123	204/123	89
5	n-SiO2	4	145/141	218/104	76

2.3. Graphene Oxide combined with other nanomaterials in cementitious paste

In [21] the combination of Graphene Oxide (GO) and single-walled carbon nanotubes (SWCNTs) leads to around 72.7% enhancement in flexural strength of cement, higher than the one obtained with the only addition of GO (51.2%) or of SWCNTs (26.3%). In [24] the properties of cement paste reinforced by GO and carbon nanotubes (CNTs) composites are investigated: GO with CNTs composite improves of the 21.13% and 24.21 % the compressive and flexural strength of cement paste respectively, which is much higher than cement paste reinforced by only CNTs (6.40% and 10.14%) or by only GO (11.05% and 16.20%), see Table 2. In [25] GO combined with SiO2 nanoparticles (SiO2-NPs) are studied obtaining a hybrid cement having better performances with respect to the ones given by the single use of GO or SiO2. In the maturation time, up to 28th day, the compressive strength progressively improves, the incorporation of 0.02wt% leads to an improvement of the compressive strength of (about) 30.68%, 25.43% and 24.58% at 3, 7 and 28 days, respectively. Very similar results are reached by SiO2-NPs but with 1.0 wt%, it could mean GO has better reinforcing effects than SiO2-NPs, especially in the first days of the maturation time. The improved mechanical strength of GO-cement samples is attributed to a combination of the accelerated cement hydration, to an excellent interfacial bonding, and to a refined microstructure. However, for 0.04 wt% and 0.06 wt%, there is a little decrease in compressive strength with respect to the maximum value, [24].

Table 2: Mechanical behavior of cement paste with different contents of CNTs and GO, adapted from [24]

specimen	compressive strength(MPa)	Flexural Strength(MPa)	Young's Modulus(GPa)
Cement paste	25.6	13.64	12.12
0.05 wt. % CNTs/cement	27.24	15.06	12.63
0.05 wt. % GO/cement	28.43	15.85	14.31
0.025 wt. % GO/0.025 wt. % CNTs/cement	31.01	16.93	15.42

2.4. GNS combined with Ultra-High-Performance Concrete (UHPC)

Considering as Ultra-High-Performance Concrete (UHPC) the concrete with 0.5% steel microfibers, 5% silica fume and 40% fly ash, it is worth noting recently GNS has been studied to increase the mechanical strength of concrete as an alternative to the use of Carbon Nano fibers (CNFs), [26]. Varying the content of nanomaterials from 0 to 0.3% of the cementitious material weight, two GNS sizes are proposed the GNP-C with 2 nm diameter and the GNP-M with 30 nm diameter, both with about 5 nm thickness. A slight increment of the compressive resistance is achievable, at 28 days, averagely of the 2.5-3.0% with a content of nanomaterials from 0.05% to 0.3% (GNP-C shows best performance among the nanomaterials). Regarding the tensile strength, increasing the nanomaterials content from 0 to 0.30%, the tensile strength increases (averagely) of the: 56% with CNF-s, 40% with GNP-C and 45% with GNP-M, in addition, the incorporation of nanomaterials does not have a significant effect on the density of the UHPC (similar results have been detected in [27]). Experimental tests with different sizes of graphene products are deepen not only for GNP, but also for GO, [28]. For different GO sizes, after 28 days, the GO have indifferently led to an improvement of the compressive strength ranged in 63%-86%. It is interesting to notice that the compressive strength of the concrete increases in the first days of the maturation up to about the14th days, later it gradually decreases with respect to the maximum value.

2.5. GNS with Carbon Fibers

The abundant oxygen-containing groups of GO have been also exploited in [83] to increase the hydrophilicity and roughness of carbon fibers (CF), improving their dispersion in the cement matrix and their interfacial zone with the cement. In [29] CFs coated with GO have shown, by scanning Electron Microscope (SEM) observation, a better dispersion in the cement matrix, this is an important advantage since the mechanical behavior of cement-based materials reinforced by carbon fiber (CF) greatly depends on the dispersion of CF and on the interfacial properties between the CF and cement matrix. In [30], by introducing GNP and CF in the autoclaved aerated concrete (ACC), used for precast construction, it has been observed an increase of the compressive strength of the concrete mix from 12 MPa to 27.5 MPa. This improvement can be due to the presence in the GO of carboxyl, hydroxyl, and epoxy functional groups which significantly act as binder between GO nanosheets and cement matrix. Similarly, the tensile strength also increased from 2.22 to 2.87 MPa (improvement of the 29.3%).

2.6. GNS with Recycled aggregate concrete

The use of GNS is promising in recycled aggregate concrete (RAC), which has shown reduced mechanical and durability properties, therefore its application result still limited. GNS has great potential to enhance the performance of RAC, as it is pointed out in [31] in which the 0.05%wc of GNS has improved the mechanical strength and the sulfate resistance of mortars produced by recycled fine aggregates. Nevertheless, investigations about GNS as reinforcement for recycled concrete are still limited. In [31] moreover, the incorporation of graphene into fly ash cement mortars (70% of cement and 30% of Fly Ash) has been studied for different mix of graphene in fine recycled aggregates (FRA) or fine natural aggregates (FNA) in mortars (the mixes are M1 with 0.0% of graphene and 100% of FNA, M2 with 0.0% of graphene and 100% of FRA, M3 with 0.05% of graphene and 100% of FRA and M4 with 0.10% of graphene and 100% of FRA). Among the mixes, M3 gives a maximum increase of 8% and 13% with respect to FNA mortar in compressive and flexural strength respectively. Also, an excellent resistance to sulfate attack in M3 composite could be achieved with minimum loss in compressive strength (around 21%). The best results in terms of strength and resistance to sulfate attack are shown by M3 while the least performances are noticed for the M2 (without graphene). Furthermore, M3 also depicts the least decrease in strength under different cycles of sulfate attacks, because graphene offers a large surface for the mobile ionic entities present in the pore solution.

3. DURABILITY IMPROVEMENTS IN THE CEMENT-BASED STRUCTURES BY GRAPHENE

3.1. Microporosity variations

Existing concrete structures are susceptible to various forms of deterioration for aggressive elements (such as CO2, SO42- and Cl-), alkali-silica reaction (ASR), calcium leaching, freezing and thawing cycles, fire, thermal cracking and bacterial attack [32]. The existent concrete constructions durability, in relation to the aggressive agents, is mainly governed by its pore structure and permeability, considering [33] the addition of GNS in new concrete parts can led a longer durability with a reduction of the water and gas permeability, and an encreased resistance to the aggressive elements [34]. By using mercury intrusion porosimetry (MIP) it was observed for cement pastes [35] and mortars [36] a nanostructure modification of the cement matrix; this modification is partially responsible for the reduction to the penetration of aggressive agents through the matrix of GO-composites. Moreover, in [36] mortars with 0.01%wc of GO have shown a five-fold reduction in chloride penetration compared to the usual mortars. In [37] it is suggested that the layered structures of GO may also trap and reduce the ingress depth of chloride. At the same time, in [38] mortars with GO, after an exposure of 18 months in a carbonation chamber, have displayed a five-fold decrease in carbonation depth compared to standard mortar). Similar results are detected in [39] where the water penetration depth, chloride diffusion coefficient, and chloride migration in mortar with GNP are compared to the ones of usual mortar. Here, the experimental tests have demonstrated that the addition of 2.5% GNP can cause a significant decrease of 64%, 70% and 31% for water penetration depth, chloride diffusion coefficient, and chloride migration coefficients respectively. The reduced ions attack can be partially attributed to the reduction of the critical pore diameter of about 30%, as validated by mercury intrusion porosimetry (MIP) tests results. By increasing GNP, the durability in terms of water penetration resistance is higher in comparison to standard cement mortars [40].

3.2. Freeze-Thaw resistance variations and Thermal diffusivity

Another important aspect is the improvement of the freeze-thaw resistance by GO as shown in [41] where mortars containing 0.06%wc of GO have shown a weight loss of about 0.25% after 540 freeze-thaw cycles compared to that of a reference sample without GO of the 0.8%. The enhancement of freeze-thaw resistance by GO can be linked to the increase of nanopores over mesopores, because lower temperature is required to freeze the water in smaller pores [42]. Good results in terms of freeze-thaw resistance are widely discussed in [43], where samples with different additions of GNP are exposed to

200 freeze-fhaw cycles, About the thermal diffusivity, the use of GNS is valid in order to improve the inner heat dispersión, decreasing the effect of thermal cracking. In [44] experimental tests performed by Time-Domain Thermo-reflectance method exhibited the use of 5% and 10%wc of graphene increases the thermal diffusivity of the cement pastes by 25% and 75% in the first 44 hours.

4. CONCLUSIONS

The use of GO in cement paste or concrete can led to important improvements in terms of strength and durability, in particular combined with concrete it can allow to reduce the thickness of the new concrete parts in the replacement of the degraded ones. GO can be added without or with other elements discussed in Section 2 (i.e. SWCNTs, CNTs, CNFs, CFs, RAC). The most relevant results obtained from experimental tests are discussed in the references of the present paper. Summarizing the improvements (in percentage terms) with respect to the cementicious paste or to the mix design without graphene, the following results can be underlined. In cementicious paste: GNS combined to SWCNTs lead to an increase of 72% in flexural strenght, GNS combined to CNTs lead to an increase of 21% in compression strenght and 24% in flexural strenght, GNS combined to SiO_2 lead to an increase of about 30% in compression strenght. At the same time, the introduction of GNS in OPC matrix have shown an increase of about 35% in compression strenght, 37% in tensile strenght, while the contribution in flexural strenght is included in the range 41-59%. Important results are also obtained for GNS in UHPC, especially in terms of tensile strenght (increasing about 40-45%) while the contribution in compression strenght is negigleble (about 2.5-3.0%).On the contrary, GNS in NSC have shown significan improvements in terms of compression strenght (with results included in the 63÷86% range). Finally, in NSC, GNS combined to CNFs have shown the higher improvement in compression strenght (about 125%) and a significan tensile improvement (about 29%); if combined to RAC, GNS lead to a low increase in terms of compression strenght (included in the range 8-13%). GNS, especially in the form of GO and GNPs, shows positive influence on the durability and mechanical performance of different types of cement composites, including OPC. The ~~mechanica~~l reinforcement mechanisms are often associated with GNS' nucleation effects on cement hydration and with the capability to interlock different hydration products; the durability improvements, especially those one concerning the permeability to aggressive agents and freeze-thaw resistance, are attributed to GNS's ability tuning the matrix porosity, reducing the number of the larger pores while increasing the ones of nanopores. Neverthless, a challange in the use of GO in concrete is represented by the reproducibility of high quality and low-cost GNS at industrial scale. Clearly a deeper knowledge of these nanomaterials may foster the use of GNS in construction materials, but further tests are still required to make them widely accepted in the construction field.

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