Graphene Oxide Application in Cement-Bound Materials—State of the Art

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Abstract: In recent years, the incorporation of nanoparticles in the cementitious matrix has been regarded as a prominent strategy in the research effort. This paper reviews the influences of the nanomaterial GO (graphene oxide) in cement bound materials, as GO has become one of the most well-known inclusion nanoparticles in the cementitious matrix in the last few years. This study describes (i) the influences of the GO on enhancing hydration mechanism in the cementitious materials; and (ii) the improved performance of the cementitious materials, which are highly dependent on the functionalizing behavior of the GO. All this improves the properties of the matrix. The paper reports the influences of GO on the workability of the mixtures and the durability enhancement of the cementitious composites. Therefore, it demonstrates promising results of employing GO in the fabrication of novel building materials. However, tremendous progress in utilizing GO in scientific domains like materials technology has achieved a significant level. Remarkable progress has been achieved by applying the GO in different fields such as solar cells and super capacitors. Hence, more intensive research is required to achieve comparable improvement in building materials which constitutes a significant future challenge.

Key words: GO (graphene oxide), cementitious materials, GO enhanced hydration, workability, durability.

1. Introduction

Cementitious materials have been used widely, and it is one of the primary materials for building and construction facility especially during the 21st century. Currently, the traditional cementitious materials could not meet the special engineering requirement under severe conditions due to the advancement of technology and society needs. Hence, improving novel high-performance cementitious materials with reduced comprehensive cost and reduced energy consumption during the infrastructure service life is significant for the ecological environment and promotes sustainable development [1, 2].

The strength and durability are the main characteristics considered in the design and service life of the concrete to control the efficiency of the final products. Speaking about the first main property of concrete, strength, which was defined as its ability to withstand all types of stress (compressive, shear, tensile, etc.), is determined by a variety of factors such as mix composition, structural design, curing process, and so on. The second main property of concrete, durability, can be defined as the ability of the concrete to resist chemical attacks, environmental conditions, and other service life influences [3]. In the past two decades, a literature survey shows that there have been intensive efforts to formulate the strength properties of the concrete. Eventually, the necessity of obtaining trustworthy concrete in every practice is demonstrated by continuing to study the acceptable formulations with vigour. The complying of the concrete structure to its designed functions during the specified project service life is essential and one of the practical approaches to adhere to the sustainability of concrete because of the high contributor of Portland cement in global emissions of green gases, which is used extensively as a binder in concrete fabricating [4].

GO (graphene oxide) is a kind of nanoparticle with a two-dimensional structure and can be formed by the arrangement of carbon atoms in a packed hexagonal...
structure. GO is produced by the oxidation of graphite with strong acid; then, by the resultant oxide exfoliation, GO is derived. As a consequence of the oxidation, it has hydrophilic active groups, such as hydroxyl (-OH), which are placed at the basal plane of a two-dimensional structure sheet and the carboxyl (-COOH) groups at the sheet edges, as shown in Fig. 1 [5]. Those functional groups alter the non-hydrophilic property of graphene to the hydrophilic property of GO; hence, planes of GO can provide nucleation sites for the formation reaction of the cement hydration products C-S-H and Ca(OH)$_2$ in the cementitious materials.

Due to the unique structure of GO, it can enhance the properties of cementitious materials [6-8]. The influences of GO on cementitious composites are variously explained. One is “nano and nucleation effects”. Belonging to nanoparticles, GO can enhance the cement hydration rate, reduce the pore volume and cement paste [9-12]; the polymerization degree of calcium silicate hydrate (C-S-H) gels can be increased due to the nucleation effects [13]. The other is “ion diffusion and transport resistance effects”. Due to the presence of divalent calcium ions, the ion diffusion process is accelerated [14], and the transportation resistance is increased under the action of GO-addition [15], which accelerates the cement hydration reactions, increases the compressive strength and tensile strength of the mortar, reduces the pore volume, and strengthens cement properties. The interlocking of GO to different anionic and cationic ions has a good effect on composite carbonation [16]. GO has a good effect on the mechanical property of cementitious materials. It can improve the properties of the concrete; with the addition of about 0.02 wt% GO in cement, the compressive and flexural strength and the toughness and modulus of elasticity can be improved over 30% at early days. GO can improve the durability of concrete as well [17].

Recently, graphene-based materials, which may be regarded as a novel type of nanomaterials, have been investigated in several studies; thus, incorporating such materials into the matrix of cementitious materials can acquire new properties. This paper reviews the state-of-the-art on properties of cementitious materials containing GO, which is considered one of the most well-known graphene materials. The first section contains the enhancing mechanism of the cementitious materials under the influence of GO; then (Chapter 2), the performance of the cementitious composite in the presence of GO is discussed (Chapter 3). The last section presents the conclusion and recommendation with a view on future challenges (Chapter 4).

2. Graphene-Oxide Influenced Hydration Mechanism in Cement-Bound Materials

Many researchers have conducted an intensive microstructural investigation with the help of various characterization methods and instruments to explore the mechanism beneath the improved properties of the mechanical and durability performance of cement
composites incorporating GO. The following sections summarize the influences of GO on the microstructure of cement composites based on the latest literature, concentrated mainly on the hydration and pore structure of the cementitious materials.

2.1 Hydration

The main two steps in the mechanism of the hydration effects in the cementitious materials incorporating GO are: (i) GO adsorbed on cement particles and orders hydration product formation due to the (ii) acceleration of the hydration reaction by GO [18]. The hydration products define the performance of the cementitious materials. Many researchers [19-22] have shown the impressive influences of GO in cement hydration products. The formation mechanism of the cement hydration products containing GO is illustrated in Fig. 2 [23]. Lv et al. [21] show that the hydration products exhibited a well-ordered petal-like or crystalline structure, as shown in Fig. 3.

SEM (scanning electron microscopy) imaging technique has been used to observe the influences of GO on the microstructure of the hydration products; it shows that the hydration products become more uniform and compact in the presence of GO; thus, the pores become uniform and smaller as the GO had the sheet layers and high strength and toughness, hence improving the growth of the cement hydration products [21]. However, Horszecaruk et al. [24] showed that the GO addition has no significant effect on information shapes of hydration products. Lv et al. [23, 25] have explored more to understand the formation mechanism and shapes of hydration products in the cement matrix involving GO nanosheets. According to the research above, it can be concluded that the influence of the GO on the promotion of the hydration reaction depends on the oxygen functional group of GO nanosheet, which adsorbs on cement particles and influences the hydration.

![Formation mechanism in holes/cracks](image1)

![Formation mechanism in dense environment](image2)

Fig. 2  The formation mechanism of hydration products in well-ordered petal-like shape or crystalline structures.
The figure is taken from Ref. [23].
2.2 Pore Structure

The presence of the pores structure in cement composites due to the porous nature of these materials is regarded as the decisive parameter for mechanical and durability properties. The analysis of the microstructure of cement matrix involving GO shows a denser structure, and in addition, GO can improve the pore structure and reduce the porosity.

An intensive investigation has been carried out on the effects of the pore structure of cementitious materials containing GO using MIP (mercury intrusion porosimetry) test results of GO-modified cementitious materials.

Fig. 3  Cement hydration products in petal-like shapes or crystalline structures. 
The pictures is taken from Ref. [21].

Fig. 4  Mercury intrusion porosimetry test results of GO-modified cementitious materials. 
The figure is taken from Ref. [26].
intrusion porosimetry). It shows the porosity of cement composites reduced with increased GO content as shown in Fig. 4 [26]; this phenomenon occurred due to two mechanism factors which have been stated: (i) the first factor responsible for the refined pore structure is due to the pore-filling effect of nanoscale of the GO sheets and (ii) the other is assisted with seeding effect of the GO that facilitates more hydration products to fill in the pore space, resulting in more compact microstructure and eventually associated to the improvement in mechanical and durability performance [27-38].

Further research was also conducted to simulate the hydration process using the molecular dynamics method adopted by Hou et al. [39] and Fan et al. [40] and establish a microstructure model of hydration products. In order to understand the complex reinforcing mechanisms of GO and achieve the desired performance of composite materials, in-depth investigations with accurate and rigorous methods are required, and it can target on altering the microstructure of the cement composites reinforced by GO.

3. GO Performance in Cement-Bound Materials

The two-dimensional GO nanosheet has unique features such as functional groups, large and rough surface area, and these features have an efficient influence on the performance properties of the cement composite materials. The inclusion of a small quantity of GO as 0.01%-0.05% by weight of cement led to improved mechanical and durability properties impressively. The utilization of GO becomes more competent for cement application as a reinforcement additive, not only in electronic industries due to the strong influence on cementitious materials properties and its ability to convert the physicochemical properties to an utmost level. This section presents the influence of GO on the performance properties of cementitious materials involving workability and durability.

3.1 Workability Properties

The workability of the cementitious composites is a significant property; it affects the construction performance, especially the demand of the applications of high-rise and long-span structures increased recently and need best concrete performance. Furthermore, its ease of transport, placement, homogeneous distribution of cement materials, and suitable compaction is essential. However, moderate viscosity and high flowability are essential [29]. Nevertheless, many researchers [34, 41-44] have reached a consensus and indicated that the GO is not favourable to the consistency and would increase the viscosity and reduce the cement slurry’s fluidity due to the hydrophilic nature.

The existing hypotheses for this occurrence are mostly as follows: (i) the distribution of functional groups and the large surfaces area of GO can accelerate the hydration and adsorb more free water in cement slurry [45, 46]; (ii) the nano size of the GO affects the interaction between the water reducing agent and the cement particles, resulting in the weakening of the repulsive force between cement particles and decreasing the fluidity [44, 47, 48]; (iii) due to the formation of the agglomerate of GO trap in a high degree, the free water in the system, consequently, the fluidity of the cement materials decreased [47, 49]; (iv) the van der Waals force between GO flakes makes cement particles attract each other, resulting in a decrease in the fluidity of cement composites [50]. Table 1 presents GO influences on the workability of cement composite, which has been the subject of several studies.

Some research indicates that the inclusion of SF (silica fume) and FA (fly ash) can improve the impact of GO and the workability of the cement composites [48, 51]. Moreover, others proposed applying various methods to compensate for the negative impact by GO, in which application of a water reducing agent is a
Table 1  The influence of GO on the workability of fresh cement composites.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>w/c</th>
<th>GO content (wt%)</th>
<th>Method</th>
<th>The change of fluidity/slump</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paste</td>
<td>0.5</td>
<td>0.03</td>
<td>Mini-slump test</td>
<td>The diameter of the minis-lump is 34.6% lower [29]</td>
</tr>
<tr>
<td>Paste</td>
<td>0.5</td>
<td>0.05</td>
<td>Mini-slump test</td>
<td>The slump diameter is reduced by 41.7% [43]</td>
</tr>
<tr>
<td>Paste</td>
<td>0.4</td>
<td>0.03</td>
<td>n.a. (^b)</td>
<td>The fluidity has markedly decreased by 54.4% [20]</td>
</tr>
<tr>
<td>Paste</td>
<td>0.29</td>
<td>0.05</td>
<td>Mini-slump test</td>
<td>The slump flow diameter was reduced by 21% [47]</td>
</tr>
<tr>
<td>Mortar</td>
<td>0.37</td>
<td>0.05</td>
<td>GB/T2419-2005(^c)</td>
<td>The fluidity is reduced by 15.2%, and the apparent viscosity is increased from 988.5 mPa·s to 19,284.0 mPa·s [34]</td>
</tr>
<tr>
<td>Mortar</td>
<td>0.5</td>
<td>0.1</td>
<td>Mini-slump flow</td>
<td>The slump flow was 27.8% lower [52]</td>
</tr>
<tr>
<td>Mortar</td>
<td>0.66</td>
<td>0.2</td>
<td>Mini-slump test</td>
<td>The workability decreased by 18.8% [26]</td>
</tr>
<tr>
<td>Concrete</td>
<td>0.2</td>
<td>0.03</td>
<td>Mini-slump test and flow</td>
<td>The slump and slump flow were reduced by 8.3% and 15.6%, respectively [34]</td>
</tr>
</tbody>
</table>

\(^a\) By weight of cement; \(^b\) Not available; \(^c\) Digital rotary viscosity meter.

more commonly used method. Further research is needed to improve the workability of cement-based materials and reduce the slump loss [22, 53, 54].

3.2 Durability Properties

The durability properties of cementitious materials indicate that these materials could resist different severe environments that cause materials degradation and reinforcement corrosion, which are influenced by many factors such as alkali-aggregate reaction, freeze-thaw cycle, chloride, and carbonation effects etc. which will have a negative impact on the mechanical performance and designed service life. Compared to the mechanical performance, the GO reinforced cement composite in durability aspect has not been sufficiently explored. This section highlights the improvement brought out forth by GO in the durability performance of the cement composites based on the recent literature.

The primary consideration of the durability issue is the transport properties of these materials, such as permeability, sorptivity and diffusion, which are nominated as a vital mechanism that could clarify the movement of corrosive elements in the pore structure of the cement past [55, 56]. The microstructure of the cementitious matrix, as reflected by the volume and connectivity of the pore network, affects these transport parameters. Incorporating GO nanosheets in cement composite to investigate the durability performance significantly reduces the ingress of corrosive chemicals, thereby increasing durability [57].

The primary transmission routes of corrosive chemicals inside cement composites are cracks and pores. Lv et al. [23] stated that GO is significantly decreasing cracks and pore number by regulating the crystal structure of cement hydration products, resulting in improving the inner porosity of cement mortar and the weak area of interface transition to form a regular and dense microstructure that can better resist to external corrosion factors. They investigated that the cement composite including GO indicates permeability depth reduction by 72% and raises the elastic modulus by 78% after 100 freeze-thaw cycles, followed by a reduction in carbonation depth by 66%. The enhanced durability by adding the GO nanosheets in cement composite was due to the orderly formed crystal-like hydration products consequently, reducing cracks and pores in the microstructure; hence the resistivity of freeze-thaw cycle and transport properties improved [23]. A conducted study has used 0.06 wt% GO in cement composite, and it was found that the sorptivity coefficient reduced by 24.8% compared to the reference mixture, thus indicating the durability improvement in cement composite [58].

Mohammed et al. [59] have investigated the water sorptivity and chloride penetration of cement mortar. It shows that adding GO nanosheets significantly
Fig. 5  Water sorptivity depth and chloride penetration depth of the GO-modified mortar: G0/CM without GO, G1 with 0.01 wt% GO, G2 with 0.03 wt% GO, and G3 with 0.06 wt% GO. 
The figure is taken from Ref. [59].

As illustrated in Fig. 6, the chloride front is represented by the white AgCl precipitation area on top of the specimen. The chloride penetration depth was 26 mm in the CM (control mix) compared to just 5 mm in the G1 mix. This could be linked to the unique lamella structure of GO nanosheets which will form a sponge structure in the mortars and improve the performance of the cement mortars against chloride penetration by limiting the chloride penetration depth. It also shows that GO inclusion in cement composite can improve carbonation and frost resistance [59].
Researchers have investigated the influence of GO on chloride ion penetration in concrete. They achieved an 80% reduction in chloride penetration because of the cement matrix’s pore refinement and increased tortuosity. However, higher dosages of GO beyond 1.5% caused agglomeration of these particles and hence reduction in the effectiveness of GO [64, 65].

The carbonation resistivity is a significant durability indicator of the concrete structure since the carbon dioxide diffuses into the concrete matrix; the carbonation reaction affects alkalinity, resulting in rapid degradation of the hardened concrete and corrosion consequences of the steel reinforcement. The studies by Mohammed et al. [17] showed the reduced carbonation depth for the GO-modified mortars, as shown in Fig. 7. The carbonation depth is only 3 mm after 18 months of carbonation, which is 18% of the control group [16].

The limitation of carbonation is related to two primary reasons: (i) the pore structure refinement, which is a rise in gel pores and reduction in capillary pores, and (ii) the interlocking of GO nanosheets to carbonate and calcium ions. Furthermore, Table 2 represents the durability enhancement of GO-based cementitious composite according to recent studies.

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**Table 2** Durability performance of GO-based cementitious composite.

<table>
<thead>
<tr>
<th>GO wt%</th>
<th>w/c</th>
<th>Durability improvement</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.344</td>
<td>Reduction in chloride penetration by 75% [59]</td>
</tr>
<tr>
<td>0.06</td>
<td>0.448</td>
<td>Reduction in loss of weight through the freeze-thawing cycle by 50% [28]</td>
</tr>
<tr>
<td>0.10</td>
<td>0.544</td>
<td>Reduction in loss of weight through the freeze-thawing cycle by 80% and loss in strength under chemical attack by 30% [62]</td>
</tr>
<tr>
<td>0.04</td>
<td>0.30-0.45</td>
<td>50% mitigation in strength loss when exposed to 800 °C [63]</td>
</tr>
<tr>
<td>0.03</td>
<td>0.5</td>
<td>Modifying the cement matrix at the nanoscale significantly reduces the entry of aggressive chemicals through GO-induced cement composite and enhances its durability [29]</td>
</tr>
</tbody>
</table>

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![Graph showing carbonation depth of GO-modified mortars](image-url)
4. Conclusions and Future Recommendations

In an attempt to summarize the current state of GO incorporation performance in cement composites, based on the literature and recent advancement, the main conclusions are illustrated as follows:

- The availability of GO large surface area, nucleation sites of GO interaction, and various oxygen-based functional groups; forms a linkage and contribute to unusual behaviour to the cementitious matrix’s.
- The addition of GO can accelerate the cement hydration reaction; thus, the hydration products can form ordered regular and dense microstructure that reduces the pores and cracks in the cement matrix.
- The reduction in capillary pores and the rise of gel pores are the direct benefits of using GO. As a result of this microstructural refinement, cement hydration improves and hence, mechanical and durability properties of cement composites are enhanced remarkably.
- Mechanical properties and microstructure were the most frequently studied targets; microstructure has been found with significant interaction with cement hydration.
- The main challenges were difficulties in dispersion, adverse effects on workability and fluidity properties on higher dosages; thus, the polycarboxylate ether-based superplasticizers could maintain the workability of cement materials.
- The incorporation of GO in cement composites shows significant improvement in transport properties by decreasing the water sorptivity and chloride penetration, and it also shows better freeze-thaw behaviour.
- The refined pore structure and the effect of GO in interlocking the carbon dioxide molecules are the main reasons for the limitation of the carbonation reactions.

Further studies are needed in the near future to meet the requirements of the advanced engineering materials:

- The practical methods in improving the workability of cementitious materials when reinforced with GO.
- How to adapt the microstructure of GO reinforced cement composites to achieve the targeted properties of composites.
- Experimental studies and applications of GO in concrete from both the material and structural perspectives.
- Extend the durability evaluation of GO-reinforced cement composites based on different GO types (e.g., nanosheets, nanotubes, and GO with fibres, etc.).

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