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EFFECT OF GRAPHENE NANO SHEETS REINFORCEMENT ON THE PHYSICAL PROPERTIES OF CEMENT PASTE

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Graphene nanosheets (GNSs) have unique physical properties that make them effective reinforcing materials. In this study Graphene Oxide (GO) was synthesized by oxidation of graphite flakes via modifed Hummer's method. The produced GO was thermally reduced (exfoliated) at 350 °C for 6 hours to produce graphenenano sheets. The influence of GO and GNSs reinforcement on mechanical properties, pore structure, thermal stability and electrical characteristics of the hardened cement composites was investigated. GO and GNSs were added at different percentages of 0, 0.01, 0.02, 0.03, 0.04 and 0.05 wt. % of cement. Compressive strength was determined at 28 days of curing. Thermo-gravimetric analysis (TGA) was used to detect the phase decomposition, the pore structure was studied using nitrogen adsorption at 77.35 °K technique, the microstructure was examined using scanning electron microscopy (SEM), and finally, electrical conductivity of GO/graphene-cement composites was also studied. Results revealed that, considerable enhancements in compressive strength by about 33% have been achieved by incorporating GNSs into cement matrix by about 0.04%. The integration of graphene into cement has significantly reduced the pore size of the pastes and led to a considerable improvement in the microstructure, with a consequent improvement in the electrical conductivity of these composites.

Keywords: Graphene nanosheets, Cement paste, Mechanical strength, pore structure, Thermal analysis, electrical properties.

1. Introduction

Cementitious materials are the most widely utilized for many decades for different sorts of structures [1]. Although; cement based materials are used over a wide range of a structural applications, they are brittle and possess poor tensile strength. The brittleness of cement structures comes from the inferior characteristics of the cement pastes in the hardened state [2]. Enhancing the strength of cement materials generally can be achieved by using reinforcing microfibers, such as steel fibers [3], carbon fibers [4] polymeric fibers [5, 6] and natural fibers [7]. These reinforcing materials can greatly improve the strength characteristics as a whole and increase the stress at which cement starts to crack, i.e. they delay the crack growth in the cementitious matrix however do not inhibit the crack formation [8].

Nowadays, nanotechnology (NT) has provided nano - scale particles /fibers; including, nano silica (NS), carbon nano tubes (CNTs) and nano graphene oxide (NGO); these might be utilized as reinforcements to inhibit the formation and delay the propagation of micro cracks. The use of nano fibers for improving the mechanical performance of cementitious materials are found to be more efficient than ordinary steel fibers (at millimeter scale) as they help in restricting cracks before they develop into micro cracks. NS and nano metakaoline were found to enhance the mechanical performance of cement-based materials [9-14].

Nowadays, great attention was paid to graphene and graphene oxide nanoplatelets (GONPs) being the most beneficial nano reinforcing materials. It is used as a nano reinforcement in different matrices like polymer, ceramic or cement for improving their mechanical and electrical properties [15].

The characteristics of graphene oxide (GO) - cement composites were studied by some researchers; the introduction of GO by 0.05 wt.% of cement has increased the compressive strength considerably by 15 – 33%; in addition, an enhancement of about 41–59% has been achieved in the flexural strength [2], the incorporation of GONPs by 0.03 wt.% of cement can enhance the compressive strength of GO – cement composite and tensile strength by more than 40%; also the total porosity (TP) of cement paste decreased [16]. When GO was added to plain cement and cement mortar at different percentages 0.01, 0.02, 0.03, 0.04 and 0.05 wt.% of cement, significant improvements in the flexural and compressive strengths of the hardened cement pastes by about 90.5 and 40.4% have been attained at 28 days of hydration, respectively. The flexural and compressive strengths of cement mortar modified with GO at ratios of 0.01, 0.03 and 0.06% increased by 70.5 and 24.4 wt.% after 28 days of hydration, respectively [17]. Incorporating graphene into geopolymers at concentrations of 0.00, 0.10, 0.35 and 0.50% by weight has improved the microstructure

and resulted in pore free condensed composites with enhanced mechanical performance, previous work reported an enhancement in flexural strength and Young's modulus by 134 and 376%, respectively [18].

It was found from the literature survey that, there are many conflicts regarding the development of GONPs/graphene reinforced cement especially in the GO/graphene incorporation ratios and the percentages of enhancements achieved. The main issue to be addressed in this work is to add an extended study to investigate the role of graphene in enhancing the physical properties of hydrated cement by using different analytical techniques.

2. Materials and Methods

Graphene Oxide (GO) was synthesized according to the modified Hummer's technique [19]. Typically, add 1 g of graphite + 0.5 g of $NaNO_3$ in a flask, then add 50 ml of H_2SO_4 (98%) under constant stirring at 5^oC for 1h, after that, add gradually 3 g of $KMnO_4$ (1g every 15 min.) taking into consideration that, the temperature of the solution have to be less 20 ^oC to avoid overheating and explosion. Dilute the solution by slowly adding100 ml warm distilled water, and then treat the solution with 3 ml of 30% H_2O_2 solution and 100 ml of distilled water to be sure that, $KMnO_4$ is completely reacted. After that, wash the mixture with HCl and water, respectively, then filtrate and dry to get GO, as a final step GO was thermally reduced for 6 hours to eliminate oxygen functionalities from the surface of GO to get the final product graphene sheets.

In this investigation, ten mixes of cement-Graphene composites were studied. GO and GNSs were added to ordinary Portland cement (OPC) by different ratios 0, 0.01, 0.02, 0.03, 0.04 and 0.05% by weight of cement. Firstly the as prepared GO and GNSs were dispersed in the mixing water through ultrasonication process (at 250 Watt and frequency of 20 KHz) for 20 min. to be sure of good dispersion and to prevent agglomeration of GO/GNSs. Now the mixing water with Graphene sheets dispersed in it can be added to cement to prepare the cement composites. The chemical composition of the used OPC is presented in table (1), while the mix composition was presented in Tables (2&3).

Table 1. **The chemical composition of OPC**

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	L.O.I.	Na_2O	K_2O	Total
21.54	4.02	2.93	61.82	1.59	3.48	3.64	0.42	0.25	99.69

Table 2. **Mix Design of Cement – GO Composites**

Mix Designation	OPC, (%)	GO, (%)	W/C Ratio
A	100	0.00	0.2500
F1		0.01	0.2830
F2		0.02	0.2925
F3		0.03	0.3000
F4		0.04	0.3025
F5		0.05	0.3075

Table 3. **Mix design of cement – nano graphene composites**

Mix designation	OPC, (%)	GNSs, (%)	W/C ratio
A	100	0	0.25
D1		0.01	0.26
D2		0.02	
D3		0.03	
D4		0.04	
D5		0.05	

The cement composite pastes were casted into 20 mm cubes for compressive strength test. The molds were vibrated for 1 min. to eliminate any contained air bubbles. The fresh pastes were kept in their molds at 100% relative humidity for 24 h, and then the samples were demolded and cured under tap water for 28 days [2].

3. Testing

3.1. Compressive strength

The Compressive strength of the samples was performed after 28 days of hydration on 20 mm cubic specimens as per a previous study for cement pastes [20] using RMU testing equipment hosted in HBRC, 57-2400 BERGAMO ITALY using loading rate 0.5 kn/sec. with a maximum force 1500 kn. Three specimens at each age were tested and the average compressive strength was calculated.

3.2. SEM

The microstructure of the freshly fractured surface of the specimens was examined using environmental scanning electron microscope (ESEM- Inspect S, FEI Company, Holland) equipped with Energy-dispersive X-ray analysis (EDX).

3.3. Thermal analysis

Thermogravimetric analyses of the samples were conducted using a DSC-TGA thermal analyzer (STD-Q600, USA) instrument from 25°C up to 1000°C at a heating rate of 10°C/min. The sample chamber was purged with nitrogen gas at a flow rate of 100 ml/min.

3.4. Pore structure

The Nitrogen adsorption - desorption isotherms were obtained for the hardened composites at 77.35 °K using a NOVA2000e (Quantachrome, USA) instrument. The pore - size distribution curves were obtained using non local density function theory (NLDFT) kernel.

3.5. Electrical conductivity

For the electrical conductivity measurements, pellets with thickness of 3mm and 10mm diameter were prepared, see Fig.1. A programmable automatic RLC bridge, model Hioki 3532 Hitester, was used for these measurements. The parameters such as phase angle φ, impedance Z, resistance R and capacitance C were measured in the applied range of frequencies 42 Hz – 5 MHz. The conductivity,σ, is calculated from the relation:

$$\sigma = \frac{d}{Az}. \quad (1)$$

Where: A is the cross-sectional area and d is the thickness of the pellet [21].

Fig. 1. Samples for electrical measurements

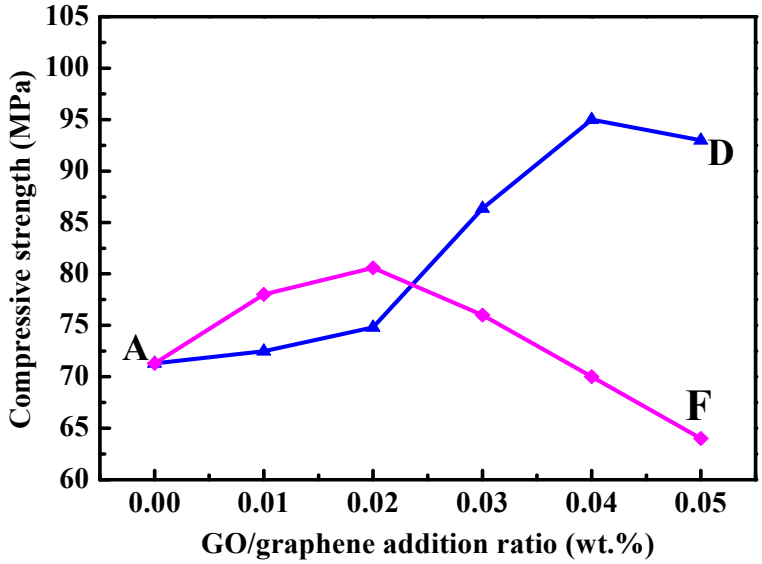

Fig. 2. Compressive strength of the hardened GO/GNSs - OPC composites

4. Results and Discussion

4.1. Compressive strength

Fig. 2 shows the compressive strength results of the cured OPC pastes with different GO/ GNSs additions. Evidently, the compressive strength of the hardened specimens increase with increasing GNSs percentage up to 0.02 GO and 0.04% GNSs, by further increase weight of GO/GNSs dosage in OPC leads to a gradual decrease in the compressive strength. As shown in this figure, D4 and F2 composites exhibited an enhancement ratios of about 33.24 and 13% increase in compressive strength compared with that of the control composite (A), that can be explained by improvement in mechanical interlocking caused by wrinkled appearance of GO and graphene sheets, strong interaction between cracks and GO/ graphene due to the 2D sheet – like structure and high aspect ratio, enhancement of the hydration process and formation of strong interfacial forces resulted from chemical interactions between oxygenated functional groups and hydration products [2], and the reduction of the pore structure in cement composite [16]. Also the gradual decrease may be interpreted by the agglomeration of the GO and graphene that resulted in difficulty to achieve uniform distribution of GO and graphene throughout the cement matrix.

4.2. Pore structure analysis

The hardened cement paste is composed of the solid part of hydrated cement and the pores. There are different reasons for the presence of pores in the hardened cement paste among them the excess water and air. These pores affect the strength, durability and shrinkage. In this study, the pore sizes and their distribution were determined by nitrogen adsorption technique. There are four main pore size distribution categories in cement paste:

pores of size >1000 nm are called large pores, capillary pores are of size between 100 to 1000 nm, meso – pores or transitional pores have size ranges from 10 to 100 nm and finally the gel pores have size <10 nm. Based on this classification, the pores in our samples are mainly meso - pores and gel pores. Moreover, macroscopic pores (>50 nm) contribute to permeability and strength, while microscopic pores (<50 nm) may affect the dry shrinkage and creep [22, 23].

Results of Figs. 3, 4 indicate that, the addition of GO/GNSs can efficiently improve the pore structure, through reducing the pore size and making the cement paste more compact.

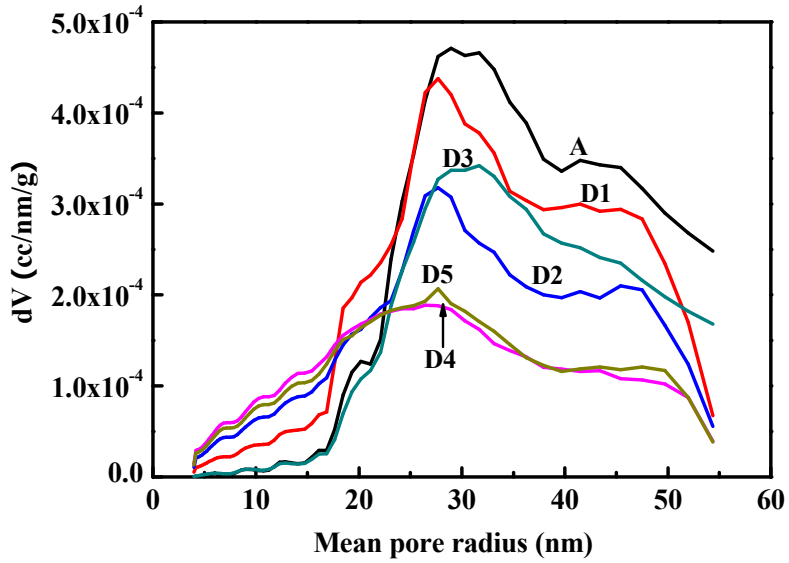

Fig. 3. Pore- size distribution curves of graphene-cement composites

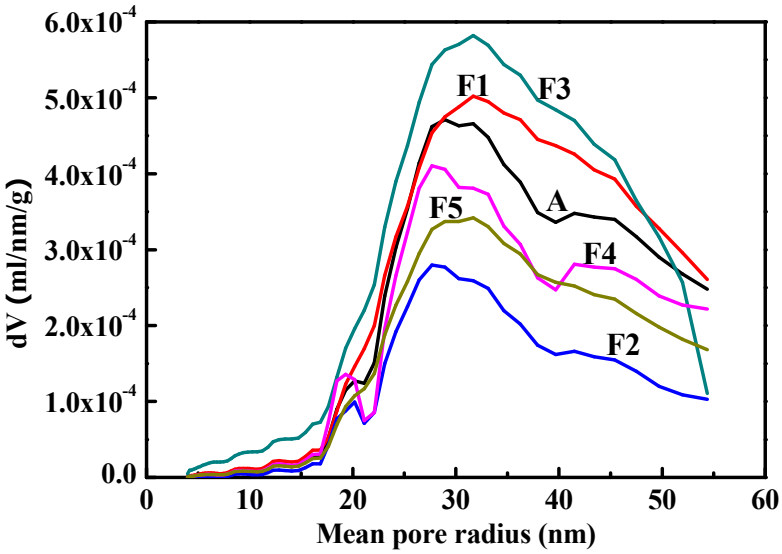

Fig. 4. Pore- Size Distribution Curves of GO- Cement Composites

The concentration of 0.02 and 0.04 wt.% for GO and GNSs, respectively, yielded the lowest intensity in the pore size distribution and consequently, the highest compressive strength values; the intensity of the peak is an indication for the number of pores having the transitional pore size (meso- pores) and the location of the peak represents the sizes of these pores. Therefore, the addition of 0.04% graphene resulted in a decrease in the number of transitional pores (meso - pores) and modified the pore structure of the hardened composites, this may explain the reinforcing action mechanism of GO and graphene, including both chemical and physical contributions.

4.3. Thermogravimetic analysis (TGA)

TGA was used to estimate the thermal stability of the prepared samples. Figs. 5, 6 represent the thermograms of cement paste reinforced with

different GO and graphene ratios in comparison with the plain cement mix (A). It can be noticed that, all the steps characterizing the calcium hydroxide (CH) and calcium carbonate (CC) phases of the prepared blended mixes are shifted to higher temperature relative to the plain mix (without GO/graphene) which confirms that the thermal stability of the hydration products increased by the addition of GO/graphene sheets.

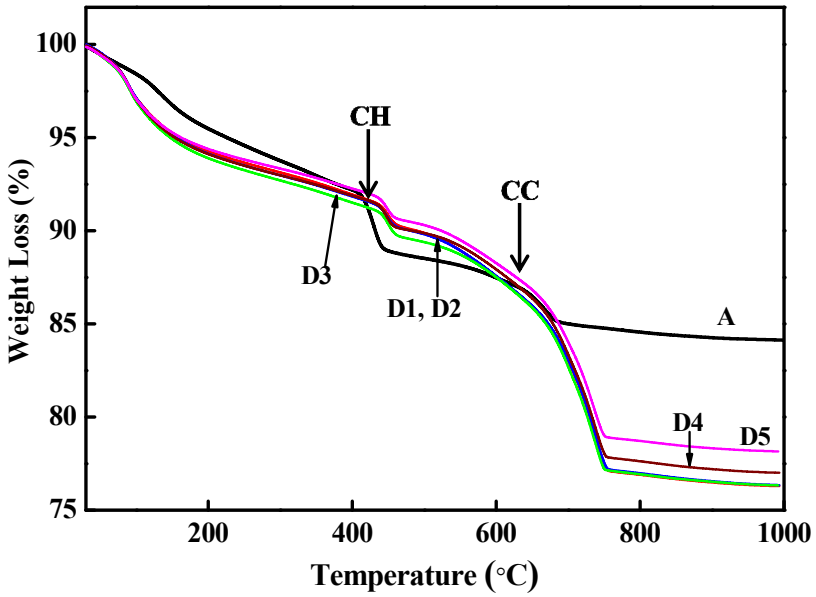

Fig. 5. The TGA thermograms of graphene– cement composites

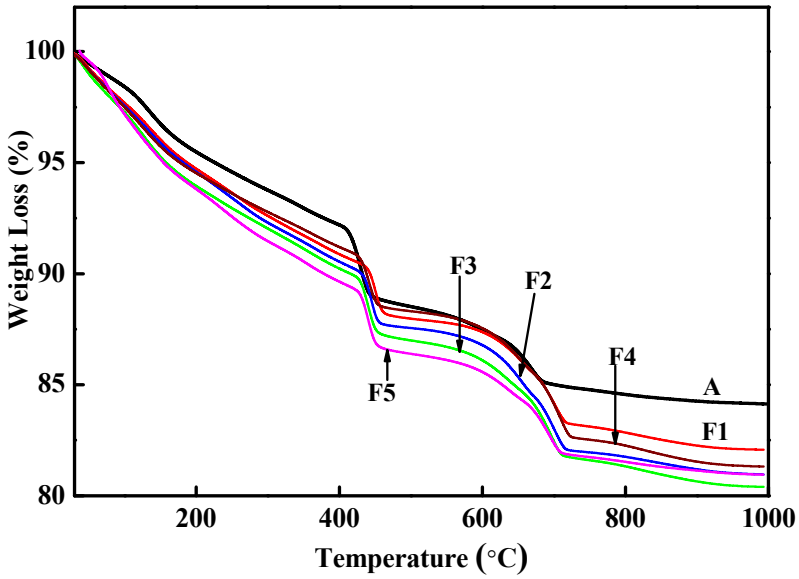

Fig. 6. TGA Thermograms of GO – Cement Composites

4.4. Morphology and microstructure

The mechanical properties of cementitious materials are determined by their microstructure characteristics. In order to determine the reasons of mechanical strength improvements and to get visual evidence of the microstructural characteristics responsible for these improvements, the morphology and microstructure was performed for the graphene-cement composites as presented in Figs. 7-9. The SEM micrograph of plain mix (OPC) revealed non-uniform distribution of the hydrated phases; furthermore, macro pores and micro cracks are observed as shown in Fig. 7 (A, B). The addition of GO/GSs has generally modified the microstructure and resulted in more uniform and compact structure as they cause bridging (2D reinforcement) between cement hydrates as presented in Fig. 8 (A, B) and Fig. 9 (A, B). Evidently, the microstructure of the hardened specimens made of OPC – GO/GSs composites displayed the formation of interlocking fi-

bers and wrinkled foils of CSH; so the number of binding centers in the hardened specimens increased leading to an increase in the hydraulic properties of these specimens. The microstructure obtained for the specimens made until 0.02% addition of GO and 0.04% addition of GSs, appeared to have larger points of contact in C-S-H, leading to the maximum improvement of the mechanical properties; this provides a strongly hydraulic structure having an increase in the total contents of binding centers. Furthermore, Nucleation of hydration products on nanoparticles further promotes and accelerates cement hydration and results in enhanced strength [24, 25].

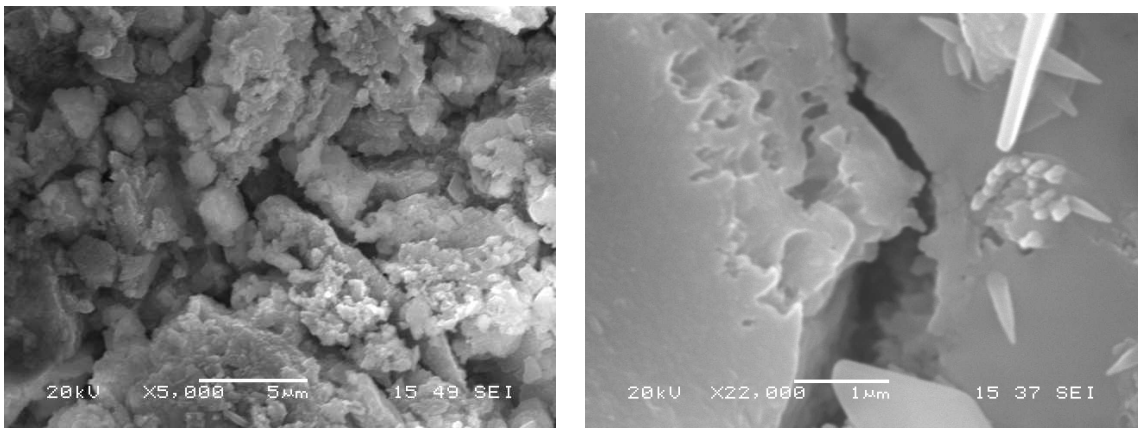

Fig. 7. SEM images of plain cement paste

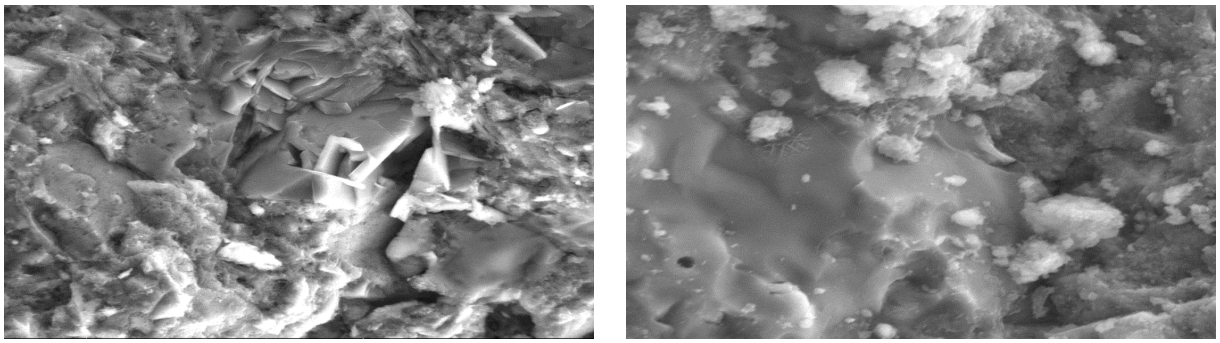

Fig. 8. SEM images of cement paste modified with graphene sheets.

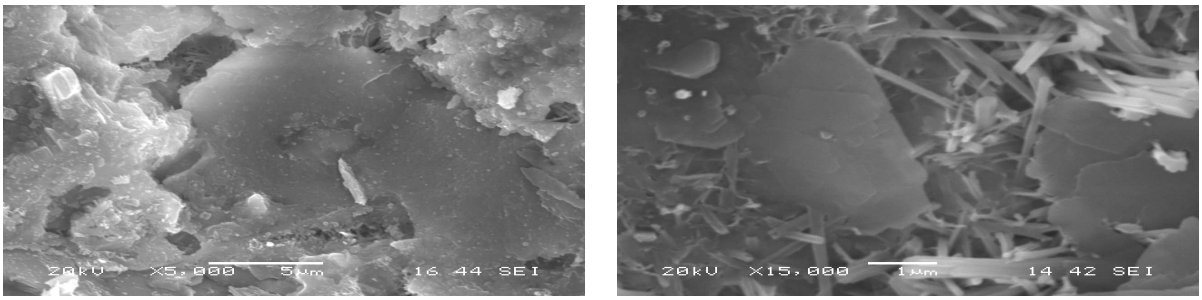

Fig. 9. SEM images of cement paste modified with GO sheets

4.5. Electrical conductivity

Electrical conductivity of cement paste occurs primarily due to ion transport through the pore solution in the cement based system [26]. During hydration, the capillary pores in the cement are gradually filled up with hydration products such as C-S-H, CH, ettringite and the conductivity decreases with increasing hydration time**.**

Graphene and its derivatives are used to enhance the electrical conductivity of cement composites.

In this study, the specimens tested were oven dried to avoid the ionic conduction. As a result, the

conduction that was observed probably was due to the electronic conduction.

Fig. 10 shows the electrical conductivity of neat cement paste as a function of frequency (42 Hz – 5 MHz), it is observed that the conductivity of the neat cement paste reached about 3.19×10^{-8} $\Omega^{-1}cm^{-1}$, while Figs. 11, 12 present the electrical conductivity of cement composites reinforced with different ratios of graphene and GO, from these figures; it was observed that, the highest conductivity of each mix was as follows; 9.4×10^{-6} Ω^{-1} cm^{-1} for composite D2 and 1.42×10^{-5} Ω^{-1} cm^{-1} for composite F2, which means that, the incorporation of GO and graphene greatly enhanced the electrical conductivity of cement paste.

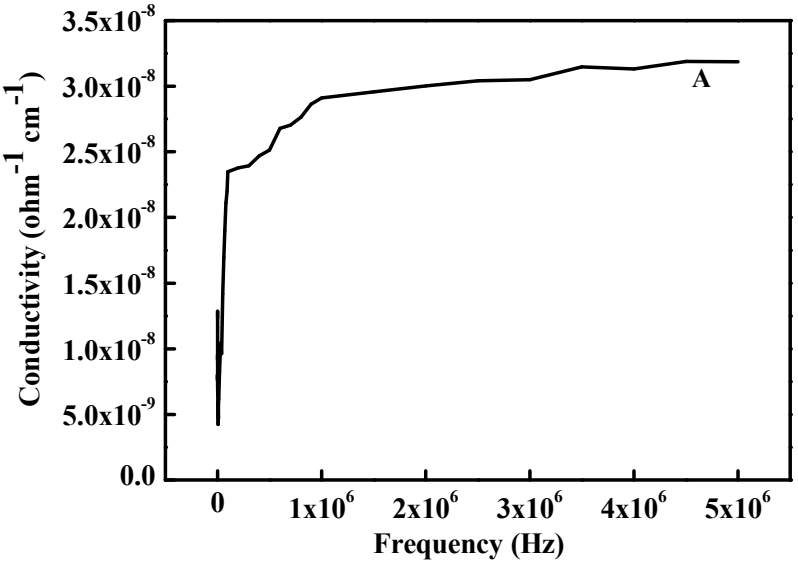

Fig. 10. Electrical conductivity of neat cement paste

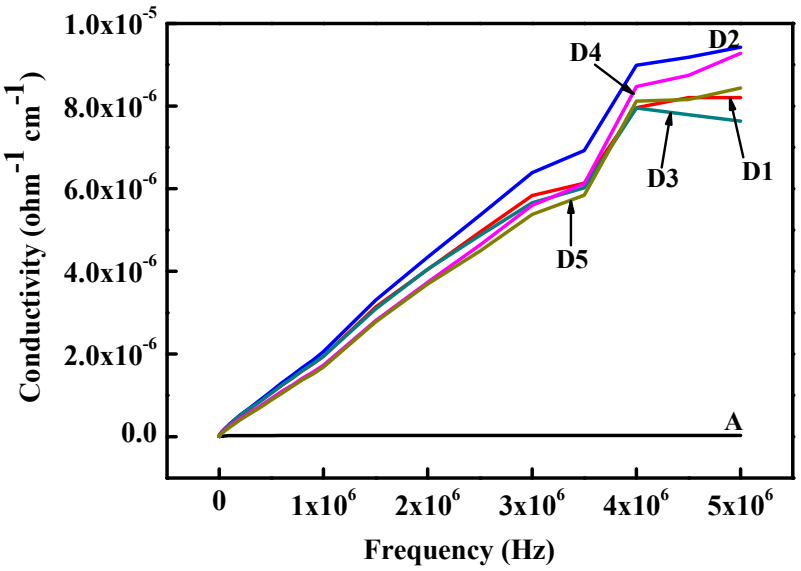

Fig. 11. Electrical conductivity of graphene - cement composites

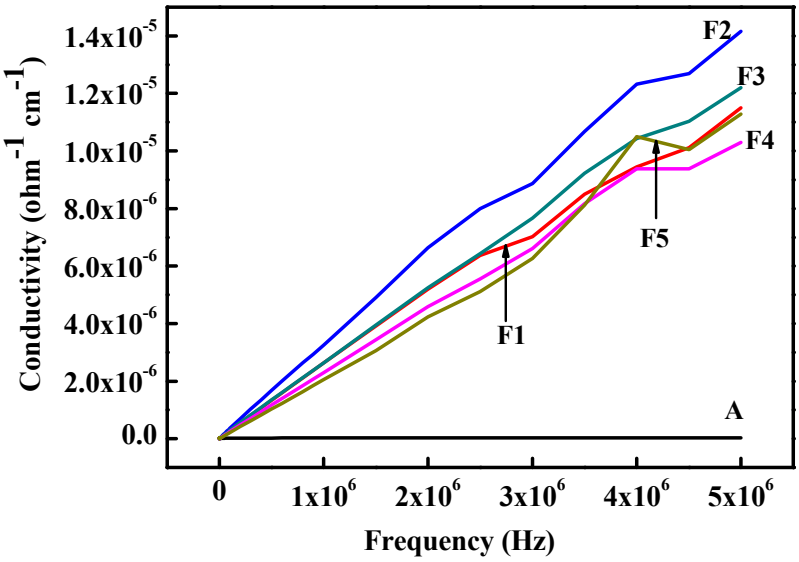

Fig. 12. Electrical Conductivity of GO- Cement Composites

5. Conclusions

The influence of GO/GNSs dosage on the microstructural characteristics, mechanical performance and electrical conductivity of cement composites were investigated. The results indicated that:

- In contrast to many previous studies it can be concluded that, small ratios of GO/GNSs about 0.02-0.04% can enhance the physico-mechanical characteristics of hardened OPC – GNSs composite pastes.
- The addition of GO and GNSs at ratios of 0.02 – 0.04 % significantly increased the compressive strength of cement composites, by about 13 and 33%.
- GO and graphene addition has modified the pore structure, through reducing the number of pore and making the cement paste more homogenous and compact.
- The addition of GO/graphene increased the degree of thermal stability of the hydration products especially of CH and CC phases.
- Finally, the electrical conductivity of cement pastes markedly enhanced by the addition of GO and graphene nanosheets.

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О влиянии графеновых нанопластинок на физические характеристики цементного раствора

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Графеновые нанопластинки (ГН) обладают уникальными физическими характеристиками, которые делают их эффективными армирующими материалами. В этом исследовании оксид графена (ОГ) синтезировали окислением графитовых флюсов с помощью модифицированного метода Хаммера. Полученный оксид термически восстанавливали (расслаивали) при 350 °С в течение 6 часов для получения графеновых нанопластинок. Исследовано влияние введения оксида графена и графеновых нанопластинок на механические свойства, структуру пор, термическую стабильность и электрические характеристики затвердевших цементных композитов. ГН и ОГ добавляли в различных количествах: 0, 0,01, 0,02, 0,03, 0,04 и 0,05 % от массы цемента. Прочность на сжатие определяли на 28-е сутки. Для определения температур деструкции использовался термогравиметрический анализ (ТГА), структура пор была исследована с использованием метода адсорбции азота при 77,35 К, микроструктура – с использованием сканирующей электронной микроскопии (СЭМ), и, наконец, была изучена электропроводность ОГ/графен-цементных композиций. Результаты исследования показали, что значительное повышение прочности на сжатие (примерно на 33 %) было достигнуто за счет введения ГН в цементную матрицу в количестве 0,04 %. При этом размер пор значительно уменьшился и было достигнуто значительное улучшение микроструктуры цементного раствора и, как следствие, улучшение электропроводности этих композитов.

Ключевые слова: графеновые нанолисты, цементный раствор, механическая прочность, структура пор, термический анализ, электрические характеристики.

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