Graphene Oxide Impact on Hardened Cement Expressed in Enhanced Freeze–Thaw Resistance

A. Mohammed[1]; J. G. Sanjayan[2]; W. H. Duan[3]; and A. Nazari[4]

Abstract: Graphene oxide (GO) is a newly invented material with extraordinary properties. This paper presents the effect of graphene oxide addition on freeze–thaw resistance in hardened cement. GO is incorporated in the cementitious matrix in ratios of 0.01, 0.03, and 0.06% by weight of cement. Freeze–thaw cycle tests show a weight loss of approximately 0.8% after 540 cycles in the control mix compared to approximately 0.25% in 0.06% GO mix. Several tests were conducted to investigate the reasons behind this result. The tests included nitrogen and water adsorption, air content, and compressive strength. The results showed that GO mixes have finer pore structure than the control mix. Moreover, the results indicated that GO addition increases air content in the mix and shows high compressive strength compared to the control mix. The enhancement of freeze–thaw resistance due to GO addition can be because of the modification of pore structure where water hardly freezes in small pores. Also, the resistance of nanocracks propagations can limit the development of frost damages, in addition to the entraining air in the mix by GO addition that creates room to release osmotic pressure. **DOI: 10.1061/(ASCE)MT.1943-5533.0001586.**

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Introduction

In recent years, nanotechnology, which has many applications in different engineering fields, has grown, including in the construction industry. In the last few years, the literature on incorporating nanoparticles into the cement matrix has increased significantly (Björnström et al. 2004; He and Shi 2008; Yazdi et al. 2011; Oltulu and Şahin 2013; Babak et al. 2014). A multiphase composite material, such as concrete, consists of an amorphous phase, microscale- to nanoscale-sized crystals, and bound water. The reactions within this structure can occur in macroscale, microscale, and nanoscale (Sanchez and Sobolev 2010). Therefore, incorporation of adequate nanoparticles into concrete can affect these reactions and subsequently alter the properties of the produced concrete. Graphene, which is one carbon atom thick and has fascinating characteristics, is a promising nanomaterial that has the capability to push the current boundaries of the use of concrete in construction. The discovery of graphene has brought substantial innovations in science and engineering. Graphene materials have been considered outstanding with remarkable applications in construction industry. Graphene oxide (GO), one of the graphene-based materials, is a hexagonal network of carbon atoms with sp^2 and sp^3 hybridized orbitals. There are many functional groups with GO structure consisting of hydroxyl and epoxide groups found mostly on its basal plane, and carbonyl and carboxyl groups found on the edges (Geim and Novoselov 2007; Gómez-Navarro et al. 2007; Behabtu et al. 2010). These functional groups help in the dispersion of GO in polar solvents, such as water. However, GO has been reported as an amphiphilic molecule that has both hydrophilic and hydrophobic regions (Cote et al. 2011). Utilizing GO in the cement matrix has recently gained considerable attention. Mohammed et al. (2015) have reported that GO incorporation in the cement matrix has enhanced its pore structure and produced a cement matrix with high resistance for chloride ingress. Horszczaruk et al. (2015) investigated the mechanical properties of cement-based composites with 0.01 and 0.05% GO. The results showed highest compressive strength in the mix with 0.05% GO compared with a pristine cement paste and 0.01% GO mix. It has been suggested that heterogeneous nucleation of C-S-H gel is the reason for the increase in compressive strength. Pan et al. (2015) addressed the addition of GO in the cement matrix using a load fraction of 0.05% by cement weight and water-to-cement ratio of 0.5. Mechanical test results significantly showed an improvement in strain capacity. Thus, it is suggested that the initiation of microcracks is delayed because of GO sheets. Furthermore, the effective reinforcement by GO addition in cement mix could be due to strong interfacial adhesion between the cement matrix and GO.

The aim of this study is to investigate the effects of GO addition on freeze–thaw resistance and compressive strength of hardened cement. It is envisaged that by studying freeze–thaw resistance, the mechanisms involved in the impact of GO addition in hardened cement can be explored in depth.

The most widely used method for increasing the freeze–thaw resistance is air entrainment. However, the mechanisms by which air entrainment work to prevent freeze–thaw damage are not entirely

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Table 1. Chemical Composition of Cement

Test	Percentage
Sulfur trioxide	2.6
Chloride	0.01
Equivalent alkalis	0.5
Crystalline silica	<1
Portland clinker	85–94
Gypsum	5–7
Mineral addition	Up to 7.5

Table 2. Chemical Composition of GO (Data from Graphenea Company 2015)

Element	Percentage
Carbon	49–56
Oxygen	41–50
Nitrogen	0–1
Sulfur	0–2
Hydrogen	0–1

understood. By investigating freeze–thaw resistance, the mechanism may become clearer, as well as the effect of GO on the microstructure development of cement hardening be understood.

Materials and Samples Preparation

General-purpose ordinary portland cement, according to the Australian standard AS3972 (Australian Standard 2010), was used to make the mortar mix; the chemical properties are shown in Table 1. Washed sand from Sibelco Australia and New Zealand Materials in north Sydney was used.

GO in the form of 4 mg/mL water dispersion graphene oxide was supplied from Graphenea Company, San Sebastian, Spain. The properties of GO are described in Table 2. GO can be found as both powder and colloidal dispersions (Compton and Nguyen 2010; Park and Ruoff 2009). In this study, GO was used as a water dispersion solution, which is more appropriate to mix in cement mortar.

The control mix (CM) (GO-free) was made following the proportions shown in Table 3. GO was added to the cement mixture in three different percentages of 0.01, 0.03, and 0.06% by weight of cement. The fraction of GO was calculated based on its concentration in water. The 4 mg/mL GO water dispersion was further diluted to 2 mg/mL. This would help to have better dispersion of GO sheets.

Mixing Method

The dry contents were first mixed for 2 min in an automatic mortar mixer in compliance with EN 196-1 [British Standards Institution (BSI) 2005a], EN 196-3:2005 (BSI 2005a), and EN 480-1 (BSI 2014) specifications. The speed was 285 rotations per minute (rpm) for the revolving action and 125 rpm for the planetary action. In a separate container, GO was mixed with distilled water and stirred mechanically for 2 min. Then, the GO solution was added to the dry contents and stirred for 3 min at 285 rpm and 2 min at 125 rpm. The fresh mixture was cast into cylindrical molds of 100-mm diameter and 50-mm height, and compacted to remove entrapped air. After that, the specimens were covered with plastic sheets to prevent evaporation from unhardened mortar mixes. Finally, all specimens were demolded and moist cured at 23 ± 2°C for an additional 28 days. Two samples per mix were put through each of the following tests.

Freeze–Thaw Test and Results

Freeze–thaw test for cement mortars was conducted following the ASTM C666 method (ASTM 2003): rapid freezing–thawing cycles in water. This method is used to determine the resistance of cementitious material to rapidly repeated freeze–thaw cycles. The samples were standard prisms of $25 \times 25 \times 280$ mm dimensions. The age of specimens was 28 days at the commencement of the test. A suitable chamber was used to conduct the freeze–thaw cycles; it had the necessary refrigerating and heating equipment and was set to produce continuous cycles at specified temperatures. All samples were placed in suitable containers and covered with water to 1–2 mm; then the containers were placed in the chamber. Each freeze–thaw cycle was run for 4 h and repeated automatically. The cycle started at −18°C for 3 h, and continued for 1 h after raising the temperature to 4°C. The weight loss of each specimen was measured at the beginning of the test and after a specified number of cycles.

The results of the freeze–thaw test showed surface damage of the mortar specimens, especially after 378 cycles. The degree of damage varied among the samples. Fig. 1 shows a significant weight loss in the control mix in comparison to the mixes with GO. Furthermore, as seen in Fig. 2, it was observed that the damage in the control mix occurred intensively at the specimen's edges—there were many broken edges with falling parts. The CM sample also had a spongelike surface by the end of the test. A significantly lesser weight loss was determined in GO cement mortars compared to the control mix. This indicates a considerable capability of GO to keep matrices together. However, as Fig. 2 shows, there is surface damage in G1 mix, particularly at the corners of the specimen. G3 mix exhibits the lowest weight loss due to freeze–thaw cycles; this result is obvious from the early cycles. By the end of the test, as Fig. 2 illustrates, G3 mix sample surface shows less damage and scaling than the other samples. As can be seen in the results, GO addition makes significant improvements to the freeze–thaw resistance although the addition of GO was very small. However, the mechanisms by which the GO works is unclear, and this is an impetus to research and understand how GO interacts with the cement matrix to increase its freeze–thaw resistance. To achieve this goal, a number of tests have been conducted. GO has been reported as a surfactant material, which is a similar activity as air-entraining agents. That is why the air content test is used to

Table 3. Cement Mortar Mix Proportions

Mix identification	Cement (g)	Sand (g)	Water content (mL)			GO (%)	GO (mg)
			Distilled water	Water with 2 mg/mL GO dispersion	Total water		
CM	225	675	101	0	101	0	0
G1	225	675	90.0	11.0	101	0.01	22.5
G2	225	675	67.8	33.8	101	0.03	67.5
G3	225	675	33.8	67.8	101	0.06	135

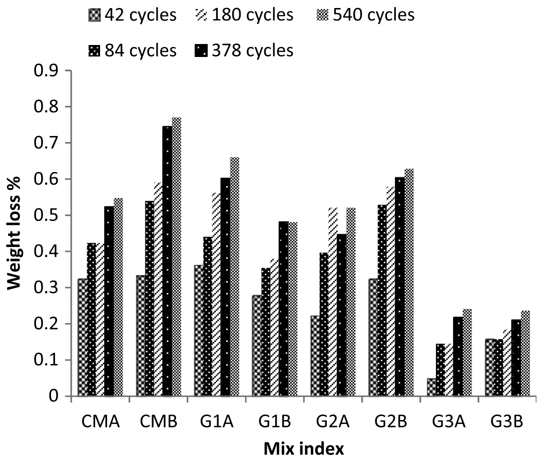

Fig. 1. Freeze–thaw cycles of different cement mixes

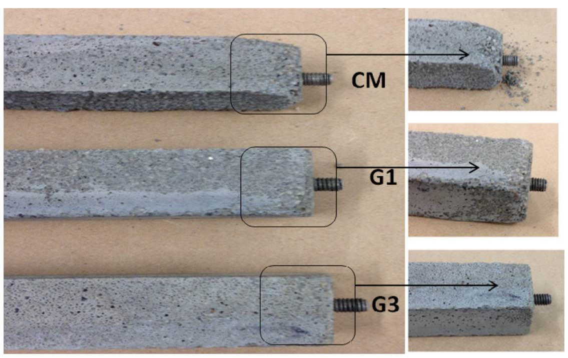

Fig. 2. Freeze–thaw damages of different cement mixes

investigate whether GO can entrain air in the mix or not. A test was conducted to measure the total water absorption and voids of hardened cement. Hence, water absorption is an important factor to control freeze–thaw damage. To investigate the pore structure of the cement matrix, nitrogen absorption test was used. Finally, compressive strength is the main property that is negatively affected due to the addition of an air-entrainment agent. The compressive strength was tested to investigate the influence of GO addition on this property. The results of the tests are discussed here.

Tests to Identify the Reasons for Superior Freeze–Thaw Resistance

The air content, Burnauer–Emmett–Teller (BET) isotherm, and strength tests were conducted to explore the reasons why very small amounts of GO make significant improvements in freeze–thaw resistance.

Air Content Test in Mortars

The ASTM C185 method (ASTM 2015) was followed to measure the air content in fresh cementitious mixtures. All cement mortars were prepared according to the mixing proportions shown in Table 3. A measure of known volume and mass was used to place the mortar in it in three layers and compact each layer 20 times using a suitable rod. The air content was measured using the following equation:

Table 4. Air Content by Volume of Fresh Cement Mortar Mixtures

Mix identifier	Air (%)	GO (%)
CM	8.1	0
G1	9.7	0.01
G2	11.2	0.03
G3	13.5	0.06

$$\text{air content, volume\%} = 100\left[1 - \left(\frac{W_a}{W_c}\right)\right] \quad (1)$$

where W_a = actual mass per unit of volume; and W_c = theoretical mass per unit of volume.

Air content of different cement mixtures are shown in Table 4. The air content of CM is 8.1% and it has increased by adding GO to reach 13.5% in G3, which indicates a nearly 40% increase in air content. The results show that by increasing GO content in the mix, the air content increases, which may indicate the surfactant nature of GO.

GO is a sheetlike surfactant and has an edge-to-center arrangement of hydrophilic and hydrophobic groups. It would be expected that smaller sheets are more hydrophilic because of higher edge:base ratio (Cote et al. 2011). Thus, by increasing GO content in the mix, more large sheets are included. This means that the size of hydrophobic nanographene regions is increased and subsequently more air content is entrained in the mix. According to BS 8500 (BSI 2015), the required air content in paving concrete for freeze–thaw resistance is normally between 4.5 and 5.5%. However, in mortars with no coarse aggregates, the air content is approximately twice of that in concrete. Results in Table 4 indicate that G2 and G3 mixes have adequate air content to resist freeze–thaw cycles. It is the hypothesis of this study that incorporation of GO in a cement matrix as a surfactant agent lowers the surface tension of the water to facilitate formation of air voids. The diameter of air voids can be much smaller than any other air-entraining agent and ranges in nanometers, which should not have an effect on the required compressive strength. It is expected that by entraining air in cement mixture, the resistance for freeze–thaw damages subsequently increases. Matrixes with sufficient air content for freeze–thaw resistance are produced by incorporating GO in the mix. Additionally, it is clear that the air system produced by the addition of GO has no negative effect on compressive strength. In fact, GO addition increases compressive strength, as shown subsequently in Fig. 6.

However, the effect of GO on a cementitious mixture may be different from any other traditional air-entrained admixture because of the nano nature of GO. Hence, the air voids produced due to GO addition could much smaller than that produced by traditional air-entraining agents.

Total Water Adsorption

This test is adopted to determine the density, total adsorption, and percentage of voids in hardened cement mortars. The ASTM C642 method (ASTM 2013) is used for this test. Cylindrical samples of 100-mm diameter and 50-mm height were used from each mix which were aged 28 days. First, a dry mass of each specimen was determined by placing the samples in an oven at 110°C for 24 h. After cooling to approximately 25°C, a sample mass was recorded as the dry mass. Then, the specimens were immersed in water for no less than 2 days. After removing the surface moisture from the samples, the sample immersion weight was recorded. Then, the saturated samples were placed in a suitable container, covered with tap water, and boiled for 5 h. All samples were allowed to cool naturally for no less than 14 h, and the soaked, boiled mass was determined after removing the surface moisture. Finally, the immersed

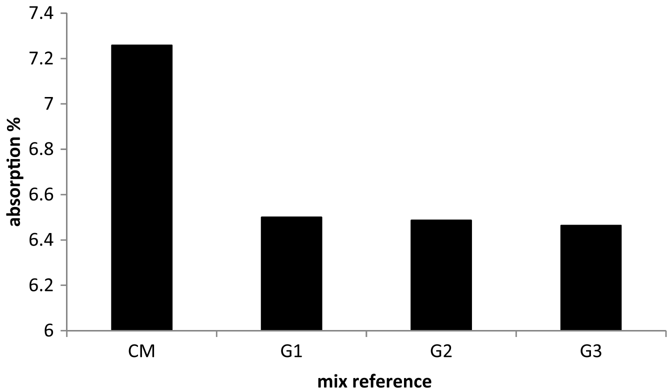

Fig. 3. Total water adsorption of different cement mixes

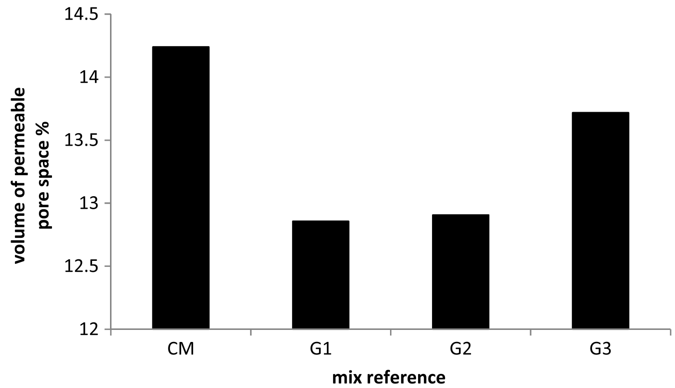

Fig. 4. Volume of permeable pore space of different cement mixes

apparent weight was determined by suspending the immersed samples in water using a wire and recording the sample weight.

Fig. 3 shows that water adsorption of GO cement mortars is less than the control mix. It is well known that the size and distribution of pores have a significant effect on the ease and rapidity of liquids to transport through pore system of cementitious materials. It is supposed that GO in the cement mix effectively fills the spaces among pores in different scales ranging from micropores to macropores. This is because of GO, which has a sheet-size distribution ranging from a few nanometers to several hundreds of micrometers (Aboutalebi et al. 2011; Compton and Nguyen 2010; Sun et al. 2008; Liu et al. 2012). Peyvandi et al. (2013) have reported that the addition of nanoscale materials, such as graphite nanomaterials, cannot effectively interact with microscale crystals of cement hydration. Thus, it may still be just a physical contribution of nanomaterials to block and restrict the connection among pores. This is also supported by the results shown in Fig. 4; the permeable pore space of GO mixes is lower than the CM. This shows that a great part of the pore system of GO mixes is impermeable.

The G3 mix has an adsorption percentage similar to other GO mixes, but the volume of permeable pore space is higher. This could be attributed to the high resistance to water ingress due to the increase of tortuosity of pores in the cement matrix (Liu et al. 2011). High tortuosity of pores can be a result of the connection of GO sheets and the other cement matrix ingredients, which cause the production of an effective barrier against water movement through pores. Low water adsorption of the cement matrix enhances the freeze–thaw resistance significantly. Hence, the majority of the expansion is from water absorption due to osmotic pressures (Qian et al. 2014; Jensen and Hansen 2001).

BET Isotherm Analysis

The BET isotherm is a well-established method to determine the surface area and adsorption properties of a wide range of materials (De Belie et al. 2010). In this study, BET isotherm graves were used to investigate the pore structure of cement composites in the range of 1 to 500 nm. Application of gas adsorption method to study the effect of GO addition on pore structure of the cement matrix is highly effective when the pore range is less than 100 nm. Mercury-intrusion porosimetry (MIP) method has accuracy limitations in small pore range due to the high incremental pressure required to press mercury in these pores, which could affect the pore structure. Samples with weight less than 1 g were removed from each mix and preconditioned prior to the adsorption by degassing the samples at 105°C for 24 h under vacuum (<10 μm − Hg). Each specimen was kept under vacuum and heated until the gassing out rate of < 0.66 Pa/min (<0.005 torr/min) was reached. This usually occurs in 16–24 h of beginning the degassing process. The preconditioning process is necessary to ensure removal of any adsorbed foreign liquids. After that, the weight of the degassed sample and the glass tube was recorded to determine the weight of the analysis sample. Then, the sample was placed on the analysis port of the device and the gas adsorption–desorption process begun.

The nitrogen adsorption isotherms for cement mixtures are shown in Fig. 5. Addition of GO decreases the amount of nitrogen adsorption significantly in G3, which has the highest GO loading, compared to the control mix, as Fig. 5(c) shows.

This exhibits a reduction in mesopore volume with an increase in GO amount. Additionally, the hysteresis loops of G2 and G3 gradually become thinner and less pronounced in comparison to the CM hysteresis loop, which mainly occurs at high pressures ($p/p0 > 0.6$). It also indicates a reduction in porosity of G2 and G3, and it is an indication of smaller pore volume for these mixes in comparison to CM having a very pronounced hysteresis loop. This could be attributed to the small number of pores induced by GO addition. The size of freezeable water depends on the size of the pore and it is limited by the water:cement ratio. Small pores show great surface tension, which could reduce their freezing ability (Powers 1945). Thus, gel pores with very small radii exhibit high freeze resistance because temperatures can never drop enough and water in large capillary pores freeze before water in smaller pores. It is true to say that the governing parameter of freezing capability is the pore size of the cement pore structure. Mohammed et al. (2015) reported that GO addition in cement mortar produces a finer pore structure matrix compared to the normal mix. Such cement matrix could have high freeze–thaw resistance.

Water in gel pores with very small radii cannot freeze at temperatures higher than −78°C (Pigeon et al. 1996). In practical conditions, such temperatures are not reached, which means that the number of small pores in a cement mix can enhance the freeze–thaw resistance of cementitious materials.

Compressive Strength

Compressive strength test was conducted on the control mix and other mixes containing GO. The samples have a cylindrical shape with diameter of 100 mm and height of 50 mm and they are aged 28 days at the time of the test.

Fig. 6 shows the compressive strength test results of the control mix and mixes with GO. This figure demonstrates that the compressive strength of cement mixes with GO is higher than the control mix. The increase in compressive strength is more significant in the G2 mix and it is nearly 30% of the CM compressive strength. Chuah et al. (2014) reported a similar increase in cementitious material compressive

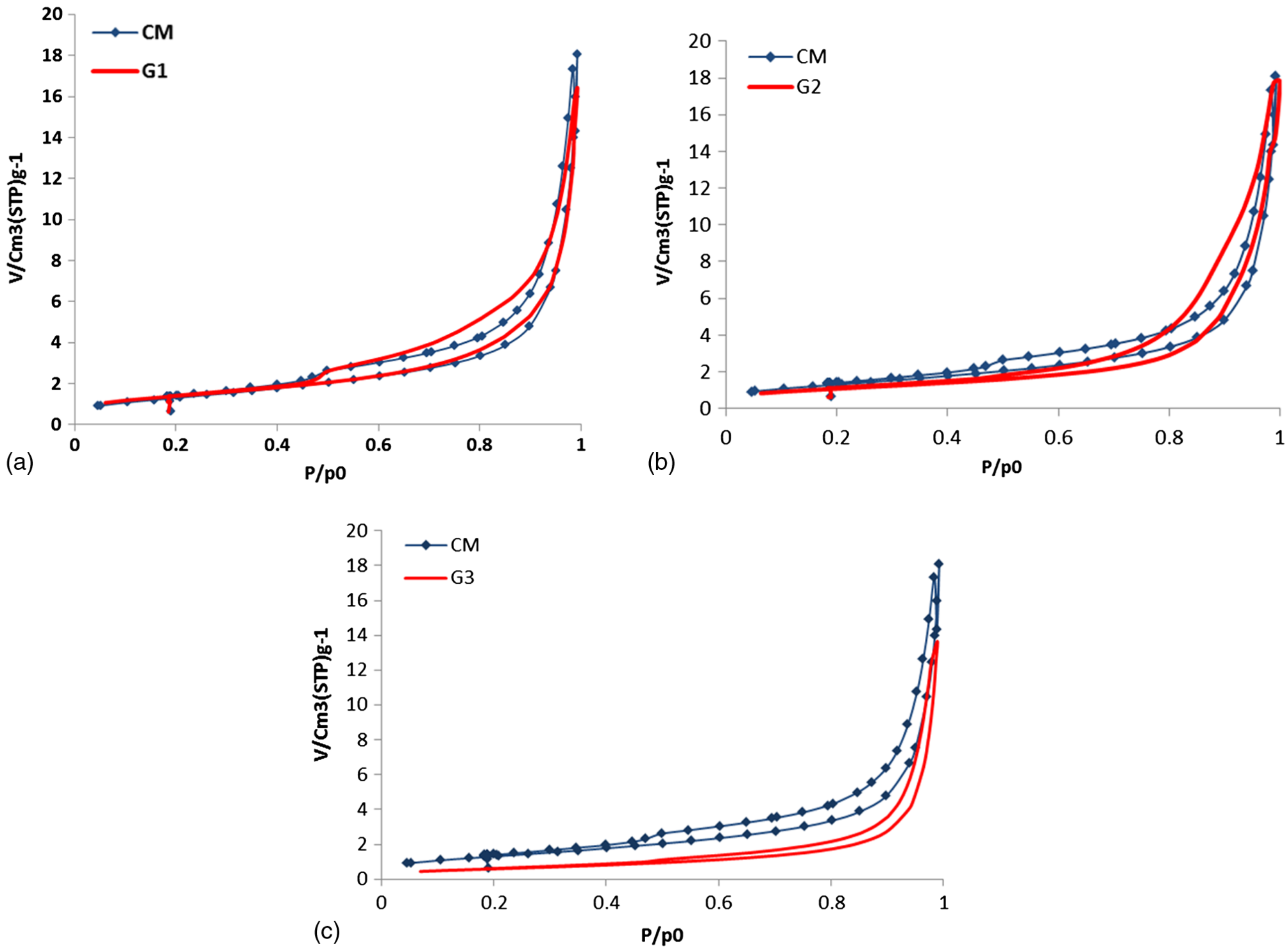

Fig. 5. Nitrogen adsorption isotherms of (a) G1; (b) G2; (c) G3 cement mixes

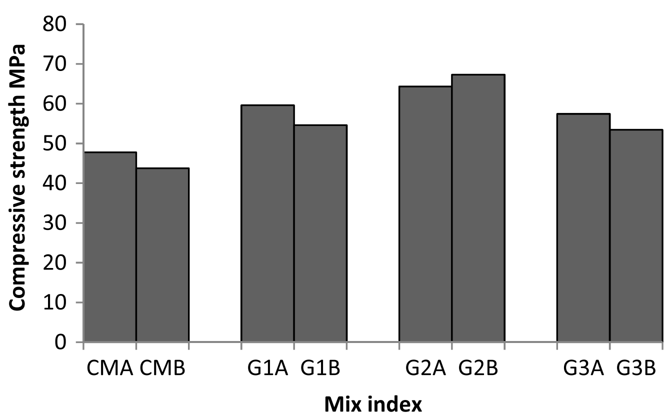

Fig. 6. Compressive strength of different cement mixes

strength due to GO addition. This shows the advantage of using GO as an air-entraining agents that can maintain high strength and freeze–thaw resistance. On the other hand, using a traditional air-entraining agents causes a reduction in compressive strength recorded because for every 1% of air entrained, the strength falls by typically 5–6%. The reduction of strength can be attributed to the air system induced by air-entraining agents. The air voids range in microscopic size and represent around 11% of the volume of mortar. The key to achieve the required freeze–thaw resistance is to provide a good distribution of small-sized entrained air voids (Giridhar et al. 2013). It can be concluded that this was acquired by using GO in the mix. One of the main causes of concrete deterioration in cold weather regions is the freezing–thawing cycle. When water freezes, it expands and as a result produces a pressure in the pores of the cement matrix. When the pressure exceeds the tensile strength of concrete, damage can take place (Neville 2012). This damage can be described as scaling, cracking, and decaying of concrete. Air entrainment is used to cope with this problem; however, the diameter of air-entrained voids is mostly less than 1 mm, which causes a reduction of compressive strength (Jensen and Hansen 2001; Wei et al. 2012).

The enhancement of compressive strength of GO cement mixes could be attributed to the effects of GO on the microstructure of the cement matrix. It includes the presence of interaction surfaces between cement hydration products and the GO sheets, which can effectively hinder the propagation of nanocracks. Due to the extremely small size of a GO sheet, normally ranging from a few nanometers to several micrometers, it is believed that the GO sheet can contribute to resist crack initiation at very early stages, which are measured by nanocracks. Maintaining strong interaction surfaces between GO sheets and cement products can increase the load-transfer efficiency from the cement matrix to the GO sheet. Subsequently, the mechanical properties can improve. It is observed from Fig. 6 that increasing of GO content causes a reduction in compressive strength enhancement due to the incorporation of GO in the cement matrix. This is compatible with the results of the air content test that showed that by increasing GO in the mix, the air content increases as well. It is clear that more air addition in the mix can negatively affect the compressive strength.

Conclusions

The results of freeze–thaw cycles showed a positive effect of GO addition on enhancement of freeze–thaw resistance. Cement mixes with GO exhibit less weight loss during freeze–thaw cycles, especially the mix with the highest GO addition. In addition, GO mixes showed few scaling damages on the specimen's surfaces compared to the control mix. The results of the air content test for GO mixes showed an increase of 40% compared to the air content of the mix without GO. Furthermore, GO addition modifies the pore structure and produces a matrix with less mesopore volume as is evident from the nitrogen absorption test. Water absorption test results revealed that GO mixes have less water absorption compared to the control mix. Test for compressive strength showed that GO addition has increased the compressive strength. It can be concluded that GO has the potential to modify cement matrix to exhibit high freeze–thaw resistance. The mechanism of how GO enhances freeze–thaw resistance can be explained by, but not limited to, the following: the amount of entrained air due to GO addition, enhancing pore structure, and increasing compressive strength.

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