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Mechanical Behavior and Microstructure of Graphene Oxide Electrodeposited Carbon Fiber Reinforced Cement-Based Materials

Siyue Wang 1,*, Xuezhi Wang 1,*, Jingjing He 2 and Ming Xin 1

1 School of Civil and Architectural Engineering, Liaoning University of Technology, Jinzhou 121000, China; xmyemail@163.com
2 Power China Northwest Engineering Corporation Limited, Xi’an 710065, China; hejing_86@126.com
* Correspondence: wsy1037992263@163.com (S.W.); myemailwxz@163.com (X.W.)

Abstract: In this study, graphene oxide (GO) was prepared by an improved Hummers’ method, and the graphene oxide–carbon fiber (GO-CF) hybrid fibers were prepared by electrophoretic deposition (EPD) with the above GO. The microstructure and mechanical properties of GO, CF and GO-CF cement matrix composites were studied by X-ray diffraction (XRD), SEM and mechanical tests. X-ray diffraction (XRD) and SEM results showed that the surface modification of CF with GO could effectively improve the dispersion of CF in the cement matrix, the template action of GO providing nucleation sites for cement hydration, which significantly enhanced the interface bond between CF and the cement matrix. The mechanical properties test results showed that the early compressive strength and flexural strength of cement matrix composites were significantly improved by GO. Adding CF into the cement matrix significantly improved the flexural strength, although the compressive strength was not improved, even exhibiting a downward trend when the CF content exceeded 0.5%. The flexural and compressive strength of GO-CF cement matrix composites were clearly improved, its 7 d flexural strength and compressive strength increased by 30.89% and 17.56%, respectively, and its 28 d flexural strength and compressive strength increased by 38.37% and 14.32%, respectively. The research results indicate that a new method was provided which used GO as a dispersant and surface modifier to improve the dispersion of chopped CF in a cement matrix, and the interaction between CF and the cement matrix interface could also be applied to the functional aspects of cement matrix composites.

Keywords: graphene oxide; carbon fiber; cement composite; compressive strength; flexural strength; microstructure

1. Introduction

Cement-based materials are the most widely used building materials in the construction industry, but due to their inherent shortcomings—such as low tensile strength and poor fracture toughness—the development of cement-based materials has been limited in many aspects [1,2]. Fiber-reinforced cement-based materials are one of the most promising materials for high-performance structural and functional applications [3–5]. The effect of adding fiber to a cement matrix is different due to the shape and size of fibers, their surface textures, the interfacial bond strength between the fibers and the matrix, crack bridging ability, and energy dissipation during crack propagation. Various fibers have been widely used in cement-based materials—including steel fibers [6,7], carbon fibers (CF) [8,9], and polypropylene fibers [10,11], etc.—to improve their strength and toughness. Among these, CF has attracted increased attention due to its advantages of low density, light weight, high specific strength, and good thermoelectric performance [12–14].

Sun et al. [15] conducted an experimental study on the mechanical properties of carbon fiber cement-based composites (CFRC). Their results showed that the bending strength of
the CFRC increased linearly with increasing CF content, while the compressive strength increased initially before decreasing—as the mechanical properties of CF had a toughening effect—and prevented the formation and development of cracks. However, when the CF content was too high, it led to reuniting in the cement base material, resulting in a decrease in the compressive strength. Moreover, with increasing CF content, the mixing time was longer, producing a large number of bubbles in the cement matrix, which also caused a decrease in the compressive strength.

Jacopo et al. [16] investigated the mechanical properties of CFRC by means of introducing different dosages (2%, 3%, and 4% by weight of cement) of short CF. The study found that with increasing CF content, the flexural strength of cement-based composites increased, but the compressive strength did not improve. Safiuddin et al. [17] reported that CFRC with a water:cement ratio of 0.35 exhibited a higher density and smaller porosity than CFRC with a water:cement ratio of 0.5. When the CF content was 0.25%, the CF was evenly distributed in the concrete, its flexural strength and toughness increased by 3.6% and 41.4%, respectively. According to the existing literature, the addition of CF to cement usually substantially improves the flexural strength of the cement matrix, but different research results have shown different compressive strength trends. Adding fiber to cement only improves the strength and toughness of the cement matrix but does not fundamentally improve the hydration process and cement microstructure or inhibit the development of microcracks in the cement matrix [18]. Moreover, CF easily agglomerates and has poor dispersion in the cement matrix, and the interface adhesion between them is poor, greatly affecting its role in the cement matrix. Consequently, seeking a method to fundamentally improve the dispersion of CF in aqueous solutions and the cement matrix, and modify CF to make its surface more active, has considerable potential in engineering applications.

To improve the dispersion of CF in the cement matrix and the interaction between them, scholars began to study the surface modification of CF, the main methods including plasma treatment, electrophoretic deposition (EPD), and γ-ray treatment [19,20]. Among these methods, the EPD method can effectively deposit carbon nanomaterials on the surface of CF and modify it. Graphene oxide (GO), a graphene derivative, is a novel two-dimensional carbon nanomaterial [21] that has many hydroxyl, epoxy, carbonyl, and carboxyl groups on the nanosheet surface and edges. These oxygen-containing functional groups have high hydrophilicity, which can better disperse GO in water [22,23]. GO has excellent mechanical properties, and the tensile strength of multi-layer GO can reach 130 MPa [24]. Moreover, GO exhibits a good bond with the cement matrix, further improving the mechanical properties of cement matrix composites. Many scholars have added GO to the cement matrix to study its influence on the properties of cement-based composites [25–29]. Additionally, GO can be prepared from graphite at a lower cost using an improved Hummers’ method, laying a good foundation for its widespread use. Consequently, GO is considered to be a good material for CF surface modification. Zeyu Lu et al. [13] prepared GO-CF hybrid fiber using the newly designed EPD method and mixed it into the cement matrix. Their experimental results showed that the GO-CF surface exhibited high chemical reactivity, enhancing the bond between CF and the cement matrix, and significantly improved the mechanical properties of the cement matrix. Juan Chen et al. [30] used the EPD method to deposit GO on CF to prepare GO-CF cement-based composites and found that GO-CF improved the electromagnetic interference shielding performance of cement-based composites, but had little influence on their mechanical properties.

Based on existing studies, few scholars have systematically examined the effects of GO-CF hybrid fiber on the microstructure and mechanical properties of cement-based composites. In this study, GO was prepared using the improved Hummers’ method and GO-CF was prepared using the EPD method. The GO was then used to modify the surface of CF, improve the dispersion of CF, and the bonding properties of its interface with the cement matrix. The microstructure and mechanical properties of the GO-CF cement matrix composites were then experimentally studied.
2. Experimental

2.1. Materials and Equipment

The raw materials and reagents used in our tests are shown in Table 1. The experimental instruments used are shown in Table 2. The physical properties of the CF are shown in Table 3. The main components of P·O 42.5 ordinary Portland cement are shown in Table 4.

Table 1. Reagents and raw materials used in the experiment.

| Materials and Reagents | Note | Manufacturer                                      |
|------------------------|------|---------------------------------------------------|
| deionized water        |      | Homemade Access                                   |
| graphite powder        |      | Jinzhou Senmao Chemical                           |
| carbon fiber (CF)      | T700 | Toray Carbon Fiber (Guangdong) Co., Ltd.          |
| polycarboxylate        | 45%  | Sinopharm Chemical Reagent Co., Ltd.              |
| superplasticizer (PC)  |      | Jinzhou Senmao Chemical                           |
| Concentrated sulfuric | analytically pure | Jinzhou Senmao Chemical                           |
| acid (H₂SO₄)           |      | Shenyang Reagent Factory No. 4                    |
| hydrogen peroxide (H₂O₂)| 30% | Shenyang Reagent Factory No. 4                    |
| potassium permanganate | analytically pure | Jinzhou Senmao Chemical                           |
| (KMnO₄)                |      | Tianjin Tianli Chemical Reagent Co., Ltd.         |
| hydrochloric acid (HCl)| analytically pure | Liaoning Jinzhong Cement Factory                  |
| Calcium oxide (CaO)    | P·O 42.5 | Liaoning Jinzhong Cement Factory                  |
| cement                 | river sand |                                                |
| sand                   |      |                                                   |

Table 2. The equipment and instruments used in the experiment.

| Equipment                                    | Model     | Manufacturer                                             |
|----------------------------------------------|-----------|----------------------------------------------------------|
| scanning electron microscope                 | Zeiss Sigma500 | Carl Zeiss (Shanghai) Management Co., Ltd.              |
| Electric magnetic stirrer                    | JJ-1      | Shenzhen South China City                                |
| centrifugal machine                          | TG16-WS   | Shanghai Pudong Physical Optical Instrument Factory     |
| Mechanical ultrasonic cleaning machine       | 410T      | Shenzhen Jietuo ultrasonic cleaning Equipment Co., Ltd.  |
| Ultraviolet spectrophotometer                | UV-1000   | Tianjin Port East Science and Technology Development Co., Ltd.  |
| Electronic balance for analysis              | JM2002    | Yuyao Jiming weighing calibration Equipment Co., Ltd.    |
| Box type resistance furnace                  | SX-5-12   | Beijing Yongguangming Medical Instrument Co., Ltd.       |
| cement paste mixer                           | JJ-5      | Xian County Yaxing Highway construction instrument Factory |
| Electronic universal testing machine          | WDW-300   | Changchun Kesin Experimental Instrument Co., Ltd.        |
| Cement compression fixture                   |           | Wuxi Zhongke Building Materials Instrument Co., Ltd.    |

Table 3. Physical properties of carbon fiber.

| Length (mm) | Diameter (µm) | Tensile Strength (MPa) | Tensile Modulus (GPa) | Density (g/cm³) |
|-------------|---------------|------------------------|-----------------------|-----------------|
| 3           | 7             | 3500                   | 228                   | 1.75            |

Table 4. The main component of P·O 42.5 grade ordinary Portland cement.

| Main Ingredients | CaO | SiO₂ | Al₂O₃ | Fe₂O₃ | SO₃ | MgO |
|------------------|-----|------|-------|-------|-----|-----|
| Proportion (wt%) | 66.30 | 19.60 | 6.50 | 3.50 | 2.50 | 0.70 |

2.2. Preparation of GO

The GO was prepared using a modified Hummers’ method. It was characterized using NaNO₃ and strong oxidant KMnO₄, and anhydrous concentrated H₂SO₄ to oxidize the graphite, avoiding the problem of insufficient and repeated oxidation. Using the traditional Hummers’ method, scholars have found KMnO₄ in concentrated H₂SO₄ oxidation to be much stronger than NaNO₃, completely replacing it to promote acid intercalation. At the same time, NaNO₃ produces NO₂, N₂O₄, and other toxic gases during its use. Consequently, the modified Hummers’ method was adopted in this study [31]. A schematic diagram of the preparation process is schematized in Figure 1 [32]. The GO structure diagram in this figure
is a possible structure of GO. The process was as follows: We measured 23 mL concentrated H$_2$SO$_4$ and placed it in a beaker in an ice water bath, controlling the temperature so that it did not exceed 2 °C, and slowly added 1 g graphite powder under conditions of magnetic stirring, the process being controlled to finish within 25~40 min. We then added 3 g KMnO$_4$, stirring the mixture with a glass rod, the process being controlled for approximately 3 h. Magnetic stirring was then used to continue the reaction for 1~2 h, all carried out under the conditions of an ice water bath. Ultrasonic dispersion was then carried out for 8~12 h, after which 46 mL deionized water was added, the reaction lasting for 15 min. Next, 120 mL (75~90 °C) deionized water was added for dilution, and 10 mL 30% H$_2$O$_2$ solution was added under agitation to treat the remaining KMnO$_4$ in the mixture, the solution turning a golden yellow in color. The precipitate was centrifuged while it was hot, then washed twice with 5% dilute HCl, after which it was centrifuged using a large volume of deionized water at 10,000 r/min for 10 min. The supernatant and black precipitation at the bottom were then removed; this step was repeated seven times until the supernatant was neutral, and the GO solution was obtained, as shown in Figure 2.

![Diagram of GO preparation process.](image)

**Figure 1.** Diagram of GO preparation process.

![GO solution.](image)

**Figure 2.** GO solution.

### 2.3. GO/CF Hybrid Fibers Using the EPD Method

Figure 3 shows a schematic diagram of the electrophoretic deposition process. A copper box was used as the working electrode, with CF being installed in it. A hole was drilled on either side of the copper box to ensure that the GO electrolyte could pass through and make full contact with the CF. To avoid CF leakage from the container, a screen was placed between the hole and the copper box. Power was supplied using the MP3030D DC power supply. The copper strip acted as the counter electrode, the distance between the two electrodes being fixed at 5 cm. Before its deposition, the surface of commercial CF has a layer of commercial sizing agent [20], the existence of which affects the GO wrapping
of the CF. Consequently, the surface desizing of the CF should be carried out before the deposition process.

![Diagram of EPD](image)

**Figure 3.** Diagram of EPD.

The pH of the GO electrolyte was adjusted to 10.0 by adding a NaOH solution, the GO electrolyte concentration being 1.5 mg/mL. The voltage was set to 15 V, the deposition time to 40 min, and the process conducted at a constant temperature. After EPD, the GO-CF mixed fiber was removed from the copper box, washed with deionized water and dried to obtain the GO-modified CF (GO-CF).

### 2.4. Cement Mortar Preparation

The standard consistency water consumption was tested based on the GB/T 1346-2011 standard—that is, the “Cement Standard consistency Water consumption, Setting Time, Stability Test Method”. The cement mortar compressive strength and flexural strength were measured using an electronic universal testing machine (WDW-300), based on the GB/T 17617-1999 standard—that is, the “Cement mortar strength testing method”. P·O 42.5 ordinary Portland cement was used for the cement, and the sand was classified as river sand with a maximum particle size of 2 mm.

#### 2.4.1. Determination of Water Use for Standard Consistency

Due to the existence of many oxygen-containing functional groups on the surface of GO, it has strong hydrophilic properties—that is, the water adsorbed by functional groups on the GO surface is not released over time [33,34]. When GO is mixed into the cement mortar, it thickens it and reduces its fluidity. Consequently, we tested the water consumption for the standard consistency of cement with different GO content by using Vicat apparatus and by referring to the GB/T 1346-2011 standard—that is, the “Test Method for Water Consumption, Setting Time, and Stability of Cement standard Consistency”. The cement net slurry sunk into the test bar and was taken to be a net slurry of a standard consistency (6 ± 1 mm away from the bottom plate).

#### 2.4.2. Preparation of GO Cement Matrix Composites

For the GO cement mortar preparation, the cement:sand ratio was 1:2, the PC content was 0.5% of the cement mass, the GO content was 0, 0.01%, 0.03%, 0.05%, 0.07%, and 0.1% of the cement mass, respectively, and the water:cement ratio was 0.375. With increasing GO content, the water consumption increased based on the measured standard consistency water consumption. In the preparation process, the GO solution was first dispersed ultrasonically for 30 min, as shown in Figure 4. PC was then added, mixed evenly, and poured into the cement mortar mixer containing the cement and sand, which was mixed based on the mortar mixing standard and poured into a 40 × 40 × 160 mm test mold for insertion and tamping. After insertion and tamping, it was placed on a vibrating table and demolded for maintenance after 24 h. Both compressive and flexural strength tests were conducted with the 40 × 40 × 160 mm specimens.
dispersed ultrasonically for 3 min, as shown in Figure 4. PC was then added, mixed evenly, and poured into the cement mortar mixer containing the cement and sand, which was mixed based on the mortar mixing standard and poured into a 40 × 40 × 160 mm test mold for insertion and tamping. After insertion and tamping, it was placed on a vibrating mold for 10 s, then removed from the mold, and cured at 20 ± 2 °C and 95% RH for 24 h, and then demolded, and cured at 20 ± 2 °C and 95% RH for 7 d or 28 d.

Figure 4. GO dispersion.

2.4.3. Preparation of CF and GO-CF Cement-Based Composites

The preparation method of the CF and GO-CF cement-based composites was the same as that described in Section 2.4.2, with the content of the CF or GO-CF accounting for 0, 0.1%, 0.3%, 0.5%, 0.7%, and 1% of the cement volume, respectively. Six specimens were prepared for each group, including three specimens with a curing age of 7 d and another three specimens with a curing age of 28 d. A total of 36 specimens were prepared for compressive and flexural strength tests.

2.4.4. Flexural and Compressive Strength Tests

Based on the GB/T 17617-1999 standard—that is, the “Cement mortar strength testing method”, the flexural and compressive strength of the cement mortar specimens was tested (Figure 5). In the flexure test, the loading speed was 50 ± 2 N/s (until specimen failure), and in the compression test, the loading speed was 2400 ± 200 N/s (until specimen failure). The test results of each group were the average of the test results of the three specimens.

Figure 5. Diagram for bending and compression tests.

3. Results and Discussion

3.1. The Morphology and Structure of GO Sheets

Scanning electron microscopy (SEM) was used to characterize the morphology of GO prepared using the improved Hummers’ method, the GO SEM images of which are shown in Figure 6. As can be seen from the figure, GO presents a multi-lamellar structure with an irregular lamellar boundary and smooth surface. Due to the existence of oxidation functional groups, the edge presents a state of wrinkles. There are several white spots on the surface of the GO lamellar which may be caused by unwashed sediment.
Figure 6. SEM characterization of GO.

3.2. Characterization of GO-CF

Figure 7 shows the surface morphology of the desized CF and GO-CF. As can be seen, the surface of the CF is flat and smooth, there is little physical friction when pulled from the cement matrix, making it easy to slide out from the matrix, reducing its enhancing effect on the toughness and ductility of cement-based materials. Figure 7b shows the CF after deposition of GO. Folded GO covers the CF surface, evenly distributed without stacking. The CF surface after GO modification is rough, and greater physical friction is generated when the CF is pulled from the matrix, thus improving the enhancement effect of CF on the mechanical properties of cement-based composites.

Figure 7. SEM images of the surface morphology of CF and GO-CF hybrid fibers. (a) desized CF, (b) GO-CF.

3.3. Dispersion of GO-CF in Water

The dispersion of CF and GO-CF in deionized water is shown in Figure 8. By comparing the dispersion of CF in water before and after GO modification, it can be seen that CF without modification has poor dispersion in water and is prone to agglomeration, while GO-CF improves the dispersion and does not produce bulk reunion. The GO-modified CF has many oxygen-containing functional groups on its surface, increasing the hydrophilicity of the CF and laying a good foundation for improving the dispersion of CF in the cement matrix.
3.4. Workability

The measurement results are shown in Figure 9. With increasing GO content, water consumption also increases, proving GO to have strong hydrophilic properties. In previous studies, the author has discussed the optimal quantity of PC as a dispersant of GO—that is, if the viscosity of the mortar can be improved by changing the quantity of PC, the dispersion of GO in the cement matrix is affected. Consequently, the amount of water in the experimental process should be adjusted based on the quantity of GO—that is, a unified water consumption value should not be adopted.

Figure 9. Water consumption for standard consistency with different GO contents.

3.5. Mechanical Properties

3.5.1. Mechanical Properties of GO Cement Matrix Composites

Figure 10 shows the compressive and flexural strength of the cement mortar test blocks with different GO content—that is, 0, 0.01%, 0.03%, 0.05%, 0.07%, and 0.1%—after 7 and 28 d of curing, respectively. It can be seen that the flexural strength and compressive strength of the cement mortar increase initially, before decreasing with increasing GO content. When the GO content is 0.07 wt%, the maximum flexural strength is reached, the 7 d and 28 d flexural strength being 6.79 and 8.13 MPa, respectively. Compared with ordinary cement mortar, the 7 d and 28 d flexural strength increases by 29.70% and
27.27%, respectively. When the GO content exceeds 0.07 wt%, the flexural strength begins to decline, the reduction being sizeable. The 7 d and 28 d compressive strength of the cement matrix composite with GO content of 0.07% is 52.79 and 69.86 MPa, respectively. Compared with ordinary cement mortar, the 7 d and 28 d compressive strength increases by 32.03% and 30.92%, respectively. When the GO content exceeds 0.07 wt%, the GO exhibits agglomeration due to the excessive GO content and the surface of the cement hydrated crystals is rough, thus leading to a reduction of compressive strength.

Analysis of the reasons: When the GO content is 0–0.07 wt%, GO can be evenly dispersed in the cement matrix. It provides nucleation sites for cement hydrated crystals and acts as a template to accelerate the generation and development of hydrated crystals [35], having a regulatory effect on them and making the microstructure more compact, thus improving the compressive strength. Moreover, the incorporation of GO also plays a bridging role in the cement base [36]. For the hydrated crystals with loose structures, the bridging effect is more obvious, which makes the cement hydrated crystals and the GO more closely connected, thus improving the compressive strength [26].

It can be seen from the above data that GO improves the compressive and flexural strength of cement-based composites. The cement mortar with 0.07 wt% GO exhibits the maximum flexural strength and compressive strength.

3.5.2. Mechanical Properties of CF and GO-CF Cement Matrix Composites

Figure 11 shows the compressive and flexural strength of the CF and GO-CF cement-based composites after 7 d and 28 d. It can be seen from Figure 11a that the 7 d flexural strength of the CF cement mortar increases with increasing CF content. When the CF content is 1.0 wt%, the flexural strength of the cement mortar test block reaches 6.98 MPa, which is 24.42% higher than that of the blank group. The 7 d flexural strength of the cement mortar test block mixed with GO-CF is the same as that of the cement mortar test block mixed with CF, exhibiting an increasing trend, but the degree of improvement is greater than that of the CF cement mortar. Compared with the blank group, the 7 d flexural strength of the GO-CF cement matrix composite material increases by 30.89%.

Figure 11b shows the 7 d compressive strength of the CF and GO-CF cement mortars. The 7 d compressive strength of the cement mortars mixed with CF shows an increasing trend initially before decreasing. When the CF content is 0.1 wt%, the maximum compressive strength is 40.14 MPa. The reason for the decrease is that the CF surface is smooth and the bond between the CF and the cement matrix interface is poor. A gap between the CF and the cement matrix interface exists, which leads to a reduction in compressive strength. Conversely, the poor dispersion of CF in the cement matrix leads to increasing porosity of

![Figure 10](image-url)
the cement matrix composites, thus reducing the compressive strength of the cement mortar test blocks [37]. However, the 7 d compressive strength of the cement mortar test block mixed with GO-CF exhibits an increasing trend with increasing GO-CF content. When the GO-CF content is 1.0 wt%, the compressive strength of cement mortar is 44.65 MPa, which is 17.56% higher than that of the blank group.

![Figure 1](image_url)

**Figure 1.** Effect of GO on mechanical properties of cement mortar. (a) 7 d flexural strength, (b) 7 d compressive strength, (c) 28 d flexural strength and (d) 28 d compressive strength.

Figure 11c shows the 28 d flexural strength of the CF and GO-CF cement-based composites. As can be seen, the 28 d flexural strength of the cement mortar test blocks mixed with CF and GO-CF exhibits a rising trend. When the CF/GO-CF content is 1.0 wt%, the flexural strength of the CF cement mortar and GO-CF cement mortar is 7.73 and 8.18 MPa, respectively. Compared with the blank group, the 28 d flexural strength of GO-CF increases by 30.89% and 38.37%, respectively, and the flexural strength of GO-CF increases even more.

Figure 11d shows the 28 d compressive strength of the CF and the GO-CF cement matrix composites. The 28 d compressive strength of the CF cement mortar test block exhibits the same trends as those of the 7 d samples, rising initially before decreasing. When the CF content is 0.5 wt%, the maximum compressive strength is 43.26 MPa, which is 9.81% higher than that of the blank group. The optimal dosage of the CF cement-based composites for 7 d and 28 d compressive strength, differs—that is, the optimal dosage is 0.1 wt% for 7 d and 0.5 wt% for 28 d. This is because CF has little influence on the early
strength of the cement mortar. After 28 d, the cement hydration improves, enabling the CF to play a better role. The 28 d compressive strength of the GO-CF cement mortar increases with increasing GO-CF content. When the GO-CF content is 1.0 wt%, the compressive strength is 45.03 MPa, 14.32% higher than that of the blank group.

Based on the experimental results, adding CF to the cement matrix can improve its flexural strength, although the compressive strength is not improved to as great an extent, even exhibiting a downward trend when the quantity is too high. The flexural strength of the GO-CF cement matrix composites is the same as that of the CF cement matrix, exhibiting a rising trend, although the increase is greater than that of the cement mortar mixed with CF. Moreover, the 7 d and 28 d compressive strength of the GO-CF cement mortar exhibits a rising trend, which improves the compressive strength of the cement matrix. The optimal content of GO-CF was 1.0 wt%.

Compared with the above test results, it can be concluded that the mechanical properties of cement matrix composites improved by CF alone are not ideal. Both GO and GO-CF can improve the compressive strength and flexural strength of cement matrix well. However, considering the high cost of GO, the amount of GO alone is large. Therefore, GO-CF is the best choice to improve the mechanical properties of cement-based materials.

3.6. Microstructure Analysis

3.6.1. XRD

Figure 12 shows the XRD patterns of cement-based composites with mixtures of 0.05% and 0.07% GO, respectively, the detected phases being cement hydration products. It can be seen that the main cement hydration products after GO incorporation include calcium silicate hydrate (C-S-H) gel, AFt, and dicalcium silicate (C2S), which are consistent with the hydration products of ordinary Portland cement, indicating that GO incorporation does not change the cement hydration products themselves. Additionally, C3S and C2S in cement clinker react with water to produce C-S-H gel and calcium hydroxide (CH). When GO is mixed into the cement base, the active group on the surface of the GO reacts with the active components of the cement—such as C3S and C2S—to form the hydration product growth point. The shape of GO and the active point on the surface become the template with which to control the shape of the hydration product [38]. As can be seen, with increasing GO quantities, the diffraction peak intensity of the CH crystal weakens, while that of the C-S-H gel strengthens. This demonstrates that GO plays a template role in the cement hydration process and promotes cement hydration to produce C-S-H gel, which improves the strength and volume stability of cement-based composites.

3.6.2. SEM

Figure 13 shows the SEM images of the GO cement-based composite morphology. The improvement of the cement-based macro properties is achieved by changing the microstructure. As can be seen from Figure 13a, when GO is not added, the crystals generated by cement hydration have many voids and defective grid structures, and more needle-like and rod-like products can be seen. These products are mainly AFt, AFm and other hydration products generated by cement hydration, although the degree of hydration is relatively low. When the GO dosage is 0.03 wt%, as shown in Figure 13b, the hydration products exhibit a folded shape, and the number of needle-like and rod-like crystals decreases considerably. In the cement sample with a GO content of 0.05 wt%, as shown in Figure 13c, the block structure can be seen, the hydration products being polyhedral, which promotes the generation of C-S-H gel [39]. When the GO content is 0.07 wt%, as shown in Figure 13d, the hydration products begin to appear lamellar with a smooth surface and more dense structure. The degree of cement hydration improves, which is also why the compressive and flexural strength increase. When the GO dosage is 0.1 wt%, as shown in Figure 13e, the hydration products are folded and have a small number of rod-like crystals, with too close a structure. Moreover, the hydration products
are not evenly distributed, and agglomeration occurs, their connections with each other being reduced, leading to a reduction in mechanical strength.

Figure 12. XRD patterns of cement-based composites with different GO content.

Figure 13. SEM morphology of GO cement matrix composites. (a) without GO, (b) 0.03 wt% GO dosage, (c) 0.05 wt% GO dosage, (d) 0.07 wt% GO dosage and (e) 0.1 wt% GO dosage.
Figure 14 shows SEM images of the CF and GO-CF morphology in the cement matrix, and the changes in their flexural and compressive strength were analyzed. The reason the flexural strength of the CF cement mortar exhibits a rising trend is that CF itself has good toughness, which prevents the formation and development of cracks, effectively improving the flexural strength of the cement matrix, while the change of compressive strength depends on the interaction between the CF and the cement matrix interface.

![Figure 14](image)

Figure 14 shows SEM images of the CF and GO-CF morphology in the cement matrix, and the changes in their flexural and compressive strength were analyzed. The reason the flexural strength of the CF cement mortar exhibits a rising trend is that CF itself has good toughness, which prevents the formation and development of cracks, effectively improving the flexural strength of the cement matrix, while the change of compressive strength depends on the interaction between the CF and the cement matrix interface.

Figure 14a shows that there is a large gap between the CF and the cement matrix interface. The surface of the CF is smooth and there is no hydration product wrapped on it. The bond between the CF and the cement matrix interface is poor, which is the main reason for the reduction of the cement mortar compressive strength [40].

Figure 14b shows SEM images of the interface morphology between the GO-CF and the cement matrix. It can be seen that the CF surface has many cement hydration crystal packages, which greatly improve the interface bonding performance between the CF and the cement matrix, enhancing the interaction of the CF and filling the interface gap. Consequently, the microstructure is more compact and the macroscopic mechanical properties improve.

Figure 14c shows that GO provides nucleation sites for cement hydration crystals on the CF surface. The CF surface modified by GO contains GO with many oxygen-containing functional groups, which provide nucleation sites for cement hydration products, playing a template role and making the CF surface properties more active. In addition, the GO on the CF surface also has a bridging effect, which makes the CF more closely connected with the cement hydrated crystals, effectively improving the physical friction and chemical bonding on the CF surface [41]. This results in the CF and the cement matrix interface interacting more fully, thus improving the mechanical properties of the cement matrix.

Figure 15 shows the interaction between the CF and the cement hydrated crystal before and after modification. It can be seen that due to the smooth surface of the CF,
there is a large gap between the cement hydrated crystals and the CF surface, and the bond performance between them is poor. On the surface of the GO-CF hybrid fiber, the GO provides nucleation sites for the cement hydrated crystals, which have a regulatory effect on the cement hydration products. Consequently, the hydrated crystals aggregate and embed in the GO surface. The bond between the CF and the cement matrix improves, and the GO-CF cement matrix composites exhibit excellent mechanical properties.

![Figure 15. Schematic illustration of Hybrid effect of GO-CF to cement material.](image)

Moreover, the GO-CF hybrid fiber has strong electrostatic repulsion and space stability, and the dispersion of GO-CF in the cement matrix is better than that of the CF in the cement matrix. It can be seen from Figure 14d that GO-CF is well dispersed in the cement matrix, and good dispersion is a prerequisite for improving the mechanical properties. Consequently, the compressive and flexural strength of the GO-CF cement-based composites are superior to the CF cement-based composites. Moreover, GO itself has good mechanical properties. As described in Section 3.5.1, adding a small amount of GO to the cement matrix can greatly improve its compressive and flexural strength. Therefore, adding GO-CF to the cement matrix can significantly improve its mechanical properties.

4. Conclusions

From the current investigation, we can draw the following conclusions:

1. The compressive and flexural strength of cement-based composites can be significantly improved by adding GO to cement-based composites. The optimal dosage of GO is 0.07%. When the dosage of GO is 0.07%, the 7 d and 28 d compressive strength of the GO cement matrix composites increased by 32.03% and 30.92%, respectively, and the 7 d and 28 d bending strength increased by 29.70% and 27.27%, respectively.

2. Compared with the CF cement mortar, GO-CF further improved the compressive and flexural strength of the cement mortar. The 7 d and 28 d flexural strength were further improved by 6.47% and 5.82%, respectively. As for the compressive strength, not only was it further improved, but the compressive strength curve did not exhibit any downward trend and was always increasing. This showed that the GO-modified CF could improve the phenomenon of compressive strength decline caused by excessive fiber content. Compared with the blank group, the 7 d flexural and compressive strength of the GO-CF cement mortar increased by 30.89% and 17.56%, respectively, and the 28 d flexural and compressive strength increased by 38.37% and 14.32%, respectively.
3. XRD and SEM test results showed that GO played a template role in cement hydration, providing nucleation sites for hydration crystals, and promoting the cement hydration reaction to generate hydration products such as CH and C-S-H gel. GO improved the surface roughness of CF, improving the physical and chemical properties of CF, resulting in better CF dispersion in the cement matrix. Moreover, GO provided nucleation sites for the cement hydrated crystals on the CF surface to promote cement hydration. Similarly, GO also played a bridging role on the CF surface to improve the bond between the CF and the cement matrix interface, thus improving the macroscopic mechanical properties of the cement matrix.

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Abbreviations

| Abbreviation | Description |
|--------------|-------------|
| C2S          | Dicalcium silicate |
| C-S-H        | Calcium silicate hydrate |
| CF           | Carbon fiber |
| CFRC         | Carbon-fiber-reinforced cement |
| CH           | Calcium hydroxide |
| EPD          | Electrophoretic deposition |
| GO           | Graphene oxide |
| SEM          | Scanning electron microscopy |
| XRD          | X-ray diffraction |

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