Experimental investigation into graphene’s effects on the mechanical properties of cement mortar under specific sonication parameters

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Abstract. Graphene and its derivatives have been studied as nanomaterials in many different fields owing to their various interesting properties. Many researchers have investigated the mechanical properties of different graphene cementitious composites, and the current study investigates the effect on the mechanical properties of cement mortar of adding graphene with and without the use of an ultrasonic homogeniser. To examine this effect, all other testing conditions and requirements such as mix design content, mixing procedure, curing time, specimen size and sonication parameters were maintained at the same levels across tests. Cement mortar specimens containing different percentages of graphene (0, 0.003, 0.006, 0.009, 0.012 and 0.03% by weight of cement) were experimentally tested after 7 and 28 days to determine the effect of graphene dosage on their quasi-static strengths. The results showed an obvious enhancement in both compressive and flexural strengths after adding each graphene dosage to the mix without sonication; the compressive strength was increased by 12% with a 0.006% dose of graphene and the flexural strength was increased by 27% at a 0.009% dose of graphene. On using the sonicator at the specified parameters, the compressive strength increased by 33% for the 0.006% dose of graphene, offering an increment of 20% in strength due to the sonication effect; however, there was no noticeable effect on the flexural strength.

Keywords: sonication; graphene reinforced cement; compressive strength; flexural strength; nanocomposites.

1. Introduction
Graphene refers to single atomic planes of graphite, making it an inexpensive material that is available in practically unlimited amounts. It has been known of and studied since 1917 as graphite oxide [1], though one of the major challenges is that this substance does not readily exfoliate to provide individual graphene sheets [2], increasing the cost of production and meaning that it could not be readily incorporated into practical applications that require the mass-production of graphene [3]. Graphene nanosheets (GNSs) and graphene oxide nanosheets (GONSs) are new kinds of nano-materials consisting of graphene stacks of graphene sheets [4], however, and a new method of producing graphene at lower cost known as Flash Graphene (FG) has also emerged, with flash joule heating of any inexpensive carbon sources allowing gram-scale graphene to be produced for an electric cost of 7.2 kilojoules per gram [5].
Graphene is an ideal nano-filler for the modification of cementitious materials [6]. The various impressive properties of graphene such as its structural strength and durability enable many developmental applications to be accomplished, and its anti-corrosion properties lend it to use in self-cleaning surfaces and energy-saving developments [7]. This range of applications is supported by its low cost as compared to other nanomaterials such as carbon nanotubes and nanosilica [8].

Recently, researchers have indicated that enhancements can be gained by adding graphene to various cementitious composites at both early and later ages of development; experiments in adding 2 vol.% of multi-layer graphene to cement paste increased the compressive strength and elastic modulus by 54% and 50%, respectively [9]; adding 0.05% of graphene nanoplatelet GNP to concrete enhanced the compressive and flexural strength by up to 7.5% and 23.5%, respectively [10]; adding 0.15% of GNP to cement paste increased the compressive and flexural strength by about 49.4% and 27.5%, respectively [11]; adding 0.03% of GNP to cement paste increased the compressive and flexural strength by about 1.3% and 16.8%, respectively [12]; adding 0.8% of GNP to mortar increased the compressive strength up to 87.5% [13]; adding 0.1% of GNP increased the compressive strength to 19.3% [14], and adding 0.1% of GNP to concrete increased the compressive strength to 14.2% at 7 days and the flexural strength to 4.0% at 3 days of curing [15].

There are many factors affecting the mechanical strength of concrete, such as the selected matrix, the water/cement (w/c) ratio, curing time, dispersion and mixing procedures, and the type, size and functional groups of graphene derivatives involved [16]. In this research, dispersion is thus considered and studied as a key factor affecting the mechanical behaviours of cement mortar. As part of verifying the influence of dispersion on the composite behaviours, enabling good dispersion of graphene in cementitious composites should be considered [17]; this may be achieved by using modified chemical dispersant treatments, ultrasonic dispersion techniques, or an alternating electric field method. Many previous studies have used different dispersant materials, such as silica fume [18], alkylphenol polyoxyethylene ether [19], graphene oxide [20], and alkylbenzenes [21]. Recently, however, some researchers have dispersed graphene using ultrasonic process techniques [19, 22-29], and in this research, the ultrasonic process technique was used to ensure the dispersion of graphene, based on the different parameters that control efficiency and should thus be considered, such as process time, frequency, power output, and probe nature.

This research’s main aim was to experimentally examine the effect of adding graphene to cement mortar in very small dosages in a manner that has not been studied before as well as to investigate the effect of dispersion, using specific sonication parameters, on the mechanical behaviours of the cement mortar.

2. Materials

General purpose (Portland) cement of type GP was used as a binder in this research, as this is a high-performance concrete with strong setting, hard wearing, and durable properties as required by Australian Standard AS3972 [30]. Table 1 presents the ingredient properties of Portland Cement as mentioned in the Safety Data Sheet (Independent Cement & Lime Pty Ltd).

| Ingredient | Portland cement clinker | Lime stone | Gypsum | Clinker Kiln dust | Chromium (VI) hexavalent |
|------------|-------------------------|------------|--------|------------------|------------------------|
| Formula Proportion | Not available >92% | CaCO₃ 0-7.5% | CaSO₄·2H₂O 3-8% | Not available 0-2.5% | Cr⁶⁺ Trace |

Graphene-mortar specimens were prepared and tested after curing for 7 and 28 days at room temperature. In this research, 1,200 g of GP cement, 1,400 g of course sand with a grade of 16/30, 1,000 g of fine sand with a grade of 30/60, and 600 g of water were used in all cement mortar mixes. The fineness
moduli for the coarse and fine sand were 5.8 and 4.9, respectively. The mix proportions of the cement mortar component are listed in Table 2.

Table 2. Proportions of cement mortar component.

| Material | cement | Water | Sand |
|----------|--------|-------|------|
| ratio    | 1      | 0.5   | 2    |

Graphene was used as an additive nanomaterial. Graphene powder may form combustible dust concentrations in air that have negative effects on human health on inhalation, ingestion, or skin and eye contact; an aqueous graphene paste was thus used, with features as indicated in Table 3.

Table 3. Aqueous graphene paste features.

| Graphene content | 55.0-60.0% |
|------------------|-------------|
| Purity           | 99.8%       |
| Carbon content   | 99.6%       |
| Average flake thickness | 2-3 nm |
| Average number of layers | 5-7 |

Six different graphene dosage percentages (0, 0.003, 0.006, 0.009, 0.012, and 0.03%) were added to six portions of cement mortar mix to get six different graphene mortar mixes. These were labelled Mix0, Mix3, Mix6, Mix9, Mix12 and Mix30, respectively. The proportions and weights of graphene and graphene paste are shown in Table 4, with the graphene calculated as a mass fraction of cement. Mix0 is the reference mix and Mix30 was added later to examine the predictions of the behaviours trend in resulting strength as the graphene percentage increased.

Table 4. Proportions and weights of graphene in each mix.

| Mix#  | Graphene % | Graphene (g) | Cement (g) | Graphene Paste (g) |
|-------|-------------|--------------|------------|--------------------|
| Mix0  | 0           | 0            | 1200       | 0                  |
| Mix3  | 0.003%      | 0.0360       | 1200       | 0.0857             |
| Mix6  | 0.006%      | 0.0720       | 1200       | 0.1714             |
| Mix9  | 0.009%      | 0.1080       | 1200       | 0.2571             |
| Mix12 | 0.012%      | 0.1440       | 1200       | 0.3429             |
| Mix30 | 0.030%      | 0.3600       | 1200       | 0.8571             |

3. Mixing procedure and specimen preparation

The same mixing, moulding, and preparation procedures were used for all mixes. To ensure a more homogenous structure, an Intelligent Ultrasonic Processor/Homogeniser (Sonicator) was utilised to improve the graphene dispersal into water, as shown in Figure 1. The specific sonication parameters were fixed for all mixes, with ultrasonic power equal to 1,200 W, voltage/frequency equal to 230V/50 Hz, and sonication time set to two minutes. In each case, the cement and sand were added into the mixer and blended together for two minutes at a medium speed, with one further minute at high speed. After that, the mix was poured into lubricated moulds to create $40 \times 40 \times 160$ mm$^3$ prisms used for flexural strength tests, as shown in Figure 2. Finally, the mix was kept in a closet for 24 hours at room temperature, then immersed in water tank for curing for 7 and 28 days. The mixing process steps for graphene mortar was thus as outlined in Tragazikis [31]. In addition, $40 \times 40 \times 40$ mm$^3$ cubes were used for compressive tests.
4. Testing

4.1. Flexural Tests
Three-point bending tests were conducted at 7 and 28 days on the prisms created following the above method in order to determine the flexural strength. An MTS machine was used, with the flexural apparatus added separately to suit the machine, for flexural strength testing. Data were collected directly from the machine for each specimen.

4.2. Compressive Tests
After completing the flexural strength tests, cubes with dimension 40 × 40 × 40 mm$^3$ were cut from the remaining un-deformed prisms for compressive tests per ASTM C349 [32]. The same MTS machine was used, with compression apparatus added to fit the cube specimens. As this machine provides the stress and the maximum load for specimens for both compression and flexure, there was no need to calculate the flexural and compressive strengths; however, the strain rate was not obtained from these flexural and compressive tests.

5. Results and Discussion

5.1. Graphene Dosage without Sonication
As shown in Figures 3a and 4a, increasing the graphene dosage in the mix increased both compressive and flexural strengths. The compressive strength was enhanced by 16.2% and 7.1%; 21% and 11.7%; 24.7% and 7.2%; and 21.2% and 0.8% after 7 and 28 days curing for Mixes 3, 6, 9 and 12, respectively as compared with the strength of Mix0 (without graphene), while the comparable flexural strength was enhanced by up to 15.1%, 21.3%, 27%, and 10.7% after 28 days curing for Mixes 3, 6, 9 and 12.

5.2. Sonication
In order to study the effects of sonication on the mechanical behaviours of the graphene mortar, quasi-static compressive and flexural tests were conducted after curing for 7 and 28 days for each mix with and without an ultrasonicating step. As noted, prisms were used to conduct the flexural strength tests and cubes were used to conduct the compressive tests; however, for this comparison, Mix0 was omitted, as it did not contain any graphene. Figure 3 (a) and (b) show the relationships between compressive strength and the percentage of graphene in each mix without any sonication and with 2 minutes of sonication.
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sonication, respectively. The compressive strength was enhanced by up to 6.58%, 19.06%, 12.26% and 7.18% by the sonication process after 28 days curing for Mixes 3, 6, 9 and 12, respectively, as compared with the strength of their counterpart mixes without sonication.

Figure 4 (a) and (b) shows the relationship between flexural strength and the percentage of graphene dosage in each mix both without any sonication and with 2 minutes sonication, respectively. Here, there is no noticeable effect from sonication at the specific sonication parameters used on the flexural strength of graphene mortar.

The enhancements of the compressive and flexural strengths of graphene mortar, including sonication, are equal to 32.8% and 23.9%, respectively. These enhancements are higher than those reported in previous studies investigating the effect of graphene on the mechanical properties of cement mortar [33-35].

5.3. Optimum Graphene Dosage

Based on Figures 3b and 4b, increasing the graphene dosage in the mix causes both compressive and flexural strengths to increase to reach a maximum at a single dosage, taking sonication into account. For compressive strength, the optimum graphene dosage percentage is 0.006%, here used in Mix6, with a
maximum compressive strength of 52.07 MPa. For flexural strength, the optimum graphene dosage percentage is 0.009%, Mix9, with a maximum flexural strength of 9.38 MPa. Mix6 and Mix9 are thus the optimum choices.

To examine the trend of the obtained results for the relationship between the strength and the graphene dosage percentage, a 0.03% graphene mix, Mix30, was created, as shown in Figures 3b and 4b. Adding 0.03% of graphene to the mix decreased the compressive strength to 34.73 MPa, about 18.84% less than at a graphene dosage of 0.012%. Moreover, the flexural strength also decreased to 6.89 MPa, around 23.3% less than that of Mix12.

This decrement in strength was expected for two reasons. The first one is that graphene agglomeration, the dispersion state of graphene, means that graphene particles are likely to cluster and stay suspended together at higher concentrations, which is known to have significant effects on material behaviour, such as decreasing conductivity [36]. The second reason is that sonication parameters such as sonicating time were kept identical across all concentrations; two minutes sonicating was applied to all mixes. However, 0.03% graphene would require more sonicating time for effective dispersal in water than 0.003% graphene. This highlights the need to change the sonicating time with respect to the percentage of graphene in each mix as well as to consider other parameters.

There are three main factors that contribute to the mechanical enhancement of graphene cementitious material: The first is the interfacial bonding that occurs between the filler and matrix that reduces the stress concentration by distributing and transferring the efficient load from the matrix to the reinforcement so that the composite can resist more loading. The next is that the large specific surface area of graphene controls water demand and thus setting and hydration reactions by offering additional sites for hydration products [37]. The final factor is the 2D geometry of graphene; 2D sheets have a high aspect ratio that increase stress transfer to graphene based on shear lag theory and thus also increases the modulus and stiffening effect.

6. Conclusions
In this research, graphene was used as an additive nanomaterial for cement mortar at different dosages; a sonication process technique was also used as a dispersion method, with specific sonication parameters. The results clearly show that graphene offers enhancement to the mechanical properties of cement mortar after proper sonicating; the enhancement to compressive and flexural strength due to graphene are equal to 11.7% and 21.3%, respectively, without sonication, and 32.8% and 23.9%, respectively, in sonicated graphene. In terms of increasing the graphene dosage added to the mix, different sonication parameters are required to reduce the effect of graphene agglomeration. Mix6, with only 0.006% graphene, was thus identified as the optimum mix in this research, based on it having the largest quasi-static compressive and flexural strengths.

7. References
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