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Effects of using aqueous graphene on behavior and mechanical performance of cement-based composites

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Abstract

This paper presents the results of an investigation into aqueous graphene (AG) in Portland cement (PC) mortars for the first time. The investigation found that AG can be used to replace powdered pristine graphene nanoplatelets (PG) in PC mortar because AG has fewer agglomerates than PG. Thus, AG not only has lower manufacturing and carbon costs compared to PG, it is also shown to outperform PG in improving the compressive strength of PC. Using AG increases cement gel nucleation seeding and prolongs PC hydration thereby improving the content and morphology of the hydration products with the resulting compressive strength of AG mortar samples being about 13\% higher than PG mortar samples (70 vs 62 MPa).

Keywords: graphene, agglomeration, dispersion, nucleation seeding, compressive strength

1 Introduction

Portland cement (PC) has been widely used due to its low cost and high compressive strength. Current global PC production is about 4.4 billion tons and is expected to increase due to growing infrastructure demand [1]. PC is however the largest contributor to CO\textsubscript{2} emissions from the construction industry: the production of PC clinker is responsible for about 8\% of global CO\textsubscript{2} emissions (~3 Gt of CO\textsubscript{2} annually) [2]. Many efforts have been made to reduce CO\textsubscript{2} emissions through the use of alternative fuels (e.g. biomass) [3], and the use of supplementary cementitious materials (SCMs) such as fly ash or blast-furnace slag as clinker replacement [4-6]. Reducing PC clinker ratio by SCMs is straightforward but they generally reduce early hydration and strength development which is particularly impactful on the usage of SCM’s in precast and repair concretes.

The hydration of PC is associated with formation, swelling, and binding of hydration products (e.g., C-(A)-S-H and ettringite). These products reduce pore volume and provide a network structure
to enable PC-based materials to harden and gain strength. Isothermal calorimetry results of PC indicate five stages of its hydration process, this is illustrated in Fig. 1 [7-9]. Stage I is the dissolution period in which PC is dissolved in water along with an associated high heat release. The dissolution period is followed by an induction period (Stage II), which is characterized by very low activity. The low hydration rate of stage II is attributed to the difficulty in nucleating hydration gels [10] and the formation of a thin protective layer on PC particles which acts as a diffusion barrier to dissolving ions. During Stage III (the acceleration period), the hydration rate to produce hydration gels (e.g., C-(A)-S-H) drastically increases for several hours. Afterwards (stage IV), the reaction rate decreases rapidly to a lower level. Finally, reaction rate descends to a much lower reaction rate in the last hydration period (stage V). The low hydration rate of stages IV and V is widely agreed to be controlled by the slow diffusion of ions through the layers of hydrates depositing over the PC particles.

To overcome the slow hydration activity and improve the mechanical and durability performance of PC-based materials, nanoparticles have been investigated to accelerate the hydration process of cement [11-13]. When nanoparticles are well-dispersed in PC paste, they act as seeds and provide heterogeneous nucleation sites and increase surface area on which hydration products can grow. The precipitation of hydration products on the nanoparticles, instead of on clinker particles reduces the diffusion barrier effects in the dissolution of PC clinker [14-16], thus the presence of nanoparticles stimulates the hydration of PC at stage II, facilitates the formation of hydration gels at stage III, and facilitates continual hydration of PC at stage IV. Additionally, nucleation in the pore space removes calcium and hydroxide ions from the solution, thereby creating a local concentration gradient away from the clinker particles, which further accelerates PC clinker dissolution [17, 18].

![Fig. 1 Rate of heat evolution during hydration of PC: stage I dissolution period, stage II induction period, stage III acceleration period, stage IV deceleration period, stage V slow ongoing hydration](image-url)

Fig. 1 Rate of heat evolution during hydration of PC: stage I dissolution period, stage II induction period, stage III acceleration period, stage IV deceleration period, stage V slow ongoing hydration
In recent years, graphene has been deployed as nanoparticles to enhance the performance of cement-based materials [19-23] due to its outstanding properties to form graphene-reinforced cement composites for smart infrastructures. Graphene, a single-layer of sp2 bonded sheet of carbon atoms arranged into a 2D honeycomb lattice pattern (with an interlayer thickness of ~0.335 nm), has intrinsic high mechanical properties (i.e., the strength of ~100 GPa and the Young’s modulus of 1 TPa [24]) therefore has potential to greatly improve the mechanical properties of cementitious materials. This nano-sized material can act as (i) a nano-filler which can fill coarse voids to form finer voids, and (ii) a nucleation site for promoting cement hydration [25], leading to a denser microstructure of the cement matrix. The single-layer of carbon atoms in graphene sheets results in a high aspect ratio (i.e., defined as the ratio between the lateral size and the thickness, which can reach more than 2000) and high surface area (i.e., maximum theoretical surface area is 2600 m²/g) [26]. The greater exposed surface area of graphene sheets generate more potential nucleation sites for PC hydration and improve bonding between graphene and the cement matrix. The experimental results of Ho [28] show that improvements in hydration and microstructure of mortar samples using 0.07% graphene (by weight of cement) result in an increase in the compressive and tensile strength by 34 and 27%, respectively. However, in order to achieve the aforementioned improvement, graphene (or any nanoparticle) should be very well dispersed inside the cement-based material.

Currently, three techniques are used to disperse graphene in the cement matrix: dry dispersion, wet dispersion without ultrasonication, and wet dispersion with ultrasonication [27]. In the dry dispersion technique, graphene is directly mixed with dry cement by a concrete mixer or high-speed shear mixer for up to 72 h. However, this method of graphene dispersion in cement material has been found to not be effective [27, 28]. In the wet dispersion technique, superplasticizer is added to weaken the Van der Waals force between graphene sheets to improve the dispersion of graphene into the water [29-31]. The backbone of the superplasticizer molecules absorb on the surface of graphene sheets. The negative charges of the side chain of superplasticizer molecule are thought to generate electrostatic repulsion force to repel graphene sheets from each other [32, 33]. The wet dispersion without ultrasonication disperses graphene in water and superplasticizer by mechanical stirring, then mixing the dispersed graphene solution with the dry cement. However, this dispersion technique has been shown to be ineffective in enhancing mechanical performance of graphene cement paste samples due to poor dispersion of graphene particles because the electrostatic repulsion force created by the superplasticizer is unable to exfoliate monolayer graphene from stacks of graphene [27]. Therefore, the wet dispersion with ultrasonication technique has been developed to enhance the dispersion of graphene. In this technique, the strong hydrodynamic shear-force and
cavitation effects generated by the sonicator can exfoliate graphene primary particles by overcoming the binding energy in agglomerates, thereby allowing many more superplasticizer molecules to absorb on the surface of graphene particles [27, 34, 35]. The wet dispersion with ultrasonication technique has been found to be the most effective technique to achieve uniform dispersion of graphene in aqueous solution. This method was shown to increase the compressive and flexural strengths by ~20% for mortar samples [27, 36] and ~40% for concrete samples [37, 38].

However, the wet process with ultra-sonication to achieve uniform graphene dispersion in cement-based materials is energy-intensive. This method has a high energy demand due to sonicated graphene flakes restacking and re-agglomerating when used in a concentrated graphene dispersion [39]. To reduce the cost of graphene dispersion, this study proposes to use aqueous graphene (AG). AG (consisting of 80% water and 20% PG, without any other by-products) is an intermediate product of electrochemically exfoliated powder graphene (PG), and it is supplied as a paste form without drying in contrast to PG which is dried. Therefore, AG is cheaper and more ready form of graphene than PG, which brings with it advantages of lower cost and lower environmental impact. More importantly, in paster form, AG has the potential to be better dispersed in composite because it can more easily facilitate the adsorption of superplasticizer due to a higher number of free platelets compared to PG. Since dispersion of graphene is a critical factor affecting the performance of graphene modified cement-based composites, it is essential that the expected improvement of AG dispersion is thoroughly investigated and confirmed and its effects on the properties of graphene modified cement-based composites are quantified. This is the main aim of the paper.

While some levels of agglomeration of graphene are reversible, e.g. through ultra-sonication, some agglomeration is irreversible due to strong Van der Waals interactions, precipitation, and incompatibility with water [40]. Irreversible agglomeration that results in large graphene flakes is thought to result in decreased mechanical properties of cement-based materials at high graphene contents due to increased defects caused by large graphene flakes inside the cement-based matrix. Large agglomerates also block water inside the graphene flocs which is necessary for hydration of the cement paste [25].

Thus, while AG is expected to improve dispersion of graphene compared to PG, AG may not improve irreversible agglomeration of graphene. The aim of this paper is to carry out detailed experimental investigations to provide insight into the effects of graphene on mechanical properties of cement-based materials. This paper investigates the use of AG, which is an intermediate product in the graphene manufacturing process, for potential application in cement-based materials for the first time. The replacement of AG for PG is expected to provide cheaper and lower carbon cementitious materials. In particular, this paper compares the effects of agglomeration and re-
agglomeration of graphene in powder form (AG) and in aqueous form (PG) on various qualities of the cement-based material. It is possible to assess whether graphene is better dispersed through comparison of PC hydration with AG and PG. Hydration will be probed by conducting a variety of chemical analysis tests (Ultraviolet-visible test, Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric (TG), scanning electron microscopy (SEM) and backscattered electron (BSE). On the other hand, irreversible graphene agglomeration would cause effect on flowability, setting time and the optimal level of graphene dosage at which the compressive strength of cement-based matrix peaks. A comparison of the effect of using AG and PG on these values would help to resolve whether AG has any benefit in reducing irreversible agglomeration. However, it should be noted that at this stage, the concept of reversible and irreversible agglomeration is a hypothetical concept and it is not possible to provide detailed measurements. Nevertheless, this concept potentially leads to a new understanding of the mechanism of how graphene affects the behavior of cement-based material.

2 Materials and Methodology

2.1 Materials

The PC used in this study was CEM1 52.5N from Hanson-UK with the chemical composition shown in Table 1. The addition of additives and/or supplementary cementitious materials to CEM2 cement could affect the hydration of pure cement, which would not reflect the full influence of graphene on cement hydration. As a result, CEM1 cement was chosen for the experiment. Furthermore, CEM1 52.5N was used because it is more readily available than CEM1 42.5N. The specific surface area of the PC was 383 m²/kg. The AG and PG were provided by First Graphene (UK). Except for the drying process of PG production, the AG and PG have undergone a similar manufacture process, hence they have the same physical dimensions shown in Table 2. A polycarboxylate-based superplasticizer (SP) (ADVA 650, UK) was used to enhance dispersion and stabilization of PG and AG in the mixing water [29, 30, 41]. Fig. 2, provided by the supplier, presents SEM images of PG and AG platelets (dark particles) dispersed in a latex polymer (i.e., 30% w/w graphene) which reflects similar behavior as PG and AG platelets in water. AG (Fig. 2 (a)) shows better dispersion than PG (Fig. 2 (b)) as seen by the smaller AG flakes than PG flakes.

<table>
<thead>
<tr>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>Fe₂O₃</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>TiO₂</th>
<th>MnO</th>
<th>SO₃</th>
<th>L.O.I</th>
</tr>
</thead>
<tbody>
<tr>
<td>65.08</td>
<td>20.15</td>
<td>5.06</td>
<td>2.52</td>
<td>1.99</td>
<td>0.86</td>
<td>0.41</td>
<td>0.23</td>
<td>0.06</td>
<td>-</td>
<td>3.03</td>
</tr>
</tbody>
</table>

Table 1. Chemical composition of PC CEM1 52.5N in this study (%) (provided by supplier)
Table 2. Physical properties of PG and AG

<table>
<thead>
<tr>
<th>Layer number (layers)</th>
<th>Thickness (nm)</th>
<th>Lateral size (µm)</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>16.7</td>
<td>5.3</td>
<td>1.65</td>
</tr>
</tbody>
</table>

![Fig. 2. SEM image of (a) PG and (b) AG dispersed in latex polymer](image)

2.2 Methodology

UV-vis spectroscopy was used to evaluate stability of PG and AG after sonication in water. FTIR, XRD, TG, SEM and BSE analyses were performed to investigate the influence of PG and AG on hydration of PC and microstructural development of PC matrix. Setting time and flow table tests were used to compare the influence of PG and AG on fresh properties of PC composites. Compression strength test at different curing durations (3, 7 and 28 days) on PC paste and mortar cubes was carried out to measure the influence of PG and AG on mechanical performance of PC composites.

2.2.1 Sample preparation

All tests were conducted on three sets of samples: control samples (CS) without any graphene, samples with PG and samples with AG. Table 3 lists the mix proportions in the three groups of samples. Graphene dosage is based on results of the research by Ho [42] which indicates that the optimal graphene dosage is less than 0.07% (by mass of cement). The amount of SP (0.9% by mass of cement) was suggested by the manufacturer. The ratio of water to binder of 0.36 ensures suitable followability of mortar.

To prepare the graphene mix suspension, SP was used to improve the dispersion and stability of graphene. SP was first mixed with water manually for 30 s, and then graphene (either PG or AG) was added into the mixture of water and SP solution, followed by sonication using a RS Pro
ultrasonic cleaner (200 W) for 30 mins. The graphene suspension was then mixed with the dry mix of cement and sand for 2 mins. After mixing, the mortar samples were cast into 50 mm cubic moulds, consolidated by a vibrating table, and finished by a trowel. All samples were demoulded after 24 hours and cured in water under the ambient temperature of 20 ± 2 °C until tested. The graphene suspensions of samples PG0.07 and AG0.07 were also prepared for the UV-vis test.

Table 3. Mixture proportion of cement-based mortar samples

<table>
<thead>
<tr>
<th>Mix label</th>
<th>Graphene type</th>
<th>Graphene dosage (%)</th>
<th>Mortar mixture proportion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PC</td>
<td>Sand</td>
</tr>
<tr>
<td>CS</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PG0.005</td>
<td>-</td>
<td>0.005</td>
<td>-</td>
</tr>
<tr>
<td>PG0.01</td>
<td>PG</td>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>PG0.017</td>
<td>PG</td>
<td>0.017</td>
<td>-</td>
</tr>
<tr>
<td>PG0.035</td>
<td>PG</td>
<td>0.035</td>
<td>-</td>
</tr>
<tr>
<td>PG0.07</td>
<td>PG</td>
<td>0.07</td>
<td>-</td>
</tr>
<tr>
<td>AG0.005</td>
<td>AG</td>
<td>0.005</td>
<td>-</td>
</tr>
<tr>
<td>AG0.01</td>
<td>AG</td>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>AG0.017</td>
<td>AG</td>
<td>0.017</td>
<td>-</td>
</tr>
<tr>
<td>AG0.035</td>
<td>AG</td>
<td>0.035</td>
<td>-</td>
</tr>
<tr>
<td>AG0.07</td>
<td>AG</td>
<td>0.07</td>
<td>-</td>
</tr>
</tbody>
</table>

2.2.2 UV-vis

Sedimentation of PG and AG in solutions was measured by UV-vis spectrophotometer. The changing UV-vis absorbance of graphene solutions over time was obtained by using UV-Vis Camspec - M550 to provide a quantitative analysis of sedimentation of PG and AG in solutions. UV absorption was recorded in the wavelength range of 250–500 nm.

2.2.3 Flow and setting time

The corresponding pastes were prepared to investigate the influence of PG and AG on flow table values and setting time. The flow table test of fresh cement paste was carried out according to ASTM C230/C230M-21 [43]. The truncated cone mould has a top diameter of 70 mm, a height of 50 mm, and a bottom diameter of 100 mm. A tamper was utilised to ensure uniform filling of the truncated cone mould with fresh mortar. The mould was then lifted vertically, and the average horizontal spread of fresh mortar was measured. The setting time was measured on paste using the Vicat test.
procedures, according to ASTM C191 −13 [44]. The reported results were the average of two measurements.

2.2.4 Microstructural analysis

After setting time measurement, all test samples were cured in water under ambient temperature of 20 ± 2 °C for other 6 days before microstructural analyses. After curing, the samples were stored in isopropanol for one day to stop hydration. The samples were then dried in a vacuum oven at 40 °C for another one day before microstructural analyses. The dried samples were ground down and passed through a 75 μm sieve for XRD, TG, and FTIR analyses.

XRD was performed on a PANaytical X’Pert Pro Diffractometer using CuK\textsubscript{α} radiation (40 kV, 40 mA) with a scanning rate of 0.02° 2θ/step from 5 to 60° 2θ. FTIR was performed by using a Bunker Vertex 70v spectrometer. The infrared spectrum was recorded in the range of 500 cm\textsuperscript{-1} to 4000 cm\textsuperscript{-1} with a resolution of 8 cm\textsuperscript{-1} by transmittance on powder samples.

TG was performed by using TGA 550 from TA instruments in a temperature range from 30 to 900 °C with a heating rate of 10 °C/min under nitrogen flow. To quantify the amounts of different phases in each sample, derivative thermogravimetry (DTG) curves were deconvoluted according to the Gaussian area deconvolution method using Origin 2017 software, which revealed the area corresponding to the decomposition of each phase.

SEM and BSE were carried out with a Tescan Mira3 SC microscope at an accelerating voltage of 10 kV. To prepare for BSE samples, the vacuum dried samples were polished to obtain smooth surfaces. Sandpapers were used prior to final polishing by diamond suspensions (6, 3 and 1 μm). Dust and diamond particles generated during the polishing process were removed by cleaning the samples with isopropanol in an ultrasonic bath twice, which was followed by drying in a vacuum oven at 40 °C for 24 hours. Afterwards, the polished samples were exposed to compressed air jet to remove any dust from their surfaces prior to being mounted onto aluminum stubs using double-sided adhesive carbon disks and coated with gold by a Quorum Q150T ES Sputter coater before BSE analysis. SEM imaging was performed on unpolished samples to observe the morphology of hydrated products. SEM and BSE imaging was carried out with a magnification of 5000 and 1000, respectively.

2.2.5 Compressive tests

Compressive strength tests were carried out in a servo-controlled hydraulic testing machine (CONTROLS 50-C56Z00) in triplicates at 3, 7, and 28 days, operated at a loading rate of 0.4 MPa/s.
3 Results and discussions on microstructure analysis

3.1 UV-vis

Fig. 3 compares the UV absorbance by AG and PG solutions at different times (0h, 1h, 2h, 4h, and 24h). The sedimentation of graphene in aqueous solution is measured as absorbance from UV–vis test. A solution having a higher absorbance with time indicates better dispersion of graphene over time. Due to the absence of sedimentation of graphene in the solution at the start of the experiment, it is highly likely that the higher absorbance of PG than AG at 0h is merely a result of measurement noise. The higher absorbance of AG suspension after 1h indicates better dispersion and maintaining stability of AG than PG. The higher absorbance of AG suspension after 1h, indicating better dispersion and maintaining stability of AG than PG. The improved dispersion and stability of AG can be attributed to the paste form of AG alleviating hydrophobic properties of PG, thereby allowing the backbone of superplasticizer molecules to absorb on the surface of AG particles to generate an electrostatic repulsion force to repel AG particles from each other and maintain their stability in the solution [32, 33]. Maintaining stability and dispersion of graphene over time is critical to accelerate the hydration of PC until it is finally set. The use of AG results in lower reversible graphene agglomeration and better acceleration of PC hydration than the use of PG.
Fig. 3. Comparison of absorbance between using AG and PG: UV-vis test results for: (a) 0 and 1 hour, (b) 2 hours, (c) 4 hours and (d) 24 hours

3.2 FTIR

Functional groups and covalent bonding of hydration products in paste samples with and without graphene can be detected by FTIR. Fig. 4 presents the infrared transmittance spectra in the range of 500 cm\(^{-1}\) to 4000 cm\(^{-1}\) of hydration phases of CS, PG0.017 and AG0.017 paste samples at the age of 7 days. The results shown that all samples have a complex group of bands of C-(A)-S-H in the range of 600-1200 cm\(^{-1}\), corresponding to the asymmetric and symmetric stretching vibrations of Si–O and Al-O bonds [45, 46]. To summarize, the correspondence between absorption band and stretching vibration of hydration products are as follows:

- \(\sim 780\) cm\(^{-1}\): Al-O bonds of the octahedrally coordinated Al and the vibrations of Al-O bond in AlO\(_4\) units [46];
- \(\sim 900\) cm\(^{-1}\) and \(\sim 1080\) cm\(^{-1}\): Si–O at Q\(^2\) sites [45];
- \(\sim 1221\) cm\(^{-1}\): Si–O at Q\(^3\) sites [45];
- \(\sim 1600\) cm\(^{-1}\) and \(\sim 3480\) cm\(^{-1}\): O-H groups in water [45, 47, 48];
- \(\sim 3660\) cm\(^{-1}\): hydroxyl group in Ca(OH)\(_2\) [45];
- \(\sim 3790\) cm\(^{-1}\): Si-OH bonds [49];
- \(\sim 2350\) cm\(^{-1}\), \(\sim 2850\) cm\(^{-1}\) and \(\sim 2920\) cm\(^{-1}\): presence of calcium carbonate, formed during sample preparation and remained after clinker calcination [50, 51].

The results in Fig. 4 confirm that using PG or AG does not alter the chemical structures of hydration products. This is expected because graphene is chemically inert. Using graphene promotes chemical reactions compared to the control sample, this is clearly demonstrated by the reduced intensities of
Ca(OH)$_2$ (band at ~3660 cm$^{-1}$) and Si-OH (band at ~3790 cm$^{-1}$), attributed to the nucleation sites of PG or AG promoting hydration reactions to accelerate the consumption of Ca(OH)$_2$ and Si(OH)$_4$ in the formation of C-(A)-S-H. However, because the physical properties of AG and PG (e.g., size, thickness and surface areas) are similar, there is little difference in infrared transmittance spectrums of PG and AG samples.

3.3 XRD

Fig. 5 shows the XRD patterns of CS, PG0.017 and AG0.017 paste samples after 7 days of hydration. The main hydration products identified in the XRD patterns are ettringite (main peak centered at ~9.09º 20) and portlandite (main peak centered at ~18.04º 20). The presence of calcite (main peaks centered at ~29.38 and 39.54º 20) can be attributed to carbonation when paste samples are exposed to the ambient condition during setting time tests and during sample preparation. The identification of C-(A)-S-H is complicated because it is predominantly amorphous and its peaks overlaps with those of calcite. The unhydrated C$_3$S, C$_2$S (overlapped main peak centered at ~32.1º 20) and C$_4$AF (main peak centered at ~33.26º 20) were also detected in samples.

As shown in the XRD results (see Fig. 5), using AG or PG in PC does not alter the crystal phases, as evidenced by the similar peak patterns, but it does influence the rate of acceleration of the hydration process of PC as reflected by the different peak intensities on the XRD patterns (higher intensity of hydration products like ettringite and portlandite (crystal phase only, not including
amorphous phase) for AG and PG, and lower intensity of unhydrated $C_3S$, $C_2S$, and $C_4AF$ for CS). This again is a result of graphene (either in AG or PG form) and does not affect the nature of chemical reactions, but their speed and intensity. However, due to similar properties of AG and PG, the peaks of hydrated and unhydrated phases of AG and PG samples show similar intensities.

Fig. 5. XRD patterns of paste samples after 7 days of hydration
3.4 TG-DTG

Fig. 6 shows TG-DTG results of CS/PG/AG paste samples after 7 days of hydration. Three major mass losses can be observed in the TG-DTG curves: strong endothermic peak at ~100 °C, indicating dehydration of water bonded to ettringite and C-(A)-S-H; endothermic at ~430 °C corresponding to decomposition of portlandite, accompanied with dehydroxylation; two further endothermic peaks at ~600 and 750 °C representing decarbonation of calcite. These decomposition steps are consistent with the results of previous studies by others [52-54]. Table 4 summarises and compares mass loss values associated with different decompositions of CS/PG/AG samples.

Most of the mass lost is dehydration of ettringite and C-(A)-S-H. In line with FTIR and XRD results that show improved hydration of PC grains through the provision of additional nucleation sites, the inclusion of graphene (in either PG or AQ form) results in higher mass loss due to increased dehydration and dehydroxylation in PG0.017 and AG0.017 samples when compared to CS (14.86 and 14.9 vs. 14.53 %). The nuclei of hydration products not only form on the surface of PC grains but also around the PG/AG dispersed within the pore space, thus making the microstructure of PG0.017 and AG0.017 samples denser, leading to lower carbonation degree in these samples compared to the CS (8.05 and 8.00 vs. 8.20 %). The higher total mass loss of PG0.017 and AG0.017 samples than the CS (22.81 and 22.90 vs. 22.73 %) suggested higher formation of hydration products in these samples than the CS. Comparing the results between AG and PG samples, AG samples experienced slightly higher total mass loss indicating improved performance of AG over PG in facilitating dehydration of PC.
Fig. 6. TG-DTG results of paste samples after 7 days of hydration: (a) CS, (b) PG0.017 and (c) AG0.017
Table 4. Comparison of mass loss values of paste samples after 7 days of curing.

<table>
<thead>
<tr>
<th>Mix</th>
<th>Dehydration (≈50-250 °C)</th>
<th>Dehydroxylation (≈250-500 °C)</th>
<th>Decarbonation (≈500-850 °C)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS</td>
<td>9.81</td>
<td>4.72</td>
<td>8.20</td>
<td>22.73</td>
</tr>
<tr>
<td>PG0.017</td>
<td>9.91</td>
<td>4.95</td>
<td>7.95</td>
<td>22.81</td>
</tr>
<tr>
<td>AG0.017</td>
<td>9.88</td>
<td>5.02</td>
<td>8.00</td>
<td>22.90</td>
</tr>
</tbody>
</table>

### 3.5 SEM

Fig. 7 shows SEM images of AG/PG/PC paste samples after 7 days of hydration. Needle-like formation of ettringite (diameter ~0.1 μm, length ~1 μm) can be observed in the CS sample (Fig. 7 (a)). The use of PG or AG significantly improves the morphology of needle-like ettringite which is shown as increased crystals (diameter ~0.2 μm, length ~3 μm) in PG0.017 (Fig. 7 (b)) and AG0.017 (Fig. 7(c)) samples. Graphene flakes (either in AG or PG) enables formation of larger crystals of hydration products. Improved hydration filling effect also enable PG and AG to link small crystals into massive solids. The crack in the AG0.017 sample was due to sample preparation for SEM operation, not reflecting performance of the AG sample.

While SEM images of CS/PG/AG samples show better performance of PG/AG samples over CS sample, they do not show improvement using AG compared to using PG. The later can be seen in Fig. 8 which compares BSE of different samples. BSE observation was carried out in many areas of the samples, and Fig. 8 shows a typical distribution of unhydrated cement particles in CS/PG/AG samples. A quantitative statistical analysis shows that PG and AG samples have much smaller sizes of unhydrated PC particles (typically from 20 to 40 μm) than CS samples (many >40 μm, up to ~80 μm). Furthermore, sample AG0.017 has smaller sizes of and fewer unhydrated PC particles than sample PG0.017. This is further evidence that AG0.017 sample has better hydration than the PG0.017 sample due to better dispersion of AG than PG in the cement matrix, thus accelerating hydration of the AG sample more than the PG sample.
Fig. 7 SEM images of paste samples after 7 days of hydration: (a) CS, (b) PG0.017 and (c) AG0.017
Fig. 8 BSE images of paste samples after 7 days of hydration: (a) CS, (b) PG0.017 and (c) AG0.017
3.6 Summary of the influence of AG and PG on PC hydration

As a summary of results of various detailed tests presented in the previous section, the effects of AG and PG on PC hydration are as follows:

1. Using AG can achieve a better (more stable) graphene dispersion than PG, as shown by slower sedimentation of AG in water, evidenced by a reduction in UV-vis absorbance over time (Fig. 3).

2. Graphene, in AG or PG form, does not change the chemistry and crystallinity of hydrated PC, this is confirmed by FTIR patterns (Fig. 4) and XRD patterns (Fig. 5).

3. However, AG or PG will accelerate hydration of PC, which is exhibited by differing intensities of hydrated products and unhydrated products in FTIR, XRD tests (Fig. 4 and 5), mass loss of hydration products in TG tests (Fig. 6), improved morphology of hydration products (Fig. 7), and reduced unhydrated products in SEM/BSE images (Fig. 8).

4. It is well known the reduced hydration of cement and reduced performance of cement composites can be directly attributed to poor dispersion and agglomeration of graphene [42, 55, 56] in the composite. The UV-vis results can be used to directly confirm better dispersion of AG over PG because AG and PG are not affected by chemical cross-linking caused by dissolved cement positive ions like graphene oxides [57]. The consistent better results of AG over PG from FTIR, TGA, XRD, and SEM tests are confirmation that AG is better dispersed than PG in the composite.

4 Comparison of effects of AG and PG on macro engineering performance of PC mortar

The different effects of AG and PG on PC mortar, as shown in sections 3.1-3.5 in detail, and summarized in section 3.6, are reflected in a number of macro engineering properties of PC mortar, including flow and setting times, and compressive strength, as presented in the next two sections.

4.1 Flow table and setting times

Table 5 compares setting times and flow table values between CS, and AG/PG samples at different dosages. The results in Table 5 indicate that acceleration in PC hydration due to AG and PG leads to slight shortening setting times (5.5h and 12.25 h for CS compared to values of slightly lower values than 5.5 h in most cases and slightly lower than 12.25 h respectively when AG and PG is used). However, the differences are too small to be considered useful advantages for PG and AG samples.
The inclusion of AG/PG may affect the hydration of cement in its initial state, which could change the setting time of cement paste. On the other hand, beyond a certain dosage, graphene reduces the workability of cement-based materials [42]. However, the flow table and initial setting time values show that there is a slight difference, which means that graphene levels between 0.005-0.07 % have an insignificant effect on workability and hydration in the initial stage. Nevertheless, as hydration proceeds, the improvement in hydration within graphene samples stimulates the formation of hydrated cements and thus shortens the final setting times of PG and AG samples by 1 hour (i.e., 11.0–11.25 h for PG samples and 11.0–11.5 h for AG samples vs. 12.25 h for CS samples).

Table 5. Setting times and flow table values of paste samples

<table>
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<tr>
<th>Mix label</th>
<th>Setting times (h)</th>
<th>Flow table (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Final</td>
</tr>
<tr>
<td>CS</td>
<td>5.5</td>
<td>12.25</td>
</tr>
<tr>
<td>PG0.005</td>
<td>5.5</td>
<td>11.25</td>
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<td>PG0.01</td>
<td>5.0</td>
<td>11.0</td>
</tr>
<tr>
<td>PG0.017</td>
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<td>11.0</td>
</tr>
<tr>
<td>PG0.035</td>
<td>5.25</td>
<td>11.0</td>
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</tr>
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</tr>
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</table>

4.2 Compressive strength

Fig. 9 compares compressive strengths PC mortar samples at different ages up to 28 days. The effects of AG and PG on the compressive strength of PC are in line with the results revealed by UV-vis, FTIR, XRD, and TG-DTG results, as follows:

(a) Using graphene, in either PG or AG form, enhances the compressive strength of PC mortar, due to increased hydration, cement hydrates form at nucleation sites and form a denser microstructure in PC mortars.
(b) Enhancements in compressive strength of PC mortar due to using AG and PG are especially impressive at the earlier age and then decrease with time because of a decreasing rate of hydration of PC over time. For example, for 0.017% graphene dosage, the compressive strength increases are 28% and 35% respectively for PG and AG samples at 3 days, compared to 4% and 13% respectively at 28 days.

(c) As a result of better stability of AG than PG (UV-vis result in Fig. 3), using AG enables more hydration than using PG (as revealed by increased mass loss of hydrate products in TG-DTG results, and fewer unhydrated PC particles in SEM observation), therefore, the compressive strengths of AG samples are higher than that of PG samples. For example, comparing AG and PG samples, for 0.017% graphene dosage, the increase in PC compressive strength due to using AG over PG is 13% at 7 days and 8% at 28 days.

(d) When either AG or PG is used, an increase in graphene dosage does not lead to continued increase in compressive strength of PC mortar, as has been consistently observed in number of other studies [42, 58, 59]. The enhancement reaches a peak value at a certain graphene dosage. In this research, this dosage is 0.005-0.017% for both AG and PG. At this stage, it is hypothesized that this is a result of some re-agglomerated graphene flakes become irreversible. As the dosage of graphene (either in AG or PG) increases, the irreversibly agglomerated graphene flakes increase in size. After reaching a critical size, the agglomerated graphene flakes would contain defects at their interface with PC mortar, which leads to reduction in compressive strength of PC mortar. AG and PG are physically very similar forms of graphene and hence using either would result in the same sizes of agglomerated graphene flakes. Therefore, using either AG or PG would likely not change the graphene dosage at which enhancement in compressive strength of PC mortar reaches the peak, as observed in this research.
5 Conclusions

This paper investigates the effects of using aqueous graphene (AG), as a cost-effective way of incorporating graphene in cement-based mortar, to replace powdered graphene (PG). Several different microstructure and macro engineering tests were carried out to compare the effects of using AG and PG in PC mortar. The main conclusions are:

- There is no change in types of chemical reactions by using AG or PG, and this is confirmed by FTIR test results.
- The paste form of AG enables it to achieve better dispersibility and stability in water. This is shown in the results of UV-vis tests.
- The better dispersion of AG than PG in water helps to improve hydration of PC. This manifests as greater concentrations of hydration products in AG samples evidenced by the results from TG-DTG and SEM/BSE tests.

Fig. 9. Compressive strength of mortar samples
AG offers better performance for PC-based materials than PG and demonstrates its suitability for industry applications as a replacement for PG due to its ready availability, lower cost, lower embedded carbon footprint, and ease of distribution. For example, at the optimal level of graphene dosage at 0.017% for both AG and PG samples, using AG leads to an increase in compressive strength from 62 MPa for PG sample to 70 MPa for AG sample).

However, using either AG or PG reaches peak improvement in compressive strength of cement-based material at very similar graphene dosage, suggesting similar irreversible agglomeration. This is potentially a new finding to explain the consistently observed result of stunted improvement or reduction in compressive strength of PC mortar and concrete at high graphene dosage over a certain value.

In summary, this paper has confirmed the good potential of using AG, which is cheaper and has lower embodied carbon than conventional PG, to improve the dispersion of graphene and to obtain better performance of graphene modified cement mortar. However, the reversible and irreversible agglomerations of AG/PG in the cementitious materials have not been measured. Further research should focus on measuring the degree of irreversible agglomeration of AG and PG.

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