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ORIGINAL ARTICLE

Production and investigation of mechanical properties and electrical resistivity of cement-matrix nanocomposites with graphene oxide and carbon nanotube reinforcements

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Abstract

In this study, two groups of the cement-matrix nanocomposites (CMNC) were produced. The first group was reinforced with either carbon nanotubes (CNT) or graphene oxide (GO), where the equivalent weight% of cement equaled 0.05, 0.1, and 0.15. The second group was reinforced with the hybrid CNT–GO, where the equivalent weight% of cement equaled 0.05 CNT–0.1 GO and 0.1 CNT–0.05 GO. Before producing nanocomposites, the distribution of the nanoreinforcement in water had been investigated using spectrophotometric analysis, scanning electron microscopy, and transmission electron microscopy. The physical and mechanical behaviors of different samples of the produced nanocomposites were evaluated by electrical resistivity and compressive strength tests. The effects of the types and the percentages of the nanoreinforcements on the electrical and mechanical properties of the produced nanocomposites were measured. The results showed that the electrical resistivity of the produced composites decreased with increasing the percentage of CNT, whereas the compressive strength of the cement paste initially increased and then decreased. Also, with increasing the percentage of GO, the compressive strength of the produced composites increased, while the electrical resistivity decreased. Moreover, in comparison with the composites reinforced with either CNT or GO, by using the hybrid reinforcement (CNT/GO), the compression strength increased, while the electrical resistivity decreased.

Keywords Cement-matrix nanocomposite · Carbon nanotubes · Graphene oxide · Electrical resistivity · Compressive strength

1 Introduction

Cement-matrix nanocomposites (CMNC) reinforced with carbon nanotubes not only have health monitoring structures for the static load conditions, but also are capable of sensing dynamic load variables [1]. The high aspect ratio of CNT leads to the formation of a conductive network even at low percentages (equivalent weight% of cement equals 0.1). In addition, the electromechanical properties (piezoresistivity) of CNT, with improved mechanical properties, have provided potential applications for CMNC, including the multiple capabilities of stress assessment of concrete structures, damage detection, and traffic assessment in highway structures. That is, the electrical properties of the cement-matrix nanocomposites equipped with CNT (CMNC-CNT) can change under the stress/strain [2].

Calcium silicate hydrate (C–S–H), which is close to the amorphous material, is the main hydration product of Portland cement and forms about 60% of cement paste volume. C–S–H is the main connecting factor in the cement paste and is responsible for important properties, such as strength and contraction. To understand and predict mechanical and physical behaviors, the structure of concrete should essentially be analyzed on nanoscale [3]. The use of CNT, as a reinforcement in the cement paste, increases the number of hydrate crystals, thus changing their morphologies. Researchers have also shown that CNT can enhance the strength of cement-matrix composites [4]. Makar et al. [5] demonstrated that the

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compressive strength of CMNC increased about 68.5% and 47% in the mortars with 0.06 and 0.12 wt% of CNT, respectively, after 28 days of curing. The great tendency of CNTs for agglomeration and their weak bonding with the cement matrix, however, have mainly limited their applications [4]. Equipping CNTs with reinforcement increases strength, hardness, fracture toughness, and flexural strength of cement composites through microcrack bridging mechanism [5]. Lu et al. [6] showed that 0.05 wt% of graphene oxide (GO) increased the compressive strength of GO-CMNC up to 33%. Likewise, Lv et al. [7] found that the GO nanosheets could regulate the formation of the cement hydration crystals. The GO nanosheets carried a large number of oxygen-containing groups, mainly –OH, –O–, –COOH, and $–SO_3H$. These functional groups provided places for the hydration products to grow. Then, the hydration reaction continued with the formation of the thicker rod-like crystals. These rod-like crystals were composed of CH, C–S–H, etc. They could form flower-like and polyhedron-like crystals due to the effects of the GO nanosheets on the whole reactions. These flower-like and polyhedron-like crystals created a coherent structure improving the toughness of CMNC [7, 8].

In comparison with carbon nanotubes and carbon nanofibers, CMNC reinforced with GO (CMNC-GO) has many advantages, such as easier dispersion processing, excellent mechanical properties, and self-repairing behavior of CMNC [7].

Other researchers showed that the simultaneous use of hybrid CNT/GO reinforcements in the cement mortars with and without polycarboxylate additive could increase the compressive strength up to 23.8% and 9.1%, respectively [9]. In this study, CMNCs reinforced with either carbon nanotubes or graphene oxide were produced, where equivalent weight% of cement equaled 0.05, 0.1, and 0.15. The hybrid nanocomposites with two types of reinforcements (carbon nanotubes and graphene oxide) were also produced, where the equivalent weight% of cement equaled 0.05 CNT–0.1 GO and 0.1 CNT–0.05 GO. Before the production of these composites, the distribution of reinforcement in water had been investigated by spectrophotometric analysis, scanning electron microscopy, and transmission electron microscopy. The aim of this paper is to investigate the relations between the ordered microstructure and the strength and electrical resistance of the nanocomposite samples. The effects of various parameters, such as types and percentages of reinforcement, on these properties were also studied.

2 Experimental procedure

2.1 Materials

In this research, Portland cement type II and the standard silica sand (Table 1) were used for the production of the cement paste. The resistance of the Portland cement type II to the formation of the sulfate compounds is moderate at the contact surface of the electrodes with the cement paste. In the multi-walled carbon nanotubes with carboxyl functional groups (MWNTs-COOH), used in this study, the outer diameters of CNTs were in the range of 10–20 nm, and their lengths were around 10–30 µm. Reduced graphene oxide (rGO), whose layers varied from one to ten and whose thickness changed between 0.55 and 3.74 nm, was used to better disperse the particles in water and to create more and stronger chemical bonds with the cement matrix.

2.2 Dispersion of CNT reinforcement in aqueous solution

In order to produce CMNCs reinforced with CNTs (CMNC-CNT), CNTs must uniformly and effectively be dispersed in water, and a suspension must be obtained containing CNTs and water. Thus, sodium dodecyl sulfate (SDS), equal to 0.025 wt% of solution, was initially added to distilled water. This mixture was stirred by a magnetic stirrer for 5 min. Next, the specific weight of CNTs (equivalent weight% of cement = 0.05, 0.1, and 0.15) was measured; this was then added to the SDS solution and dispersed in ice-water bath by using a 480-W ultrasonic homogenizer for 15 min. The ice-water bath not only prevents the evaporation of water but also protects the reinforcement from being damaged by the heat generated by the ultrasonic waves. Eventually, CNTs suspended in water were achieved.

2.3 Dispersion of GO reinforcement in aqueous solution

To produce CMNCs reinforced with GO (CMNC-GO), rGO must uniformly and effectively be dispersed in water. Thus, after measuring the specific weight of rGO (equivalent weight% of cement = 0.05, 0.1, and 0.15) to enhance the distribution of GO in the cement matrix, acetone solution was used. Therefore, in ice-water bath, GO was mixed with 30 ml of acetone and dispersed by a 300-W ultrasonicator for 15 min. Then, the prepared suspension was stirred by a magnetic stirrer in order for the acetone to be evaporated and

Table 1 The specifications of standard silica sand mixture

Square mesh size (mm)	Cumulative retained (%)
0.08	99 ± 1
0.16	87 ± 5
0.5	67 ± 5
1.00	33 ± 5
1.60	7 ± 5
2.00	0

the functionalized graphene to remain in the reaction. The dried GO was dispersed in distilled water in ice-water bath using the 480-W ultrasonicator for 15 min. Eventually, GO suspended in water was achieved.

2.4 Dispersion of hybrid reinforcements CNT/GO in aqueous solution

In order to produce CMNCs reinforced with hybrid CNT/GO reinforcement (CMNC-CNT/GO), CNTs and GO must uniformly and simultaneously be dispersed in the cement matrix. Therefore, the GO surface was initially functionalized with acetone and then heated with the magnetic stirrer to be dried. Next, the certain weight of GO and CNTs (equivalent weight% of cement = 0.05 CNT–0.1 GO and 0.1 CNT–0.05 GO), having surface functionalization (–COOH– functional group), was dispersed in distilled water in ice-water bath by using the 480-W ultrasonicator for 15 min. Eventually, CNT/GO suspended in water was achieved.

2.5 Production of cement-matrix nanocomposite

Following the dispersion of the reinforcements in water, the polycarboxylate super plasticizer was added to the produced suspension, and the mixture was mixed for 1 min. The specified amounts of the cement and the sand (according to standard C109) having mechanical turbulence were added to the suspensions. This mortar was prepared according to the standard C109 and molded in a lubricated metal mold whose dimensions equaled $5.08 \times 5.08 \times 5.08\ \text{cm}^3$. As schematically shown in Fig. 1, two stainless steel mesh electrodes were embedded in the molded samples at a distance of 2 cm from each other and a distance of 1.5 cm from the mold wall. After molding, the produced composite samples were placed in a humid room for 24 h. The produced samples were cured in water for 28 days (the temperature of humid room was 23 ± 2 °C according to the standard). In this study, CMNCs reinforced with varying amounts of single or hybrid reinforcements were produced using the aforementioned procedure and were characterized by the standard tests. Different types of composites (at least eight specimens for each condition) were produced in this study; the amounts of their reinforcements are shown in Table 2.

2.6 Evaluation of physical and mechanical properties

The microstructures of the produced CMNCs were evaluated by scanning electron microscopy and transmission electron microscopy. The stability and distribution of the reinforcements were investigated using ultraviolet–visible

Table 2 The types of produced composite samples in this research and the amounts of their reinforcements

Samples	Percentages of reinforcement
Plain cement paste (PC)	–
CMNC-CNT	PC + 0.05 wt% CNT PC + 0.1 wt% CNT PC + 0.15 wt% CNT
CMNC-GO	PC + 0.05 wt% GO PC + 0.1 wt% GO PC + 0.15 wt% GO
CMNC-GO/CNT	PC + 0.1 wt% GO + 0.05 wt% CNT PC + 0.05 wt% GO + 0.1 wt% CNT

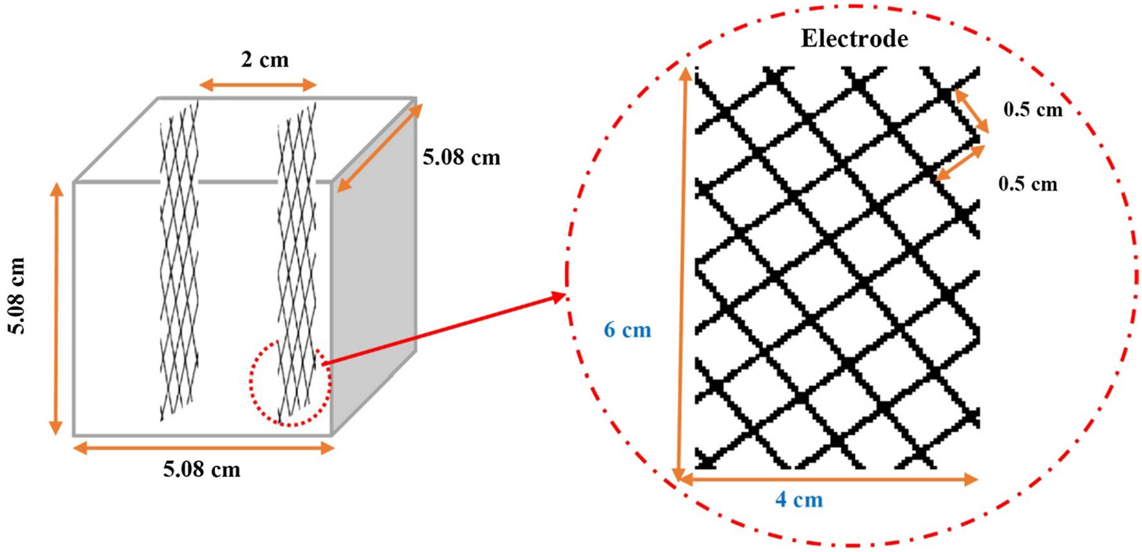


Fig. 1 Schematic illustration of the electrodes embedded in the cement mortar

spectroscopy (UV–Vis) in the aquatic environment. To study the effects of the types and the percentages of different reinforcements on the compressive strength of different samples of the produced composite, having the dimensions of $5.08 \times 5.08 \times 5.08$ cm^3, the 20-ton press machine was used. The effects of the types and the amounts of reinforcement on the electrical properties of the produced composite samples were assessed by a type of electronic test equipment used to measure the inductance (L), capacitance (C), and resistance (R) of an electronic component (LCR meter) with 0.0001 Ω precision. AC and two probes were used for measuring the electrical properties of the produced samples. The connection setup of the equipment used for measuring the electrical properties of the produced composites is shown in Fig. 2.

3 Results and discussion

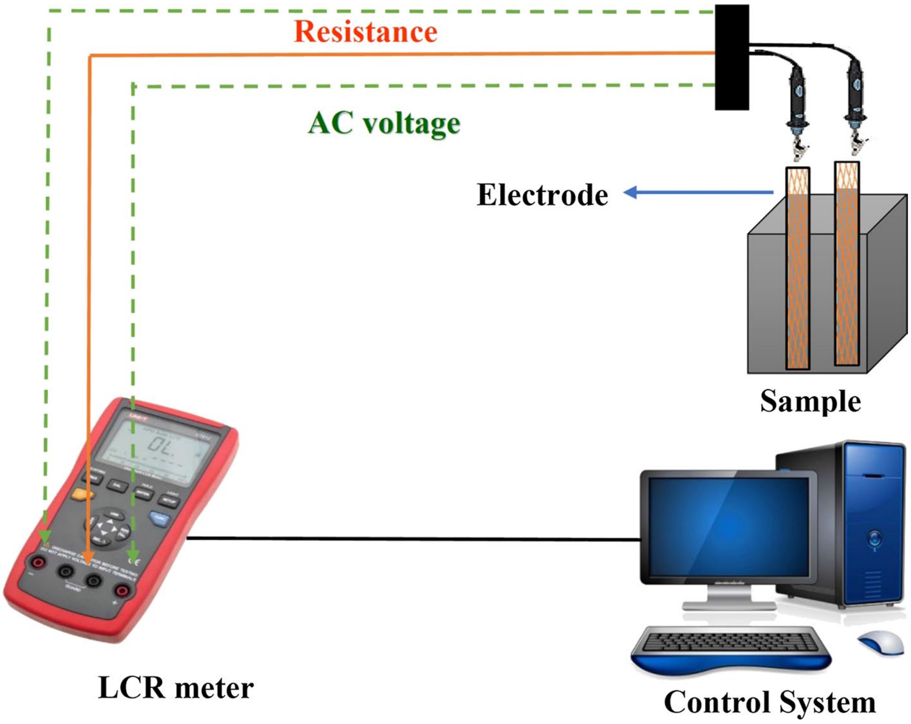
3.1 Investigation of reinforcement dispersion in aqueous solution

As shown in Fig. 3a, after being mixed by the ultrasonic homogenizer, CNTs were well dispersed in the aqueous SDS solution consisting of 0.1 wt% of cement. Figure 3b also indicates that GO was well dispersed in the aqueous solution consisting of 0.1 wt% of cement after being dispersed in acetone and water twice. Figure 4 shows the SEM images of the hybrid GO/CNT reinforcements, where 0.05 wt% of CNT was combined with 0.1 wt% of GO, following dispersion in water. It can be seen in Fig. 4 that the carbon nanotubes better dispersed in the aqueous solution of the hybrid reinforcements than that of the single reinforcement. This can be attributed to the effects of the GO nanosheets on the dispersion of CNTs in the aqueous solution. The GO nanosheets whose force of surface gravity is exerted on the places where there are lattice defects in contact with CNTs (or with their functional groups) make CNTs be dispersed in the hybrid suspension better [9].

The transmission electron microscopy (TEM) images of the prepared reinforcements, shown in Fig. 5a and b, indicated the networks of the CNTs and GO reinforcements dispersed in water, respectively. The networks of the hybrid CNT/GO reinforcements were formed in water after the dispersion process (Fig. 5c). As previously mentioned, in the suspension of the hybrid CNT/GO, the graphene nanosheets acted as a dispersive material, which made CNTs be separated from each other, thus improving their dispersion in water (Fig. 5d) [6].

The stability of the reinforcements in different produced aqueous solutions was studied using the UV–Vis spectrophotometry test. Figure 6a shows results of the UV–Vis spectroscopy as to the CNT solutions at different static times. This figure shows that the absorption peak occurred at wavelength of 215 nm, which was related to the transmission of electron $\boldsymbol{n} \rightarrow \boldsymbol{\pi}^*$ of C=O bond, caused by carboxyl-group carbon and SDS surfactant bonds, respectively. It also shows the higher absorption peak occurring at a wavelength of 257 nm due to transmission of electron $\pi \rightarrow \pi^*$

Fig. 2 The connections set up equipments for measuring the electrical properties of produced composite samples



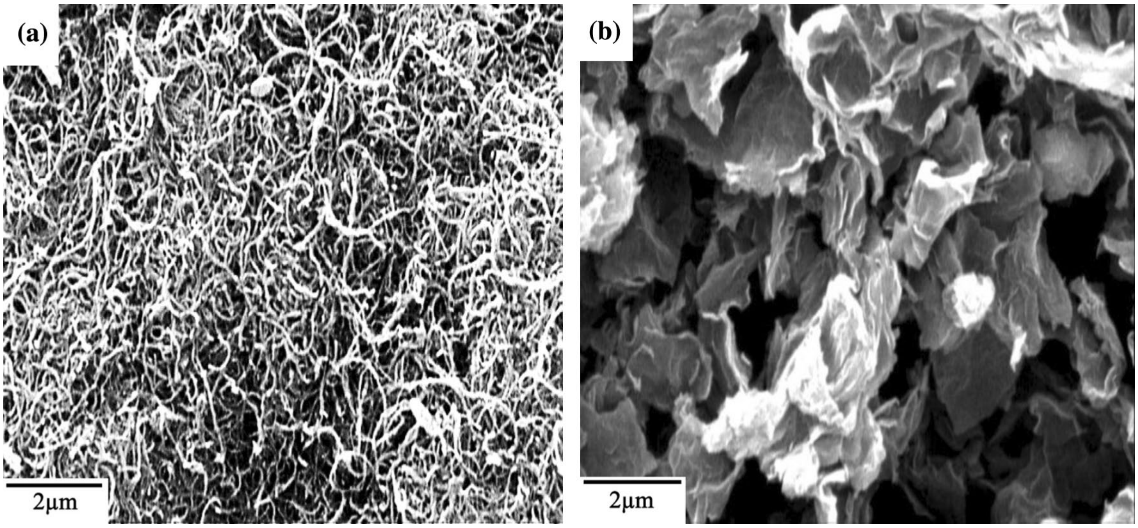


Fig. 3 The SEM image of **a** the CNTs equal to 0.1 wt% of cement after dispersion in water, **b** the GO nanosheets equal to 0.1 wt% of cement after dispersion in acetone, then in water, respectively

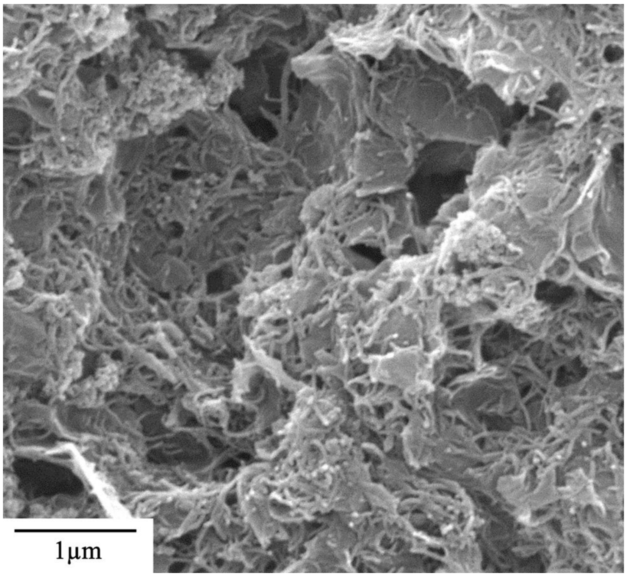


Fig. 4 The SEM image of the mixture of GO/CNT after dispersion in aqueous solution

of C=C bonds [9]. It can be seen that the absorbance of CNTs decreased at different times. Thus, at the characteristic absorption peak (257 nm), the absorbance of the suspension varied from 1.703 (0 h) to 1.623 (6 h). These results indicated that the carbon nanotubes tended to agglomerate in water due to strong van der Waals interaction forces.

The suspension of GO showed the absorption peaks at the wavelengths of 230 nm and 263 nm (Fig. 6b). After different static times, the variations of the absorption peak were negligible for the GO suspension at the peak of 263 nm. The variations of the absorbance stability of the GO suspension, with the passage of time, indicated the reluctance of the GO nanosheets to agglomerate in the aqueous solutions because of the repulsive forces between the atomic groups on their surfaces. The absorbance of the hybrid CNT/GO colloidal solution at different static times is shown in Fig. 6c, indicating a higher absorption peak at the wavelength of 262 nm. This increase in the absorbance of CNTs in the hybrid CNT/GO solution was due to the existence of strong electrostatic repulsions between the GO nanosheets having a negative charge. Moreover, with the addition of CNTs to the GO suspension, the zeta potential of the GO nanosheets reduced; the CNTs were then adsorbed by the GO nanosheets, and the steric effect could overcome the van der Waals interaction forces between CNTs. The dispersion of CNTs in the hybrid CNT/GO solution eventually improved [9].

Figure 7 shows that the UV absorption spectrum of GO could overcome the UV absorption spectrum of the CNT suspension in the hybrid CNT/GO suspension (0 h of time). The absorption spectrum of the hybrid CNT/GO suspension was also similar to that of the GO suspension. This was due to the strong van der Waals interaction forces between CNTs which could overcome the effects of the GO dispersion as reported in the previous researches [6, 9].

3.2 Investigation of compressive strength of produced CMNC samples

3.2.1 Effects of CNTs on compressive strength of CMNC-CNT

As presented in Table 3, the compressive strength of the cured CMNC-CNT having different amounts of CNTs was higher than that of the plain cement paste having no

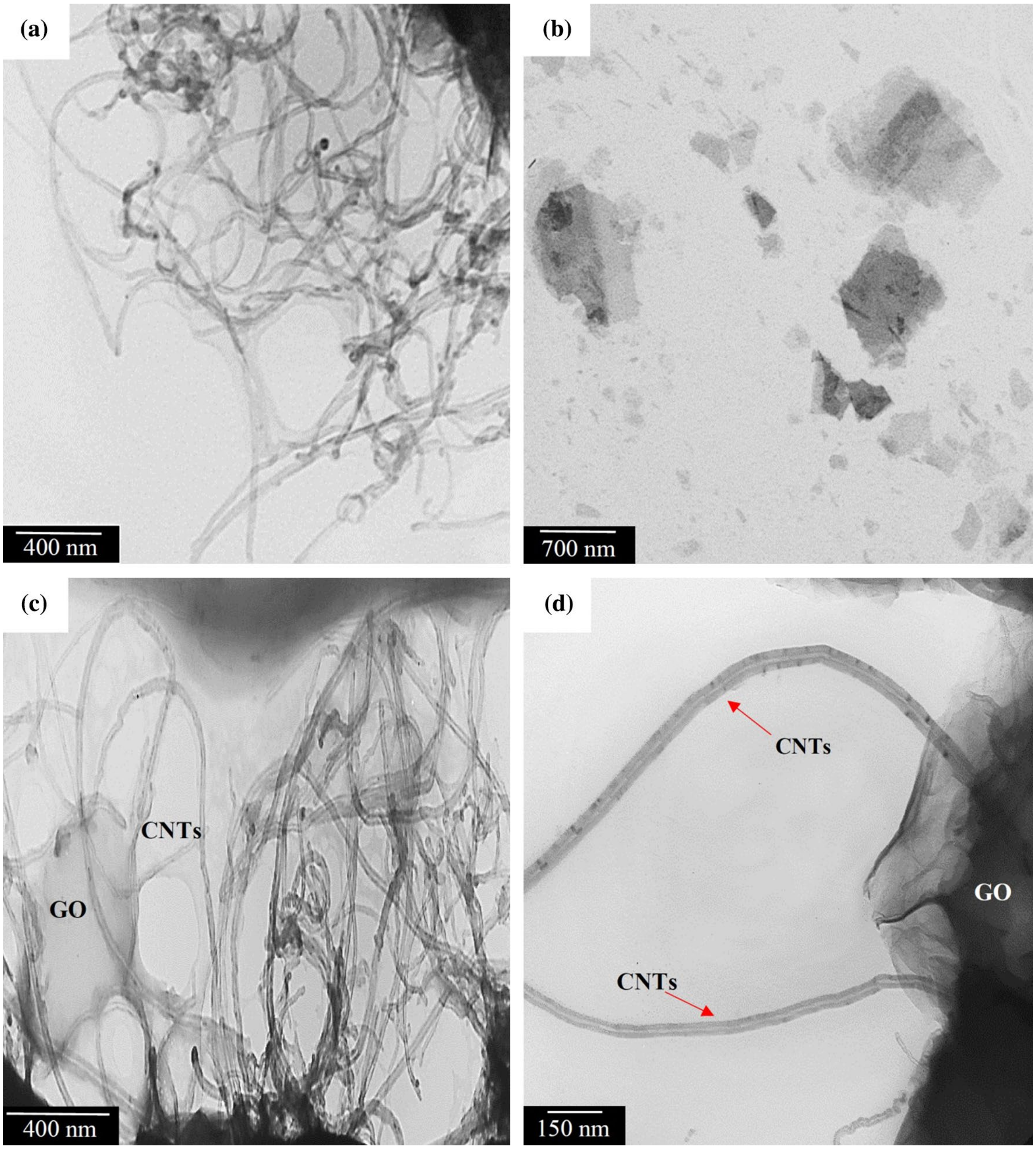


Fig. 5 The TEM image of **a** CNTs, **b** GO nanosheets, **c** the mixture of CNT/GO, after dispersion in water, and **d** the effect of GO nanosheets as dispersive material in hybrid suspension of CNT/GO in water

reinforcements as shown by other researchers [10]. Also, the compressive strength of CMNC-CNT decreased by increasing the percentage of CNTs (Table 3). This behavior might result from the tendency of CNTs to agglomerate, which was also confirmed by the spectrophotometric analysis [5].

Different mechanisms have been proposed to improve the compressive strength of CMNC-CNT having varied amounts of CNTs. The most common mechanism is the bridging effect of CNTs (Fig. 8a, b) [5]. In the image shown in Fig. 8c, it can be seen that the network of the CNTs was covered with the hydration products. The carboxyl functional groups on the surface of CNTs are places for nucleation and growth of hydration products. As a result of the interaction between the conductive network of CNTs and the hydration products, a spider-web structure was created (Fig. 8d) with high strength CMNC-CNT composites.

The effects of the crack bridging of CNTs and of the intertwined network of the hydration products on the strength of the CMNC-CNT composite were determined by the SEM images taken from the fracture surfaces of CMNCs having 0.1 wt% of CNTs (Fig. 9). Figure 9a clearly indicates that CNTs prevented the growth of the given products

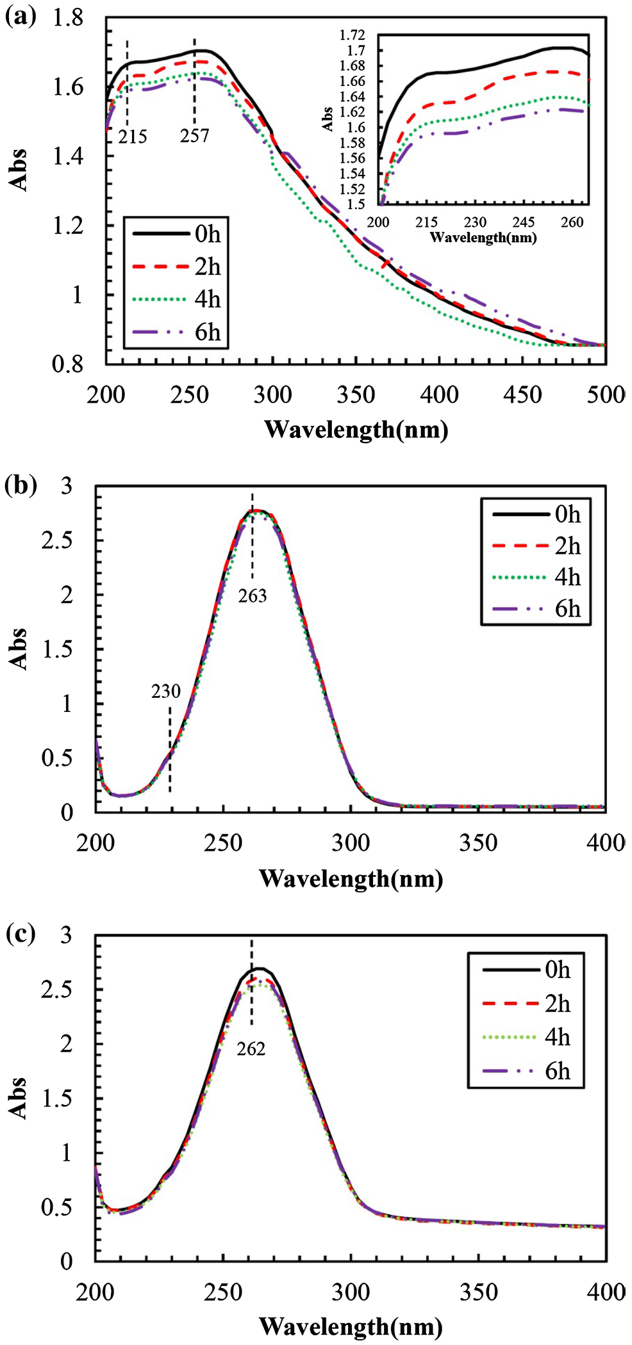


Fig. 6 The UV–Vis spectroscopy results of **a** CNTs at a concentration of 0.02 mg/ml, **b** GO suspensions at a concentration of 0.01 mg/ml, and **c** CNT/GO hybrid suspension at a concentration of 0.02CNT/0.01GO mg/ml, at different period of static time

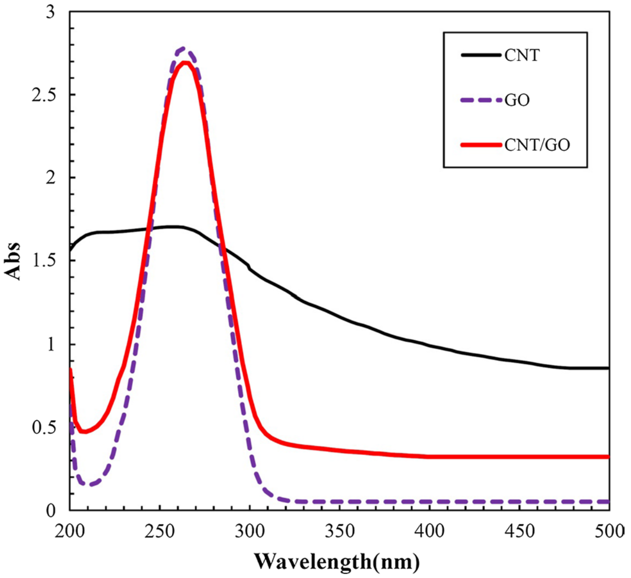


Fig. 7 The comparison of UV–Vis spectroscopy results of the CNT, GO, and CNT/GO suspensions at a concentration of 0.02, 0.01, and 0.02CNT/0.01GO mg/ml, respectively

Table 3 The variation of the compressive strength of samples

Percentages of reinforcement (wt%)	Compressive strength (MPa)
0	48 ± 2.6
0.05% CNT	66.6 ± 3.68
0.1% CNT	57.2 ± 3.32
0.15% CNT	55.2 ± 2.51
0.05% GO	54.2 ± 4.15
0.1% GO	67.7 ± 3.77
0.15% GO	61.7 ± 4.66
0.1% CNT + 0.05 GO	58.4 ± 3.05
0.05% CNT + 0.1% GO	67.2 ± 2.98

by bridging both sides of the cracks. With the continued pressure of crack bridging, however, CNTs were broken and separated from the cement matrix (Fig. 9b).

As can be observed in Fig. 10, with increasing the amount of CNT to 0.15 wt%, a part of CNT was agglomerated in the cement matrix. Therefore, in agreement with the other researchers [11], irrespective of their added amounts, CNTs could not show their maximum potential for improving the composite strength (Table 3).

3.2.2 Effects of GO on compressive strength of CMNC-GO

In comparison with the plain cement paste, the compressive strength of the cured CMNC-GO, having different amounts of GO, increased (Table 3). The compressive strength of the composites also increased with increasing the percentage of GO up to 0.1 wt% and decreased when using 0.15 wt% of GO. As observed in the spectrophotometric analysis, the reason for these results can be attributed to the unwillingness of the GO nanosheets for agglomeration. The reduction in the compressive strength of composites when increasing

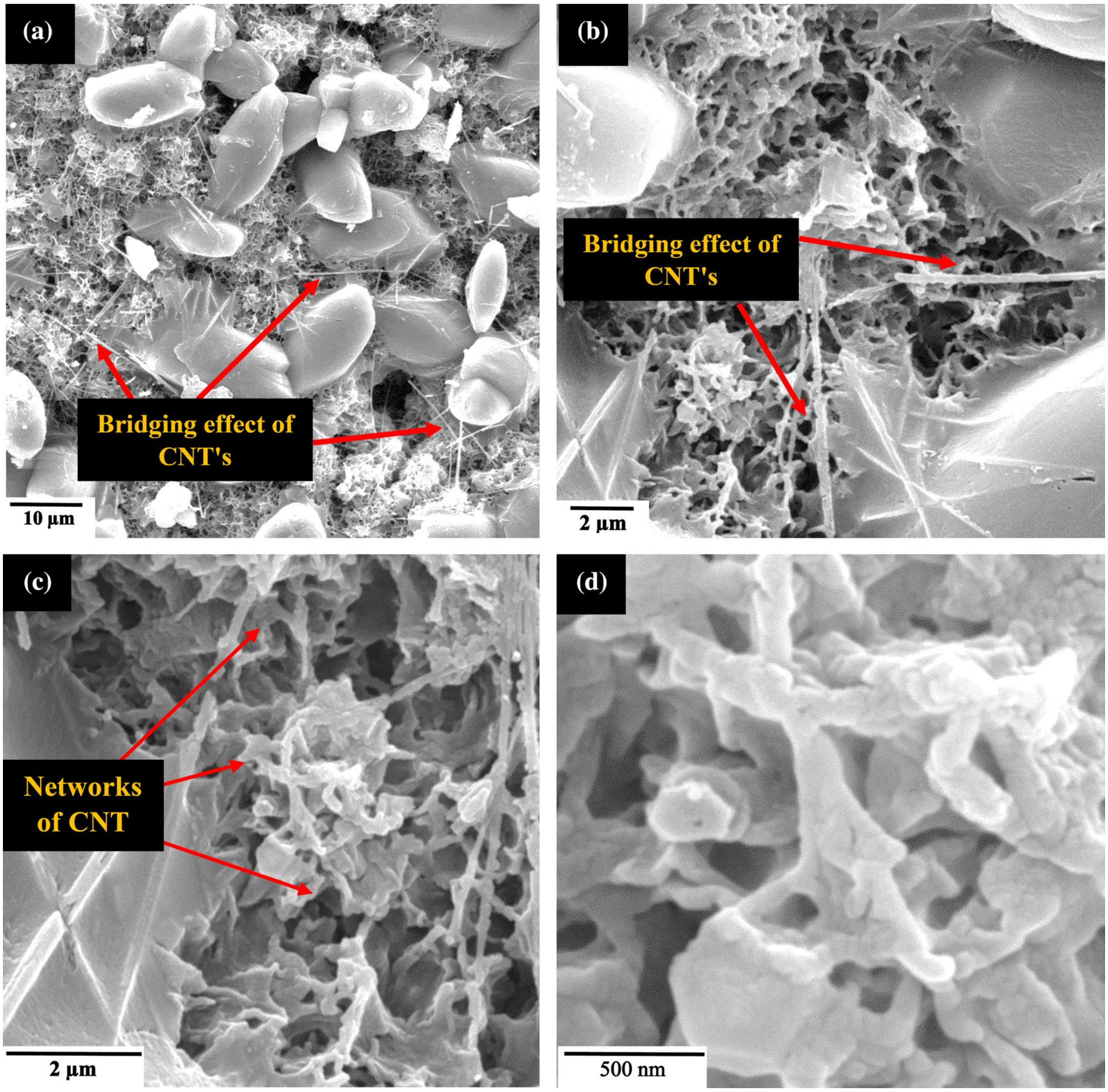


Fig. 8 The SEM image of CMNC-0.1 wt% CNT at the different magnifications **a** ×1000, **b** ×12,500, **c** ×25,000, and **d** ×100,000

the amounts of GO to higher than 0.1 wt% of cements (up to 0.15 wt%) may be the result of the action of the GO sheets during the dispersion of graphene in the cement. In this condition, any slips between the layers of the GO nanosheets under stress could lead to failure and reduce the mechanical properties of the composite [12]. Such conditions occur when the interface of the GO nanosheets with the cement matrix is poor. In the present study, because of the high percentage of GO, better dispersion was needed to prevent reduction of strength in the cement [12].

The SEM images, Fig. 11, showed the growth of the hydration products on the GO nanosheets, indicating that the presence of the GO nanosheets made the hydration products of the cement follow a regular growth mechanism. The hydration crystals followed polyhedron-like growth patterns and eventually created a more compact structure in the cement mortar (Fig. 11a). Figure 11b demonstrates the dense structure of the crystals with a spherical or rod-like shape, growing from the surface of the GO sheets. Also, the hydration products of CMNC-GO followed the flower-like growth mechanism in low-density positions, such as pores and cracks, and showed a self-repairing behavior in the cement matrix, i.e., reduction in size of holes in composites (Fig. 12).

Based on different growth mechanisms of hydration products observed in the cement matrix in the presence of CNT and GO reinforcements, it can be concluded that GO had more significant effects on the compressive strength of the cement paste in comparison with CNT when the reinforcement percentages exceeded 0.05 wt% due to the following reasons:

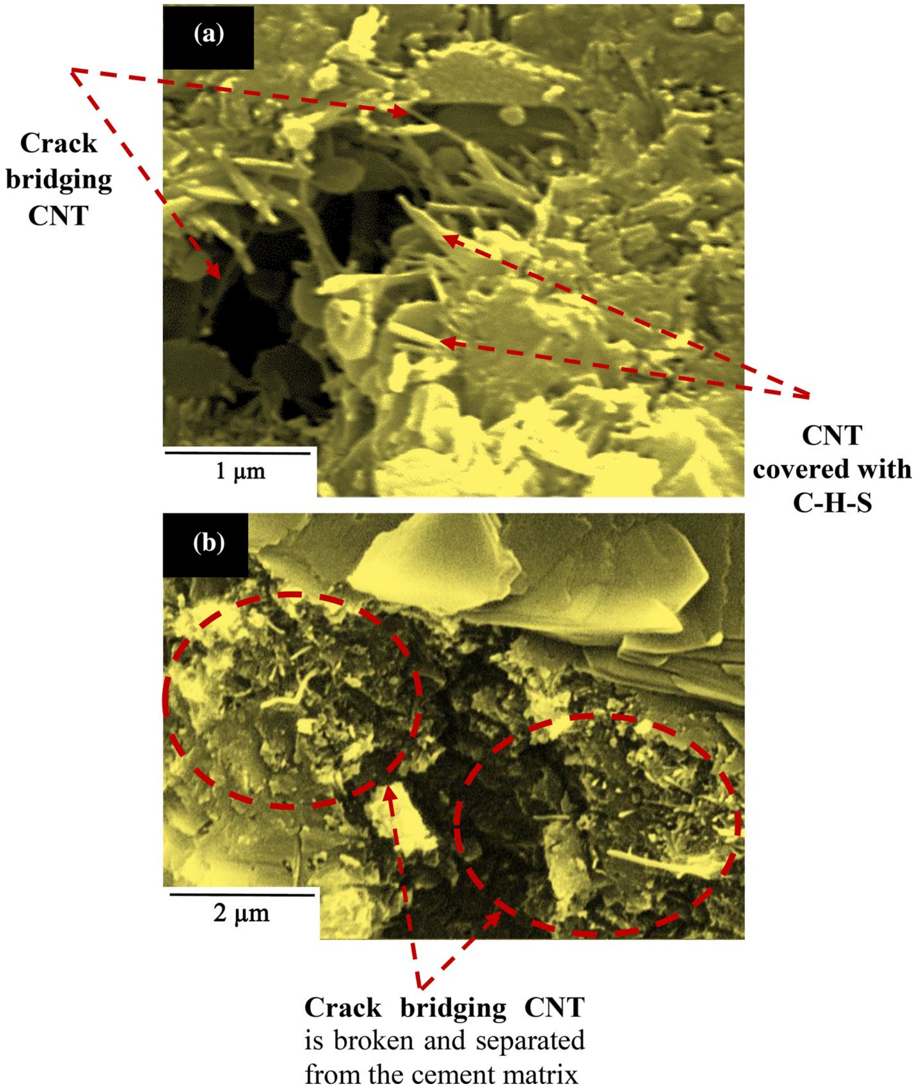


Fig. 9 The SEM image of the fracture surface of CMNC-0.1 wt% CNT at different magnifications **a** ×50,000, **b** ×25,000

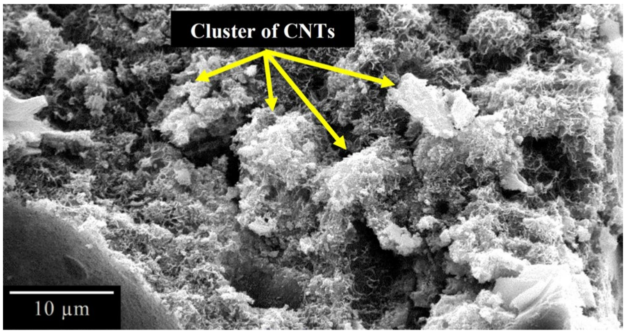


Fig. 10 The SEM image of the fracture surface of the CMNC-0.15 wt% CNT

(i) The denser composite structures of CMNC-GO in comparison with the composite structures of CMNC-CNT because of the polyhedron-like growth patterns of the hydration products in CMNC-GO.
(ii) Lack of agglomeration in the GO nanosheets due to the zeta potential of the GO nanosheets in comparison with more willing CNTs which tended to agglomerate due to strong van der Waals forces.
(iii) Self-repairing behavior of GO, resulting in reduction in pore size and a decrease in the number of voids in the cement matrix.
(iv) The role of GO as an adhesive material in assembling the crystals of the hydration products regularly.

Therefore, the higher compressive strength of CMNC with 0.05wt. % of CNT in comparison with that with 0.05wt. % of GO was caused by the lack of agglomeration in CNTs and the absence of a fully dense structure in CMNC having a low percentage of GO, i.e., 0.05 wt%.

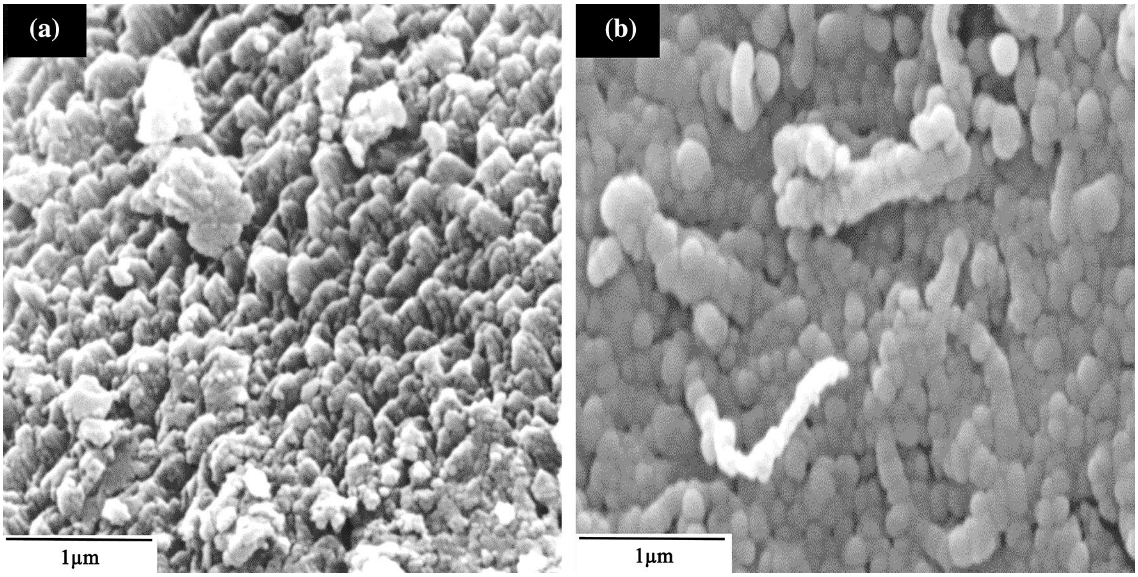


Fig. 11 The SEM image of CMNC-0.1 wt% GO **a** polyhedron-like crystals, **b** rod-like crystals

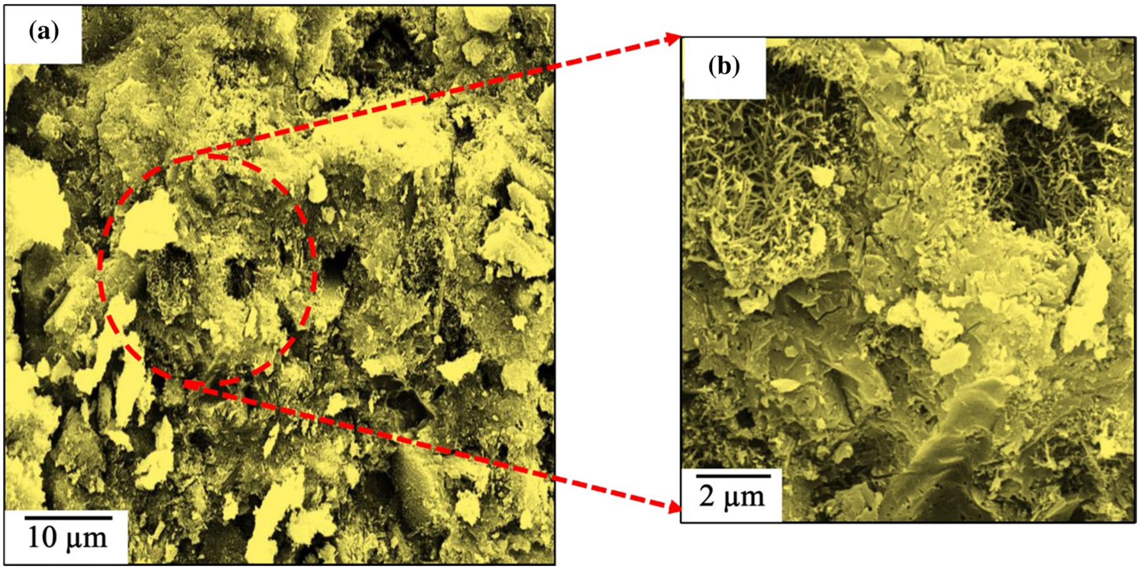


Fig. 12 The SEM image of the fracture surface of CMNC-0.1 wt% GO at different magnifications **a** ×3000, **b** ×15,000

3.2.3 Effects of hybrid CNT/GO reinforcements on compressive strength of CMNC-CNT/GO

Table 3 indicates that the compressive strength of CMNC-CNT/GO with different percentages of two types of reinforcement increased after 28-day curing in comparison with that of the plain cement paste. Also, the compressive strength of the hybrid composite samples was higher than that of the simple composite samples (Table 3). These results can be attributed to more uniform distribution of CNTs in the hybrid reinforcements and the denser structure due to the growth of the hydration products on the GO nanosheets. Figure 13 shows the microstructures of two types of hybrid composites, i.e., CMNC-0.1CNT/0.05GO and CMNC-0.05CNT/0.1GO. It can be seen that the density of the structure enhanced with increasing GO. In other words, by increasing the amount of GO, the flower-like growth in the pores of the cement matrix and the polyhedron-like growth patterns in the hydration products promoted in CMNC. Figure 13c shows that CNTs were mostly coated with the hydration products in CMNC-0.1CNT/0.05GO. Also, Fig. 13d shows the compact structure of the polyhedron germination of the hydration products created on the GO nanosheets.

3.3 Investigation of electrical resistivity of produced CMNC samples

3.3.1 Effects of CNTs on electrical resistivity of CMNC-CNT

Table 4 shows that the electrical resistivity of CMNC-CNT with different amounts of CNT exceeded that of the plain cement paste without any reinforcement, and the electrical resistivity of CMNC-CNT decreased with increasing the percentage of CNT reinforcement. This decrease in the electrical resistivity of CMNC-was due to the formation of a conductive network in the cement matrix because of the presence of CNTs [13]. In fact, because of the one-dimensional structure of the carbon nanotubes, electrons had ballistic transfer in the carbon nanotubes. Thus, the electrical resistivity significantly decreased in CMNC-CNT.

3.3.2 Effects of GO on electrical resistivity of CMNC-GO

Table 4 shows that the electrical resistivity of CMNC-GO decreased with increasing the percentage of GO reinforcement. This decrease in the electrical resistivity of CMNC-GO was due to the formation a conductive network in the cement matrix. As previously mentioned, the hydration products grew on the GO nanosheets (Fig. 11). Therefore, a conductive substrate formed between the hydration products and enhanced the electrical conductivity of this composite. Furthermore, the self-repairing effect of GO on reducing the porosity and pore size of the cement matrix increased the conductivity of this composite [7].

By comparing the effects of GO and of CNT reinforcement on the electrical resistivity of CMNC-GO and CMNC-CNT with different percentages of reinforcements, it can be concluded that the effects of CNT on increasing the conductivity were greater than those of GO with the same amount of reinforcement in this cement-matrix composites due to the following reasons:

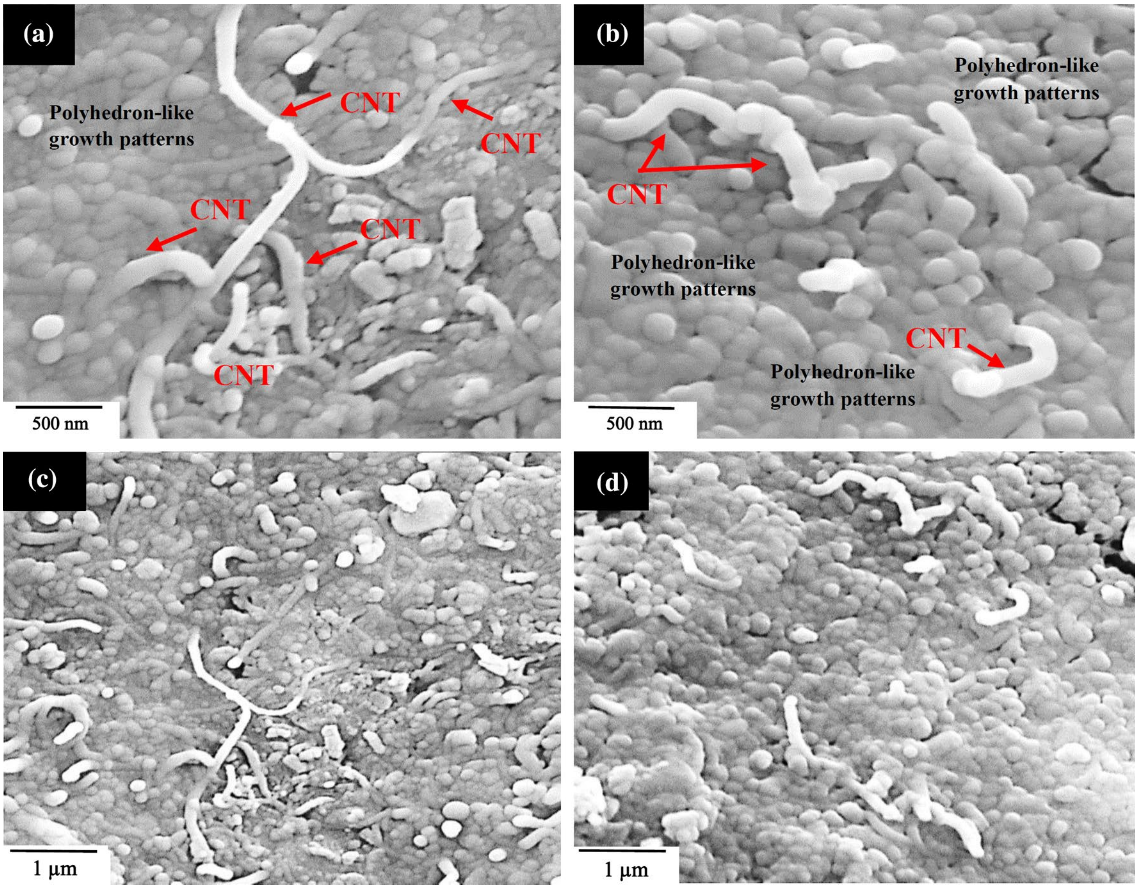


Fig. 13 The SEM images of the CMNC-0.1CNT/0.05GO surface at magnification **a** ×60,000, **c** ×3000, respectively, and the SEM images of the CMNC-0.05CNT/0.1GO surface at magnification **b** ×60,000, **d** ×3000, respectively

Table 4 The variation of the electrical resistivity of samples

Percentages of reinforcement (wt %)	Resistivity (kΩ cm)
0	85.42 ± 3.12
0.05% CNT	73.68 ± 2.27
0.1% CNT	37.84 ± 0.90
0.15% CNT	18.48 ± 0.65
0.05% GO	83.44 ± 2.96
0.1% GO	44.8 ± 1.40
0.15% GO	25.5 ± 0.85
0.1% CNT + 0.05 GO	13.01 ± 0.44
0.05% CNT + 0.1% GO	8.64 ± 0.52

(i) The electron transfer in the CNTs was one-directional ballistic transfer with no external or internal barriers, whereas the electron transfer in the GO nanosheets was two- or three-directional diffusion transfer. As a result, the rate of electron transfer in CNT was higher than that in GO. Therefore, the conductivity of the CMNC-CNT composites was higher than that of the CMNC-GO with the same percentage of reinforcement.

(ii) The GO nanosheets used in this study, made up of the reduced graphene oxide, due to the particular method of synthesis, had numerous oxygen-containing functional groups, such as carboxyl, epoxide, and hydroxyl groups, on its surface. Many atomic defects also occurred on the surfaces. These two factors disrupted and reduced the speed of the electron transfer in reduced graphene oxide. Thus, the electrical conductivity of rGO was less than that of CNT and other types of GO [14].

(iii) The electric field around the material is proportional to the charge density (i.e., the ratio of the number of charges on the reinforcement to the cross section of reinforcement). In the CMNC-CNT composites, the charge density increased due to the nanoscale structure of the tip of CNTs. Therefore, a strong electric field formed around the carbon nanotubes. Also, due to the capacitive and tunneling effects, the electron transfer helped to further increase the electrical conductivity of CMNCs with CNT reinforcement [13, 15].

3.3.3 Effects of hybrid CNT/GO reinforcements on electrical resistivity of CMNC-CNT/GO

As shown in Table 4, the electrical resistivity of CMNC-0.1CNT/0.05GO and CMNC-0.05CNT/0.1GO decreased with respect to the electrical resistivity of the cement matrix. This increase in the conductivity can be attributed to better dispersion of CNTs into the GO nanosheets, the role of self-repairing of GO in reducing porosity and pore size [8], the decrease in the number of the GO defects due to CNT adsorption, and the ballistic electrons transfer in the attributed CNTs. The sheets of rGO had a lot of atomic defects and functional groups; these structural defects had considerable energy and a tendency for reaction with other atoms, and in turn, reducing their energy. Thus, reducing the functional groups and defects on the surface of GO could increase the electrical conductivity [14]. By adding CNT to the GO solution, the force of surface gravity of the GO nanosheets in places that have lattice defects contacts with CNTs [9]. Thus, by the adsorption of CNT into the defects and functional groups of GO, not only did the dispersion of CNT into the hybrid solution of GO/CNT improve, but also the electrical conductivity of GO nanosheets increased due to reduction in the number of the atomic defects and functional groups. Therefore, the electron transfer, which was the sum of the electron transfer mechanisms of GO and CNT, increased in the hybrid reinforcements [16]. Hence, compared with CMNC-CNT and CMNC-GO, having equal reinforcements, greater conductivity was achieved in the hybrid CMNC-CNT/GO composites.

4 Conclusion

According to the results of this research as to the production of CMNCs with different hybrid reinforcements, the following results can be summarized:

1. In the process of making CMNCs, it was observed that GO, as a reinforcement in the hybrid CMNC-GO/CNT composites, could improve the uniform dispersion of CNTs in water and cement.
2. The CMNC-GO has denser structures in comparison with the CMNC-CNT because GO can be used to control the formation of Portland cement hydration products into polyhedron-like crystals. Also the self-repairing behavior of GO results in reduction in pore size and a decrease in the number of voids in the cement matrix.
3. The interaction between the conductive network of CNTs and the hydration products was created a spider-web structure with high strength composites. The effects of the crack bridging of CNTs prevented the growth of the given products by bridging both sides of the cracks.
4. While considering the properties of the CMNC-GO and CMNC-CNT samples, it was observed that the strength and electrical resistivity of CMNC-GO was higher than that of CMNC-CNT with the same percentage of reinforcement.
5. In comparison with the plain cement paste, in the CMNC-CNT samples, with increasing the amounts of CNTs (equivalent weight% of cement = 0.05, 0.1,

and 0.15), the compressive strength of the composites increased by 38%, 19%, and 17%, respectively, and the electrical resistivity decreased by 14%, 56%, and 78%, respectively.

6. In comparison with the plain cement paste, in the CMNC-GO samples, with increasing the amounts of GO (equivalent weight% of cement = 0.05, 0.1, and 0.15), the compressive strength of the composites increased by 13%, 41%, and 29%, respectively, and the electrical resistivity decreased by 2.3%, 48%, and 70%, respectively.
7. In comparison with the plain cement paste, in the hybrid composites, where the equivalent weight% of cement equaled 0.05 CNT–0.1 GO and 0.1 CNT–0.05 GO, it was observed that the compressive strength increased by 27% and 40%, respectively.
8. In comparison with the plain cement paste, in the hybrid composites, where the equivalent weight% of cement equaled 0.05 CNT–0.1 GO and 0.1 CNT–0.05 GO, it was observed that the electrical resistivity decreased by 84% and 90%, respectively.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Ethical issues Authors state that the research was conducted according to ethical standards.

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