Investigation of the dispersion of multi-layer graphene nanoplatelets in cement composites using different superplasticiser treatments

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Highlights:

- A combination of a mechanical method and a surfactant, results in better dispersion of multi-layer graphene nanoplatelets (GNPs)
- Commonly used superplasticisers can be effective in dispersing the graphene nanoplatelets in the cement matrix
- A polycarboxylate superplasticiser is the most effective dispersant

Keywords: Graphene nanoplatelets, Cement, Dispersion, Superplasticiser
The emergence of nanomaterials research over the past decades, allows the construction sector to turn the cement-based structures into fully digitised, cognitive assets with additional functionalities and improved durability and sustainability performance. Multi-layer graphene nanoplatelets (GNPs) is one such nanomaterial that could be used in cementitious structures. However, the homogenous dispersion of commercially available GNPs has been found to be a key challenge in the literature. This study aimed to develop a practical dispersion protocol to promote the use of GNPs in cementitious systems. Four different commonly used superplasticisers were tested, including a lignosulphonate, a naphthalene-based and two polycarboxylates, along with sonication. The GNPs were characterised using Scanning Electron Microscopy (SEM), Thermogravimetric Analysis (TGA) and X-Ray Diffraction analysis (XRD). The effect of the different superplasticisers on the GNPs dispersion in water was tested with zeta-potential, while UV-Vis spectroscopy was used to examine the effect of the superplasticiser dosage. This was followed by rheology testing that assessed the impact of the superplasticisers on dispersing the GNPs in cement paste. It was found that dispersion of GNPs in water with sonication is not sufficient and a chemical treatment is also needed. The polycarboxylates that work by a steric hindrance mechanism, by physically separating the GNPs and cement particles, were found to be more effective compared to the plasticisers that work by electrostatic repulsion. This research provides a practical dispersion protocol for GNPs in cementitious systems to promote more advanced construction materials.
1. Introduction

Cement based composite materials - such as concrete, mortar and paste - are widely used for infrastructure projects, including buildings, bridges, tunnels and airports. However, the construction materials currently employed in infrastructure are passive and inert, far from being carbon neutral, maintained reactively and serve no additional functionality [1–3]. Over the past few decades, there has been increasing research interest in the use of nanomaterials that have at least one dimension in the range of 1-100nm [4–6]. The use of nanomaterials could allow the infrastructure industry to turn the cementitious structures into fully digitised, cognitive assets with additional functionalities and improved durability and sustainability performance [7–10].

One such nanomaterial is graphene, which was isolated in 2004 through graphite exfoliation, and its properties include high strength and electrical conductivity, high flexibility and toughness, low weight and thickness as well as barrier properties to aggressive atoms [11,12]. Graphene is a 2-dimensional material (one atom thick), however, at one-layer thickness it is very expensive and currently it would be prohibiting to use at a large scale for civil engineering applications (for example, 500 mg of graphene powder cost £398 in January 2021 prices [13]). There are many different fabrication techniques for graphene-related materials, and each production method would result in varying fundamental properties, including number of layers, average lateral size and carbon-to-oxygen (C/O) atomic ratio and it will also have an effect on cost and scalability [12,14]. Depending on the production technique, graphene can come in many different forms and graphene-related materials include graphene oxide (GO), reduced graphene oxide (rGO), multi-layer graphene nanoplatelets (GNPs) as well as natural graphite which is the starting material for graphene fabrication. GNPs are of interest for use in
cementitious composites because they are suitable for production at scale for bulk structural applications and a common production technique is the liquid phase exfoliation \([12,14,15]\). GNPs are comprised of many layers of graphene sheets (usually between 10-100 layers) and have a diameter of several micrometers, which makes them a more economical alternative to the single layer graphene \([16]\). Furthermore, GNPs do not possess any oxygen functional groups, which makes it possible to generate an electrically conductive network within the cementitious matrix that could ultimately lead to advanced functionalities, such as a self-sensing mechanism, where the material can sense its own environment and condition \([17–19]\).

A key challenge with using currently available GNPs in cementitious composites is their homogenous dispersion, because their large surface area can lead to high van der Waals forces (attractive forces) between the individual particles \([20]\) and also because of their hydrophobic nature which leads to their aggregation in aqueous systems \([21,22]\). Researchers have used a variety of dispersion techniques for GNPs, which can be categorised as mechanical or chemical methods (or a combination). The mechanical methods include high speed shear mixing, ball milling, magnetic stirring and ultrasonication \([23,24]\). The chemical methods include covalent or non-covalent functionalisation; the first involves chemical modification of the material using acids and oxidants, which could introduce defects in the material; and the latter is based on a non-covalent interaction from surfactants that preserve the GNP structure \([24]\). In terms of mechanical methods, sonication is one of the most commonly used techniques \([25]\) and it works by mechanical vibrations that are transferred in the liquid and create pressure waves. These waves cause the formation and collapse of microscopic bubbles (cavitation) which in turn aids the dispersion of materials \([26]\). The key sonication parameters include, frequency, power input, duration, type of sonication and temperature \([27]\) and the sonication can be performed using
either a bath sonicator or a probe/tip. However, the use of sonication can lead to a temperature increase in the suspension due to the release of high energy levels [28] and therefore, the temperature of the sonicated liquid must be carefully controlled to ensure that the water does not evaporate (which would affect the w/c). The sonication duration has been the subject of a number of studies and the consensus is that a duration of 60 minutes is appropriate, while a more prolonged mixing could induce damage to the material [27,29,30].

In terms of chemical methods, the use of surfactants and admixtures (non-covalent functionalisation), would be an appropriate mixing technique for cementitious systems as these admixtures are already widely used in construction. Superplasticisers are water soluble organic polymers that are used to improve the fluidity of the mix. There are different types of superplasticisers, including lignosulphonates, sulphonated naphthalene-based and polycarboxylates and their dispersion capability is achieved by wetting, electrostatic repulsion and/or steric hindrance [19]. Lignosulphonates and naphthalene-based superplasticisers work by electrostatic repulsion; their negatively charged molecules attach to the positively-charged cement particles and make them repel each other [31]. On the other hand, polycarboxylate-based superplasticisers work primarily by steric hindrance; the polycarboxylate polymers adsorb on to the cement particles and create a physical barrier between them to prevent agglomeration [31,32]. Some studies have investigated the effect of superplasticisers on the dispersion of carbon nanomaterials and there is an agreement that polycarboxylates are effective in uniformly dispersing carbon nanomaterials [33–37]. However, there is limited literature on other commonly used superplasticisers and a holistic comparison of the different types. At the same time, it is difficult to directly compare different studies, due to the differences between the inherent GNP properties and the various mixing methods that are employed by authors.
Even though the mechanical and chemical mixing are sometimes used in isolation, the literature shows that a combination of the techniques would be beneficial for the dispersion of GNPs in cementitious composites [33,35–38]. The use of superplasticisers has yielded promising results, however, there has not been a targeted review on the effect of different superplasticisers on the dispersion of GNPs in the cement matrix. Unless a homogeneous dispersion is achieved, the benefits of GNPs on the mechanical, durability and electrical properties will not be fully realised. In this paper, the dispersion behaviour of GNPs (14 nm thickness which is approximate 40 layers) modified with different superplasticisers in water and cementitious composites was investigated. This material was selected as it was a commercially available product that was already produced at scale so it would be appropriate to use for bulk construction applications.

Scanning electron microscopy (SEM) and thermogravimetric analysis were used to characterize the properties of the GNPs. A combination of zeta-potential testing, rheology testing, UV–visible (UV–vis) spectroscopy and SEM were used to investigate the dispersion of GNP in water and in cement paste. These tests were preferred compared to macro-scale testing (such as compressive strength testing) as they would provide a more direct insight in the dispersion state of GNPs in the aqueous system and in the cement paste. The literature to date has shown that compressive strength results can be widely affected by a number of parameters (such as w/c, curing regime, cement properties etc.) and it would be therefore difficult to isolate the effect of GNPs and draw conclusions on their dispersion state [10]. The objective of this research was to develop a practical dispersion protocol for GNPs, that are already commercially available, so they can be used for large-scale applications in construction materials. This will enable researchers and practitioners in the civil engineering industry to modify their cementitious structures and take advantage of emerging nanomaterials research.
2. Experiments

2.1 Materials

The materials used in this research are Portland cement, GNP, and superplasticisers. Portland Cement CEM I 52,5N, supplied by Hanson Cement, was used for preparing the fresh cement paste and its properties are summarised in Table 1. GNP was supplied by Nanesa in paste form in a paste form and the product was called G2NanPaste. This product was chosen as it was commercially available and produced in bulk, hence it would be suitable to use in construction applications. The paste contains approximately 95% water and 5% active GNP. The GNP within the paste have a carbon content > 97%, an approximate thickness of 14 nm (equivalent to 40 layers), an average particle size of 30 µm ($D_{50} = 25$ µm) and a specific surface area of 30 m$^2$/g. The surface state, defects and stability of the G2NanPaste product have been experimentally investigated and the results are presented in Section 3.1. Four different superplasticiser types were supplied by BASF and tested at different concentrations (recommended dosages provided by the supplier). These superplasticisers were chosen as they are representative of the admixtures already used in industry and they would result in a practical dispersion method for GNP in cementitious structures. The superplasticiser types and corresponding properties are summarised in Table 2 and the superplasticisers dispersed in water are shown in Figure 1.

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Mean size (µm)</th>
<th>Surface area (m$^2$/g)</th>
<th>Density (g/cm$^3$)</th>
<th>Loss on ignition LOI %</th>
<th>CaO</th>
</tr>
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<td></td>
<td></td>
<td></td>
<td>2.2</td>
</tr>
<tr>
<td>Superplasticiser type</td>
<td>Product</td>
<td>Solids content %</td>
<td>Appearance</td>
<td>Specific gravity (g/cm³)</td>
<td>Tested dosages (% by weight of cement)</td>
</tr>
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<td>---------------------------------</td>
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</tr>
<tr>
<td>Lignosulphonate</td>
<td>MasterPozzolith 324N</td>
<td>40</td>
<td>Brown liquid</td>
<td>1.18</td>
<td>0.24% - 0.71%</td>
</tr>
<tr>
<td>Sulphonated Napthalene</td>
<td>MasterRheobuild1000</td>
<td>40</td>
<td>Dark brown liquid</td>
<td>1.20</td>
<td>0.84% - 1.44%</td>
</tr>
<tr>
<td>Polycarboxylate ether</td>
<td>MasterEase 3820</td>
<td>29</td>
<td>Light brown liquid</td>
<td>1.08</td>
<td>0.32% - 2.16%</td>
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<tr>
<td>Modified polycarboxylic ether</td>
<td>MasterGlenium C315</td>
<td>35</td>
<td>Off white opaque liquid</td>
<td>1.10</td>
<td>0.22% - 3.3%</td>
</tr>
</tbody>
</table>

Table 2: Superplasticisers used in this study and their properties

Figure 1: Chemical admixtures used for the dispersion of GNP s, supplied by BASF and shown dispersed in water – (a) MasterPozzolith324N (b) MasterRheobuild1000 (c) MasterEase3820 (d) MasterGlenium315C

2.2 Sample preparation

The protocol for dispersing GNP s in water included the use of a chemical admixture to improve dispersion and the use a bath sonicator, FB11203 by Fisherbrand® operating at a sonication frequency of 37 Hz and power of 100W. All four different superplasticisers were used. The GNP s
were added in paste form (G2NanPaste) in a beaker containing water and the respective superplasticiser as illustrated in Figure 2. During sonication, the temperature was controlled by replacing the water in the bath sonicator every 5 minutes. The sonication was stopped every 5 minutes for 1 minute to replace the water in the bath sonicator and this helped in maintaining the sonication temperature between 20°C - 23°C for all suspensions. In total, the sonication duration was 60 minutes.

![Figure 2: GNP suspension preparation using a bath sonicator and superplasticisers](image)

Following sonication of the aqueous suspension containing water, superplasticisers and GNPs, 13.5 ml of the solution were added to 30 g of dry cement (w/c = 0.45). The paste was then mixed by hand for 3 minutes with a plastic spoon and vibrated for 10 seconds in a vortex mixer to remove entrapped air.

### 2.3 Experimental procedures

#### 2.3.1 GNPs characterisation

The as-received GNPs were characterized with Scanning Electron Microscopy (SEM) and thermogravimetric analysis. The SEM used was a ZEISS EVO LS 15. A small layer of
G2NanPaste was left to dry in the oven at 80 °C for 4 days to remove any water and the remaining powder was examined under a 6 kV accelerating voltage. Thermogravimetric analysis (TGA), using a PerkinElmer instrument, was used to characterize the GNP material and understand its decomposition. The TGA experiment was performed in air. The temperature ranged from 40 to 1000°C, at a steady rate increase of 10 °C/min, and the gas flow rate was kept constant at 30 mL/min. X-ray diffraction analysis (XRD) was also carried out to characterise the GNP product. A Siemens D500 X-ray diffractometer was used with a CuKα source operating at 40kV and 40mA and scanning carried out between 10° < 2θ < 60° at a rate of 0.02°/step and 1s/step.

2.3.2 Assessment of dispersion effectiveness in water

The effectiveness of the different superplasticiser types on dispersing the GNPs in water was tested with zeta-potential and UV-Vis spectroscopy. Zeta potential can be used to determine the particle tendency to aggregate and it indicates the stability of dispersion. When a solid particle (>1nm) is dispersed in water, an electrochemical double layer is created. A potential (ζ) at the slipping plane between the solid particle and the liquid medium is formed and its magnitude shows the degree of electrostatic repulsion between adjacent particles, therefore zeta-potential can be used to assess the effectiveness of the superplasticisers that work by electrostatic repulsion [39–41]. The magnitude of the zeta potential shows the degree of electrostatic repulsion between adjacent particles and the closer it is to 0, the more aggregated the particles will be. A Partikel Analytik Field ESA was employed for the testing and a beaker containing 250 ml of the aqueous solution (water + superplasticiser + GNPs) was used. Approximately 20 measurements were taken for each test and a higher zeta-value indicates better electrostatic
repulsion between particles which corresponds to better dispersion. Following the successful
identification of the most suitable superplasticiser type, UV-Visible spectroscopy testing was
used to establish the optimum superplasticiser concentration. A Perkin Elmer Lamda 35
spectrometer was used and 5 samples were tested for each concentration at the wavelength range
of 200-700 nm.

2.3.2 Assessment of dispersion effectiveness in the cement matrix

The rheology of the cement paste incorporating superplasticisers and GNPs can be used to assess
the dispersion effectiveness in cementitious systems. When the viscosity increases significantly
with GNPs addition, it is an indication that the superplasticiser is not effective in de-
agglomerating the cement and GNP particles. For rheology testing a smooth-walled Brookfield
DV3T Rheometer was used with a SC4-27 spindle. Triplicate testing was undertaken for each
material concentration. 10 ml of the hand-mixed cement paste were inserted in the rheometer
sample cup and left for 5 minutes to stand before the rheology test. Measurements were carried
out at room temperature and taken every 15 s. Each sample was firstly pre-sheared for 1 minute
to account for any shearing that was experienced when the sample was mixed and transferred,
and it was then left for a further 30 s to stabilise at 0 rpm speed before the test started. The shear
speed increased progressively from 0 to 175 rpm in 25 rpm intervals (ascending rates). It was
then kept constant at 175 rpm and then decreased progressively from 175 to 0 rpm again in 25
rpm intervals (descending rates). The Bingham rheological model was then used to correlate the
shear stress, shear rate and viscosity.
3. Results and analysis

3.1 Characterisation of GNP

Scanning electron microscopy images of the dried GNP are shown in Figure 3, where a wrinkled and folded morphology can be observed. The SEM images were taken at 4 locations of the dried GNP paste product to ensure that they are representative of the material. Individual sheets are agglomerated together and form large clusters and therefore a treatment method is needed to break the GNP agglomerates and to disperse them homogeneously in the cementitious matrix. By measuring individual flakes, the approximate length is found to be around 23 µm, however, various GNP agglomerates were formed.

Figure 3: SEM images (a-d) taken at different locations of the as-received dried GNP at 6kV accelerating voltage
The results of the TGA analysis carried out to understand the behaviour and mineral decomposition of the GNPs are illustrated in Figure 4(a). It was found that the GNPs completely decomposed, losing 100% of its weight at 1000°C, however, GNPs remained largely stable until circa 600°C. The XRD results, that was employed to characterise the crystalline nature and identify the main phases of the GNPs, are presented in Figure 4(b). XRD showed a sharp and intense peak at 2θ = 26.58° which is characteristic of graphite as well as other weak peaks which represent the rhombohedral graphite phase, in agreement with a study by Chougan [42]. However, a further broad peak is observed at ~2θ = 12°, which could mean that there is some loss of crystallinity, probably due to some functional groups that are present and not completely removed during the GNP fabrication [43]. This agrees with the study by Chougan et. al who found that after oxidation of pristine graphite, the graphitic peak shifts to 2θ = 10.3° due to sp³ hybridisation of some carbon atoms [42]. However, the graphitic peak at 2θ = 26° is still very intense and therefore the sample possesses more graphitic than oxidised domains.
Figure 4: Characterisation of the GNP's product that was used in this study (a) weight loss by thermogravimetric analysis (TGA) from 100°C to 1000°C (b) X-ray diffraction peaks
3.2 GNPs dispersion in water

Preliminary testing on the dispersion of the hydrophilic graphene oxide in water, showed that a combination of a mechanical and chemical method was needed to achieve homogeneity [44]. Since GNPs are hydrophobic, their dispersion in water without a chemical treatment, was not expected to be adequate and to validate this hypothesis, zeta potential testing - which measures the degree of electrostatic repulsion between particles - was carried out to investigate the effect of the superplasticisers on the GNP dispersion. A single dosage of 0.015wt% GNPs in water was sonicated for 60 minutes, and the dosage was calculated based on an equivalent w/c = 0.45. The ζ value of GNPs in water was found to be equal to -2.15 and this value was measured at a temperature of 23°C. Sonication of the suspension can lead to an increase in temperature and in this study, the temperature was controlled by pausing the sonication for 1 minute every 5 minutes. However, to understand the effect of temperature on the zeta value, one experiment was carried out where the sonication temperature was not controlled, and it reached 31°C. A decreasing trend in zeta potential was found with increasing temperature. At 27°C, a 7% reduction in the zeta value was observed (-1.99 mV) whilst a -11% reduction was found for 31°C (-1.91 mV). Even though this variance with temperature is small, it still shows that GNPs tend to agglomerate more easily with increasing temperature. Nonetheless, for all measurements, the ζ value was very close to zero, indicating an extremely strong tendency of the particles to agglomerate in water, which agrees with the literature. One study found that when GNPs were dispersed in water only, their zeta-potential was less than 10mV [29] and another study that investigated reduced graphene oxide, which has comparable properties to GNPs, found that the zeta value was less than 30mV, indicating that graphene particles were starting to agglomerate.
Hence, the zeta-potential testing confirmed the hypothesis that GNPs do not disperse sufficiently in water without using a chemical dispersant.

This dispersion of GNPs in water was visually observed, with GNPs being added in water at 0.015 wt% concentration. From Figure 5 (a), it can be observed that GNPs settled at the bottom of the beaker and no dispersion was achieved. Figure 5 (b) shows that when a polycarboxylate superplasticiser (1.76wt% MasterGlenium C315) was added, a more homogeneous dispersion of the GNPs was achieved, as indicated by the darker colour of the suspension. However, the colour at the bottom of the beaker was much darker, meaning that most of the GNPs were agglomerated and settled at the base. Instead, after applying sonication treatment for 1 hour, the GNPs appeared visually to be more uniformly dispersed as shown in Figure 5 (c) by a homogenous dark colour across the beaker. This uniformity was maintained for at least 1 hour after sonication. These visual observations show that GNPs dispersion in water was not sufficient and that a combination of chemical and mechanical treatment is indeed needed.

Figure 5: Visual observation of the GNPs (a) in water only, (b) with polycarboxylate superplasticiser and (c) with polycarboxylate superplasticiser and 1 hour of sonication
3.2.1. Effect of superplasticisers on the dispersion of GNPs in water

Due to the poor dispersion of GNPs in water with sonication, four superplasticisers were tested within the dosages recommended by the supplier, as summarised in Table 2. Three dosages were selected for each superplasticiser (minimum – median – maximum) within the recommended range. The four superplasticisers were chosen because they represent the admixtures that are commonly used in construction and they work by different mechanisms; the lignosulphonate and naphthalene-based ones work by electrostatic repulsion, while the polycarboxylates work primarily by a steric hindrance mechanism. Initially, the four superplasticisers were tested in water without any GNPs to understand their dispersion behaviour using zeta-potential testing. As illustrated in Figure 6 (a), the zeta value of lignosulphonates was very high because they work by electrostatic repulsion and this mechanism is clearly shown with this type of test. However, the naphthalene-based superplasticiser showed a low zeta value indicating ineffective electrostatic repulsion mechanism. The steric hindrance mechanism of the polycarboxylate superplasticisers is not shown clearly with zeta-potential, since the test is used to measure the electrostatic repulsion between particles, and as expected the zeta value of the two polycarboxylates (MasterEase and MasterGlenium) was low (<20mV). These results agree with a study that showed that cement suspensions had zeta values around -10 mV with a lignosulphonate superplasticiser, circa -25 mV with naphthalene-based superplasticisers but it reduced to -10 mV for polycarboxylates that work primarily by steric hindrance rather than electrostatic repulsion [40].

The effectiveness of the four superplasticisers in dispersing GNPs was then tested with a single dosage of 0.015wt% GNPs. Figure 6(b) shows that the lignosulphonate and naphthalene-based superplasticisers are very ineffective in dispersing the GNPs. These two types of superplasticisers work by electrostatic repulsion, so their zeta-value should have been the highest.
Yet, the lignosulphonate superplasticiser only improves the $\zeta$ value by 11-25% and keep it under -3 mV, whilst the naphthalene-based superplasticiser improves the value by circa 70% (to around -3.6 mV). None of these changes are significant enough to ensure that the GNPs are well dispersed. On the contrary, because polycarboxylates work by steric hindrance, it was not expected to see a high $\zeta$ value. However, both polycarboxylate dispersions with GNPs have a value >5 mV indicating that they are more effective in dispersing the GNPs. The low zeta value (<30 mV) is not an indication of low dispersion capacity; rather it is because they work by a strong steric hindrance mechanism that is not shown clearly in a zeta-potential measurement. Between the two products, MasterGlenium has higher zeta values at all three dosages.
Figure 6: Zeta potential values of (a) admixtures in water only and (b) admixtures with 0.015wt% GNPs (by weight of cement for w/c = 0.45) in water

The relationship between the concentrations of MasterGlenium superplasticiser and GNP, as well as its time-dependency, were investigated using UV-Vis spectroscopy. As shown in Figure 5, the GNP dispersion was not sufficient in water and the superplasticiser led to a more homogenous colour of the suspension, hence, the absorbance testing can inform about the superplasticiser efficiency in dispersing GNPs. The absorbance tests were carried out at a single wavelength of 220 nm with five tests for each concentration. Absorbance does not have true units and it is commonly measured in absorbance units (or au) but it is often reported as absorbance, as shown in Figure 7. The wavelength of 220 nm was selected based on an initial wavelength scan test from 200-700 nm that showed that the highest absorbance was around 220 nm and therefore this wavelength was selected for the comparative analysis. Initially, the effect of an increasing superplasticiser dosage
from 0 to 1.76 wt% for dispersing a single GNP concentration (0.01 wt% for the equivalent w/c = 0.45) was investigated, as shown in Figure 7. The maximum concentration of 1.76 wt% superplasticiser was selected, as higher dosages led to bleeding in cement paste. By observing the blue bars in Figure 7(a), it is observed that the addition of MasterGlenium increases the absorbance of the 0.01 wt% GNP suspension at all superplasticiser concentrations, indicating enhanced dispersion of the GNPs. The control sample, with 0% of MasterGlenium, presents the lowest value for absorbance, and, as the concentration of MasterGlenium increases, the absorbance also increases, showing a visible increase in the dispersion of GNP with the increased of superplasticizer. By comparing the difference between the red line (control superplasticiser measurement without any GNPs) and the blue bars, the absorbance shows an increasing trend with higher superplasticiser content; however, a plateau is reached around 0.99% - 1.32% of superplasticiser. Increasing the superplasticiser further to 1.76% leads to better dispersion, however, at this dosage issues like bleeding could occur when this dispersion is added in a cementitious composite. A single wavelength scan was also performed at 328 nm and 500 nm which are away from the peak absorbance value (220 nm) and it was found that the 0.99 wt% MasterGlenium resulted in the highest absorbance value, and the results are tabulated in Table 3. The stability over time was also evaluated for the different superplasticiser contents with the findings illustrated in Figure 7(b). The UV-Vis scan was carried out at a single wavelength of 220 nm and measurements were taken continuously over a 1-hour period to assess the stability of the GNP suspension. The superplasticiser dosages of 0.22 % and 0.55% increased the absorbance only slightly compared to the GNP in water only, indicating that they are not enough to disperse the GNPs. The plateau is observed again for dosages between 0.77% - 1.32%. In all cases, absorbance
reduced slightly over time. Hence, the dispersion is not expected to be stable for a long period and the GNP dispersion needs to be added in the cementitious matrix as soon as possible after mixing.

**Figure 7:** UV-Vis absorbance of 0.01% GNPs with varying MasterGlenium contents (a) at single wavelength $\lambda = 220$ nm and (b) at single wavelength $\lambda = 220$ nm over time
Table 3: Effect of increasing MasterGlenium dosage on the UV-Vis absorbance of 0.01wt% GNP as measured at wavelengths 328nm and 500nm

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<th>MasterGlenium wt%</th>
<th>$\lambda = 328$ nm</th>
<th>$\lambda = 500$ nm</th>
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<td>0.22%</td>
<td>0.141</td>
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<td>1.76%</td>
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The effect of increasing the GNP content was then investigated with three GNP contents of 0.01wt%, 0.1wt% and 1wt% and the findings are illustrated in Figure 8. A single dosage of 0.99wt% MasterGlenium was used and the stability of the dispersion over 60 minutes was tested. Overall, there is an indication that an increasing GNP content also results in an increase in absorbance, however, the improved GNP dispersion would also lead in higher absorbance. It has been considered that the superplasticiser addition at an optimum content would ensure that the GNPs would remain in suspension for longer, hence, allowing for a higher absorbance. As shown in Figure 8 (a), the addition of 0.99wt% MasterGlenium led to a small improvement for 0.01wt% GNP, with the effect being more pronounced for the 0.1wt% GNPs, therefore, a superplasticiser/GNP ratio of approximately 9:1, can significantly improve the GNP dispersion and keep it in suspension over 1 hour (Figure 8 (b)). For a higher GNP dosage of 1%, the addition of superplasticiser was found to be effective in keeping it in suspension in the first 5-10 minutes, but then the absorbance decreased significantly due to the sedimentation of the GNP particles. This indicates, that even though the plasticiser can maintain the GNPs in suspension for a longer period, the effectiveness seems to be wearing off after a certain period of time and it suggests that further work is needed to identify what may be an optimum superplasticiser dosage for each GNP content.

Nonetheless, the addition of superplasticiser even at this high GNPs dosage, helped the absorbance
to decrease less abruptly compared to when GNPs were dispersed in water only. The beneficial effect of the superplasticiser for the 1% GNP concentration is also confirmed by visual observation in Figure 8 (c), where without the superplasticiser, the GNP particles started settling and segregating almost immediately after 10 minutes of sonication. Instead, when the superplasticiser was added, the settling of GNPs over time was more progressive, shown by the more uniform colour of the dispersion across the depth of the cuvette.
3.2.2. Effect of superplasticisers on the dispersion of GNPs in cement

The addition of GNPs has a negative effect on the fluidity of the cement paste because GNPs are hydrophobic and have a large surface area [20–22] which requires additional water to wet their surface and results in inter-particle friction [5,6,46]. Rheology testing was carried out to ensure that the superplasticisers can maintain a sufficient fluidity in the mix while also dispersing the increasing GNP dosages. If a superplasticiser is not effective, this would result in an increase in the viscosity of the paste as the GNPs would aggregate and cause inter-particle friction. The rheology test of neat cement paste (w/c = 0.45) with no superplasticiser showed that low dosages of GNPs (up to 0.03wt%) did not affect the fluidity of fresh cement paste, as illustrated in Figure 9. Increasing the GNP dosage had a more pronounced effect on fluidity and 0.1wt% GNP addition increased the viscosity by 75% compared to the control. The higher GNP dosages are needed for...
improved permeability and to create an electrically conductive network, therefore, the rapid
increase in viscosity with high GNP concentrations could restrict its usability for practical
applications since it would not allow for adequate compaction and it could make pumping of the
cement composite difficult.

Figure 9: Effect of increasing GNP dosage on the viscosity (mPa s) of cement paste

The effect of the superplasticisers on the fluidity of cement paste with GNPs was
investigated by measuring the rheology of the composite at different concentrations of
lignosulphonate, sulphonated naphthalene, polycarboxylate ether and modified polycarboxylic
ether. The effect of the four different plasticisers (at three concentrations each) was then
investigated, with GNP dosages varying from 0% to 0.1% by weight of cement. Starting
from the lignosulphonate superplasticiser in Figure 11 (a), it is observed that for the control
mixes without GNPs, the lignosulphonate was only somewhat effective in improving the
fluidity of the neat cement paste whilst increasing the dosage from 0.47% to 0.71% had a
minimal effect. When GNP s were added, there was only a minimal change in viscosity which
could mean that the GNP dosage was very small and could be fully dispersed. Increasing the
GNP dosage to 0.1wt%, affected the viscosity more significantly and therefore the plasticiser
was not able to disperse the higher GNP content and maintain an optimum balance between
dispersion and fluidity. On the other hand, the sulphonated naphthalene-based plasticiser
reduced the viscosity of the cement paste by circa 79%, according to the control
measurements in Figure 11 (b). With GNP addition, the viscosity increased significantly,
especially for higher GNP concentrations (0.05wt% and 0.1wt%). Furthermore, at maximum
plasticiser concentration (1.44wt.%) an incompatibility is observed with the cement which
means that plasticiser micelle concentration is too high for use in cement paste. Therefore,
both the lignosulphonate and naphthalene-based plasticisers could have a limited ability in
dispersing GNP s and therefore they are not recommended as a practical dispersion method.
Furthermore, both lignosulphonates and naphthalene-based plasticisers work by electrostatic
repulsion and the above experimental results indicate that this mechanism is not sufficient to
homogeneously disperse GNP s.
Figure 10: Effect of increasing GNP dosage and different plasticisers on the viscosity of cement paste (w/c = 0.45) (a) lignosulphonate (b) sulphonated naphthalene
Figure 11 (a), shows the effect of one of the polycarboxylate superplasticisers, and a clear trend in reducing the viscosity with increasing plasticiser dosage can be observed in the control mixes (0% GNP). When the GNPs were added at low dosages, there was minimal change in the viscosity, which meant that the superplasticiser content was sufficient to fully cover all GNPs at these concentrations. Increases of 39% - 126% were observed for the 0.1wt% GNPs compared to the control, which was less than the increases observed with the two previous superplasticisers. Therefore, the polycarboxylate superplasticiser was more effective in dispersing GNPs whilst also maintaining a good rheology compared to the lignosulphonate and naphthalene-based ones. Figure 11 (b) shows that the second polycarboxylate superplasticiser, MasterGlenium C315, was more effective than MasterEase in reducing the viscosity of the neat cement paste (reduction ranges from 67% to 75%). The minimum superplasticiser dosage at 0.22wt% appeared ineffective in dispersing the increasing contents of GNPs and therefore it was not considered further. Increasing the superplasticiser dosage from 1.76% to 3.3% also did not appear to influence the viscosity with increasing GNP content and therefore using the higher surfactant concentration is of little benefit. Furthermore, the maximum superplasticiser dosage (3.3wt%) resulted in significant bleeding of the cement paste after 24 hours and therefore it was not possible to use this concentration. This surfactant is a single polymer technology that is extensively used in the construction industry for ready mix concrete and therefore it provides a practical dispersion route.

The aforementioned rheology results are in overall agreement with the literature, however, it is not possible to directly compare the findings due to the different GNP products and mixing methods employed by the different studies that could affect the results. However,
several studies have confirmed either by mini-slump tests or rheological testing that an increasing GNP dosage reduces the fluidity and that superplasticisers have a beneficial effect in maintaining the fluidity [36,47–49]. A study by Rheman et al, who undertook a thorough investigation on the rheological properties of cement composites with GNPs, found that both the yield stress and the plastic viscosity increased with increasing GNP concentration (from 0.03wt% - 0.1wt%), however, the superplasticisers had a positive effect on fluidity [50].

(a)
Rheology testing showed that the polycarboxylate-based plasticisers were more effective than lignosulphonates and naphthalene-based surfactants. The latter work by an electrostatic repulsion mechanism which was not found to be sufficient to disperse the GNPs in water or cement paste. Instead, the polycarboxylates work primarily by steric hindrance, where the polymers adsorb onto the cement particles and create a physical barrier between them, so they prevent agglomeration, and this was found to be a more effective mechanism. Therefore, the physical mechanism of GNP dispersion that was provided by steric hindrance is more effective than the electrochemical mechanism.

In summary, this study investigated different techniques for the dispersion of GNPs in water and in a cementitious matrix. Sonication was used as a mechanical mixing method and
it was found that the use of a mechanical technique alone is not sufficient to homogenously disperse GNPs as illustrated by visual observations, zeta-potential, UV-Vis spectroscopy and rheology testing. Instead, the use of a surfactant in combination with the mechanical mixing method was necessary. In order to develop a practical dispersion protocol, four commonly used superplasticisers, were selected as surfactants for the chemical dispersion, since they are widely used in industry and practitioners are familiar with the use of these materials. Zeta-potential, UV-Vis and rheology testing, showed that all superplasticisers, in combination with mechanical dispersion (sonication), were more effective in dispersing the GNPs compared to sonication alone. From the four superplasticisers, the polycarboxylate that works primarily by steric hindrance, was found to be more efficient in the dispersion of the increasing dosage of GNPs, hence, its use is recommended for a practical mixing method of GNPs in cementitious composites.

3. Conclusions

This study successfully developed a practical protocol for the dispersion of GNPs in cementitious systems. Characterisation of the GNPs using SEM showed that the flakes are aggregated together, while XRD and TGA confirmed the graphitic phases. The investigation of the dispersion of GNPs in water using zeta-potential showed that isolated mechanical treatment of the GNPs in the form of sonication, was insufficient to homogenously disperse them in an aqueous environment. This necessitated the combination of a mechanical treatment and surfactants to ensure that the GNPs can be homogenously dispersed. Four different commonly used superplasticisers were investigated using zeta-potential to understand their dispersing capability and UV-Vis spectroscopy to find an optimum concentration. It was found that the lignosuphonate and naphthalene-based
superplasticisers that work by electrostatic repulsion, were not sufficient to achieve a homogenous and stable dispersion. Instead, the polycarboxylates superplasticisers, that work by steric hindrance mechanism, were more effective in dispersing the GNPs. The steric hindrance is a physical dispersion mechanism and the use of polycarboxylate superplasticisers that are already widely used in construction, resulted in a practical dispersion solution. Moreover, the effect of the GNPs and superplasticisers on the fluidity of cement paste was investigated using rheology tests, showing that polycarboxylates were better at maintaining a good fluidity in the mix with increasing GNP concentration. This research enables researchers and practitioners in the construction industry to benefit from a practical and scalable dispersion method for GNPs in cementitious systems.

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