Property assessment of concretes with graphene oxide mixed cement

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Abstract. In the present study a number of properties of concrete samples are evaluated, in which, graphene oxide nanomaterial is mixed with ordinary Portland cement. Workability, compressive strength, flexural (tensile) strength, modulus of elasticity and chemical resistance to acidic environments of concrete samples, in which graphene oxide with weight ratios of 0.025% and 0.05% are added to ordinary Portland cement, are assessed and compared with plain concrete. This study shows that adding graphene oxide improves the compressive and flexural strength of concrete samples, while decreases their workability. It is found that the addition of graphene oxide slightly increases the modulus of elasticity of concrete samples. In 5% hydrochloric and sulphuric acid solutions, samples with graphene oxide exhibit less mass loss at the age of 84 days, which suggests better resistance to acidic environments and durability for these types of concretes.

1. Introduction

Advances in construction technology put new demands on the properties of concrete. Therefore, in addition to main ingredients of concrete (i.e. cement, water and aggregates), admixtures are frequently used in mix designs, to improve and tailor concrete properties toward desired functions. These materials can provide concretes with properties that cannot be achieved by ordinary Portland cement (OPC) [1].

Nanotechnology is the science of tailoring materials’ structures at atomic scale so that the desired properties at macro scale to be achieved [2, 3]. Together with advances in nanotechnology, nanomaterials have been introduced into the cement and concrete technologies with the aim at improving their properties. Effects of nanomaterials, in forms of nanoparticles, nanotubes, and nanofibres have been extensively examined in the concrete technology. The research on the application of nanotechnology in the cement industry has been reflected in several review papers [1, 4, 5].

Graphene oxide (GO) is a type of nanomaterial which is known for its extraordinary electrical, mechanical and thermal properties and has been studied for applications in cement industry [4, 6]. GO consists of a hexagonal carbon network with oxygen-containing functional groups. Single layer GO is usually manufactured using Hummers modified method [7]. The particle size of GO is smaller by four orders of magnitude than OPC. In contrary to the other forms of carbon nanomaterials, GO is hydrophilic and is highly dispersible in water [8, 9]. GO, with two-dimensional atomic structure, provides a large surface with high quality connection with calcium silicate hydrate (C–S–H) phases of OPC and in this respect has some superiority to other forms of carbon-based nanomaterials such as...
carbon nanotube (CNT) [10, 11]. Presence of oxygen functional groups in GO reduces its elastic modulus and tensile strength in comparison with pure graphene [12]. Even though, the elastic modulus of GO ranges between 23 to 42 GPa and its tensile strength is around 130 MPa, which are still much higher than that of the cement matrix [13, 14].

One of the critical aspects of using any admixture in concrete is the control of hydration rate. It is known that nanomaterials generally decrease the setting time and increase the hydration rate of OPC [15, 16]. Oxygen functional groups of GO are the locations that have high reactivity with water and produce hardened phases at higher rates [11]. In addition to accelerated hydration, GO has a greater inclination towards adsorption of water onto its surface. One of the negative impacts of this characteristic is the reduction of workability of cement paste. Mini-slump tests indicate reduction in workability from 34% to 50% in different studies [6, 10, 17]; therefore, using superplasticizers are inevitable in most cases [6, 10, 8].

The increase in early age strength of cement pastes may imply that a long-term durability is achievable. Scanning electron microscope (SEM) and mercury intrusion porosimetry (MIP) experimental data indicate that the application of GO decreases the capillary porosity (that ranges between 10nm to 10μm) while increases 1 to 10 nm pore volume in standard cement pastes [10, 11]. This is attributed to the higher hydration rate of GO [6, 11]. However, these opposite impacts make the effects of GO in concrete durability an open question. Moreover, oxygen functional groups of GO usually reduce the pH of the environment [19]; thereby, the alkaline phases are to some extent neutralized. Reduction of pH makes the concrete more vulnerable to environmental conditions.

The feasibility of application of GO as a nanoscale reinforcement to OPC has been studied by researchers [1, 10]. So far, majority of these studies have been conducted on mortars or pastes, in which GO has been added to OPC as a binder. The results of such studies on concrete samples may be quantitatively different. In this study, 0.025% and 0.05% (by weight of cement) GO is incorporated with OPC, and the mechanical properties of the resulted concretes in terms of workability, compressive strength, flexural strength (modulus of rupture) and modulus of elasticity have been measured and compared with plain concrete. The test procedures are based on the known standards of ASTM. In order to evaluate the chemical resistance of these types of concretes to acidic environments, samples with 0.05% of GO are tested in 5 % HCl and 5 % H₂SO₄ solutions and their mass reductions are compared with plain concrete samples.

2. Methodology

2.1. Materials Used

Single layer graphene oxide was used in this study. It was produced base on modified Hummer’s method and provided in a slurry form. The elemental analysis of the used GO is presented in Table 1. The particle sizes of applied GO were ranging from 2.7 to 6.8 μm with dispersion pH of 3.5. The monolayer content was more than 95%. The atomic force microscopy (AFM) shows that the atomic thickness of the used GO sheets lied between 0.8 to 1.1 nm.

The cement used for this study was Portland cement type I, as per ASTM C150. Crushed granite aggregates were used in this study. The maximum size of aggregates were 13mm (Grain size 1) and 19 mm (grain size 2). In this study, it was necessary to use Polycarboxylate ether based superplasticizer, in some tests.

| Table 1. Elemental analysis of applied GO. |
|-----------------|-----------------|
| Element         | Atomic concentration |
|-----------------|-----------------|
| Carbon          | 60%             |
| Nitrogen        | 1%              |
| Sulphur         | 1%              |
| Oxygen          | 38%             |
2.2. Mixing Procedure
In this study, 0.025% and 0.05% (by weight of cement) GO were incorporated with OPC concrete. Table 2 shows different mix proportions that were used in this study. One of the key parameters in application of nanomaterials in concretes and mortars is the dispersion of these types of materials in fresh concrete mixes. In spite of the fact that GO is highly dispersible in water [8, 9], its dispersion in the fresh concrete is a challenge. It has been shown that using high speed shear mixer can help GO to remain dispersed in the fresh mix [17]. Although the applied GO was in slurry form, in this study a hand mixer with a rotation speed of 2000 rpm has been used for remixing the product with cement and water for 5 minutes, before adding to the rest of concrete ingredients.

Table 2. Mix proportions.

| Mix No. | Water kg/m³ | Cement kg/m³ | GO g/m³ | Fine Aggregate kg/m³ | Course aggregate (Grain size 1) kg/m³ | Course aggregate (Grain size 2) kg/m³ | Superplasticizer kg/m³ |
|---------|-------------|--------------|---------|----------------------|---------------------------------------|--------------------------------------|-----------------------|
| OPC1    | 168         | 365          | -       | 810                  | -                                     | 990                                  | -                     |
| OPC2    | 168         | 365          | -       | 810                  | 990                                   | -                                    | -                     |
| GOPC1   | 168         | 365          | 182.5   | 810                  | -                                     | 990                                  | -                     |
| GOPC2   | 168         | 365          | 182.5   | 810                  | -                                     | 990                                  | 0.65                  |
| GOPC3   | 168         | 365          | 182.5   | 810                  | 990                                   | -                                    | 0.325                 |
| GOPC4   | 168         | 365          | 182.5   | 810                  | 990                                   | -                                    | 0.65                  |

2.3. Experiment Method
2.3.1. Compressive Strength. For determining the compressive strength of specimens, the standard test method of ASTM C 39-04a has been adopted. Tests were conducted on 150mm diameter by 300mm tall concrete cylinders. Specimens were cured under water at 20 ± 2°C and tested at the ages of 7, 14, 28, 56 and 84 days. Specimens from OPC1, GOPC1 and GOPC2 mixes were used for compressive strength tests (see Table 2).
2.3.2. Flexural Strength Test. A third-point loading test method was used for assessment of flexural strength (tensile strength). Specimens with dimensions of 550mm×150mm×150mm were used in this type of test. Span length of test apparatus was 500-mm. Other specifications of the test were in accordance with ASTM C 78-02.
2.3.3. Slump Test. Slump tests were in accordance with ASTM C143 test method.
2.3.4. Modulus of Elasticity. Chord modulus of elasticity was measured based on ASTM C469-02.
2.3.5. Chemical Resistance Test. Tests on chemical resistance were conducted in conformity with the ASTM C 267-01 “Standard Test Method for Chemical Resistance of Mortars, Grouts, and Monolithic Surfacings and Polymer Concretes”. Specimens were cured under water for 28 days, at 20 ± 2°C, and then they were immersed for 84 days in 5% HCl and 5% H₂SO₄ solutions. At the ages of 7, 14, 28, 56, and 84 days, the specimens were washed with water, cleaned, and dried in the air and then their weights were measured. Weight changes of specimens were calculated using equation (1):

\[ Weight\ loss, \% = \left( \frac{W - C}{C} \right) \times 100 \]  

(1)

in which, \( C \) is the conditioned weight of the specimen (gram), and \( W \) is the weight of specimen after immersion (gram).

3. Results and Discussion
3.1. Fresh Concrete Workability
Figure 1 compares slump test results of samples containing GO (GOPC1 and GOPC2 with 0.05% GO) and plain concrete (OPC1) at 15minutes and 120 minutes after mixing ingredients. As it can be seen from the figure, 15minutes after mixing, samples containing GO without superplasticizer (GOPC1) have considerable lower slump (5mm) in comparison with plain concrete (60mm); therefore, for the
rest of the tests polycarboxylate ether based superplasticizer has been applied (Table 2) to the mixes containing GO (GOPC2). The amount of superplasticizer has been determined experimentally to have identical slump with that of plain concrete at 15 minutes after mixing. The results show that adding graphene oxide to the fresh concrete causes significant loss of workability. The reduction of workability, as a result of introducing graphene oxide to cement paste, has been reported in literature (for example in [6, 10]). This is generally attributed to the large specific surface of graphene oxide that adsorbs more free water onto its surface. The lack of free water increases the frictional resistance between mix ingredients.

![Slump loss versus time](image1)

**Figure 1.** Slump loss versus time in plain concrete (OPC1), concrete containing 0.05% (of the cement weight) graphene oxide without superplasticizer (GOPC1) and concrete containing 0.05% graphene oxide with superplasticizer (GOPC2).

![Compressive strength development](image2)

**Figure 2.** Compressive strength development of plain concrete (OPC1), concrete containing 0.05% (of the cement weight) graphene oxide (GOPC2) and concrete containing 0.025% graphene oxide (GOPC3).

3.2. Compressive Strength

Figure 2 shows the strength development of wet cured samples of plain concrete (OPC1), samples with 0.05% GO (GOPC2) and 0.025% GO (GOPC3) with time. Comparison between samples containing 0.05% GO with plain concrete shows that the addition of graphene oxide increases the compressive strength of samples to about 18% at the age of 14 days and about 15% at 28 days. The long-term strength development at the age of 90 days shows an increase in compressive strength of about 14% in samples with 0.05% graphene oxide. Moreover, the test results of concrete samples with 0.025% graphene oxide (by weight of cement) suggest that the increase of compressive strength is almost linear when GO content is within the range of 0% to 0.05%.

In reference [10] the compressive strength of OPC paste samples, mixed with graphene oxide, are compared with those of plain OPC paste samples; it is reported that the samples containing 0.03% (by weight of OPC) graphene oxide exhibit 46% improvement in compressive strength. It is generally known that the mechanical properties of cement pastes and concrete samples might be substantially different, partly because there are less cementitious materials in unit volume of concrete samples. Moreover, as it was mentioned before, oxygen functional groups on the surface of GO are the locations that produce hardened connection with the cement matrix. It is believed that this mechanism enhances the mechanical properties, such as compressive and tensile strength [11, 15].

3.3. Modulus of Elasticity

Comparison between chord moduli of elasticity between plain concretes (OPC1) and concretes containing 0.05% graphene oxide (GOPC2) is given in Table 3. An approximately 7.1% increase in
modulus of elasticity is observed in the concrete samples containing 0.05% GO. The samples were wet cured for 28 days before testing. Modulus of elasticity increases with increase in the compressive strength of concrete, but there is no agreement on the form of the relationship [20]. It is also known that the modulus of elasticity is affected by the quality of the bond between cementitious matrix and aggregate phases of concrete. When the bond is stronger [20], as is in the case of concretes containing GO, the modulus of elasticity is usually higher.

3.4. Flexural Strength
The results of third-point loading tests on 28-day flexural strength of concrete samples with 0.05% GO (GOPC2) and plain concrete are shown in Table 3. Test results show that the flexural strength of the samples with 0.05% GO is approximately 9.4% higher than that of plain concrete. In reference [10] it is reported that the flexural strength of the paste samples containing 0.05% GO is approximately 50% higher than that of the plain cement paste samples. The improvement in tensile strength could be a result of refinement of pore structure in samples containing GO [10]. In addition, it is generally recognized that GO is able to suppress propagation of nanoscale cracks in the cementitious matrixes [3], which is another possible reason for the increase in flexural strength of these types of concretes.

Table 3. Comparison between flexural strength and elastic modulus of plain concrete (OPC1) and concrete containing 0.05% graphene oxide (GOPC2) at 28 Days.

|                  | OPC1     | GOPC2    |
|------------------|----------|----------|
| Flexural strength (MPa) | 4.87     | 5.33     |
| Elastic modulus (GPa)    | 39.19    | 41.97    |

3.5. Chemical Resistance
Test results on weight loss of specimens that were immersed in 5% HCl and 5% H2SO4 aqueous solutions, are shown in Figure 3 and Figure 4 respectively. All specimens’ masses are decreased with time. At the age of 84 days, for specimens immersed in HCl the mass losses are 60% for the samples made with OPC and 57% for the samples containing 0.05% of graphene oxide. Likewise, for specimens immersed in H2SO4 the mass losses are 41% for the samples made with OPC and 35% for the samples containing 0.05% of graphene oxide at the age of 84 days.

An acidic attack to concrete involves chemical reactions between the acid and other components of the concrete. Acid attack dissolves the binder from the concrete surface. The acid permeation is highly dependent on the amount and structure of pore and cracks inside the concrete [21]. Previous studies show that inclusion of GO refines the capillary pores of cement paste [6, 10] thereby reducing the influence of acidic environment.
4. Conclusions
The results of this investigation indicate:
-Addition of graphene oxide significantly reduces the workability of concrete,
-Concrete samples containing 0.05% GO exhibit 18%, 15% and 14% increase in compressive strength at 14, 28 and 90 days of age with respect to plain concrete,
-An approximately 7.1% increase in modulus of elasticity is observed in the samples with 0.05% GO,
-Concrete samples containing 0.05% GO show 9.4% higher flexural strength at the age of 28 days with respect to plain concrete,
-Incorporation of GO slightly increases the durability of concrete in HCl and H2SO4 acid solutions.

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