Graphene Oxide as an Additive for Improving the Strength of Cemented Composites

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ABSTRACT: This research explores the feasibility of using graphene oxide (GO) as an additive to improve cementitious composite strength. A cement composite was tested for its compressive strength and pore structure, where 0.025wt percent of cement unit weight was substituted by GO. The optimal replacement ratio was previously defined as this. Comparative studies were performed on cement composites substituted with standard cement additives such as fly ash (FA), silica fume (SF), Nano-silica (NS) and ground granulated blast-furnace slag (GGBS). The cementitious composites substituted with GO had a slightly lower air content, but had compressive strength which was 10.6–41.5 percent higher than that of the plain mixture, and also higher than that obtained with other cement additives. The toughness and mechanical properties of hardened cement composites can be improved by improving the structure and enhancing the cement matrix's paste – aggregate interface; this is usually accomplished with additives and admixtures. Analysis of the Pore structure showed that most pores were microspores with diameters not exceeding 2.5 nm; this improved the strength.

KEYWORDS: Mechanical property, Cement additives, Composites, Graphene oxide, Pozzolan, Strength.

INTRODUCTION

In cementitious composites the interfacial transition zone (ITZ) between cement paste and aggregates is reduced in particles, leading to more pores and lower power. The ITZ contains comparatively more calcium hydroxide ($Ca(OH)_2$) compared to aggregates and the mass-hydrated cement paste, the two main components of cement composites [1]. Despite its wide size, $Ca(OH)_2$ has weaker bonding strength than calcium silicate hydrates (C – S – H), as well as a strong propensity to horizontally orientate at the aggregate surface, which makes the cementitious composites vulnerable to cracking. Therefore, due to its larger pore volume and directed $Ca(OH)_2$ crystals, the ITZ is considered to be the weak link in cemented composites, in terms of mechanical properties and toughness [2].

The toughness and mechanical properties of hardened cement composites can be improved by improving the structure and enhancing the cement matrix's paste – aggregate interface; this is usually accomplished with additives and admixtures [3]. The most effective approach for enhancing the properties of cementitious composites is to densify the ITZ, which occupies 20–40 percent of the total volume of the cementious matrix. For this cause, fly ash (FA), ground granulated blast-furnace slag (GGBS), silica fume (SF) and natural pozzolans are materials that boost the properties of the hardened cementitious composite by hydraulic or pozzolanic operation, or both, when used in combination with Portland or blended cement.

Pozzolans usually exhibit smaller particle size, which helps them to serve as fillers and thus lead to increased strength through the pozzolanic reaction, i.e. $Ca(OH)_2$ consumption to create secondary C – S – H. In addition, nanosilica (NS), which follows the same mechanism of reaction, directly affects the mechanical properties and toughness of cementitious composites due to its improved pozzolanic reactivity, and the effects of packing and seeding [4]. The GGBS, which exhibits hydraulic activity, reacts with $Ca(OH)_2$ formed during cement hydration to produce a C – S – H and AFm phase slag hydration substance. Thus, in the absence of ample water, pozzolans and slag, which are used for strengthening to improve the efficiency of cementitious composites, serve as fillers or as agents for densifying the ITZ by consuming $Ca(OH)_2$. Extensive work has focused on improving cementitious composites performance by incorporating carbon allotropes, specifically carbon nanotubes and graphene. Graphene oxide (GO), a two-dimensional (2D) reinforcing nanomaterial made up of carbon atoms sp2-bonded, exhibits excellent mechanical properties [5–7]. In addition to this, functionalized GO applied to cement composites increases dispersion and thus accelerates the hydration of cement particles. Hydration materials have a more compact structure that improves mechanical properties and resistance. This thesis explored the possibility of using GO as an additive to increase the compressive strength of cemented composites. Specifically, a cement composite having 0.025 wt percent of the unit weight of cement substituted with GO was investigated for workability, compressive strength and pore structure. This optimum replacement ratio has been established before. Comparison with cementitious composites including pozzolans and GGBS, which are traditional cement additives, further evaluated the efficacy of GO as an additive.

EXPERIMENTAL

Materials and mix proportions:

Graphene oxide

The experiments used a Powdered GO in figure 1. The typical nano-sheet measurements were 30μm in the lateral dimension, and 1.2 nm in the direction of thickness. The principal functional group on the surface was the hydroxyl group (–OH).

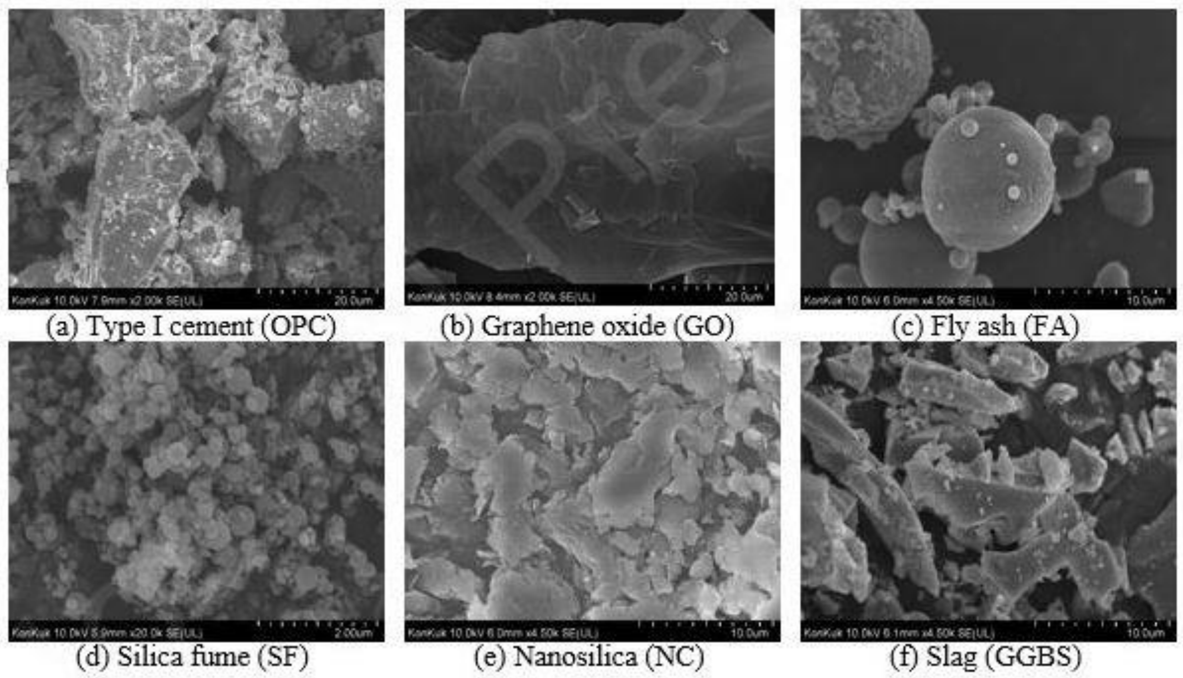
(a) Type I cement (OPC) (b) Graphene oxide (GO) (c) Fly ash (FA)
(d) Silica fume (SF) (e) Nanosilica (NC) (f) Slag (GGBS)

Figure 1. Particle Shapes Observed By Scanning Electron Microscopy.

Pozzolans and slag

As cement admixtures, FA, GGBS, SF and NS strengthen the properties of hardened cement composites, or both, by hydraulic or pozzolanic activity. Accordingly, this study used FA SF, NS and GGBS to determine GO's usefulness as a reinforcement for cementitious composites. Figure 1 presents scanning electron microscopy (SEM) images of pozzolans, slag and GO, and Figure 2 shows the difference in volume between samples with the same mass with 0.5 g.

Figure 2. Differences in Volume among Samples with the Same Amount (5 G) Of Additive.

Cement and aggregates

The tests used Type I ordinary Portland cement with a specific gravity of 3.15, fine sand aggregate with a specific gravity of 2.62 and a fine module of 2.90, and crushed stone aggregate with a specific gravity of 2.58 and a maximum size of 25 mm.

Mix proportions

This study examined the workability and mechanical properties of cementitious composites containing GO in relation to the pore structure. The performance of cementitious composites containing traditional FA, SF, NS, and GGBS additives was evaluated in order to determine the merit of using GO as cement strengthening [8]. The cemented composite was 28 days old, with a component strength of 24 MPa. The experiments used the optimal GO replacement ratio (0.025wt per cent) previously identified. Replacement ratios of FA, SF, NS, and GGBS were used at 20, 10, 0.0025, and 50wt percent of cement unit weight, respectively [6]–[8]. Different quantities of polycarboxylate-based high-range water-reducing admixture (PC-based HWRA) were integrated into each mixture to achieve the desired workability of 120 ± 20 mm for slump, and 2.0 ± 1.0 per cent for air content. No air-training agent was applied, so there was only air trapped by the cement matrix.

Compressive strength

The compressive strength calculated in accordance with the ASTM C109 standard was used to determine the mechanical efficiency of GO-reinforced cementitious composites. In a regulated setting, a cylindrical specimen (diameter: 100 mm; length: 200 mm) was prepared and initially cured for 24 h (room temperature, 23 ± 2 ° C; relative humidity, 50 ± 5 per cent). It was then isothermally demoulded and cured under water (23 ± 2 ° C) until day 28. For three separate specimens, the compressive strength of completely cured GO-reinforced cementitious composites was measured twice; the mean value is stated [9].

Pore distributions

GO-reinforced cementitious composite pore distributions were used to determine the relationship between the porosity of the cement matrix and the strength of the composite. Higher porosity indicates a less dense internal structure which results in a lower resistance. The durability of concrete, particularly reinforced concrete, can be adversely affected by environmentally harmful substances that penetrate through pores [10] . Research used a method of nitrogen adsorption to determine specimen's specific surface area, and distribution of pore size and volume. Samples (2 g) from specimens tested for compressive strength were collected on Day 28. Until adsorption of nitrogen gas the specimens were conditioned under vacuum at 200 ± 5 ° C for 4 h to eliminate any impurities and residual water [11].

RESULTS AND DISCUSSION

Workability:

In order to assess the workability of cemented composites reinforced with GO, pozzolans, and GGBS, the slump and air content were measured according to the ASTM standard. PC-based HWRA was used to achieve the cementitious composites target workability of 120 ± 20 mm for slump and 2.0 ± 1.0 per cent for air content. The PC-based HWRA's average concentration was 1.0wt per cent per unit weight of cement, which was adequate for the plain mixture to achieve the desired workability. Figure 3 contrasts the workability of the plain mixture with cementitious composites that contain the various slump and air content additives. The shaded component for each mixture reflects the target range of workability. For the plain mix that did not contain cement additives, PC-based HWRA was adequate at 1wt per cent of cement unit weight to achieve the target workability; this mixture had 10 mm slump and 2.8 per cent air content.

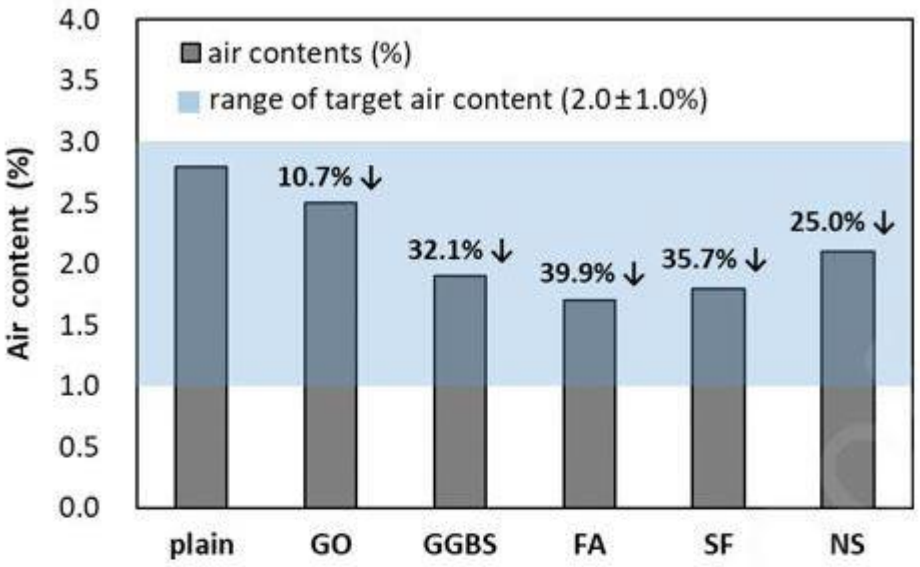

Figure 3. Workability as function of additive.

Compared to the plain mixture, the GO-reinforced mixture displayed decreased workability even when the maximum admixture content of 1.0wt percent of cement unit weight was used; the 75 mm slump was lower, 31.8 percent, and did not reach the target value. GO's adsorption of free water is related to that consequence. The hydroxyl group (–OH), the main functional group of GO and responsible for its strong dispersion in cementitious composites, and the high surface area (which requires a large amount of water for particle lubrication), result in insufficient free water within the cement matrix.

In addition, Flocks of GO – cement particles adsorb free water. The amount of free water inside the cement matrix influences cementitious composite rheological properties. Increases interparticle friction, decreases fluidity and increases viscosity and strength of yield; this leads to poorer workability. GO-reinforced cement composite air content was 2.5 percent, which was 10.7 percent lower than the simple mixture and within the target range. The GO acting as a surfactant that encouraged the creation of voids is due to this reduced air material. It is known that GO refines the structure of the pore and increases gel porosity significantly.

The slump and air content of the pozzolan and slag-containing mixtures as cement additives were lower than that of the plain mixture, but were still within the target range. The NS mixture slump was 9.09 per cent higher than the plain mixture; this is in contrast to the GO mixture, which displayed a slightly lower slump than the plain mix. The NS combination indicates a higher decrease in air content; 32.1 percent in FA, 39.9 percent in SF, 32.1 percent in air content in GGBS. This result is due to the packing result of particles smaller than cement particles filling the pores within the cement matrix, given that the replacement levels of GGBS and pozzolans other than NS were substantially higher than those of GO (400–2000 times). The spherical FA particles (Figure 1(c)) serve as ball-bearings inside the cement matrix and bind to the cement particles, thereby providing an effect that reduces the water. This helps the cementitious composite with just a small amount of admixture to reach the desired workability.

The SF mixture, containing the same amount of admixture as the plain mixture, showed decreased workability, i.e. 9.09% for slump and 35.7% for air material. The SF particles were spherical, identical to the FA particles (Figure 1(d)). The variation in reactivity was due to the disparity in the specific area; SF has the greater specific area of 20 m2/g. Thus, SF reacted quickly with Ca $(OH)_2$ within the cement matrix, forming a C – S – H gel which increased the viscosity of the cement matrix and reduced the workability. In this reaction, however, the C – S – H formed was much more crystalline than that inside the cement paste which promoted strength. Through adding the admixture at 0.8wt per cent of cement unit weight, the desired workability was achieved with the NS mixture. Nano-sized pozzolans consist mainly of SiO2, which is similar to SF, and share the same mechanism of reaction with cement particles. Nevertheless, because of their particle size, they have comparatively greater reactivity [32, 43–46]. It explains the NS mixture's greater workability relative to the simple and SF mixture, also at a lower substitution ratio.

Compressive strength:

After 28 days all the cement composites containing the cement additives achieved the compressive strength of the product. Figure 4 compares the different mixtures to a simple one. The GO mixture's mean compressive intensity was 48.1 MPa, 7.60 per cent higher than the simple mixture. This progress was credited in early stages to the rapid hydration of cement particles due to nucleation and the filling effect of 2D GO particles nano-sized. The GO-reinforced cementitious composite pore structure was more closed than the simple mixture. Research assume this feature improved the transfer of load between particles and resulted in the observed increase in compressive force.

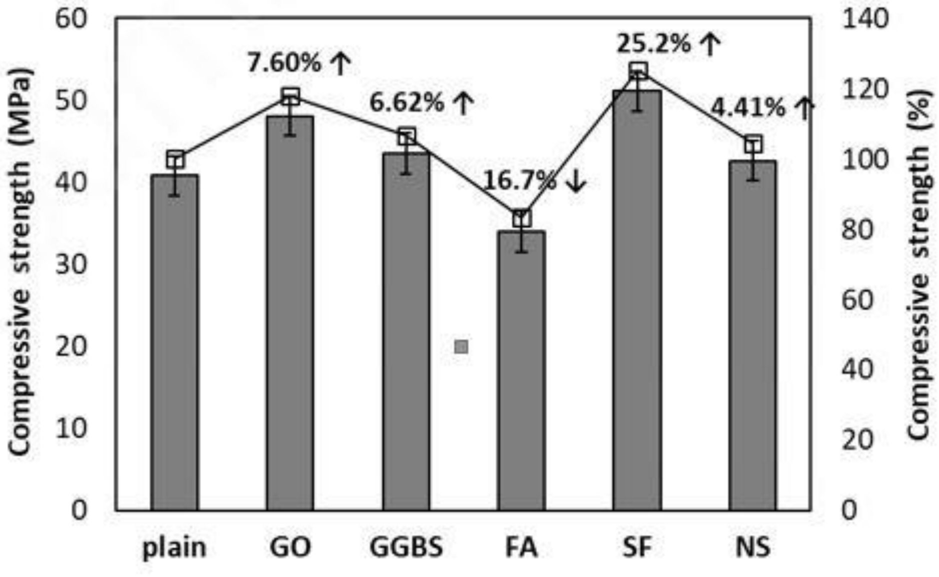

Figure 4. Compressive Strength at 28 Days as a Function of Additive.

The higher strength of cements reinforced by GGBS and FA is the product of the pozzolanic reaction caused by the $Ca(OH)_2$ produced from cement hydration. This reaction mechanism, however, postpones the reaction with $Ca(OH)_2$ until the hydration of cement starts which reduces the strength relative to that of the plain mixture. This explains why the FA mixtures mean compressive intensity was 34.0 MPa, which is 16.7 per cent lower than that of the plain mixture. The GGBS mixture displayed a mean 43.5 MPa compressive strength which is 6.62 percent higher than that of the plain mixture. With a latent hydraulic property, in the presence of $Ca(OH)_2$ GGBS hydrates and sets in the same manner as FA. While FA and GGBS share similar characteristics, compressive strength is improved by the latter because it contains at least 75% more calcium than other pozzolans. The free lime (CaO) increased reactivity for relatively rapid GGBS hydration, and ultimately increased energy.

The SF mixture displayed the highest compressive strength of 51.1 MPa, 25.2 percent higher than that of the plain mixture; as stated above, it was responsible for the positive effect of the crystalline C – S – H created at the initial stage by the small specific surface of SF. The micro-filler effect, due to the small spherical particles and the pozzolanic mechanism whereby $Ca(OH)_2$ was consumed, transformed large pores

(≥ 0.1µm) into small micro pores. It increased the bonding within the cement matrix between the aggregate and the binder at the ITZ, and strengthened the strength of the cement composite. The NS mixture, which adopted the same mechanism of reaction, exhibited a mean compressive force of 42.6 MPa, which is 4.41 percent higher than that of the plain mixture. The substitution ratio for NS, however, was very small, so it is not possible to assume that a filler effect comparable to that for SF had occurred. The nano-sized NS particles, instead, absorbed Ca2 + ions on the surface before pozzolanic reactions started. This speeded up the hydration of cement particles and resulted in improved compressive strength. To achieve the desired workability, the admixture was integrated in the higher-replacement ratio GGBS and FA mixture at 0.6 and 0.8wt percent, respectively. Content segregation occurred when 1wt per cent of cement unit weight was used, the quantity contained in the simple mixture. This is demonstrated by the surface characteristics of GGBS: When GGBS particles touch water, an impermeable acid film forms. Within the cement paste, the GGBS particles have a smooth and compact coating that only partially absorbs water and therefore strongly affects viscosity.

Pore structure:

Nitrogen adsorption method was used to assess the pore size distributions of the specimens fully cured for 28 days. No pore with a radius of 2 nm or less was observed in the plain mixture free of cement additives, while certain pores formed the majority of the pores observed in the GO, pozzolans and GGBS-reinforced mixtures. The pore radii is as follows: for plain 8.282 nm, for GO 1.879 nm, for GGBS 1.681 nm, for FA 1.681 nm, for SF 1.683 nm and for NS 1.889 nm. Pores smaller than 2 mm are known as microporous. The distributions for the pore size are shown in Figure 5.

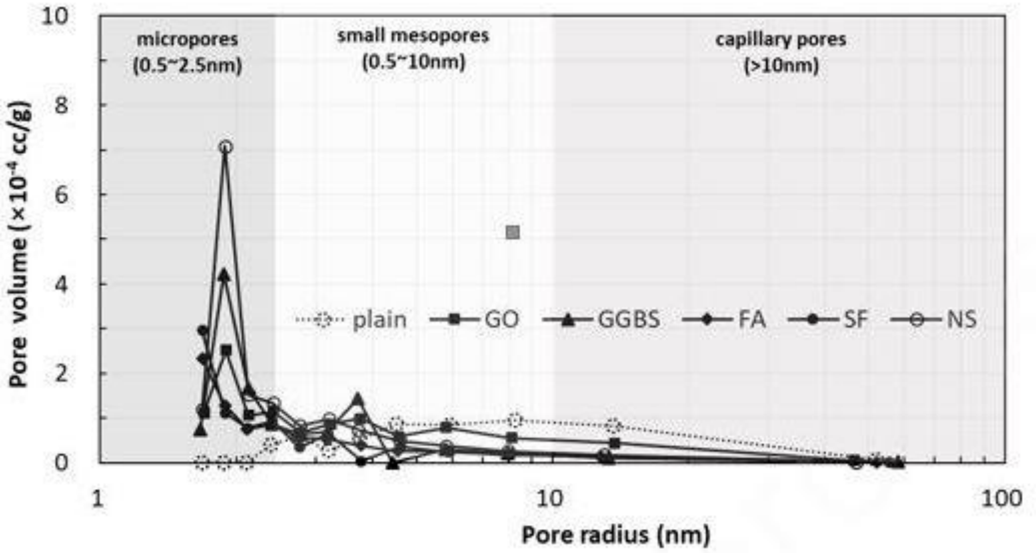

Figure 5. Pore Size Distributions.

For cement additives which contain particles smaller than cement particles, a physical filler effect is observed. The fine particles occupy spaces between the coarser particles of cement and thus increase the density. This filler effect may be responsible for the higher strength of the finer pozzolans, GGBS and NS weighed. Notably, nano-scale GO particles have been shown to fill pores into micro- and nano-sized pores within the cement matrix and to refine meso-sized pores. Research verified that pores smaller than 2 nm, free from cement additives, were not present in the simple mixture. Figure 6 shows how distributions of pore sizes have shifted. Approximately 98 per cent of the total volume of the basic mixture, free of cement additives, consisted of pores 2.5 nm or greater.

For cement-reinforced mixtures, 65.7–88.4 percent of the pore volume consisted of pores 2.5 nm or larger, but pores smaller than 2.5 nm (micropores) were 5.52 to 16.3 times greater. This explains the positive effect on compressive strength: cement additives of micro or nano size filled the voids produced by the meso-sized or larger pores, which decreased the voids to micropores. The FA mixtures' higher micro- and capillary pore volumes explain why they had less compressive power than the mixtures made with the other cement additives.

CONCLUSION

This research aimed at the feasibility of using GO as an additive for enhancing the compressive strength of cemented composites. The workability, compressive strength, and pore structure of a cement composite for which some of the cement was substituted with GO was calculated, and compared to those of cement composites containing pozzolans and GGBS (conventional cement additives). The studies conclusions are as follows:

1. Cementitious composites comprising PC-based HWRA met the criteria for workability of 120 ± 20 mm for slump and 2.0 ± 1.0 percent for air. However, the GO-containing combination had a 31.8 percent lower downturn than that of the regular mix. It is due to the GO's adsorption of free water within the cement matrix, which increased interparticle friction and subsequently decreased workability.

2. After 28 days all the cemented composites met the compressive strength of construction. The GO-reinforced mixture's compressive strength was 10.6–41.5 per cent higher than the mixtures containing slag and other pozzolans, except SF. This indicated that GO is an important additive for improving the compressive strength of cemented composites.

3. Using the nitrogen adsorption method, Pore structure was evaluated to better understand the different compressive strengths with GO, pozzolans and slags. No pores with 2.5 nm or lower radii were present in the plain mixture free of cement additives, while pores with 2.5 nm or lower radii represented the majority of pores found in the GO-, pozzolan- and GGBS-reinforced mixtures. Micro- or nano-sized cement additives filled the voids produced by the mesosized or larger pores, which decreased their size to micropores and thus increased the compressive force.

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