Effect of reduced graphene oxide on the mechanical properties of concrete

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Abstract. Reduced Graphene oxide (rGO) is a 2D nanoplane fiber that contains highly reactive hydroxyl, epoxide, carboxyl, and carbonyl functional groups. These oxygen bearing functional groups increases solubility in cement matrix and serve as a nucleation agent for C-S-H crystals. rGO can serve as a reinforcing material in cement composites and can improve the mechanical properties of cement-based materials. This paper presents the mechanical properties of concrete modified with 0.03%, 0.05% and 0.07% reduced graphene oxide by the weight of the OPC. Compressive strength of concrete was found to be increased by rGO especially the early age strength due the hydration acceleration and reinforcement of cement matrix and strong adhesion between aggregate and cement matrix by rGO. The mechanical properties, compressive strength, split tensile strength, flexural strength and modulus of elasticity are found to be maximum at 0.05% rGO replacement by the weight of the cement. The properties were found to be decreased at 0.07% of rGO content due to the formation of the agglomerated structure and poor dispersion of rGO.

Keywords: Reduced graphene oxide, mechanical properties, agglomerated structure

1. Introduction

Ordinary Portland Cement (OPC) is the most commonly used building and construction material worldwide. Cement is the principal binder holding the aggregates together to produce concrete in the presence of water for hydration. As an engineered material, concrete composites are desired for their excellent compressive strength. The major disadvantage of concrete is its brittle nature due to its poor resistance to crack formation, low tensile strength and strain capacities. Researchers have made various attempts to enhance the properties of cement composites by adding admixtures, supplementary cementitious materials and fibers.

Recent advances in nanotechnology have produced nanosized materials that have been used to improve mechanical properties and durability of cementitious materials, such as hindering the initiation and propagation of microcrack [1]. Nanomaterials having self cleansing ability, air pollution reduction and bactericidal capacity such as TiO₂ can be utilized in cementitious materials to improve their properties. Nanotechnology has the potential to be the key to a brand new world in the field of construction and building materials. Sanchez and Sobolev [2] described concrete as a nanostructured,
multi-phase composite, that composed of an amorphous phase, nanometer to micrometer size crystals, and bound water. The amorphous phase, calcium–silicate–hydrate (C–S–H) is the “glue” that holds concrete together and is itself a nanomaterial [2]. Sanchez and Sobolev [3] defined nanotechnology in concrete as the science deals with the measurement and characterization of the nano and microscale structure of cement-based materials to better understand how this structure affects macroscopic properties and performance through the use of advanced characterization techniques and atomistic or molecular level modelling.

There have been many recent studies on newly produced nanomaterials such as nanosilica, nanotitanium oxide, nanoiron oxide, carbon nanotubes (CNTs) and graphene oxide (GO) sheets. These nanomaterials may be classified according to their shape or morphology: zero-dimensional (0D) particles, one-dimensional (1D) fibers and two-dimensional (2D) sheets. Nanomaterials are treasured for their large surface areas that can be exploited for reaction with cement paste. Unlike 0D nanoparticles, 1D fibers and 2D sheets behave as reinforcing materials to bridge cracks [4]. Compared with traditional fibers, nanoscale fibers can offer several distinct advantages, namely, higher strength and stiffness, higher aspect ratio, and smaller fiber spacing, that allow them to better prohibit or hinder the development of cracks at the nanoscale level.

Graphene oxide (GO) is a graphene based material, having a hexagonal network of carbon atoms with sp² and sp³ hybridized orbitals consisting of hydroxyl and epoxide groups on its basal plane, and carbonyl and carboxyl groups on the edges. These functional groups assist such nanosheets to effectively disperse in water due to electrostatic stabilisation. Besides, its addition reduces the need for the use of surfactants in the cementitious matrix, which are typically added to prevent nanomaterials agglomeration caused by van der Waals' forces of attraction [5]. Reduced graphene oxide (rGO) has less functional groups in its structure as compared to GO [6]. Figure 1 represents rGO.

Graphene oxide is synthesized from natural graphite using the modified Hummers method. The process involves three steps, i.e. oxidation, purification, and exfoliation. GO is synthesized by treating graphite powder with H₃PO₄, H₂SO₄ and high quantity of KMnO₄. Horszczaruk et al. [7] presented a brief description of the oxidation of graphite flakes to synthesize GO using modified Hummers method. To a mixture of KMnO₄, graphite concentrated sulphuric acid and orthophosphoric acid are poured. It is then stirred for 24 h and heated to 50 °C. The resulting mixture is added to H₂O₂ (30%) and centrifuged. The separated solid product is washed with water, HCl and ethanol and kept for 12 h at 70 °C.

1.1 Effect on workability and mechanical properties

From the literatures it can be found that addition of GO decreased the workability of cement composites. Its adverse effect can be reduced by adding a polycarboxylate based superplasticizer [3]. To improve the dispersibility of GO in cement composite GO can be added with the water to the dry mix after sonication. Gong et al. [8] reported that addition of 0.03% GO lowered the workability by 34.6% than plain concrete. Wang et al. [9] studied the effect of GO on the fluidity of cement pastes at two dosages, 0.01 and 0.03 wt% of cement and found that fluidity decreases by 10.8% and 36.9 %, respectively. When GO dispersion is added to the cement matrix, a flocculation structure is formed, which is attributed to its high specific surface area and abundant oxygen-containing functional groups.
The agglomerated structure wraps a part of the mixed water and reduce the actual amount of mixed water. Also the large volume of agglomerated particles in the cement paste increases the internal friction. The combination of these two factors leads to the reduction of the paste workability [9]. Li et al. [10] also reported that Incorporation of GO reduces the workability of cement paste, due to the formation of GO agglomerates by chemical cross-linking of GO nanosheets by calcium cations.

Li et al. [11] studied the effect of GO on the early age hydration of cement pastes and found that cement hydration was accelerated. In addition to the effect of the fine GO particle size, the accelerated cement hydration might also be attributed to the increased concentration of CH in solution due to increased C3S reaction. Lv et al. [12] investigated the influence of GO nanosheets on the microstructure and mechanical properties of cement composites were investigated and reported that GO nanosheets can regulate to form flower-like hydration crystals and tensile, flexural and compressive strength of cement composites have distinctly enhanced.

Recent researches have reported that GO exhibits a high tensile strength and aspect ratio and a large surface area. Its extraordinary mechanical properties, combined with an effective dispersibility in water and inexpensive source, can make GO a promising material for enhancing the mechanical properties of composites [3]. The addition of a small percentage of the GO particles can greatly enhance the compressive strength of mortar specimens. The size of graphene nanoparticles and the functional groups of graphene oxides play important roles in the strength improvement [13].

Li et al. [14] evaluated the effect of GO on the compressive strength of cement pastes with GO dosages of 0.02, 0.04, 0.06, and 0.08% at 28 days. The compressive strengths of cement pastes incorporating 0.02, 0.04, 0.06, and 0.08% were greatly enhanced by 42.3, 43.4, 48.5, and 56.3%, respectively. The increase in compressive strength of the GO-cement pastes is more likely due to the greater contribution of the cement hydration acceleration effect and the strong interfacial adhesion between GO and the cement paste.

Gong et al. [8] reported that the introduction of 0.03% by weight GO sheets into the cement paste can increase the compressive strength and tensile strength of the cement composite by more than 40% due to the reduction of the pore structure of the cement paste. Pan et al. [3] reported an enhancement of compressive strength by 15–33% and flexural strength by 41–59% by the addition of 0.05% GO. It can be because of the outstanding reinforcement of the cement matrix provided by the GO nanosheets by the strong interfacial adhesion between GO and cement matrix. GO sheets prevents the in-plane propagation of micro cracks. Horszczaruk et al. [7] reported that graphene oxide additive in the amount of 3% by the weight of cement results in significant enhancement of Young’s modulus. Li et al. [10] found that 0.03% GO as the threshold content below which GO has no significance influence on the compressive strength of cement paste. Chu et al. [4] reported that the compressive strength and splitting tensile strength of sacrificial concrete were increased by 12.98–25.36% and 8.66–34.38 when adding 0.1 wt% graphene sulfonate nanosheets at elevated temperature.

GO exhibits better reinforcement effect and improve the mechanical properties than other nanomaterials. Murugan et al. [15] investigated the impact of rGO on the properties of OPC paste in comparison to aluminium oxide nanopowder and colloidal silicon dioxide nanoparticles. The overall results suggested that the performance of rGO was better than that of other nanomaterials, despite the significantly lower amounts that were used in the paste. Mohammed et al. [16] reported that mortars with 0.01% GO presented a five-fold reduction in chloride penetration compared to plain mortars and also the addition of 0.03% GO in mortars decreased their initial water sorptivity ratio from 0.00046 to 0.00020 mm s$^{-1/2}$. They suggested that the layered structures of GO may also trap and reduce the chloride ingestion depth.

2. Experimental programme

2.1 Materials
Ordinary Portland cement of 53 grade and manufactured by Coromandelel was used for the experimental work. rGO in the form of powder was supplied by Adnano Technologies Private
Limited, Shimoga, Karnataka. Properties of rGO given by the manufacturer are presented in Table 1. The Scanning Electron Microscopy (SEM) image and X-Ray Diffraction spectroscopy of rGO provided by manufacturer is shown in Figure 2 and Figure 3 respectively.

| Parameters                  | Description |
|-----------------------------|-------------|
| Purity                      | > 99%       |
| Number of layers            | 1-3 layers  |
| Average thickness           | 1-4 nm      |
| Average lateral dimension   | 5-10 µm     |
| Surface area                | ~220 m²/g   |

Figure 2. SEM image of rGO

Figure 3. XRD Spectroscopy of rGO

2.2 Mixing and casting
Test specimens of four mixes of concrete with a water to cement ratio of 0.43 were prepared. Three mixes was incorporated with 0.03, 0.05 and 0.07% of rGO by the weight of the cement. The other mix was plain cement concrete of grade 30 that serves as the control mix. rGO was added to the dry mix with the required amount of water after sonification. rGO was added in the form of solution to improve the dispersibility of rGO in the cement matrix. An ultrasonicator producing a sound energy of 40kHz and having a capacity of 3L was used to prepare the rGO solution. The solution was sonicated for 30 minutes till a homogeneous solution was obtained.

2.3 Mechanical property tests
For the current study slump test and compacting factor test was used to study the workability of concrete. The compression test was carried out on cubical specimens of 15cm x 15cm x 15cm size using a compression testing machine of 3000KN capacity. The test was done for all the four mixes for determining 3rd day, 7th day and 28th day compressive strength. The split tensile strength test is an indirect test used for determining the tensile strength of concrete. Test was carried out on cylindrical specimens of size 150mm diameter and 300mm height in a compression testing machine of 3000KN capacity. Flexural strength is one measure of the tensile strength of concrete. Beam tests are the most dependable tests to measure the flexural strength of concrete. It is a measure of an unreinforced concrete beam to resist failure in bending. The test was conducted on beam specimen of size 100mm x 100mm x100mm in flexure testing machine of 100KN capacity. Two point loading test was conducted as per IS 516:1959 specification. Modulus of elasticity of four mixes were determined by subjecting cylindrical specimen of size 150mm diameter and 300mm height to uniaxial compression and measuring deformations by means of dial gauge fixed between 150mm gauge length. The test was carried out as per IS 516: 1959 in a compression testing machine of 3000KN capacity.
3. Results and discussions

3.1 Workability
Workability of fresh concrete was assessed by slump test and compacting factor test. The values obtained for the four mixes are given in Table 2. From the test results it can be identified that addition of rGO reduced the workability of concrete. Low workability was found for mix with high rGO content. It is due to the formation of the flocculation structure formed by the addition of rGO. During the mixing of rGO dispersion with the dry mix a flocculation structure is formed due to the large surface area of rGO and the oxygen containing functional groups. The agglomerated particles wraps a part of the mixing water and thereby reduces the actual amount of water in the concrete. Also the agglomerated particles in the cement matrix increases the internal friction. Even though the slump and compacting factor were less it was within the safe limit. So the mix was able to cast into the mould. No superplasticizer was used to improve the workability.

Table 2. Properties of fresh concrete

| Mix | Slump (mm) | Compacting factor |
|-----|------------|-------------------|
| rGO0 | 90         | 0.9               |
| rGO1 | 40         | 0.85              |
| rGO2 | 25         | 0.83              |
| rGO3 | -          | 0.8               |

3.2 Compressive strength, split tensile strength and flexural strength
The 3 day, 7 day and 28 day compressive strength, split tensile strength and flexural strength of all the four mixes are shown in Figure 4. From the results it can be found that addition of rGO improved the compressive strength of concrete, especially the early age compressive strength. An increase in compressive strength was found up to 0.05% rGO addition. The strength was found to be decreased for mix with 0.07% rGO content. rGO can fills the voids in the cement matrix. Due to the large surface area and functional groups the hydration reaction of the cement matrix is accelerated and the formation of C-S-H crystal is enhanced. Reinforcement of the cement matrix also improved by the rGO nanosheets due to the strong interfacial adhesion between rGO and cement matrix. Also the adhesion between the cement matrix and aggregates also improved. This hydration acceleration and better reinforcement effect provided by rGO is the reason for strength improvement.

![Figure 4. Effect of rGO on the compressive strength of concrete](image-url)
The strength of the concrete also depends on the age of concrete due to ongoing hydration of cement. The effect of aging on the strength of concrete modified with rGO was studied and found that the compressive strength at 3rd, 7th and 28th day was higher than plain cement concrete. The 3rd day compressive strength of rGO modified concrete was found to be increased by 100-113% than plain cement concrete. Percentage increase was decreased at 7th day and 28th day strength. It was due to the acceleration of hydration reaction. For the rGO mix the expected design strength was obtained at the early age itself. At higher concentrations the formation of agglomerated structure increases, it reduced the compressive strength of rGO3 mix. Poor dispersion of rGO can be another reason.

**Table 3. Mechanical properties of concrete**

| Mix   | Split tensile strength(N/mm²) | Flexural strength (N/mm²) | Modulus of elasticity (N/mm²) |
|-------|------------------------------|---------------------------|-----------------------------|
| rGO0  | 2.71                         | 5                         | 33                          |
| rGO1  | 2.88                         | 6                         | 37                          |
| rGO2  | 3.07                         | 6.8                       | 39                          |
| rGO3  | 2.85                         | 5.7                       | 34                          |

Figure 5 shows the split tensile strength values of concrete specimens after 28 days. From the results it can be found that addition of rGO improved the split tensile of concrete. Highest value was found for concrete with 0.05% rGO content. The improvement in strength was due to the mechanical interlocking and reinforcement effect provided by the rGO. As the weight fraction of rGO was low the percentage increase in strength was only 5% to 13%. Even though the increase in strength was small, all the three rGO modified mixes shows higher strength compared to plain cement concrete. The decrease in strength at 0.07% rGO content may be due to the formation of agglomerated structure and poor dispersion of rGO.

The flexural strength of the four mixes after 28 days of water curing is given in Figure 6. From the results it was found that rGO improved the flexural strength of the concrete by 14% - 36%. A small weight fraction of rGO improved the flexural strength very effectively. The highest strength was found for rGO2 mix which contains 0.05% rGO. The carboxylic acid groups of rGO react with C-S-H of cement matrix and form strong covalent bond. Also the strong adhesion between the rGO and cement matrix provide a reinforcement effect to the cement matrix. These may be the reasons for enhancement of flexural strength of concrete by rGO. As in the case of compressive strength and split tensile strength flexural strength also decreased at high rGO content that is at 0.07%.
The results show that addition of rGO increased the modulus of elasticity of plain cement concrete by 3-18%. That means for the same load value rGO decreased the deformation of concrete compared to plain cement concrete. The highest value was obtained for rGO mix with 0.05% rGO content. The increase in the values can be attributed to the fact that rGO fills the voids in the cement matrix and reinforces the concrete mix. It reduces the formation of microcracks and loss of strength of the concrete. It was also found that high rGO content has less effect on modulus of concrete. The percentage increase in modulus of elasticity at 0.07% rGO content was very less. It may be due to the poor dispersion of rGO due to the increase in the formation of agglomerated structure at high concentration. So the reinforcement effect will not be same throughout the concrete.

4. Conclusions
Following conclusions are made from the comparison of properties of plain cement concrete and rGO modified concrete.

- Workability of rGO modified concrete was less than the plain cement concrete. Workability was found to be reduced by increasing the rGO content and can be attributed to the formation of agglomerated structure.
- Compressive strength of concrete was found to be increased by rGO especially the early age strength. 3 day strength was increased by 100-113%. The increased strength was due the hydration acceleration and reinforcement of cement matrix by rGO.
- The mechanical properties, compressive strength, split tensile strength, flexural strength, modulus of elasticity and impact resistance are found to be maximum at 0.05% rGO replacement by the weight of the cement. The properties were found to be decreased at 0.07%
of rGO content. It can be due to the formation of the agglomerated structure and poor dispersion of rGO.

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