

# Electrical and Mechanical Properties of Carbon Nanotube/ Graphite Oxide Cement-based Composite under the Early Age

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**Abstract.** In this study, Carbon Nanotube (CNTs) cement-based composites were investigated by adding Graphite Oxide (GO) together under the early age. The content and the ratio of GO and CNTs would significantly affect the electrical conductivity and mechanical properties of GO/CNTs cement-based composites. It was observed that the GO/CNTs composites with lower content GO (0.01 wt.%) and CNTs (0.05wt.%) could reach the percolation theory. Meanwhile, the mechanical properties (flexural, compressive strength) of GO/CNTs composites could be increased remarkably. It was also described that linear dependence between electrical conductivity and the stress of GO/CNTs cement-based composites could be found.

## 1 Introduction

Electrical cement-based composites have a wide range of application prospects in such fields as real-time traffic flow detection, green safety monitor of significant engineering structures, anti-static measures of military field, electromagnetic interference shielding, and grounding devices of power system in special industries [1,2]. In this study, a certain amount of GO will be incorporated into CNTs-based composite matrix to improve the electrical and mechanical properties of the composites. Firstly, one-dimensional CNTs and two-dimensional GO were blended in an aqueous system to prepare an aqueous suspension with a three-dimensional network of GO/CNTs hybrid materials. Secondly, the GO/CNTs cement-based composites were prepared by blending aqueous suspensions of GO/CNTs hybrid materials into cement matrix. Thirdly, the effect of GO and CNTs content and proportion on the flexural, compressive strength and electrical properties of GO/CNTs cement-based composites under the early age had been investigated.

## 2 Experiments

### 2.1 Sample Preparation

#### 2.1.1 Preparation of GO/CNTs cement-based composites sample

GO/CNTs suspensions were prepared by ultrasonic dispersion and then the suspensions were blended into cement-based matrix to prepare cement-based composites. Firstly, a certain amount of GO powder

could be added into water, stirring for 20 min. and then GO aqueous should be ultrasonically dispersed for 40 min. After sonication, GO aqueous dispersion could be prepared. CNTs were added into this GO aqueous dispersions and stirred for 20 min with magnetically stirring. Then, GO/CNTs aqueous suspension were placed in the ultrasonic disperser for 30 min. The sample No. the amounts and ratio of GO and CNTs are shown in Table1.

The prepared GO/CNTs aqueous suspension and cement were stirred in a cement stirrer pan according to the preparation process of "Test method of cement mortar strength (ISO method)" (GB17671-1999), and the formed cement pastes is loaded into the triple-mould, and finally the triple mould was set in steam curing room (curing room conditions: temperature 20 °C ± 1 °C, humidity: 90%) and cured for 7 days and then removed for performance testing.

**Table 1.** Sample No. of GO/CNTs in cement-based composites samples, incorporation amount of GO and CNTs, 7-day age flexural, compressive data, and average resistivity

Sample No.	GO/CNTs	GO (g)	CNTs (g)	Flexural strength /MPa	Compressive strength /MPa	Average resistivity Ω·m
GO/CNTs-0	/	/	/	8.4	43.0	63.3
GO/CNTs-1	1:5	0.12	0.6	10.1	58.1	31.5
GO/CNTs-2	1:4	0.24	0.96	10.2	59.7	31.3
GO/CNTs-3	1:3	0.36	1.08	11.5	59.8	29.4
GO/CNTs-4	1:2	0.48	0.96	11.6	59.6	30.1

#### 2.1.2 Preparation of GO/CNTs-r reference sample

Firstly, 0.12 g GO powder was weighed and added to the water, magnetically stirring 20 min, ultrasonic dispersion

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40 min to prepare GO aqueous dispersion. CNTs 0.6 g were added to the aqueous GO dispersion. After magnetic stirring for 20 min and ultrasonic dispersion for 30 min, the GO/CNTs-r aqueous suspension was obtained. Vacuum filtration removes excess water from the aqueous suspension, GO/CNTs-r samples were dried in an oven at 50 °C for 48 hours before testing. The mass ratio of GO to CNTs in this aqueous suspension is 1: 5, which is the same as the content of GO and CNTs in GO/CNTs-1.

## 2.2 Test methods and performance tests

### 2.2.1 Test methods of flexural and compressive strength

The sample size of the flexural strength test is 40 mm×40 mm×160 mm. The specimen was placed on the roller of the flexural testing machine. Flexural test machine is turned on, finally the specimen broke with gradually increasing the load, breaking load value of the specimen was recorded. The sample after the flexural test performed could be applied in the compressive test. The test machine gradually increased with the load after turning on until the sample is crushed, load value of the sample was recorded when crushed.

### 2.2.2 Test methods of electrical properties

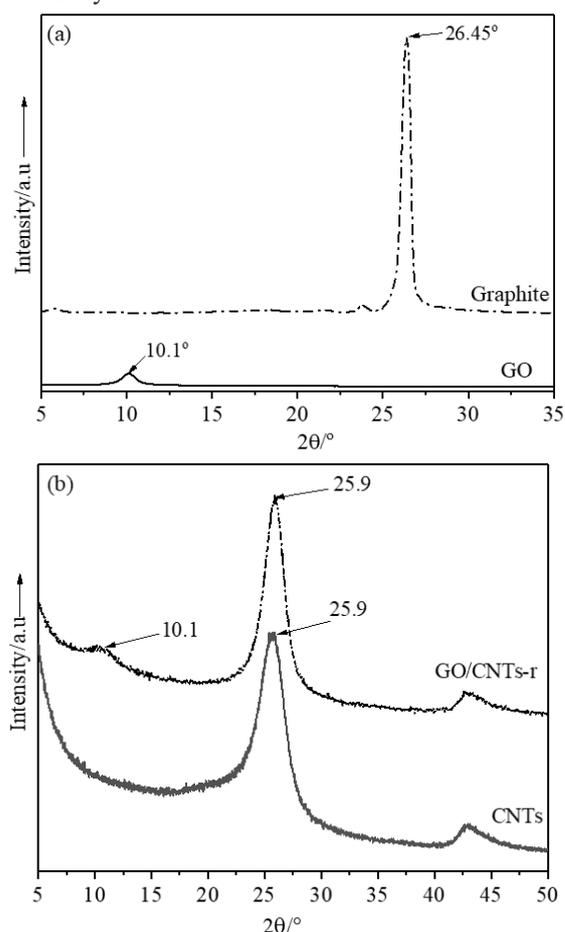
The experiment uses the four-electrode method to test the resistivity of the sample. In the experiment, the voltage of the power source was adjusted to read out different voltage values U and I from voltmeter and ammeter.

## 3 Results and discussion

### 3.1 XRD analysis of GO, CNTs and GO/CNTs

Figure 1 (a) shows that graphite has a very sharp diffraction peak at  $2\theta=26.45^\circ$  as the characteristic peak of graphite, indicating that the graphite layers are arranged in a very regular manner with very high crystallinity[3]. The interlayer distance of graphite could be calculated by the Bragg equation, the interlayer distance is 0.335 nm, consistent with the reported distance between graphite layers. At the same time, we can see that GO shows a weak, slightly broad diffraction peak near  $2\theta =10.1^\circ$ , indicating that some oxygen-containing groups were formed on GO surface through oxidation, and these oxygen-containing groups adsorbed a large amount of water molecules to improve GO hydrophilic performance. At the same time, it can be shown that majority of the GO layers that have undergone the oxidation process are in a peeled state, and a few of the GO layers are stacked. Under these conditions, the GO sheets are more likely to hybridize with CNTs in an aqueous solution and form well dispersion. Figure 1(b) shows the XRD results of acidified CNTs and hybridized GO/CNTs-r. As can be

seen from the XRD images, both samples show a sharp diffraction peak at  $2\theta = 25.9^\circ$ . This peak is due to the characteristic diffraction peaks of multi-walled carbon nanotubes formed by multi-layer graphite. The results show that the acidified carbon nanotubes do not destroy the basic structure of carbon nanotubes, and the peak of GO/CNTs-r can be found again at  $2\theta = 10.1^\circ$  belonging to GO weak diffraction peaks, which indicate that GO/CNTs- 1 has a small amount of GO. This result confirms the hybrid samples have been prepared successfully.



**Figure 1.** XRD spectrum of samples: (a) Graphite and GO; (b) CNTs、GO/CNTs-r

### 3.2 SEM figures of GO, CNTs and GO/CNT-r

Figure 2 (a) is a SEM image of GO, GO presents a smooth, uneven folds of large flakes, and has a large specific surface area. Figure 2(b) is an SEM image of CNTs. The CNTs appear linearly and reunite together and entangle together. From the figure Figure 2 (c) and (d) , it can be found that GO and CNTs exhibit intermingling three-dimensional network structure. The CNTs are linear and scattered randomly between GO layers. Some CNTs are attached to the surface of the GO bulk, like a large layer of GO wires connected by a root, which play the role of constructing GO/CNTs three-dimensional network wires.

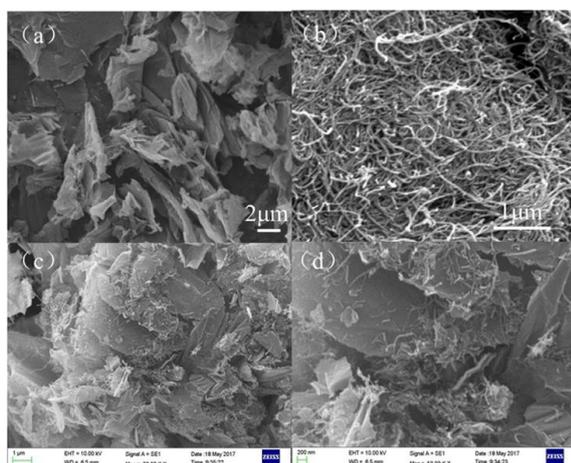


Figure 2. SEM images of dried samples of GO, CNTs, GO/CNTs-r aqueous suspensions:(a) GO, (b) CNTs, (c) GO/CNTs-r(2000-fold), (d)GO/CNTs-r(5000-fold)

### 3.3 Electrically conductive performance of GO/CNTs cement-based composites

After incorporation of CNTs and GO into the cement matrix, the electrical conductivity of cement-based composites can be significantly improved. The averaged electrical resistivity of the blank cement-based sample is about  $63.3 \Omega \cdot m$  in Figure 3; The averaged resistivity of the GO / CNTs-1 decreased to  $31.5 \Omega \cdot m$ , when the ratio of GO to CNTs was about 1: 5 for the three-dimensional conductive network in the cement matrix. With the ratio of GO to CNTs (1: 4, 1: 3 and 1: 2), the averaged resistivity of GO/CNTs-2 and GO/CNTs-3 did not change significantly, but reached a relatively balanced numerical. This result indicates that only 0.01 wt.% GO and 0.05 wt.% CNTs are incorporated into the cement matrix, the electrical conductive paths in the composite material could be formed substantially.

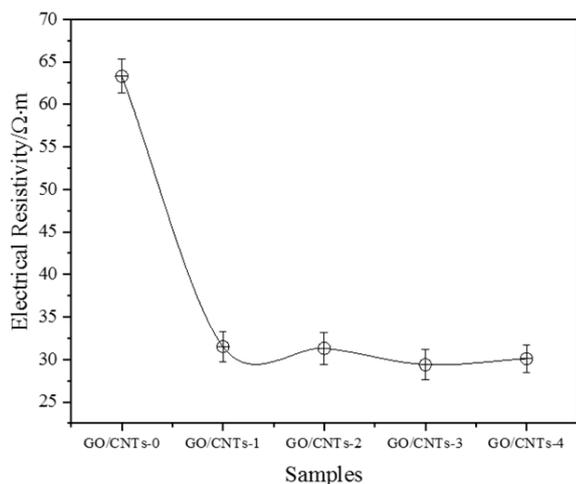


Figure 3. The average resistivity test results of GO/CNTs cement-based composites

### 3.4 Flexural and compressive strength performance of GO/CNTs cement-based composites

In this study, the data of the flexural strength, compressive strength of GO/CNTs cement-based composites are summarized in Table 1. The tendency of the flexural strength and compressive strength of the GO /CNTs samples with different GO and CNTs dosage are shown in Figure 4. For GO/CNTs cement-based composites, when loading 0.01 wt.% GO and 0.05 wt.% CNTs, the flexural strength of cement matrix obviously increased to 10.1 Mpa, which is higher than that of the blank sample nearly 20.2%. The flexural strength of GO/CNTs series samples increased with the addition of GO and CNTs, the compressive strength of GO/CNTs-3 reached 11.5 Mpa. Furthermore, the flexural strength of GO/CNTs-4 approached 11.6 MPa, increased by nearly 38% as compared with the blank sample. From Figure 4 (b), it could be observed that the compressive strength of GO/CNTs cement-based composites also behaved a similar variation. With the addition of GO and CNTs, the compressive strength of GO/CNTs cement-based composites increased gradually from 43.0 MPa for blank sample to 58.1 MPa for GO/CNTs-1, which increased by 35.1%. The compressive strength of GO/CNTs-2 and GO/CNTs-3 reached 59.7 and 59.8 Mpa, respectively. However, the compressive strength of GO/CNTs-4 decreased slightly.

In this study, the tendency of flexural and compressive strength of GO/CNTs samples is mainly attributed to the change of the content of CNTs and GO in the sample. The content of CNTs and GO in GO/CNTs-3 and GO/CNTs-4 is higher, the flexural strength of GO/CNTs-3 and GO/CNTs-4 cement composites reached 11.5 and 11.6 MPa, respectively, while the addition of excess CNTs and GO will cause the decrease of compressive strength of cement composites. The main reasons are as follows: when adding excessive amounts of GO and CNTs, their dispersion in aqueous solution will decrease, and mechanical stirring will increase CNTs to agglomerate and coagulate, causing more CNTs to form local agglomeration and entanglement in the cement hydration products. Some defects such as honeycomb and pinholes may even occur. The overall structure of the hydration products is fluffy and inhomogeneous. So that the mechanical properties of cement-based composites decrease[4].

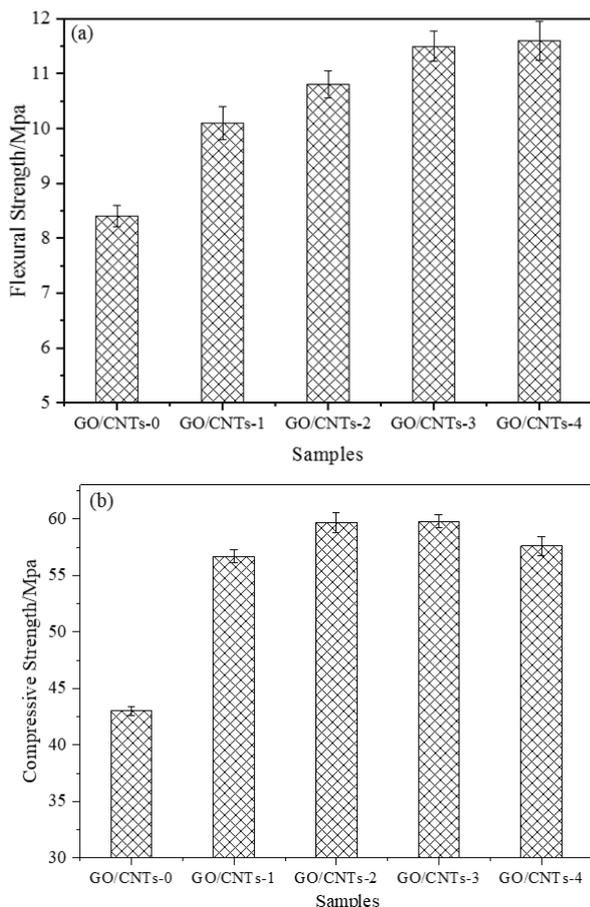


Figure 4.(a) Flexural and (b) compressive strength of GO/CNTs-0, GO/CNTs-1, GO/CNTs-2, GO/CNTs-3, GO/CNTs-4

This result could be proved by SEM images of blank sample GO/CNTs-0 and GO/CNTs-3 in Figure 5 (a) and (b), respectively. A lot of large and small holes could be found in the microstructure relaxed structured of cement matrix. There are a lot of radiated ettringite scattered on the surface of the cement matrix. However the structure of cement matrix could be improved, the size of the holes could be decreased and the compactness of cement could be increased after incorporating GO and CNTs into the cement matrix. Peng et.al[5]reported that GO can participate in the cement hydration reaction to improve the interfacial interaction between the cement hydration crystal and the GO surface to achieve the toughening effect; On the other hand, the huge specific surface area of GO sheet can provide a nucleation site for crystal growth in order to achieve controlled growth of crystals on the GO surface and further increase the crystallinity of the crystals so that the mechanical properties of the cement based composites greatly improve.

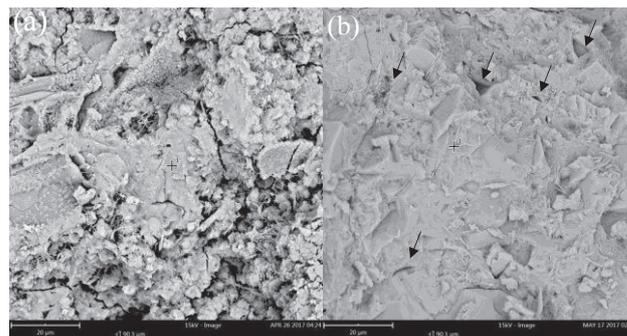


Figure 5. SEM images of GO/CNTs-0(a), GO/CNTs-3(b)

### 3.5 Piezo-resistivity performance of GO/CNTs cement-based composite

In this study, the piezo-resistivity property of GO/CNTs-3 with the best flexural and compressive strength after drying for 28 days were studied. From Figure 6, it can be found that as the external load increases from 0 to 20 KN, when load is 0, the averaged resistivity of GO/CNTs-3 cement-based composites is 68.49  $\Omega \cdot m$ . With the increase of the load, the averaged resistivity of the sample shows a significant linear decrease. The averaged resistivity of GO/CNTs-3 decreases to 32.21  $\Omega \cdot m$  when the applied stress increases to 20 KN. This phenomenon shows that GO/CNTs cement-based composites have good piezo-resistivity. This piezo-resistivity effect is mainly due to the tunneling effect and the combined effect of GO and GO, CNTs and CNTs, and GO and CNTs contact to produce electrical conductive effects.

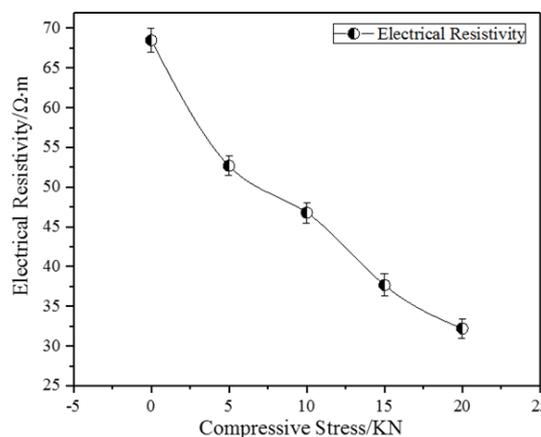


Figure 6. The tendency of average resistivity of GO / CNTs-3 cementitious composites under different compressive stress

## 4 Conclusion

1. With the increase of GO and CNTs, the flexural and compressive properties of the GO/CNTs composites increase obviously.
2. GO/CNTs cement-based composites have good electrical conductivity. GO/CNTs cement-based composites show good piezo-resistivity.

## References

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