EFFECTS OF CARBON BLACK AND GRAPHENE OXIDE ADDITIONS ON PROPERTIES OF ORDINARY PORTLAND CEMENT COMPOSITE

Abeysekara Mudiyanselage Buddhika Chandima

(159478M)

Degree of Master of Science

Department of Materials Science and Engineering

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Dissertation submitted in partial fulfilment of the requirements for the degree Master of Science in Materials Science

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Declaration

I declare that this is my own work and this dissertation does not incorporate without acknowledgement any material previously submitted for a Degree or Diploma in any other University or institute of higher learning and to the best of my knowledge and belief it does not contain any material previously published or written by another person except where the acknowledgement is made in the text.

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The above candidate has carried out research for the partial fulfilment of the requirements for the degree of Master of Science in Materials Science under my supervision.

Name of the supervisor: Mr. S. P. Guluwita

Signature of the supervisor: Date:15.06.2020

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Abstract

The effect of the carbon black (CB) and graphene oxide (GO) on the mechanical properties and microstructure of cement mortar composite were studied by preparing CB-cement composite (CBCC) and GO-cement composite (GOCC) mortars. These properties were investigated by treating the cement mortar with 0.01% to 0.1% of GO and 0.1% to 1.0% of CB of the cement weight. The results revealed that the highest compressive strength obtained for 0.4% of CBCC and for 0.04% of GOCC. The incorporation of CB and GO to the cement motor simultaneously increased the compressive strength of the samples drastically. The highest increase of the compressive strength was equal to 43.27% for specimens evaluated at the age of 2 days for the cement composite specimens of 0.4% CB and 0.03% of GO. The addition of 0.4% of CB increased the flexural strength of cement motor up to 53.54% and 0.03% of GO increased the flexural strength of cement motor up to 46.54% for 28 days. The addition of the combination of 0.3% CB and 0.04% GO to the cement composite enhanced the flexural strength by 60.61%. GO was found to be able to accelerate the hydration process by forming the flower-like cement hydration crystals which contribute to the enhancement of the early mechanical properties. The analysis of the microstructure relieved that the addition of CB provides the filling effect while GO could affect the growth form of cement hydration products.

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List of abbreviations

Abbreviation	Description
OPC	Ordinary Portland cement
IST	Initial Setting Time
CBCC	CB- Cement Composite
GOCC	GO- Cement Composite
SEM	Scanning Electron Microscope
C-S-H	Calcium silicate hydrate
CBCM	Cement based composite materials
GO	Graphene oxide
CB	Carbon Black
PCE	Polycarboxylic Ether
PC	Polycarboxylic
W/C	water/cement
CNTs	Carbon Nanotubes
CNFs	Carbon Nano Flakes
BHC	Blended Hydraulic Cement

1. INTRODUCTION

In ancient time to till the most common materials used for the construction industry are cement aggregate, water and admixtures. In the modern construction field, people are researching for the new materials without compromising on performance. Due to the blooming of nanotechnology, people use the materials at Nanoscale which offers the enhanced properties of concrete structure. On the other hand, the carbon footprint in cement production, which be achieved by lowering the clinker content of cement. Sustainable production of cement can be achieved by utilizing mineral admixture, industrial waste, Nanomaterials and this result, improves the performance of either cement product or enhances the durability of concrete structure [3], [5].

This research project disputes on the nanomaterials use in cement motor and concrete, specially graphene oxide and carbon black. Nanomaterials are defined as material with at least one-dimensional structure range approximately from 1 to 100 nm [26]. The requirement of high-performance concrete in the construction industry rises day by day and the requirement of novel material has been developed steeply. Then researcher focused more on nanomaterials since the properties of nanoparticles have diversified from the same materials at the macro or the micro scale. The types of nanomaterials used in concrete and cement are nano silica, nano alumina, carbon nano tube (CNT), polycarboxylates (PC), titanium oxide, nano kaolin, nano clay and etc, [18].

1.1. Portland Cement

Ordinary Portland Cement (OPC) of strength class 42.5N, in accordance with SLS 107:2015 standard was used for this research work [1]. In Sri Lanka it is mandatory conform the SLS 107:2015 requirement for the OPC as per Sri Lanka Standard Institution [1]. The major constituent composition of OPC is shown in the Table 1.1 [1].

Table 1.1: Composition of the OPC [1]

Designation	Equivalent cement type in BS EN 197-1	Composition % (m/m)	
		Main constituent clinker	Minor additional constituents
Ordinary Portland Cement	CEM I	95 to 100	0 to 5

1. 2 Structure of Cement

Ordinary Portland cement is the composed of various mineral oxides and cement products which represents the particular crystal structures and impurities. There are different solid phases associated with cement chemistry and main solid phases are named as Alite(C_3S), Belite(C_2S), Aluminate and Ferrite which is described in the Table 1.2 [3].

The final step of the cement production is the grinding of clinker mixed with gypsum. During the grinding process, particle sizes of cement convert to the fine powder around from 10 µm to 90 µm. Fine cement particles are reacted extensively with water and liberated heat. In the hydration process of cement "C-S-H" gel formed as the main hydration product [5]. It has a structure of very small internal pores. There is a major drawback in the cement structure which is the crack formation and results in the degradation of concrete structure. There are various research projects, conducting to overcome this issue. Cement based nano-composite played a vital role to give strength and durability of the concrete [36].

Table 1.2: The composition of cement clinker with notation [3].

Chemical Name	Oxide Formula	Mineral Name	Percentage
Tricalcium Silicate	$3CaO.SiO_2$ (C_3S)	Alite	25-50
Dicalcium Silicate	$2CaO.SiO_2$ (C_2S)	Belite	20-45
Tricalcium Aluminate	$3CaO.Al_2O_3$ (C_3A)	Aluminate	5-12
Tetracalcium Aluminoferrite	$4CaO.Al_2O_3.Fe_2O_3$ (C_4AF)	Ferrite	6-12

1. 3 Portland cement hydration

The cement hydration reactions are complex. It involves the reaction of all the cement clinker minerals such as C_3S and C_2S which are the anhydrous calcium silicate phases and C_3A and C_4AF which are the aluminate phases. C_3S and C_2S react with water to produce an amorphous calcium silicate hydrate (C-S-H) gel which is the binder of coarse and fine aggregate in the concrete mixture. The chemical reactions of hydration are represented by below equation [4].

$Ca_3Al_2O_6 \longrightarrow 3CaSO_4.2H_2O + 26H_2O \longrightarrow Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$ ----- **(1)**

C_3A **AFt rod-like**

$2Ca_3Al_2O_6 + Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O + 4H_2O \longrightarrow 3Ca_4Al_2(OH)_{12}.(SO_4).6H_2O$

C_3A **AFt** **AFm** **rod-like** **(2)**

$2Ca_3SiO_5 + 6H_2O \longrightarrow 3CaO.2SiO_2.4H_2O \longrightarrow 3Ca(OH)_2$ --------------- **(3)**

C_3S **C-S-H gel** **CH rod- and needle like**

$2Ca_2SiO_4 + 4H_2O \longrightarrow 3CaO.2SiO_2.4H_2O \longrightarrow Ca(OH)_2$ --------------- **(4)**

C_2S **C-S-H gel** **CH rod- and needle like**

In the hydration process, C_3A, C_4AF, C_3S, and C_2S (both silicates and aluminates) involve in the formation of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$,$Al_2O_3$–$Fe_2O_3$-tri(AFt), $Ca_4Al_2(OH)_{12}\cdot SO_4\cdot 6H_2O$, Al_2O_3–Fe_2O_3-mono(AFm), calcium hydroxide ($Ca(OH)_2$, CH), and calcium silicate hydrate ($3CaO\cdot 2SiO_2\cdot 4H_2O$, C–S–H) gel. As per the [5] CH, AFt, and AFm may form disorder or amorphous solid which shape rod-like, needle-like. These cement hydration products growth and agglomerate to form their own special structure while act as a binder in the concrete structure. This formation of crystal structures in the cement paste are strongly influenced by the consistency of cement which is water/cement ratio of cement paste. Water/cement ratio extensively affect to the mechanical strength development of concrete [5]. The diagrammatic representation of the development of hydrate structure in cement paste is given in Figure 1.1.

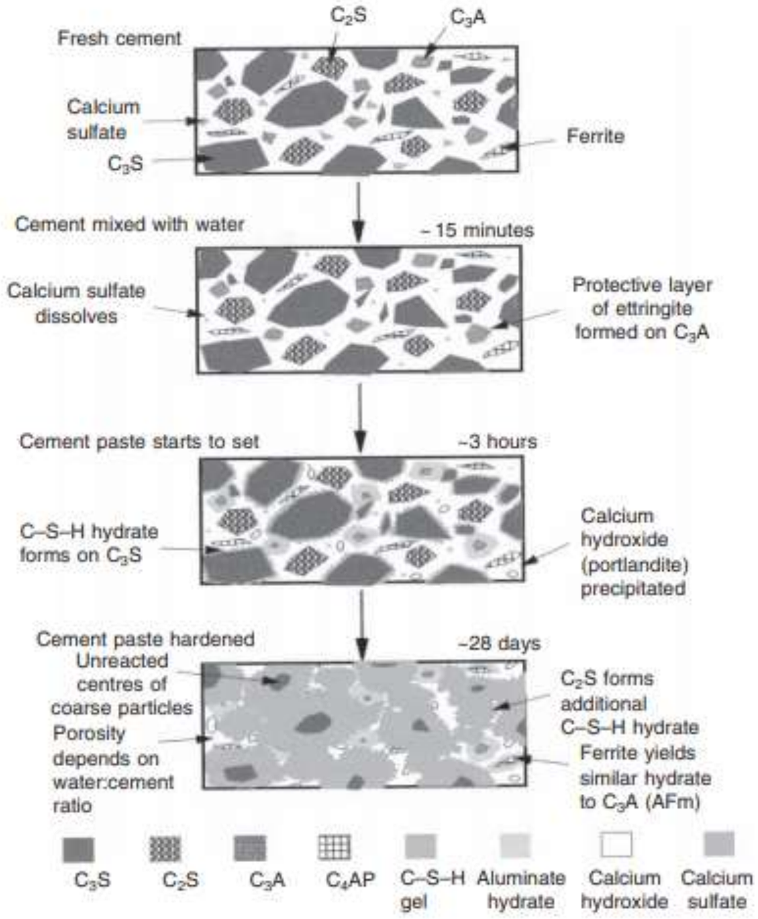


Figure 1.1: Simplified illustration of solid phase development in hydrated cement paste [3].

1.4. Concrete

Concrete is a composite material composed of cement, fine aggregates and coarse aggregates which are mixed with water to form binder in the matrix. These binder (cement paste) and filler (aggregates) are strengthening with time. There are various types of cement such as Ordinary Portland Cement (OPC), Blended Hydraulic cement (BHC) containing Portland Pozzolana Cement, Portland Fly ash cement, Rapid Hardening cement and Sulphate resistant Cement are used for concrete works which have different properties and applications. Portland cement is the commonly used type for production of concrete. During past few decades researchers tried to find out a way to increase the strength and durability of concrete [30], [32], [35]. Recently researchers checked the possibility of using nanomaterials and micro materials. There are several examples for nanomaterials such as carbon nanotube, graphene, titanium oxide, nano kaolin, nano clay, nano-silica, and nano-alumina in construction industry [23]. Preparation of nanomaterials is costly process and it gives low production. Therefore, nano materials may limit most of the applications.

1.5. Cement Composites

Although Ordinary Portland Cement (OPC) is still being used as a main type of cement in Sri Lanka construction industry, in recent time the trend of increasing usage of different materials as additive to Cement is observed. The trend is driven by demand from construction industry due to special concrete performance requirement like durability and/or temperature control. With a boom in the construction industry and major infrastructure projects, there is a good demand for high strength concrete. Engineers use high cement content to increase the strength of the concrete structure but there may another issue arises with high cement content. Concrete mixes with high cement content can cause shrinkage and excessive cracking due to differences in thermal stresses caused by cement hydration at an early age. As a solution for massive concrete structures, use of Cement composite is a good option. Further, addition of these materials improves the cement characterizations.

1.6. Nanomaterials for Construction

The usage of nanotechnology concept in cement composites is drastically growing during the past decays. Nanomaterials used in the cement industry as a reinforcing agent which provides a much higher specific surface area for interaction with the cement matrix in nanoscale. Even though, the most of the research works is based on the application of nanotechnology in cement composites for enhancement of mechanical properties, but some research works focus on usage of nanoparticles in cement industries such as Nanosilica (SiO_2), Alumina (Al_2O_3), Titanium dioxide (TiO_2) nanoparticles, nano-clay nano-calcium particles carbonate ($CaCO_3$), Carbon Nano Tubes (CNT) and Graphene oxide [6].

1.7. Graphene Oxide

Among all the nanomaterials one of the nanofibrous material; Graphene oxide (GO) exhibits pozzolanic characteristics which can enhance the internal matrix properties and interface structure. There are several methods for the preparation of GO. Graphene oxide is a compound consists of carbon, hydrogen and oxygen molecules. Graphite oxide is produced by chemically treated the graphite with strong acid. This strong acid is reacted with the graphite and removed an electron during the chemical reaction which is known as redox reaction. Graphene oxide is the result of this oxidation process as when the oxidants react with graphite, the graphite sheet increases the interplanar space. The compound that is fully oxidised in the original solution, which is the water, is then dispersed with a graphene oxide [7]. Since GO has versatile properties, it is an ideal filler of nano level for the modification of cementitious materials [8]. The drawbacks of usage of graphene are difficult to synthesis and very expensive [9]. Even though GO is expensive, researchers investigate various amazing outcomes whiles incorporate this nanomaterial into cementitious materials [10].

Graphene is a carbon allotrope. Graphite, carbon nanotubes, coal and fullerenes contain the graphene. It can also be considered as a very large aromatic molecule. It is a good example of the group of polycyclic hydrocarbons with sweet odour. Graphene has excellent physical properties, including electrical, thermal and mechanical properties. Graphene oxide (GO) is a unique material with a combination of different functional groups. It is experimentally found that epoxide, phenol, carbonyl, carboxyl and hydroxyl groups contain the GO. The interest in GO has increased considerably after graphene. It was initially hoped that GO could be a synthetic precursor of graphene [11]. The graphical representation structure of graphene oxide is revealed in Figure 1.2 [18].

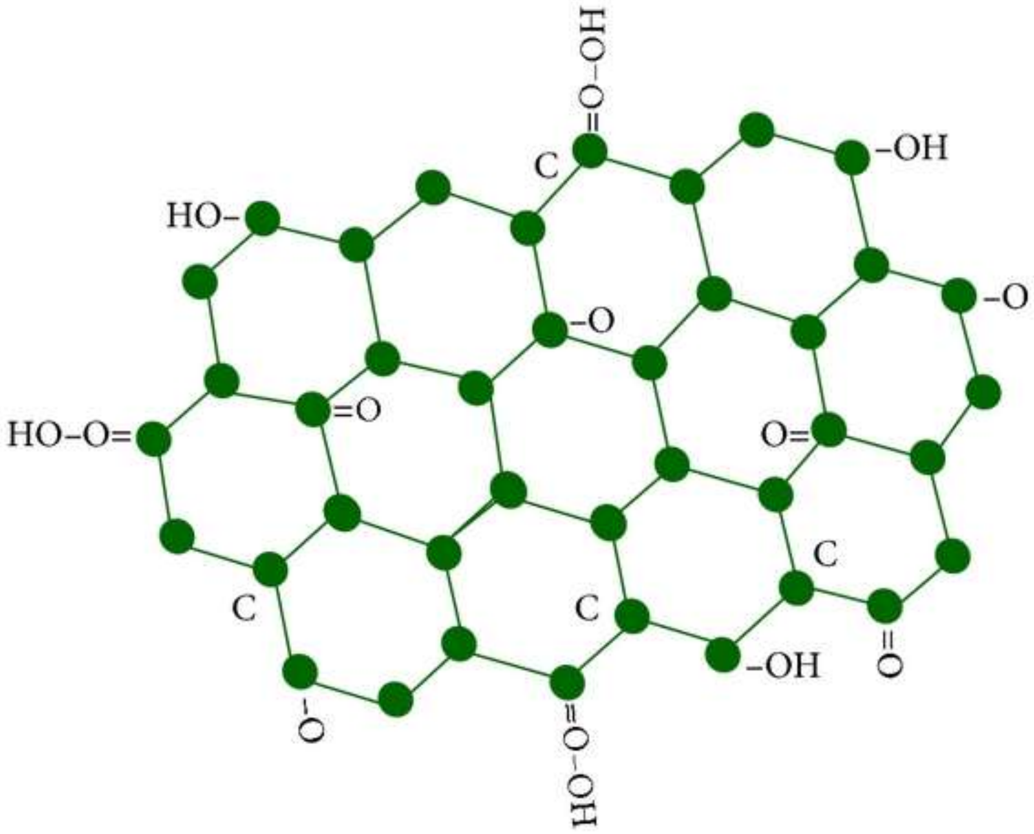


Figure 1.2: The graphical representation of graphene oxide [18].

1.7.1 Preparation of graphene oxide from graphite oxide

The numerous layers of single layered graphene arranged in the hexagonal lattice to form graphite. The oxidation process of graphite is done by using strong oxidants. Oxygenated functionalities are introduced in the graphite structure which expands the layer separation and also makes the material hydrophilic which makes GO disperse in water easily [7]. This property enables the graphite oxide to be exfoliated in water using sonication, finally producing single or few layers graphene, known as graphene oxide (GO). The difference between graphite oxide and graphene oxide is, therefore, the number of layers in which graphite oxide is a multilayer system and in graphene oxide, is a few layers of flakes and monolayer flakes can be found [12].

1.7.2 Carbon Black

Carbon black can be defined as very fine particles results from carbon possessing which is having a form of paracrystalline carbon. It is having an amorphous quasi-graphitic molecular structure. Carbon black is produced by the incomplete combustion of petroleum products and results various subtypes such as thermal black, furnace black, channel black, lamp black and acetylene black. The most significant areas of distinction are size of the particle and molecular structure. Therefore, most carbon blacks are differentiated according to the grade number depends on outer surface area and structure measurements. Carbon black is considered the pre-eminent reinforcing agent. Almost 93% of carbon black is used in rubber applications because it provides the reinforcing properties which enhanced the performance and durability. Carbon blacks are typically categorized as N100 to N900 series where N denotes functional groups contains amine which participate for the curing process. The particle size of thermal black is shown in Figure 1.3 [13].

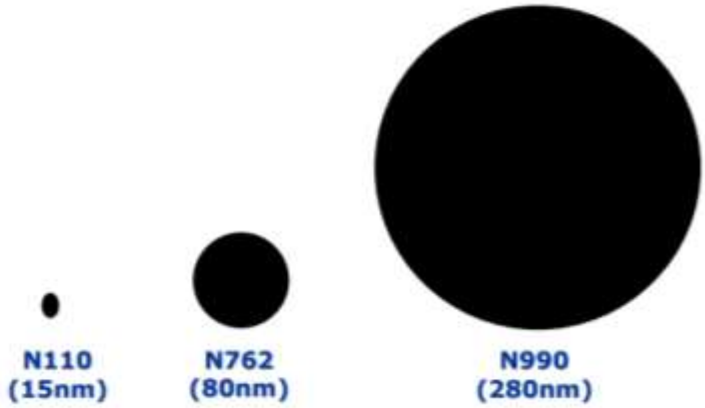


Figure 1.3: The particle size of carbon black [13]

1.8. Research Gap and significance of the project

There were several studies of the GO cement composite, performed over the last decade. There have been a number of valuable studies of enhancement of properties in cement composite using GO. However, none of these studies provide a way to reduce the cost of the materials, incorporating low cost, readily available material, such as Carbon black.

1.9. Objective:

In this study, GO-based cement composite (GOCC), and Carbon black-based cement composite (CBCC) were taken under consideration for the investigation of compressive strength and flexural strength. Microstructural investigation using Scanning Electron Microscope (SEM) technique has been employed to understand the underlying behaviour of the mechanical properties of the composites. The main objectives of this thesis are listed as follows.

1) Investigate the performance of graphene cement composite and carbon black cement composite.
2) Investigate the optimized addition percentage of graphene oxide and carbon black
3) Investigate the co-effect of graphene oxide and carbon black composite of cement motor.

2. Literature Review on topic

Production of Graphene Oxide

GO is typically produced by the chemical oxidation and exfoliation of graphite. GO forms as hexagonal 2D sheet layers with several nanometres' levels thick and several hundred manometers long. GO has ranges of reactive oxygen functional groups, and those are incorporated with cementitious materials during hydration for the formation of microstructure [9]. The functionalized of graphene is done by using three distinct methods as below [11]. Noncovalent attachment of large/small aromatic-containing molecules through stacking, grafting molecules on the basal plane of graphene and the functional groups of GO can chemically react with other molecules, together with consequent or coincident chemical reduction.

(S. Nandhini, I. Padmanaban.et.al. 2016) mentioned the preparation of Graphene oxide by modifying the Hummers method. Graphite flakes were mixed with $NaNO_3$, $KMnO_4$ and with conc. H_2SO_4 to prepare the dispersion of GO solution [14].

(B. Fakhim, et. al.,2014) [15] group of researchers used exfoliation of graphite oxide for the synthesis of GO through a colloidal suspension route which was first investigated by (S. Stankovich, D. A. Dikin et. al., 2007) [16]. During the synthesis process natural graphite powder mixed with $NaNO_3$ and Conc. H_2SO_4 in an ice bath and $KMnO_4$ added as strong oxidizing agents. The product was graphite oxide slurry and it was exfoliated by ultrasonication. The resulted mixture was then filtered. Metal ions which contains in the mixture washed with a diluted HCl solution. To neutralize the product was washed with DI water [7].

Composite of Graphene Oxide and Cement

It is required to obtain a properly dispersed graphene matrix to have good boundary interaction in-between the GO nanoparticles with cement. It gives high mechanical strength to the cement motor or concrete mixture. GO contains functional groups which are hydrophilic and highly dispersible in the aqueous medium. This unique property of GO is the reason for the better combination with cement to form composites while enhancing the mechanical properties.

(B. Fakhim, et. al.,2014) [15] mentioned the dispersion of GO within the Cement Matrix. The bundle of GO was added steadily to water mixed with PCE based superplasticizer and then ultrasonicated to obtained properly disperse individual GO flakes. Then Ordinary Portland cement, OPC was mixed with the dispersed GO at the required w/c ratio.

(A. Jinwoo et. al.,2018) [17] mentioned that wet-mix design required more energy to sonicate the GO with water to obtain a good dispersion sample. Therefore, they tested both wet-mix design and dry-mix designs. Even though wet-mix design requires more energy for sonication it exhibits the highest compressive and flexural strengths. It was revealed that from this study properly dispersed GONF-cement composite leads the high strengths, but powder form will be easy to perform.

(P. Jinchang et. al,2018) [20] investigated that, the bending strength of the GO reinforced cement based composite material and it is reported that the increase of the bending strength 23.82% was the highest value obtained for the content of GO was 0.03%.

(B. Fakhim, et. al.,2014) [15] reported that, the tensile strength of the specimens was increased gradually until it reached to the percentage of nano-GO 1.5% which was 47.8% compared with the specimens without GO flakes.

(Devasena et. al.,2015) [19] indicated that addition of GO increased the flexural strength. However, there was the optimum quantity to achieve maximum tensile and flexural strength of concrete. 0.05%, 0.1%, 0.2% of cement content were added GO to the composite and 0.1% GO-cement composite showed 4.2% and 2.34% enhancement of flexural strength for 14 days and 28 days respectively.

(Kim et. al.,20180 [25] found that the average cube and cylinder strength were increased by 10% and 29% respectively when 0.5% GO flakes were incorporated.

(Shareef et. al.,2017) [27] reported that the compressive strength of M25 concrete by replacing cement with 1% and 2% GO increased 7% and 17% respectively for 28 days.

(Wang, Q., et al.,2015) investigated the compressive strength of hardened cement paste and motor and reported the compressive strength of harden cement paste were increased by 52.4%, 46.5% and 40.4% after 3,7 and 28 days, respectively, and for the hardened motor the corresponding increased are 43.2%, 33% and 24.4% [29].

(Malgorzats Krystek, 2019) studied the compressive strength of cement motor reinforced with the 0.03% of GO. This enhanced compressive strength of cement motor by 23% and by 28% for the cubic compressive and uni-axial cylindrical compressive strength respectively [28].

(Abrishami et. al.,2016) revealed that the NH_2-functionalized GO reported higher compressive strength for 14 days of casting with compared to pure GO - cement composite motor. It increased by 39.1% of compressive strength with compared to without GO [26].

(Wang, Q., et al.,2015) investigated the compressive strength of hardened cement paste and motor and reported the compressive strength of harden cement paste were increased by 52.4%, 46.5% and 40.4% after 3,7 and 28 days, respectively, and for the hardened motor the corresponding increased are 43.2%, 33% and 24.4% [29].

(P. Jinchang et. al,2018) studied the compressive strength of cement motor by addition of GO. The mass fraction of GO was set as 0.01%, 0.03% and 0.05% and the water cement ratio was set as 0.35, 0.4, 0.45 and 0.5. The outcome of the research works was stated as below. It was found that the compressive strength was maximum with 0.03% of GO and the growth rate of compressive strength was 10.86% [20].

(Shenghua Lv. et. al.2016) indicated in their research work that, GO nanosheets have an important effect on the pore structure of GON-cement composites. These samples were prepared via doping with GO with cement composite. The outcome of this research work was interesting and the out of different pore diameters, median pore diameter and the average pore diameter were showed similar values which concluded that the pore diameter were uniform. The results indicated that GONs can enhance the formation of ordered network of micro structures due to this homogeneous distribution of pores. This property helps to increase the strength and toughness of cement [30].

Morphology

SEM (scanning electron microscope) was preferred by the researchers to investigate microstructure of cement hydration products when GO is introduced into the cement matrix. The Figure 2.1 reveals several needle-shaped ettringite projecting into the pores and the amorphous morphology of C-S-H can be clearly seen. According to the research evident of Jinwoo et. al.2018 confirmed that, the GONFs were inside the products of cement hydration which were surrounded by C-S-H which evident that GONF's act as nano-reinforcing and nano-filling ingredients.

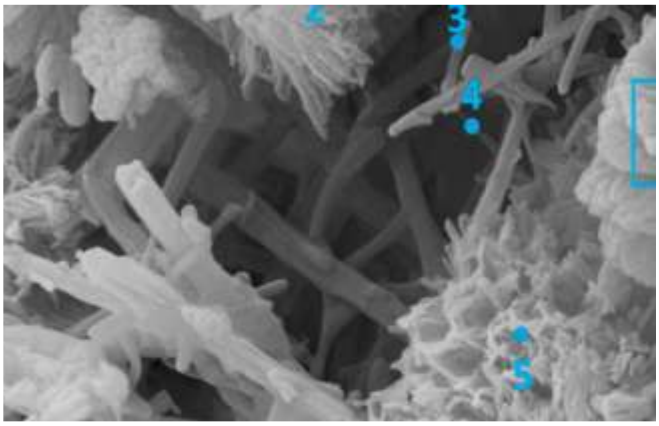


Figure 2.1 : The images of SEM analysis (GONF-combined cement paste with 0.05% GONF at 7 days) [17]

(Jinchang et. al. 2018) revealed that, GO affect the distribution and the formation of cement hydration product and it provides better filling effect, hydration effect and nucleation effect. GO has large specific surface area which provides better growth space for the hydration products. Since GO reduced the porosity results high strength and ductibility cement motor [20].

(Babak et. al. 2014) research team used ultra-high-resolution field emission scanning electron microscopy (FE-SEM) to observe the fracture surface of samples containing 1.5 wt% GO. It was indicated that the nano-GO flakes were well dispersed in the cement matrix, and it can be observed that the good bonding between the GO surfaces and the surrounding cement matrix [15].

3. METHODOLOGY

3.1 Materials

Portland cement

Ordinary Portland cement (OPC) confirming to SLS 107:2015 standard [1] of Sri Lanka Standard Institution was used as a primary binding material in casting of cement composite throughout this study. The water/cement ratio for the casting of cement composite is 0.50 by the weight of cement. OPC (CEM I) of grade 42.5 N was used in this research work. The cement was imported and all these cement samples are conformed to the requirements given in SLS 107:2015 standard [1].

Sand

The ISO standard sand (CEN standard sand) which is natural, siliceous sand and particles are rounded in shape. The silica content of this sand is at least 98 %. This sand is conformed the ISO SLS 679: 2011 standard [40]. The particle size distribution is given in Table 3.1.

Table 3.1: Particle size distribution of the ISO reference sand [40]

Square mesh size, millimeters	2,00	1,60	1,00	0,50	0,16	0,08
Cumulative sieve residue, percent	0	7 ± 5	33 ± 5	67 ± 5	87 ± 5	99 ± 1

Water

Distilled water was used to prepare the cement motor and cement paste.

Carbon Black

A commercially available Carbon Black N330 samples were used in this study. Carbon black N330 samples were used as purchased from MAKROchem sp. zo.o. Lublin, Poland without any modifications. The specification sheet is attached as Appendix A.

Graphene Oxide

A commercially available Graphene Oxide samples (Ceylon Graphene Technologies) were used in this study. Dispersed Graphene Oxide samples were used as purchased without any modifications. The specification sheet is attached as Appendix B.

Product Specification

Form:	Dispersion
Color:	Brown
Odor:	Odorless
Dispersibility:	Polar solvents (water, ethanol, DMF, etc.)
Bulk Density:	~0.5 g/cm3
Number of layers:	10-15
Elemental analysis:	Carbon: 38.0-44.0 %, Hydrogen: 3.0-4.0 %, Nitrogen: 0.1-0.3 %, Sulfur: 1.4-1.6 %, Oxygen: 50.1-57.5 %
Stability:	Stable
Conditions of instability:	Excess heat

3. 2 Method

3. 2.1 Cement Composite

Cement-based composite materials (CBCM) were prepared from CB and from GO. The water/cement ratio of all mixtures was kept constant at 0.5. The CB and GO were added as mentioned in Table 3.2 and 3.3, respectively by mass of cement.

For homogeneous the mixture, the portion of GO was dispersed in the water. Properly mixed GO via sonication was added to cement matrix. Then, the blends were mixed as the procedure mentioned in 3.2.4 for compressive strength and 3.2.5 for flexural strength. After mixing the cement composites, the samples were cast into prism moulds as mentioned in section 3.2.4. Cement motor cubes were prepared as below tables by varying percentages of GO and CB. The control sample was prepared without adding additives. Composite samples which showed the optimized compressive strength values of GO-CC and CB-CC were taken to further analyse for investigating the co-effect of both additives and the effect of Polycarboxylate admixture.

Table 3.2: Preparation of CB - Cement composite

Sample*	**Composite**				
	Cement/g	**C-Black (wt%)**	**C- Black wt/g**	**Water/ml**	**Sand/g**
Control	450	0	0	225	1350
CB – 0.1	449.55	0.1	0.45	225	1350
CB – 0.2	449.1	0.2	0.9	225	1350
CB – 0.3	448.65	0.3	1.35	225	1350
CB – 0.4	448.2	0.4	1.8	225	1350
CB – 0.5	447.75	0.5	2.25	225	1350
CB – 0.6	447.3	0.6	2.7	225	1350
CB – 0.7	446.85	0.7	3.15	225	1350
CB – 0.8	446.4	0.8	3.6	225	1350
CB – 0.9	445.95	0.9	4.05	225	1350
CB – 1.0	445.5	1	4.5	225	1350

Table 3.3: Preparation of GO - Cement composite

Sample*	**Composite**				
	Cement/g	**GO (wt%)**	**GO wt/g**	**Water/ml**	**Sand/g**
Control	450	0	0	225	1350
GO – 0.01	449.955	0.01	0.045	225	1350
GO – 0.02	449.91	0.02	0.09	225	1350
GO – 0.03	449.865	0.03	0.135	225	1350
GO – 0.04	449.82	0.04	0.18	225	1350
GO – 0.05	449.775	0.05	0.225	225	1350
GO – 0.06	449.73	0.06	0.27	225	1350
GO – 0.07	449.685	0.07	0.315	225	1350
GO – 0.08	449.964	0.08	0.36	225	1350
GO – 0.09	449.595	0.09	0.405	225	1350
GO – 0.1	449.55	0.1	0.45	225	1350

* Sample A was denoted for compressive strength and sample B was denoted for flexural strength

To investigate the co – effect of the GO and CB on cement motor specimens were prepared as per the Table 3.4. CB and GO were added simultaneously as mentioned in the Table 3.4 by mass of cement.

Table 3.4: Co-effect of the GO and CB cement composite

Sample*	**Composite**						
	Cement/g	**CB (wt)**		**GO (wt)**		**Water/ml**	**Sand/g**
		%	**g**	**%**	**g**		
Control	450	0	0	0	0	225	1350
CB – GO	448.515	0.3	1.35	0.03	0.135	225	1350
CB - GO	448.470	0.3	1.35	0.04	0.18	225	1350
CB – GO	448.065	0.4	1.8	0.03	0.135	225	1350
CB – GO	448.020	0.4	1.8	0.04	0.18	225	1350

Admixture compatibility with GO and CB were tested using the following mixture range with the addition of Hypercrete HS (Polycarboxylic based) admixture and the preparation method of the composite was mentioned in Table 3.5. The optimization of the admixture was done for the OPC by using the marsh cone test method.

Table 3.5: Preparation of CB-GO cement composite with Hypercrete HS admixture

Sample*	**Composite**							
	Cement/g	**CB (wt)**		**GO (wt)**		**0.4% Hy-HS/ml**	**Water /ml**	**Sand/g**
		%	**g**	**%**	**g**			
Control	450	0	0	0	0	0	225	1350
CB – GO I	448.515	0.3	1.35	0.03	0.135	3.6	221.4	1350
CB – GO II	448.470	0.3	1.35	0.04	0.18	3.6	221.4	1350
CB – GO III	448.065	0.4	1.8	0.03	0.135	3.6	221.4	1350
CB – GO IV	448.020	0.4	1.8	0.04	0.18	3.6	221.4	1350

*Sample A,B, C,D for compressive strength

* Sample E, F, G, H for flexural strength

* Sample I, II, III, IV for admixture compatibility

3. 2.2 Standard Consistency of cement paste

Normal consistency of a cement paste is determined by using ISO 9597:2009 standards [41].

Instruments & Apparatus

Vicat Mould and the Plunger

Balance

Graduated Cylinder

Mixer

Water

Stop Watch

Temperature & Humidity Conditions of the laboratory should be 27$\underline{+}2^0$C and >50% respectively.

Instructions:

500g of cement and 152ml of water were weighed into the bowl. The mixer machine was started at low speed and recorded the Zero time. The mixer machine was stopped after the 90s and during the next 30s, using the plastic scraper, was removed the cement paste which were adhering in the bowl. The mixture was restarted at low speed for a further 90s and therefore the total running time of the mixture was 3 min. The Vicat mould and base plate were lightly oiled. The mould was positioned on to the base plate and immediately the cement paste was transferred into the mould. Any voids in the paste were removed by gently tapping off the overfilled mould using the ball of the hand. A smooth upper surface was obtained by removing the excess using a gentle sawing motion. The scale reading was adjusted to zero when the plunger was released on to the base plate to be used. Consistency determination should be done 4 min ± 10s after zero time using the Vicat apparatus. The plunger was raised to stand by position and the mould filled with cement paste was transferred immediately centrally under the plunger. The plunger was gently moved down until it is in contact with the paste and was paused in that position for 1–2s. The moving part was quickly released and allowed the plunger to penetrate vertically into the cement paste. The scale was read at least 5s after penetration has ceased.

3. 2.3 Initial Setting Time

IST of a cement paste is determined by using ISO 9597:2009 standards [41].

Instruments & Apparatus

6kg balance

Vicat Mould

Vicat needle

Container with water

Temperature controlled cabinet

The temperature conditions were controlled as in Table 3.6.

Table 3.6: Temperature Conditions

Location	Temperature/^{0}C
Container with water	27±2
Temperature controlled curing tank	27±2

Vicat mould is filled with a cement paste made in accordance with the standard consistency procedure. The filled mould was submerged at least 5 mm in a container with water and it was stored in the temperature-controlled curing tank. After a suitable time, the filled mould was placed under the needle of the Vicat apparatus (not less than 8mm from the rim of the mould) and gently the needle was lowered until it penetrates vertically into the paste. The scale reading was read when the penetration has ceased and immediately the tested mould was kept inside the temperature-controlled cabinet. This process was repeated until the needle was giving a reading of 5. The time elapses between the zero time and the time at Vicat reading 5, was the IST of the cement.

3. 2.4 Compressive Strength

SLS ISO 679:2011 standard method [40] was used to determine the compressive strength of cement mortar. A prismatic cement mortar of 40mm x 40mm x 160mm dimensions was prepared of cement, ISO standard sand and distilled water with 1 : 3 : 0.5 ratio.

Instruments & Apparatus

6 kg Balance
Mixer machine
Jolting Table
Prism moulds with 210mm*185mm plate glass sheet of 6mm thickness
Humidity Chamber
Curing Tank
500kN Compression Testing Machine

The test prism mould (Figure 3.1) which complies with the SLS ISO 679:2011 standard conditions [40] were used to measure the compressive strength of the cement motor.

The environmental conditions (temperature and humidity) are mentioned in the Table 3.7.

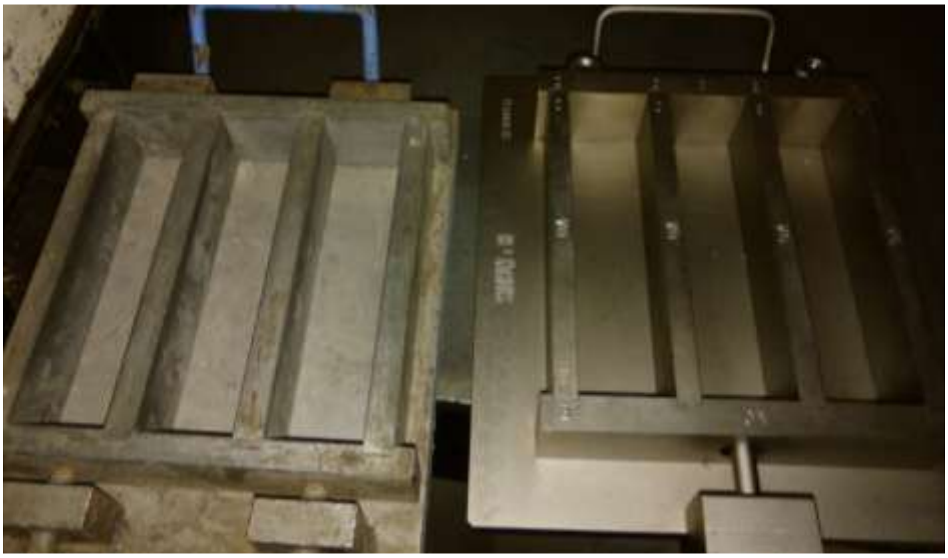


Figure 3.1: Test prism moulds

Table 3.7: Temperature & Humidity Conditions

Situation	Temp.^{0}C	Min Relative Humidity. %
Mixing Room	27±2	65
Moist Curing chamber	27±1	90
Water curing tank	27±1	-
Compression testing room	27±2	50

Mixing of mortar: The Cement, Standard sand and water were weighed as per the below Table 3.8 for preparation of the control sample.

Table 3.8: The mass and the proportion of the materials for control sample

Material	Proportion by mass	Mass (gm)
Cement	1.0	450±2
Sand*	3.0	1350±5
Water	0.5	225±1

* ISO standard sand

The cement mortar mixer machine is showed in the Figure 3.2.

Figure 3.2: Cement motor mixer machine

The water and the cement were mixed in the bowl. The machine was started immediately at low speed and mix for 30±1s. After the 30s the sand was added gradually during the next 30±1s while the mixer was in the operating position. The mixer machine was changed to the high speed and it was continued to the mixing for an additional 30±1s. The mixer was kept for 1min 30±1s. In first 15s, all the mortar adhering to the bowl was removed by a rubber scraper and the blade was placed in the middle of the bowl. Then the mixture was mixed at the high speed for another 60±1s. The total mixing time was 4 min.

Moulding of test specimens: For the compaction of cement mortar, the jolting machine was used as shown in Figure 3.3. The 300 g of cement mortar was put into each mould compartment using a rubber scoop and the first cement mortar layer was spread evenly using the larger plastic spreader. It was compacted using 60 jolts. The second 300g for each compartments of the mould were introduced and it was levelled with the smaller plastic spreader and was compacted with further 60 jolts. The mould from the hopper was removed and a smooth surface of the specimen was obtained. The moulds were labelled to identify the specimens. A glass plate sheet was placed on the mould and the moulds were immediately kept in the moist curing chamber for 24h.

Figure 3.3: Jolting apparatus

Demoulding and curing of test specimens:

The prism cubes were demoulded after 24h (1 day). Then the specimens were submerged in the curing tank until the testing date. The curing tank which use for curing purpose is shown in Figure 3.4.

Figure 3.4: Curing tank

Testing of Specimens:

Each prism, cube was split into two halves by using a flexural jig. Each half was tested for compressive strength using a 500kN Compression testing machine (Figure 3.5) with a 500 kN capacity. The machine rate was set for (2.4±0.2) kN/s. Each reading was recorded to the nearest 0.1 MPa in the worksheet and the actual values were mentioned using a calibration report. The compressive strength value was recorded to the nearest 0.1 MPa using the method described in ISO 679:2011 standards [40].

Figure 3.5: 500 kN Compressive Strength Testing Machine

3. 2.5 Flexural strength

ASTM C348 – 18: standard was used in this test programme [42].

The cement mortar was prepared by using a standard test method containing of 1:2.75 cement: standard sand by weight. The w/c ratio was kept in 0.485. The cement, motor with CB and GO were mixed in an electrically driven mechanical mixer. The temperature was maintained at room temperature, which was between 20 to 27.5 ºC and the relative humidity of the laboratory was more than 50%.

Prismatic cement mortar samples of 40mm x 40mm x 160mm dimensions were prepared using Cement, ISO standard Sand, and Distilled water with 1: 2.75: 0.485 proportions.

Procedure for mixing mortars: ASTM C 305 -82 standard test method was used for this [43]. The water and the cement were mixed in the bowl. The machine was started immediately at low speed and mix for 30±1s. After the 30s the standard sand was added gradually during the next 30±1s while the mixer was in the operating position. The mixer machine was changed to the high speed and it was continued to the mixing for an additional 30±1s. The mixer was kept for 90 ± 1s. During the first 15s, all the mortar adhering to the bowl was removed using a rubber scraper and a blade that was placed in the middle of the bowl. Then the mixture was mixed at the high speed for another 60±1s. The total mixing time was 4 min.

Prisms were kept in the humidity chamber for curing in the moulds. They were demoulded. The specimens were immediately stored for 28 days in the curing tank after demoulding. At the age of 28 days, the test specimens were removed from the curing tank. Three specimens were tested for 28 days with a loading rate of 0.5kN/s. The specimens underwent flexural tests at a central point of loading as shown in Figure 3.6 and Figure 3.7. The hardened cement mortar beam was kept in the flexural testing machine and the force was loaded in the middle of the prism until failure. The modules of raptures were calculated. It was reported as the flexural strength as follows:

Calculate the flexural strength R_f from:

$$R_f = \max \sigma_f = \frac{\max M}{W}$$

Where R_f is flexural strength (MPa)

σ_f	maximum flexural stress [MPa]
M	bending moment [N.mm]
W	sections modulus [mm^3]

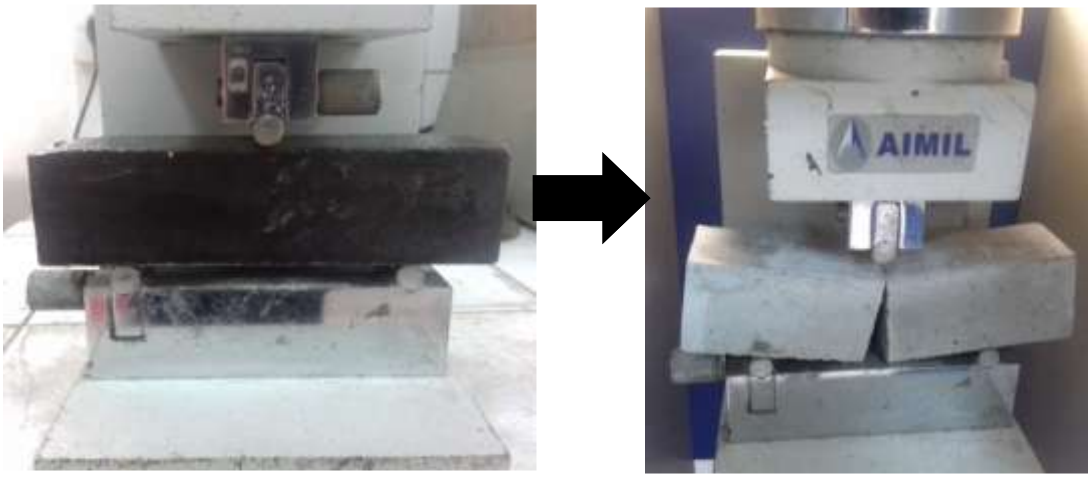


Figure 3.6: Test specimens during and after testing

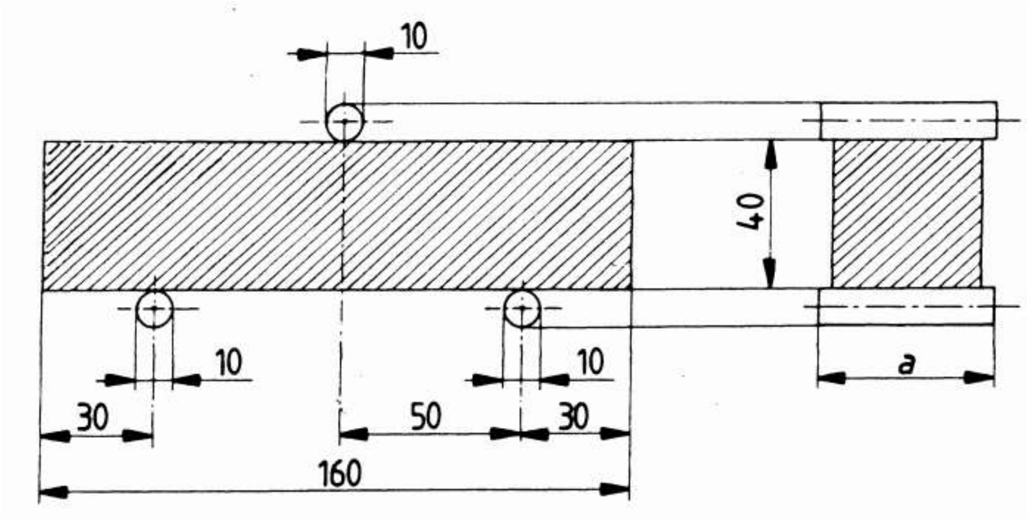


Figure 3.7: Schematic diagram of loading for determination of flexural strength

3. 2.6 Scanning Electron Microscopy

The microstructural changes of the hydrated cement composites and control samples were investigated by using SEM. ZEISS EVO 18, Scanning Electron Microscope Research was used to investigate the morphology of composite samples and the control sample.

4. RESULTS AND DISCUSSION

4. 1 Compositions of the materials

The compositions of the materials used for the research projects were analyzed as follows:

- I. Ordinary Portland Cement : As per SLS 107: 2015 standard [1]
- II. Carbon black : N330 : Specification given by the customer and SEM [45]
- III. Graphene oxide : Specification given by the customer and SEM [46]

4.1.1 Cement characterization

The chemical composition of the OPC- 42.5 N strength class is presented in Table 4.1. All the parameters of the OPC complied with SLS 107:2015 standard. The content of tricalcium aluminate (C_3A) in this cement was less than 8% and it is therefore expected that the heat of hydration is lower than the moderate heat cement. Sulfur trioxide (SO_3) was less than 3.5 which is the maximum limit of 42.5N OPC.

Table 4.1: Cement composition

Chemical Composition	**% by mass**
Insoluble Residue	0.58
Silicon dioxide (SiO_2)	19.82
Loss on Ignition	1.28
Aluminum oxide (Al_2O_3)	5.80
Ferric oxide (Fe_2O_3)	5.00
Magnesium oxide (MgO)	0.92
Calcium oxide (CaO)	62.51
Sulfur trioxide (SO_3)	3.00
Chloride	0.03
TiO_2 / P_2O_5	0.5
LSF	0.92
A/F	1.16
C_3S	49.03
C_2S	20.11
C_3A	6.92
C_4AF	15.20

4.1.2 Composition of the Carbon Black

The material specification sheet of carbon black is attached as Appendix A [45]. Prior to their incorporation in cement Carbon Black was characterized by scanning electron microscopy (SEM).

Figure 4.1 showed the SEM image of Carbon Black. Carbon black is considered a nanostructured material which is a material contains internal or surface structure in the nanoscale [24].

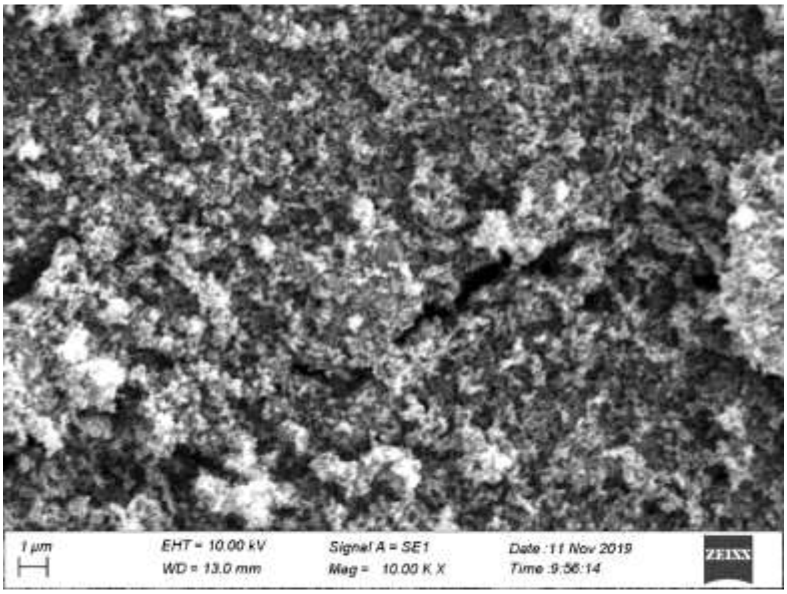


Figure 4.1: SEM image of Carbon Black

4.1.3 Composition of the Graphene Oxide

Material specification sheet of carbon black is attached as Appendix B.

The X-ray diffraction pattern of the as-received GO is presented in Figure 4.2. It is clearly shown that the characteristic peak at 2θ of 10.1 indicates the effective oxidation of graphite and the formation of graphene oxide.

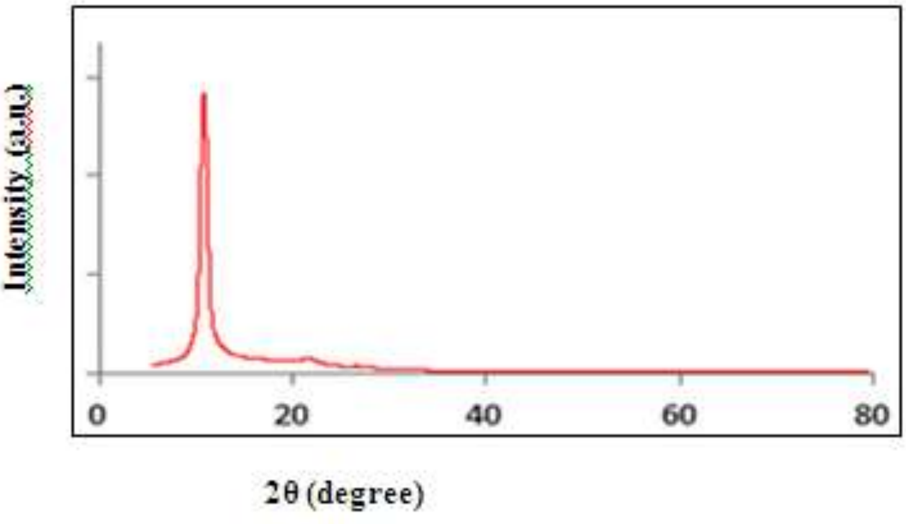


Figure 4.2: XRD patterns of the GO

The graphene oxide dispersion was examined and Figure 4.3 shows the SEM image. The SEM image of graphene oxide reveals that it contains several layers stacked on top of one another [35].

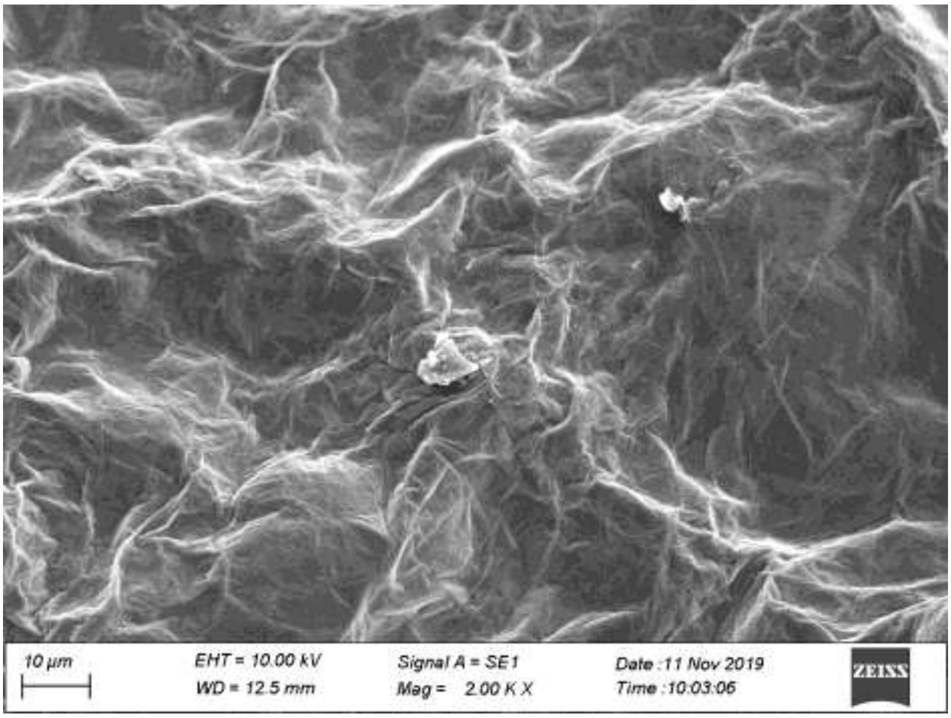


Figure 4.3: SEM image of the Graphene Oxide

4. 2 Mechanical Properties of composite

The compressive strength and flexural strength of the hardened cement mortar composites were enhanced by the incorporation of CB and GO. In general, the addition of CB and GO has increased the mechanical strength of cement composites.

4. 2.1 Compressive strength

There are varieties of samples used to measure the compressive strength of cement motor or concrete. In this study, a prism mould was used to measure the compressive strength development of composite cement, motor for Carbon black Cement composite (CBCC) and for Graphene oxide Cement composite and for the combination of both additives. For the compressive strength values, the average compressive strength of the 06 samples was taken.

I. Compressive Strength of GO Cement composite

Prepared samples of CBCC are shown in Figure 4.4.

Figure 4.4: Samples of CBCC

The compressive strength test results are presented in the below line graph (Figure 4.5). The accompanying Table 4.2 illustrates the comparison of improvement in compressive strength of CBCC with that of cement prepared without CB.

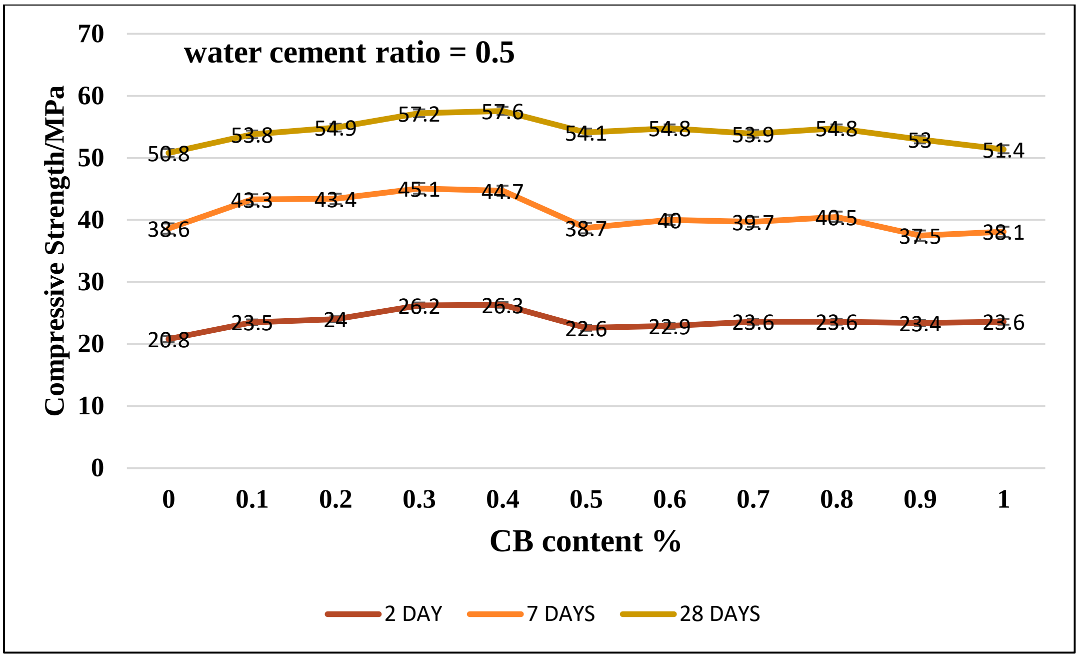


Figure 4.5: The variation of average compressive strength of carbon black reinforced cement composite

In this study, it is confirmed that adding CB to the cement, motor increased the average compressive strength. The addition of 0.3% and 0.4% gave the maximum compressive strength, irrespective from the time period of cured.

Table 4.2 indicates the test results of the compressive strength of the carbon black cement mortar samples.

Table 4.2: Compressive strength of CB - Cement composite

CB - Cement composite	Improvement in compressive strength comparison with specimens without CB (%)		
	02 days	07 days	28 days
CB – 0.1 A	12.98	12.18	5.90
CB – 0.2 A	15.38	12.44	8.07
CB – 0.3 A	25.96	16.84	12.59
CB – 0.4 A	26.44	15.80	13.39
CB – 0.5 A	8.65	0.52	6.50
CB – 0.6 A	10.10	3.63	7.87
CB – 0.7 A	13.45	2.85	6.10
CB – 0.8 A	13.45	4.92	7.87
CB – 0.9 A	12.50	-2.85	4.33
CB – 1.0 A	13.45	-1.29	1.18

It is known that the compressive strength of cement, motor enhanced with CB content. The addition of 0.3% and 0.4% of carbon black gave the maximum improvement in compressive strength of 25.96% and 26.44% for 02 days respectively with a comparison of the control sample. It is followed by 16.84% and 15.80 % of growth rates for 07 days and for 28 days 12.59 % and 13.39% growth rates were observed.

Compressive Strength of cement motoar with CB was higher than that of the control cement sample. However, increasing the CB quantity up to 0.4%, the compressive strength of CBCC shows a sudden increase by 26.44% at 2 days and 13.39 % at 28 days, compared with control samples. The effect of CB addition was highly affected for the 02 days compressive strength of the cement composite and when content of GO exceeds the 0.4% there is a reduction in the compressive strength.

Here, it is assumed that further addition of CB may cause excess CB which reduces the efficiency of the mechanical properties [39].

II. Compressive Strength of GO Cement composite

Prepared samples of GO are shown in Figure 4.6.

Figure 4.6: Samples of GO

The compressive strength values are presented in Figure 4.7. This line graph describes the variation of compressive strength of graphene oxide reinforced cement-based composite material with the different mixing amount of GO.

As shown in Figure 4.7, the influence of the mixing amount of GO on the compressive strength of the test specimens was consistent for 2 days, 7 days, and 28 days. Further, it is found that a similar pattern that is, increase firstly then decreases.

The compressive strength values were maximum when the mixing amount of 0.03% and 0.04% of GO content.

The 2 days compressive strength values of cement paste which contained 0.03% GO and 0.04% GO were 27.5 N/mm^2 and 28.5 N/mm^2 respectively. It is followed by 46.1 N/mm^2 and 46.7 N/mm^2 for 07 days and 58.9 N/mm^2 and 60.2 N/mm^2 for 28 days.

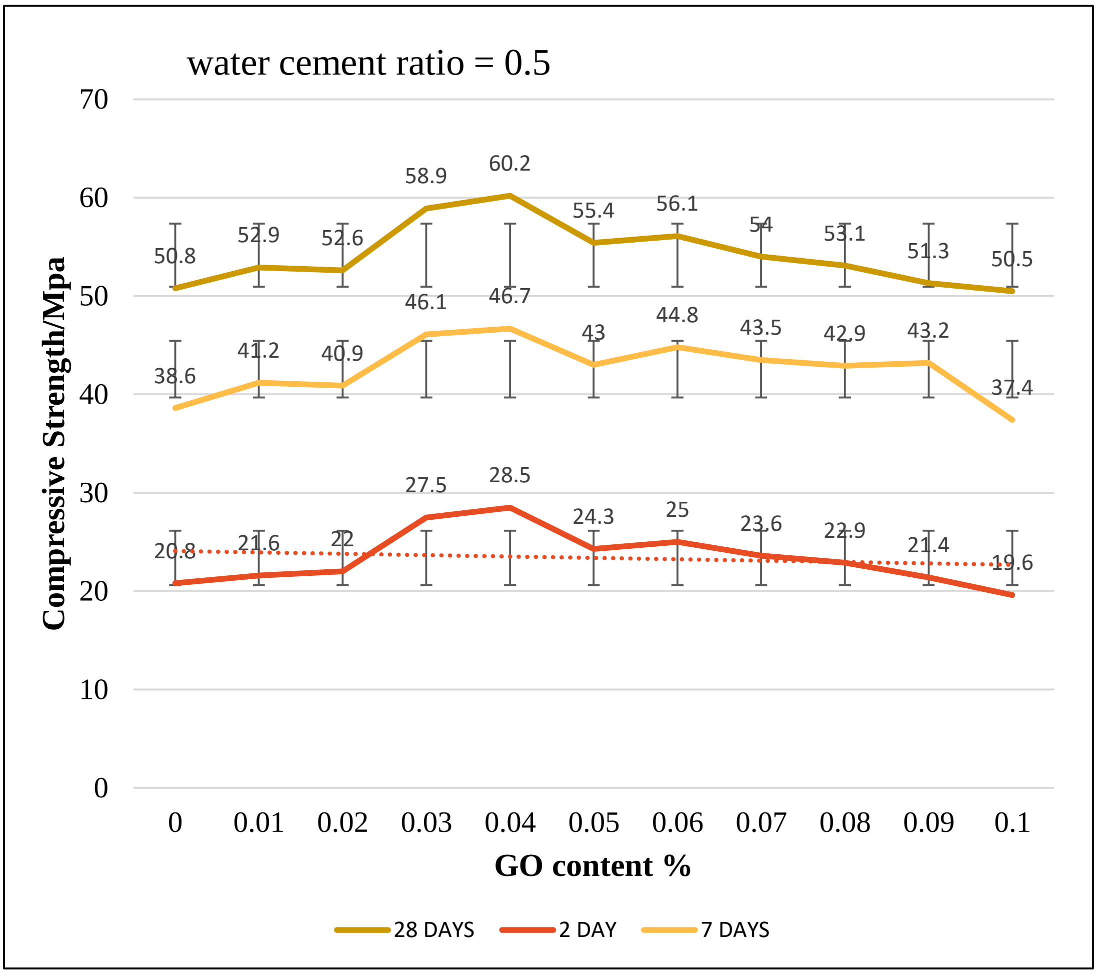


Figure 4.7: The variation of average compressive strength of GOCC

Table 4.3 illustrates the comparison of improvement in compressive strength of GO Cement composite to that of cement prepared without GO. As shown in the Table 4.3, increasing the GO content up to 0.04%, the compressive strength of GOCC shows a sharp increase of 37.02 % at 2 days and 18.5 % at 28 days, compared with control samples.

Table 4.3: Compressive strength of GO - Cement composite

GO - Cement composite	Improvement in compressive strength comparison with specimens without GO (%)		
	02 days	07 days	28 days
GO – 0.01 A	3.85	6.74	4.13
GO – 0.02 A	5.77	5.96	3.54
GO – 0.03 A	32.21	19.43	15.94
GO – 0.04 A	37.02	20.98	18.5
GO – 0.05 A	16.83	11.4	9.06
GO – 0.06 A	20.19	16.06	10.43
GO – 0.07 A	13.46	12.69	6.3
GO – 0.08 A	10.1	11.14	4.53
GO – 0.09 A	2.88	11.92	0.98
GO – 0.10 A	-5.77	-3.11	-0.59

This Table 4.3 indicates that the enhancement of the compressive strength was more noticeable when the mixing quantities up to 0.04%. When the mixing amount exceeds the 0.04%, the compressive strength decreased gradually and even became lower than that of the control specimen.

There are several reasons behind this and the first reason might be water demand raised up after the addition of cementitious materials [25]. Graphene oxide has a high specific surface area [10] and significant adsorption capacity. Therefore, there is less water amount required for the hydration reaction of cement. (Jinchang P., et al) revealed that another reason might be the agglomeration of graphene oxide due to van der Waals attraction [25].

III. Co-Effect of CB and GO

In the next stage of the research work, the improvement in compressive strength was investigated by adding both CB and GO into the cement composite. The optimized bending percentages of both CB (0.3 and 0.4) and GO (0.03 and 0.04) were used to prepare the cement motor. The outcomes of the co-effect of CB and GO are showed in Table 4.4.

Table 4.4: Co-effect of the GO and CB cement composite

Sample	Mass fraction %		Improvement in compressive strength comparison with specimens without GO & CB (%)		
	CB (wt)	GO (wt)	2 days	7 days	28 days
CB – GO A	0.3	0.03	17.79	11.92	10.83
CB - GO B	0.3	0.04	21.15	13.47	13.19
CB – GO C	0.4	0.03	43.27	19.43	18.31
CB – GO D	0.4	0.04	25.48	15.28	10.04

The incorporation of CB and GO to the cement, motor simultaneously, enhanced the compressive strength of the samples drastically. The highest increase of the strength was equal to 43.27%, 19.43%, and 18.31% of specimens evaluated at the age of 2 days, 7 days, and 28 days, respectively for the cement composite specimens of 0.4% CB and 0.03% of GO. The bar chart of Figure 4.8 illustrates the outcome further.

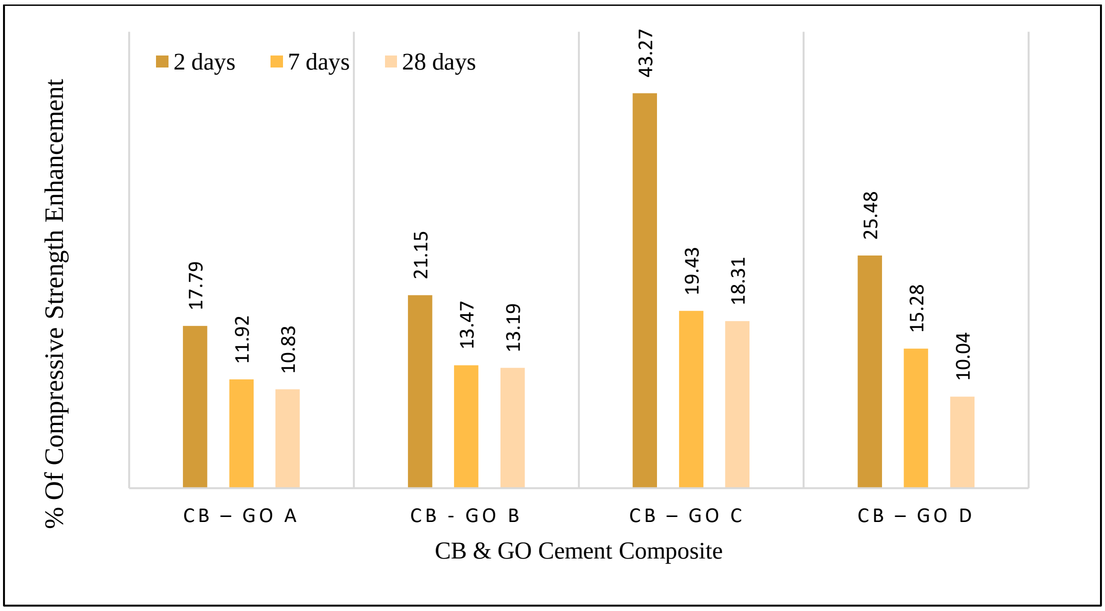


Figure 4.8: The improvement in compressive strength comparison with specimens without GO & CB (%)

It can be clearly seen that, in CBCC and GOCC specimens indicate the high compressive strength for 2 days. Interestingly, a further comparison of the mixture of GO & CB in cement composite revealed that additives have more effect on early strength rather than the late strength which at the age of 28 days. This may be due to a high water-cement ratio; properly dispersed CB and GO were prone to in the micro-pores of the cement paste which supports to have an improved structure of hydrated cement paste. Therefore, this helps to increase the early compressive strength. Further, this higher early compressive strength indicates that the GO had an ability to accelerate the cement hydration process rather than CB. This potential of GO increases initial compressive strength development [15].

During the hardening process of cement, mortar, residual water used for further reactions, and this causes the formation of large pores that cannot fill by the nanomaterials used such as CB and GO which leads to the reduction of compressive strength with respect to the early strength.

Further addition of GO may result in the restacking of GO due to Vander Waals force which reduce the efficiency of the mechanical improvement [39]. This result indicates that the right amount of CB or GO were required to improve the mechanical properties of the cement composites.

IV. Effect of PC admixture

Effect of PC admixture on the cement, motor with GO and CB cement composite was checked using a Polycarboxylic based admixture and the outcome of the research work is tabulated in Table 4.5. PC admixture enhanced the workability and it was used to improve the fluidity of cement mortar. GO has low but stable dispersibility in PC admixture which helps to proper reactions with the cement matrix which helps to enhance the compressive strength of the composite compared with other composites with PC admixture [34].

Table 4.5: Co-effect of Polycarboxylic based admixture for the GO and CB cement composite

Sample	Composite			Improvement in compressive strength comparison with specimens without GO & CB (%)		
	CB (wt)	GO (wt)	0.4% Hy-HS/ml	2 days	7 days	28 days
CB – GO I	0.3	0.03	3.6	21.2	18.4	14.4
CB – GO II	0.3	0.04	3.6	25.5	15.3	14.2
CB – GO III	0.4	0.03	3.6	38.0	19.9	21.9
CB – GO IV	0.4	0.04	3.6	30.8	19.2	14.0

Figure 4.9 shows the variation of compressive strength of CB and GO cement composite with Polycarboxylic admixture. Compare with other composites, it can be clearly seen that, 28 days compressive strength was improved than other composites.

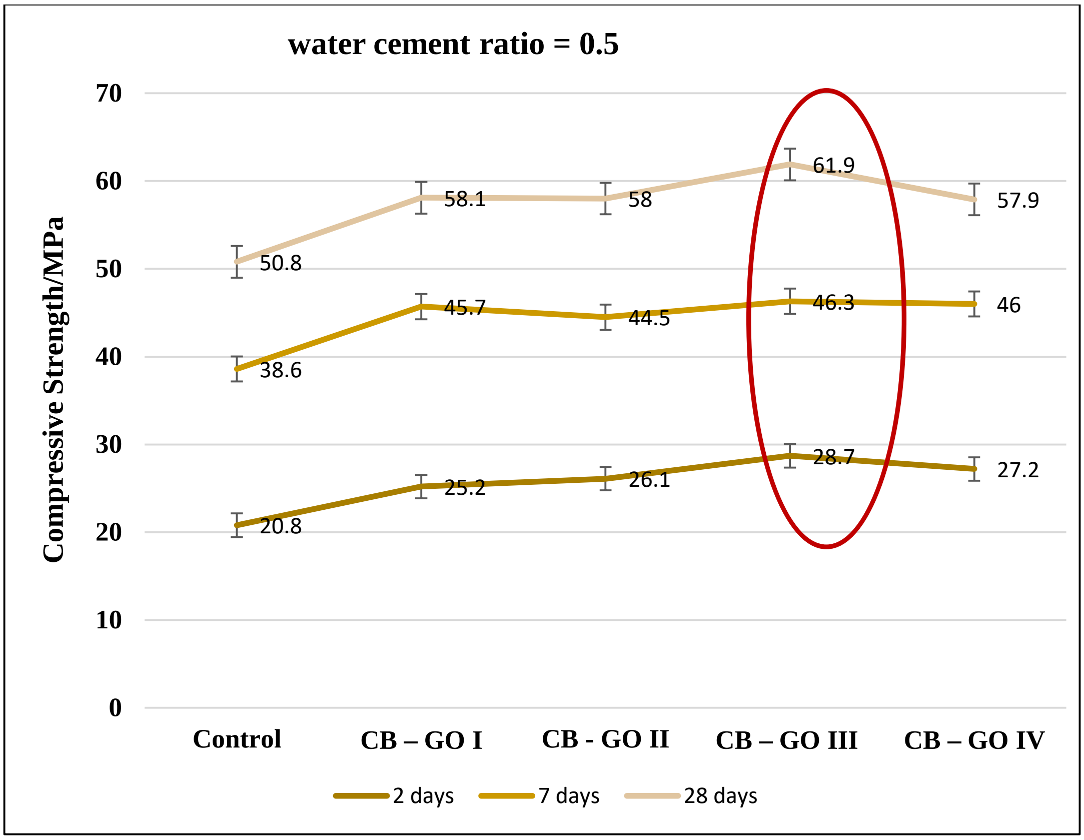


Figure 4.9: Compressive strength of CB and CO cement composite with Polycarboxylic admixture

It can be clearly seen that the same mixture of the composite without admixture, were given high 2 days strength rather than with admixture. The addition of PC based admixture enhances the compressive strength of 28 days of hardening. The addition of admixture has a positive influence on mechanical strengths, due to its filler effect and of a better dispersion in water of the cement particles, which improve the hydration processes. With the use of admixture, compressive strength can be improved in all the composites. The admixture creates electrostatic repulsion forces in the cement matrix and increases the workability of the composite. Therefore, the admixture effect on the cement hydration process physically rather than chemically. This leads to a better hydration process due to the proper dispersion of individual cement grains with admixture. Thus, this increases the water to cement ratio which causes a slight decrease in early strength.

4. 2.2 Flexural strength

Flexural strength is a measure of tensile strength in bending. OPC flexural strength testing was carried out for a 40 mm x 40 mm x 160 mm cement motor beam. In this study, a center-point loading was applied and the flexural strength was tested for 28 days of cement mortar samples.

I. CBCC – flexural strength

The flexural strength test results are shown in Table 4.6. The incorporation of 0.4% of CB enhances the flexural strength of the cement motor up to 53.54% for 28 days.

Table 4.6: Flexural strength of CB - Cement composite

Sample	CB wt%	Age/days	Average Flexural Strength/MPa	Improvement in flexural strength comparison with specimens without CB (%)
CB – 0.1 B	0.1	28	5.69	10.71
CB – 0.2 B	0.2	28	5.13	7.07
CB – 0.3 B	0.3	28	6.91	32.12
CB – 0.4 B	0.4	28	8.03	53.54
CB – 0.5 B	0.5	28	5.04	5.35
CB – 0.6 B	0.6	28	4.76	-8.99
CB – 0.7 B	0.7	28	4.67	-7.27
CB – 0.8 B	0.8	28	4.39	3.44
CB – 0.9 B	0.9	28	4.01	5.35
CB – 1.0 B	1	28	4.01	-1.91

II. GOCC –The flexural strength

The results on the flexural strength of GOCC specimens are shown in Table 4.7. The addition of 0.3% of GO increased the flexural strength of the cement mortar up to 46.54% for 28 days. For the compressive strength, there was a clear pattern that was not in the flexural strength test results indicating there may be several reasons associated with the axial loading system. Graphene oxide has extraordinary properties that adversely affect the rheological properties of the composite such as high specific surface area (2630 $m^3.g^{-1}$), high intrinsic strength (130 GPA), and firm Young's module [22]. The tensile strength of GO is very high due to its high surface energy, more dispersed GO is required to bear the stress. Therefore, the water-cement ratio may be highly affected by the flexural strength of the GO composite.

Table 4.74: Flexural strength of GO - Cement composite

Sample	GO wt%	Age	Average Flexural Strength/MPa	Improvement in flexural strength comparison with specimens without CB (%)
GO-0.01B	0.01	28	5.79	7.02
GO-0.02B	0.02	28	6.63	22.55
GO-0.03 B	0.03	28	7.93	46.58
GO-0.04 B	0.04	28	6.63	22.55
GO-0.05 B	0.05	28	5.41	-0.18
GO-0.06 B	0.06	28	5.04	-6.84
GO-0.07 B	0.07	28	5.13	-5.18
GO-0.08 B	0.08	28	4.95	-8.50
GO-0.09 B	0.09	28	4.67	-13.68
GO-0.1 B	0.1	28	4.39	-18.85

When increasing the additives, it can be clearly seen that the development of the flexural strength for 28 days is lower than that of the control mortar sample.

III. Co-effect of CB and GO Cement composite –The flexural strength

The results on the flexural strength of CB & GO Cement composite specimens are shown in Table 4.8. As shown in Table 4.8 the addition of the combination of 0.3% CB and 0.04% GO to the cement composite enhanced the flexural strength of the prism by 60.61%.

Table 4.85: Co-effect of the GO and CB cement composite

Sample	Mass fraction %		Average Flexural Strength/MPa at 28 days	Improvement in flexural strength comparison with specimens without GO & CB (%)
	CB (wt)	GO (wt)		
CB – GO E	0.3	0.03	6.72	19.89
CB - GO F	0.3	0.04	8.40	60.61
CB – GO G	0.4	0.03	7.84	49.90
CB – GO H	0.4	0.04	6.16	17.78

Noteworthy, the flexural strength test of mixed CB and GO cement composite for all four test specimens show that the flexural strength of the composite is considerably improved during 28 days of curing the condition.

The summary of the flexural strength of the cement mortar specimens at 28 days under the varying percentage of CB and GO is illustrated graphically in Figure 4.10.

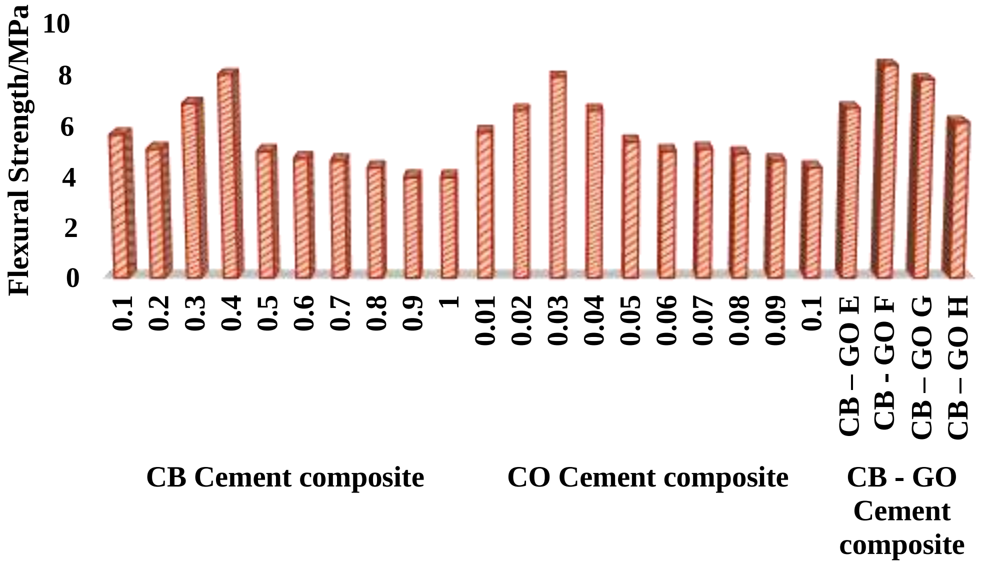


Figure 4.10: Flexural Strength of cement composite with CB and GO

The average of three test results was presented in this study. It is noticeable that the incorporation of CB and GO enhances the flexural strength of all cement mortar samples (CB-GO E, CB-GO F, CB-GO G, and CB-GO H). The flexural strength increases in a range from 7.02% to 60.61% at 28 days and the highest value indicated for 0.4% CB and 0.03% GO. Even though the rate of increase in compressive strength was higher in all specimens, but this pattern was difficult to see for the flexural strength. After the certain value of the addition of CB and GO flexural strength was decreased than the control sample.

4. 2.3 Consistency and Initial setting time

When water is mixed with the cement, it starts the hydration process and the chemical reactions between water and cement lead to the hardening of the cement mix and this gives the strength for the cement paste. The consistency is the required amount of water to be added to the cement to complete the chemical reaction to give the optimum strength of the resulted cement paste [41]. If less amount of water is used for the cement, it will decrease the water-cement ration which leads to an incomplete chemical reaction resulting in lower strength. On the other hand, it will increase the water-cement ratio resulting in low hardening property [15].

When the cement paste starts the hydration process with the added water, initially it has plasticity property which helps to mould the paste into desired shapes, but with the time, cement paste loses its plasticity and starts to set hardened. IST is defined as the time taken for a cement paste to start losing its plasticity, from the added time of water to the cement [41].

Table 4.96 shows the IST and Normal Consistency of CBCC. For the normal consistency, the water amount increased gradually and the penetration value was kept constant. This Table 4.9 indicates that when increased the CB, water demand raised.

Table 4.9: IST and Normal Consistency of CBCC

Sample	CB wt%	IST	Normal Consistency
Control	0	120	30.4
CB – 0.1 C	0.1	125	30.4
CB – 0.2 C	0.2	125	30.4
CB – 0.3 C	0.3	125	30.4
CB – 0.4 C	0.4	125	31.4
CB – 0.5 C	0.5	130	31.4
CB – 0.6 C	0.6	130	31.4
CB – 0.7 C	0.7	130	31.8
CB – 0.8 C	0.8	135	31.8
CB – 0.9 C	0.9	135	31.8
CB – 1.0 C	1	130	31.8

Table 7.10 shows the IST and Normal Consistency of GOCC. For the small addition of GO impact drastically on the consistency and the initial setting time which showed the increased in the water demand of GO.

Table 4.108: IST and Normal Consistency of GOCC

Sample	CB wt%	IST	Normal Consistency
Control	0	120	30.4
GO-0.01C	0.01	125	31.4
GO-0.02 C	0.02	125	31.4
GO-0.03 C	0.03	125	31.4
GO-0.04 C	0.04	130	31.4
GO-0.05 C	0.05	140	31.8
GO-0.06 C	0.06	150	31.8
GO-0.07 C	0.07	145	32.4
GO-0.08 C	0.08	160	32.8
GO-0.09 C	0.09	170	32.8
GO-0.1 C	0.1	170	32.8

The increase in water demand indicates that the GO required more water compared to the control sample. This can be explained by a reduced amount of free- water due to the high specific surface area of GO which can be resulted in high water absorption capacity [15], [20]. Therefore, this may result in a decrease in the availability of water in the fresh mix from wetting [31].

4. 2.4 Analysis of Scanning Electron Microscope

SEM (scanning electron microscope) was favoured by the researchers to investigate the microstructure of hardened cement mortar, especially hydration products when additives are added to the cement composites.

The variation of the mechanical strength of hardened cement mortar with the variation of additives basically depends on its microstructure mainly, solid phases, pore structure and quantity, and distribution of pore structure. SEM images correspond to the cement composite were studied to determine the relationship of mechanical strength with microstructure.

Figure 4.11 shows the microstructure of control specimens of cement motor, samples without any additives, revealed several needle-shaped ettringite projecting into the pores and the amorphous morphology of the calcium silicate hydrate (C-S-H) gel [44]. There were several pore structures in the cement mortar composite and ettringite formation (AFt) was insufficient inside the pores which lead to lower strength than other samples [32].

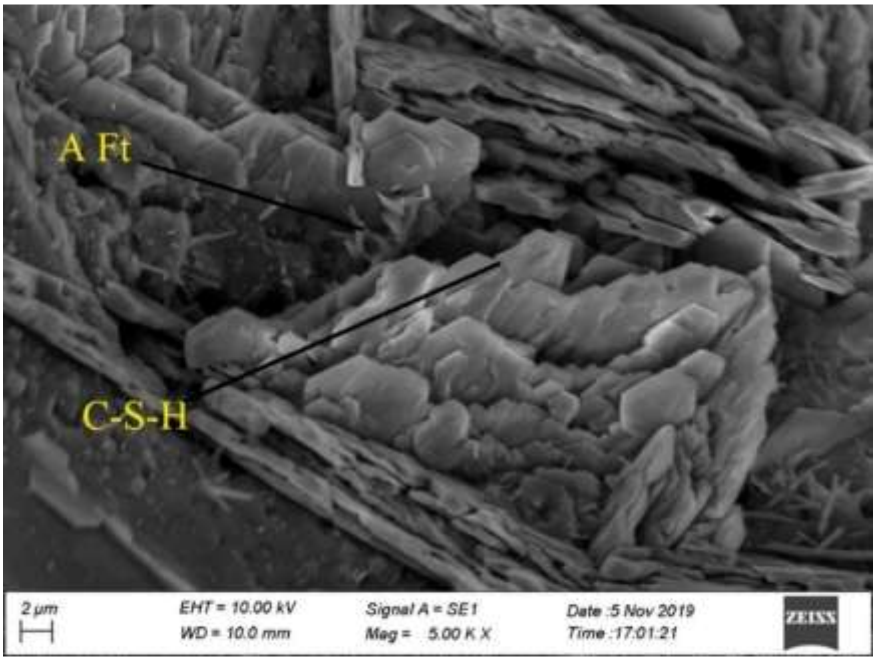


Figure 4.11: The images of SEM analysis (Control Cement motor for 07 days)

Figure 4.12 showed the images of SEM analysis of CBCC with 0.4% CB at 07 days. It is clearly visible that CB was not affected the hydration products of the cement, motor and it acts as a reinforcing and a filling ingredient of the cement matrix [13].

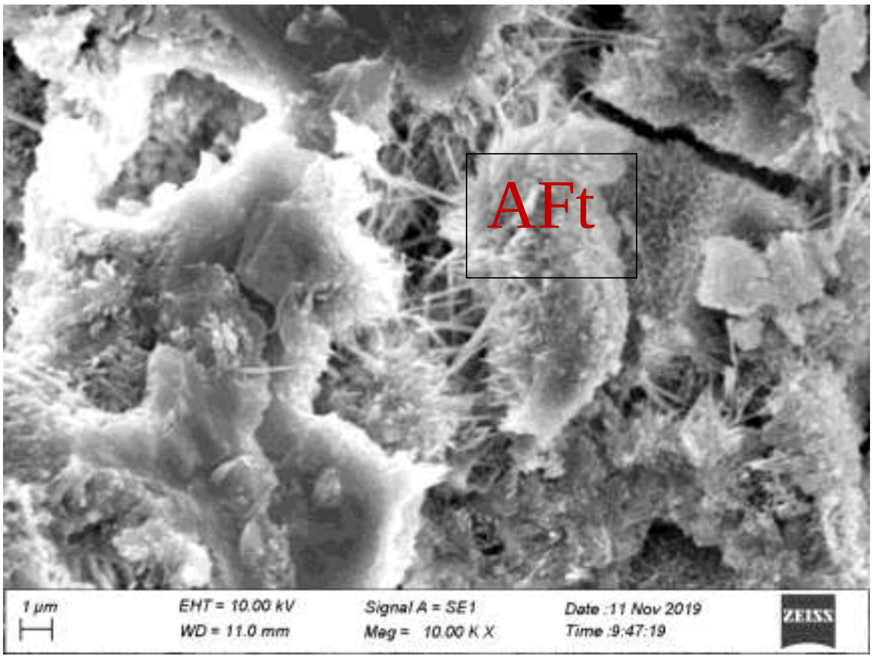


Figure 4.12: The images of SEM analysis of CBCC with 0.4% CB at 07 days

Figure 4.13 showed the images of SEM analysis of GOCC with 0.04% GO at 07 days. Interestingly, it is found that GO affect the formation of cement hydration product and it provided better filling effect and further hydration effect. GO has a large specific surface area which provides better growth space for the hydration products. For GO reduced the porosity results in high strength in cement mortar [35].

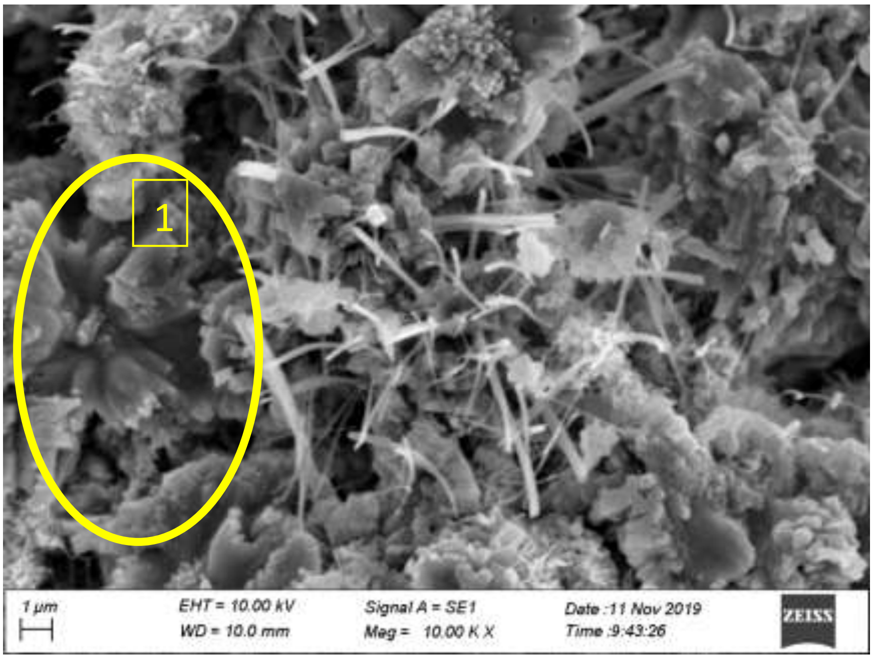


Figure 4.13: The images of SEM analysis of GOCC with 0.04% GO at 07 days

SEM images of the cement composite which were mixed with 0.4% CB and 0.03% GO contents after curing for 07 days is shown in Figure 4.14.

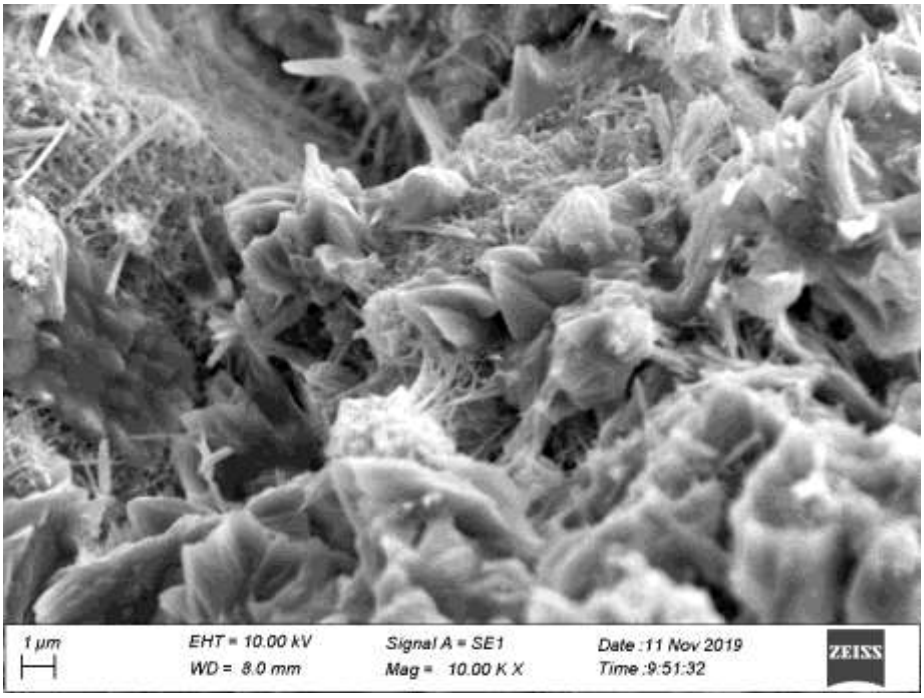
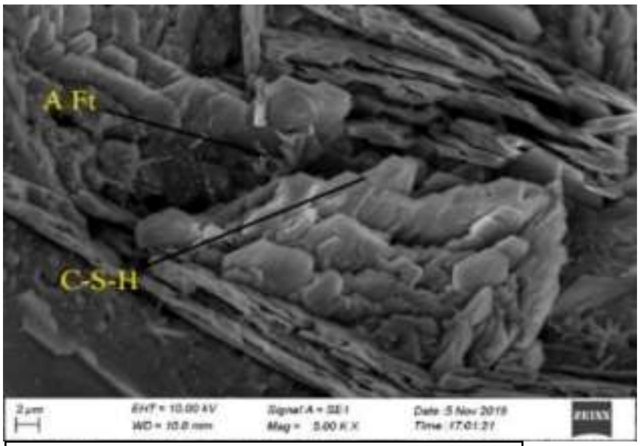


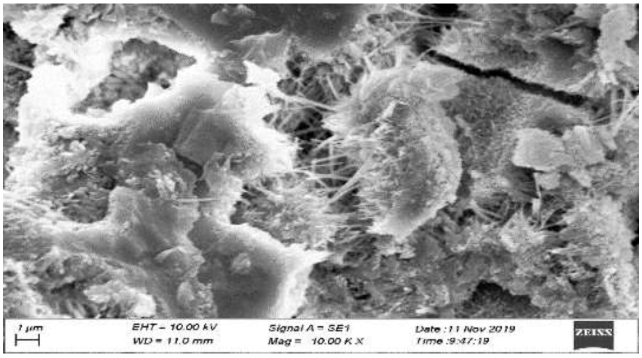
Figure 4.14: The images of SEM analysis of CB 0.4% and GO 0.03% cement composite at 07 days

Noteworthy, it can be clearly seen that in Figure 4.14, there were less pores in the hardened cement mortar and the adequate ettringite inside the pores. The structure of the control cement mortar indicates the formation of many disorganized stacked bar-shaped crystals and needle shape crystals. These can be considered as products of cement hydrations crystals such as ettringite and calcium hydroxide [32]. There were cracks and pores in the control sample, but with 0.03% Go and with 0.4% CB, the morphology of the cement mortar was significantly enhanced. The crack surfaces were covered by the needle-shaped network and filled by the particles as shown in Figure 4.14.

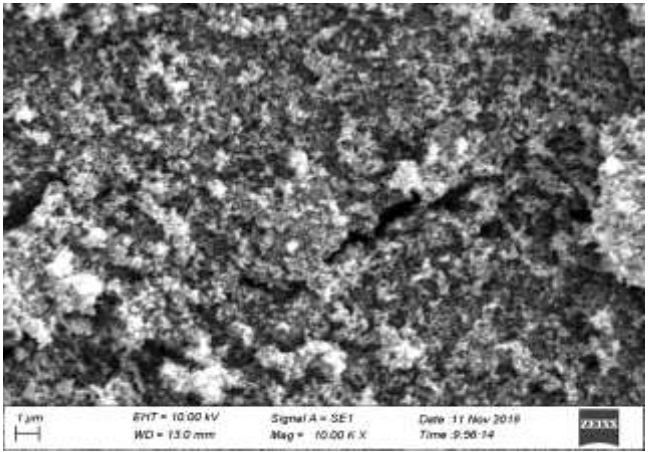
Figure 4.15 shows the summary of SEM images of different percentage of CB and the control sample.



(a): The content of CB was 0.



(b): The content of CB was 0.4%.

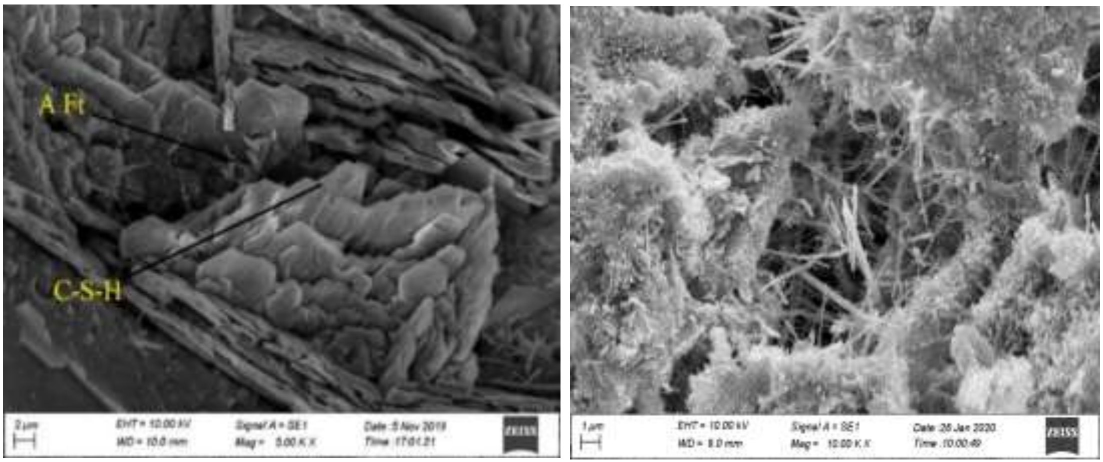


(C): The content of CB was 0.8%.

Figure 4.15: The SEM images of the test specimens under different mixing amount of carbon black.

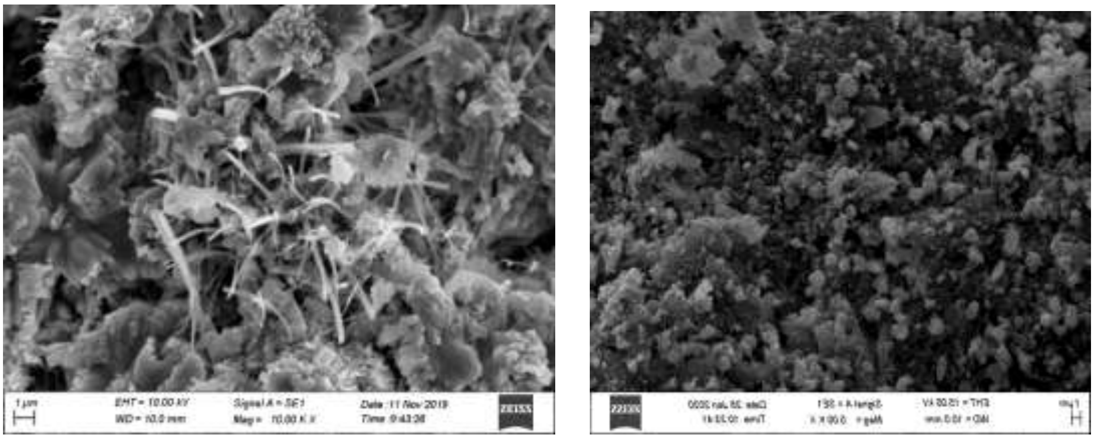
It is clearly visible that CB acts as a reinforcing and a filling ingredient of the cement matrix. With 0.4% of CB content, the hardened cement mortar sample is highly compacted with a more needle-shaped structure of crystal forms after hydration which covered from CB particles. These particles covered the fracture surface of the cement mortar.

Figure 4.16 shows the summary of SEM images of different percentage of GO and the control sample.



(a): The content of CB was 0.

(b): The content of GO was 0.01%.



(c): The content of GO was 0.04%.

(d): The content of GO was 0.08%.

Figure 4.16: The SEM images of the test specimens under different mixing amount of Graphene Oxide.

As per the previous studies of the influence of GO in the cement hydration process revealed that the cement hydration process rate is not enhanced by GO and they found the morphology of GOCC is almost similar to that of the cement mortar without GO [25]. However, recent research work elucidated that the GO has strongly influenced the hydration structure of the cement mortar which regulated the formation of flower-like hydration crystals [32].

For a dose of 0.04% of GO, the flower–like hydration crystals were shown in Figure 4.16 (c) and which confirms the GO contributes to the hydration process and further its nucleation effect [44]. The mechanism of formation of cement hydration crystals with the addition of GO is shown in the Figure 4.17 [21], [44].

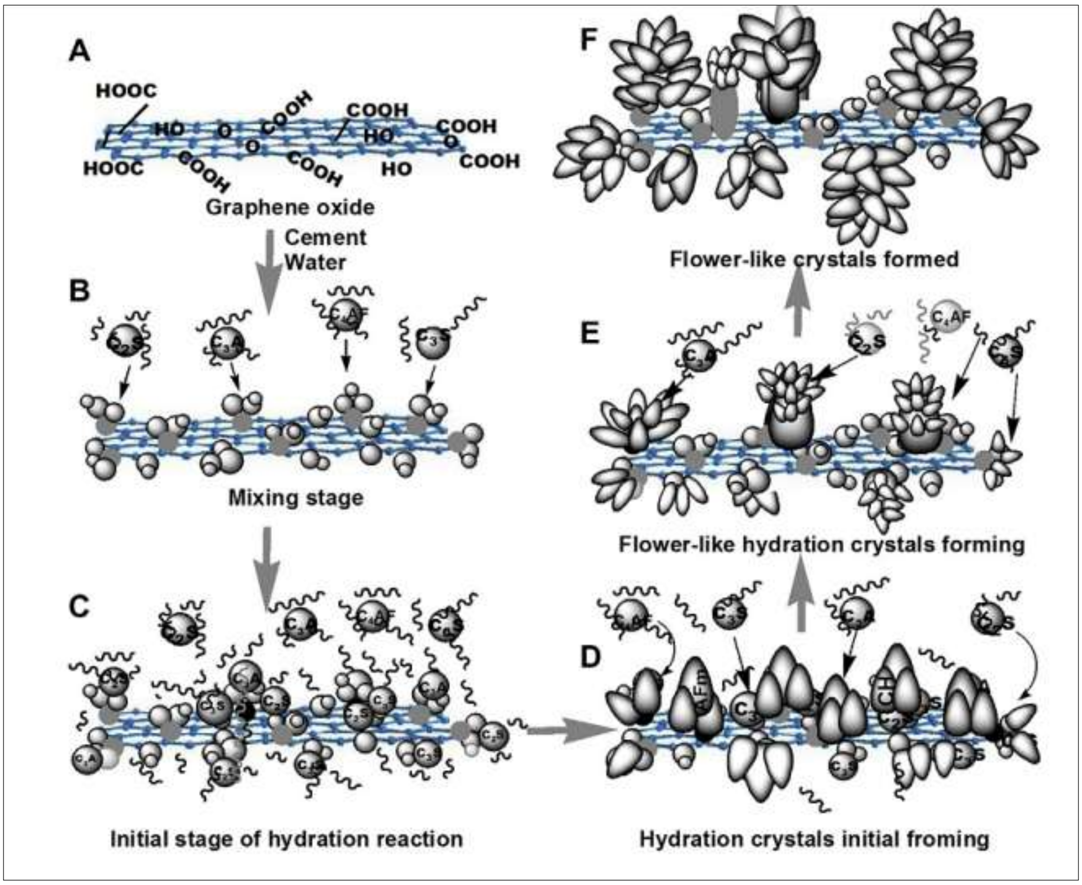


Figure 4.17: The mechanism of formation of cement hydration crystals with addition of GO [21]

When increasing the GO content further, the formation of cement hydration products decreases due to the absorption of the water by the hydrophilic groups which are on the surface of GO. This prevents the hydration process of the GO cement composite which affected the mechanical strength reduction [44]. However, this occurred extensively at a lower dosage of GO compared to the higher dosage. From 0.01% to 0.1% range of this study, GO has a considerable improvement in the mechanical properties of hardened cement mortar for the optimum content of GO is 0.04%.

The nucleation effect and cross-link effect are highly dependent on the dispersion methods and proper dispersion gives better distribution in the matrix. This helps to enhance the mechanical properties of the composite further.

4 CONCLUSION

The microstructural properties and mechanical properties of CB and GO with cementitious materials have been investigated in this research project. Incorporate of Graphene Oxide and Carbon Black in cement, mortar showed an interesting modification in mechanical and microstructural properties. It is confirmed that CB was acted as reinforcing filler which strengthens the structure of the cement composites. It finds that the high bond strength is resulted due to the influence of GO in the hydration process of cement at the molecular level. It is required to have better disperse GO to react with the cement matrix. Therefore, advanced dispersion methods are required to achieve this target.

The addition of 0.04% GO accelerates the process of cement hydration which helps in the formation of hydrated product and provided proper reinforcing of the structure resulted from the increase the mechanical strength (compressive strength and flexural strength) of the hardened cement, mortar. It was indicated that the microstructure of CBCC enhances the mechanical properties by giving a better filling effect.

Properly distributed CB and GO resulted in an increase in the percentage of GO to 0.4% and 0.03%, respectively, and reached the maximum.

The findings of this research works revealed that the addition of CB and GO significantly enhanced the mechanical properties of the cement mortar.

For a constant water-cement ratio, 0.4% CBCC and 0.04% GOCC showed the higher compressive strengths for 2 days, which were 26.44% and 37.02%, respectively compared to the control sample.

For the mixture of CB and GO cement composites, the highest compressive strength showed by 0.4% CB and 0.03% GO combination and it further enhanced when mixed with Polycarboxylic admixture.

This should be attributed to the fact that a properly dispersed CB and GO enhanced the mechanical properties of the composite which also improved the microstructure of the composite.

Future Research Work

Presently minimal research projects are available in the field of nanomaterials-based cement composite in Sri Lanka. Sri Lanka has natural graphite which gives high purity graphene. Therefore, we can utilize our own graphene oxide for various industrial applications. We can use graphene oxide as a repair material specially for old concrete buildings. Noteworthy, the finding of the research work will provide the great potential of preparation of GO and CB cement composites in the applications of nanomaterials in civil engineering.

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Research work publication:

1. Full paper presented for 10th International Conference on Structural Engineering and Construction Management (ICSECM). **Submission 60** Chandima, A. M. B., Guluwita, S. P. “A review on mechanical properties and morphological properties of concrete with Graphene Oxide” *10th International Conference on Structural Engineering and Construction Management*
2. Paper presented in 10th ICSECM conference was selected for the publication in **Springer Nature**.

APPENDICES

Appendix A: Specification sheet of Carbon black

MAKROchem S.A.
ul. M. Rapackiego 2
20-150 Lublin, Poland

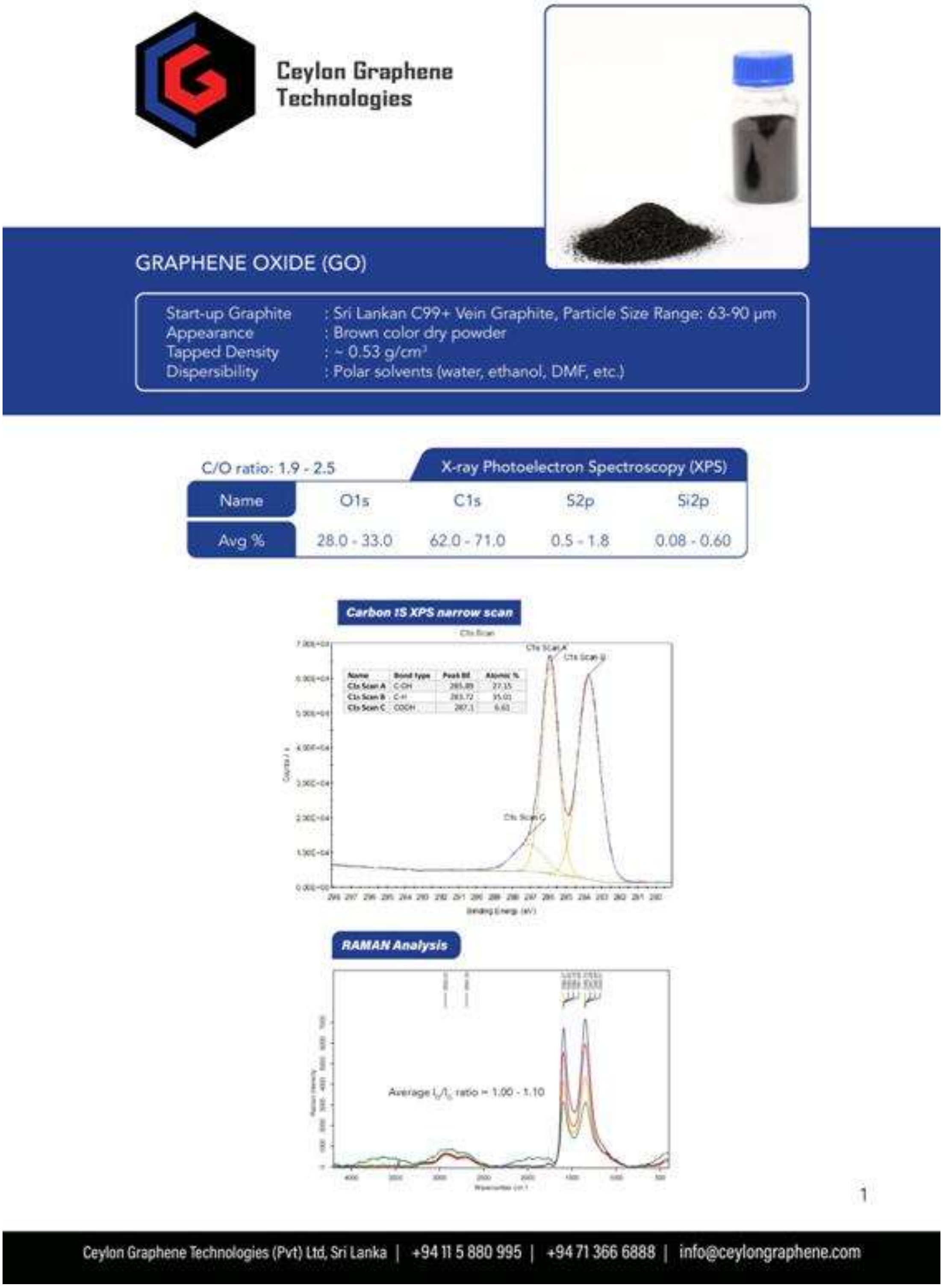
tel: +48 81 747 88 19, 740 70 74, 740 67 05, 444 15 01, 444 15 02
fax: +48 81 747 06 02,
e-mail: mc@makrochem.com
www: www.makrochem.com

MATERIAL SPECIFICATION

Carbon black N330

PROPERTY	Target	Tolerance	ASTM test method
1. Iodine adsorption, g/kg	82	± 6	D 1510
2. Oil absorption number, cm$_3$/l00g	102	± 6	D 2414
3. Sieve residue 45 µm (No.325), %		≤ 0.05	D 1514
4. Sieve residue 500 µm (No.35), %		≤ 0.001	D 1514
5. Heating loss, %		≤ 1.0	D 1509
6. Ash content, %		≤ 0.75	D 1506
7. Pour density, kg/m^3	380	± 25	D 1513
8. Fines content, %		≤ 7	D 1508
9. pH value		7÷10	D 1512
10 Sulfur content, %		≤ 1.1	D 1619
11. Individual pellet hardness (average of 20), g		≤ 55	D 5230
12 Individual pellet hardness (max of 20), g		≤ 90	D 5230
13 Toluene discoloration, %		≥ 85	D 1618
14 BET surface area (NSA), m$_2$/g	78	± 5	D 6556
15 External surface area (STSA), m$_2$/g	75	± 5	D 6556
16 Tint strength	104	± 5	D 3265
17 Oil absorption number of compressed sample, cm$_3$/100g	88	± 5	D 3493

Appendix B: Specification sheet of Graphene Oxide



Ceylon Graphene
Technologies

GRAPHENE OXIDE (GO)

Start-up Graphite : Sri Lankan C99+ Vein Graphite, Particle Size Range: 63-90 µm
Appearance : Brown color dry powder
Tapped Density : ~ 0.53 g/cm^3
Dispersibility : Polar solvents (water, ethanol, DMF, etc.)

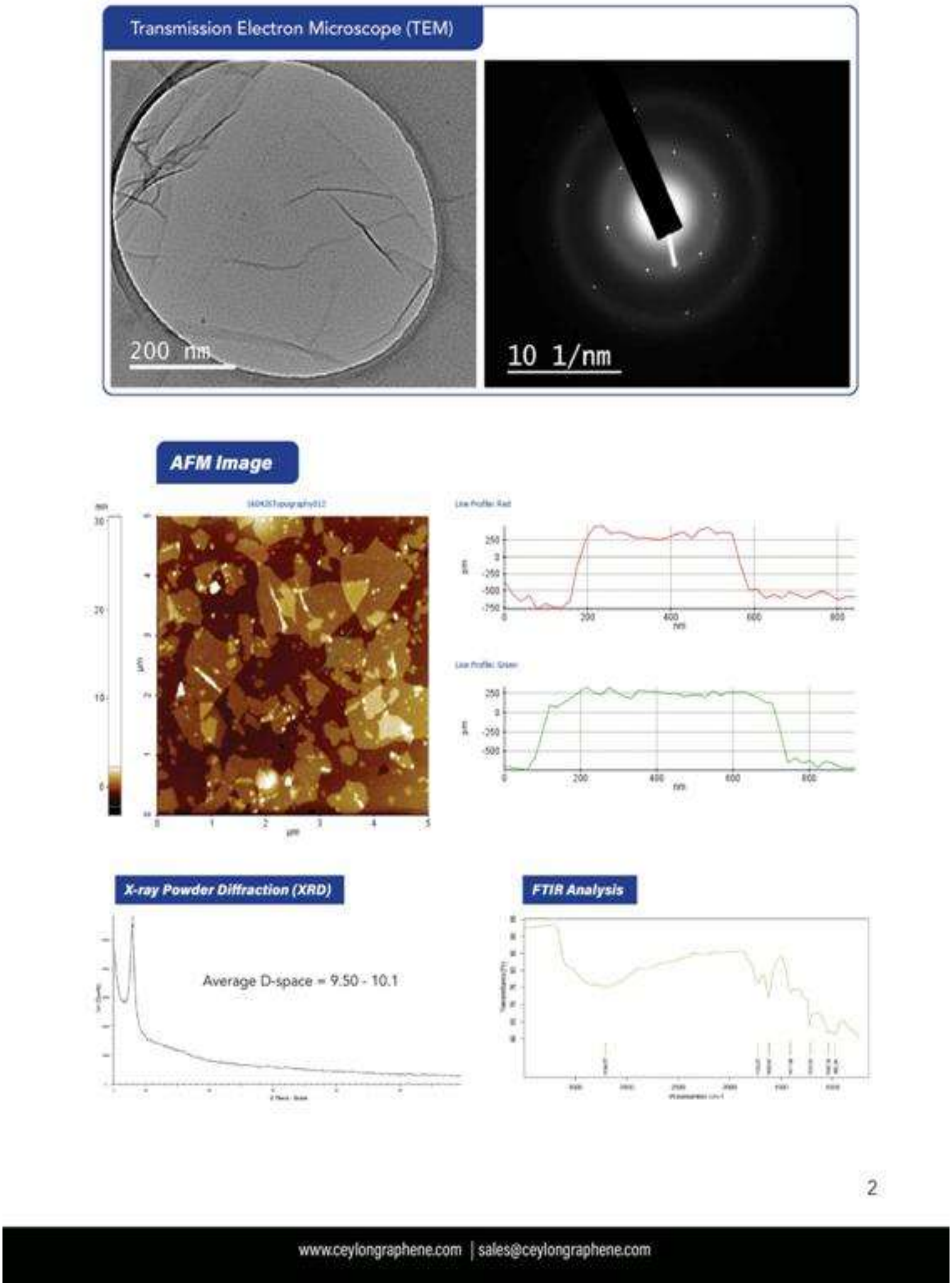
C/O ratio: 1.9 - 2.5

X-ray Photoelectron Spectroscopy (XPS)

Name	O1s	C1s	S2p	Si2p
Avg %	28.0 - 33.0	62.0 - 71.0	0.5 - 1.8	0.08 - 0.60

1

Ceylon Graphene Technologies (Pvt) Ltd, Sri Lanka | +94 11 5 880 995 | +94 71 366 6888 | info@ceylongraphene.com



Transmission Electron Microscope (TEM)

AFM Image

X-ray Powder Diffraction (XRD)

Average D-space = 9.50 - 10.1

FTIR Analysis

2

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Appendix C: Individual result of Compressive strength of CBCC

Cement /g	% CB	CB /g	Water /ml	Sand /g	Test Results														
					2 day			Mean	SD	7 day			Mean	SD	28 day			Mean	SD
450	0	0	225	1350	21.2	20.9	20.4	20.8	0.34	38.9	37.6	38.2	38.7	0.68	51	48.9	53.2	50.8	1.78
					20.3	20.9	20.9			38.6	39.1	39.5			51.1	48.5	51.8		
449.55	0.1	0.45	225	1350	23.6	24.4	23.9	23.5	0.57	43.1	43.1	43.8	43.3	0.49	54.3	52.6	54.3	53.9	0.90
					22.8	23.1	23.4			42.6	43.4	43.9			52.8	54.7	54.4		
449.1	0.2	0.9	225	1350	24.9	24.4	22.8	24.0	0.75	41.9	41.1	41.8	41.5	0.33	53.9	55.3	55.2	54.9	0.73
					24.5	23.6	23.9			41.3	41.2	41.4			55.8	55.2	54.2		
448.65	0.3	1.35	225	1350	26.4	26.1	25.6	26.2	0.53	44.9	46.6	44.6	45.1	0.99	58.6	58.2	58.8	58.2	0.67
					27.1	25.8	26.2			44	45.9	44.4			57.6	57.2	58.8		
448.2	0.4	1.8	225	1350	25.9	26.4	26.6	26.3	0.30	46.6	46.1	44.6	44.7	1.49	57.9	58.3	57.4	57.7	0.38
					26	26.6	26.4			43.2	44.7	42.9			57.3	57.6	57.4		
447.75	0.5	2.25	225	1350	22.8	23.2	22.1	22.6	0.56	40.9	38	39.5	38.8	1.19	54.4	53.8	54.4	54.1	0.59
					23.1	22.5	21.8			38.2	37.9	38.2			53.9	53.3	55		
447.3	0.6	2.7	225	1350	22.3	22.5	22.9	22.9	0.50	39.5	40.3	40.6	40.0	0.42	55.5	55.1	53.9	54.9	1.18
					23.7	23.1	23.1			40.1	39.6	40.1			56.8	53.9	53.9		
446.85	0.7	3.15	225	1350	23.1	23.7	24.7	23.6	0.64	38.8	39.9	40.1	39.7	0.53	54.7	52.4	53.8	53.9	0.92
					23	23.2	23.8			39.4	40.1	40.1			53.4	54.1	54.9		
446.4	0.8	3.6	225	1350	25.1	23.9	23.9	23.6	0.95	40.2	40.2	40.6	40.5	0.44	55.2	54.8	53.8	54.8	0.82
					23.1	23.2	22.3			41.3	40.2	40.7			56.1	54.4	54.2		
445.95	0.9	4.05	225	1350	23.1	23.4	23.2	23.4	0.34	36.7	37.3	37.9	37.5	0.57	52.4	53.2	53.4	53.0	0.51
					23.4	24	23.1			37	38.2	37.7			52.9	52.4	53.6		
445.5	1	4.5	225	1350	23.6	23.9	23.8	23.6	0.43	38.6	38.5	37.9	38.1	0.40	50.4	50.7	51.6	51.4	0.79
					23.4	24.1	22.9			37.8	37.6	38			52.5	52	51.4		

Appendix D: Individual result of Compressive strength of GOCC

Cement/g	% GO	GO/g	Water/ml	Sand/g	Test Results								
					2 day			7 day			28 day		
450	0	0	225	1350	20.6	20.9	20.7	38.4	38.8	38.6	50.9	50.9	50.8
					20.8	21	21	38.7	38.5	38.6	50.5	50.7	51
449.955	0.01	0.045	225	1350	21.5	21.3	21.9	41.4	41.1	41.2	52.8	52.9	53
					21.7	21.6	21.6	41.2	41.3	41	53	52.6	53.1
449.91	0.02	0.09	225	1350	22.1	22.3	21.6	41	40.8	41.1	52.6	52.8	52.5
					21.7	22	22.3	40.7	40.9	40.9	52.6	52.5	52.6
449.865	0.03	0.135	225	1350	27.6	27.7	27.4	46.1	46.4	45.9	58.9	58.7	59.1
					27.4	27.5	27.4	46	46.2	46	59	58.6	59.1
449.82	0.04	0.18	225	1350	28.6	28.3	28.6	46.7	46.5	46.9	60.7	60.1	60.2
					28.6	28.5	28.4	46.9	46.4	46.8	60	59.8	60.4
449.775	0.05	0.225	225	1350	24.5	24.3	24.2	42.8	43	42.8	55.6	55.4	54.9
					24.1	24.4	24.3	43.1	42.9	43.4	55.3	55.5	55.7
449.73	0.06	0.27	225	1350	24.8	25	24.7	44.7	44.6	44.9	56.1	55.9	56
					25.1	25.1	25.3	44.8	44.8	45	56.3	56.4	55.9
449.685	0.07	0.315	225	1350	23.6	23.5	23.8	43.6	43.4	43.4	54	53.7	54.1
					23.7	23.6	23.4	43.5	43.7	43.4	53.9	54.3	54
449.964	0.08	0.36	225	1350	23	22.9	23	43	42.8	43.1	53.2	52.9	53
					22.7	22.8	23	42.6	42.9	43	53	53.3	53.2
449.595	0.09	0.405	225	1350	21.5	21.4	21.2	43.2	43.4	43.1	51.3	51.5	51.7
					21.3	21.4	21.6	43	43.1	43.4	51.5	51.2	50.6
449.55	0.1	0.45	225	1350	19.7	19.3	19.7	37.5	37.4	37.3	50.4	50.9	50
					19.5	19.6	19.8	37.6	37.2	37.4	50.2	50.7	50.8

Appendix E: Flexural strength values of CBCC

Sample	Composite		Flexural Strength							
			Force /KN			Strength/MPa			Avg Strength/ MPa	% increase
	CB wt%	Age	1	2	3	1	2	3		
Control	0	28	1.9	1.9	1.8	5.32	5.32	5.04	5.23	-
CB – 0.1 A	0.1	28	2	2.1	2.1	5.6	5.88	5.88	5.79	10.71
CB – 0.2 A	0.2	28	2.1	2	1.9	5.88	5.6	5.32	5.60	7.07
CB – 0.3 A	0.3	28	2.4	2.4	2.6	6.72	6.72	7.28	6.91	32.12
CB – 0.4 A	0.4	28	2.9	2.8	2.9	8.12	7.84	8.12	8.03	53.54
CB – 0.5 A	0.5	28	2.1	1.8	2	5.88	5.04	5.6	5.51	5.35
CB – 0.6 A	0.6	28	1.7	1.7	1.7	4.76	4.76	4.76	4.76	-8.99
CB – 0.7 A	0.7	28	1.8	1.7	1.7	5.04	4.76	4.76	4.85	-7.27
CB – 0.8 A	0.8	28	1.9	2	1.9	5.32	5.6	5.32	5.41	3.44
CB – 0.9 A	0.9	28	1.8	2.1	2	5.04	5.88	5.6	5.51	5.35
CB – 1.0 A	1	28	1.7	1.9	1.9	4.76	5.32	5.32	5.13	-1.91

Appendix F: Flexural strength values of GOC

Sample	Composite		Flexural Strength							
			Force /KN			Strength/MPa			Avg Strength/ MPa	% increase
	CB wt%	Age	1	2	3	1	2	3		
Control	0	28	2	2	1.8	5.32	5.32	5.04	5.23	-
GO-0.01B	0.01	28	2.1	2.1	2	5.6	5.88	5.88	5.41	7.02
GO-0.02B	0.02	28	2.4	2.3	2.4	5.88	5.6	5.32	5.79	22.55
GO-0.03 B	0.03	28	2.8	2.8	2.9	6.72	6.72	7.28	6.63	46.58
GO-0.04 B	0.04	28	2.4	2.5	2.2	8.12	7.84	8.12	7.93	22.55
GO-0.05 B	0.05	28	1.9	1.9	2	5.88	5.04	5.6	6.63	-0.18
GO-0.06 B	0.06	28	1.8	1.7	1.9	4.76	4.76	4.76	5.41	-6.84
GO-0.07 B	0.07	28	1.8	1.8	1.9	5.04	4.76	4.76	5.04	-5.18
GO-0.08 B	0.08	28	1.7	1.8	1.8	5.32	5.6	5.32	5.13	-8.50
GO-0.09 B	0.09	28	1.7	1.7	1.6	5.04	5.88	5.6	4.95	-13.68
GO-0.1 B	1.0	28	2	2	1.8	4.76	5.32	5.32	4.67	-18.85

Appendix G: Flexural strength values of GO + CB cement composite

Sample	Mass fraction %		Force /KN			Strength/MPa			Average Flexural Strength/ MPa	Increase%
	CB (wt)	GO (wt)	**1**	**2**	**3**	**1**	**2**	**3**		
Control	0	0	1.9	1.9	1.8	5.32	5.32	5.04	5.23	-
CB – GO E	0.3	0.03	2.3	2.5	2.4	6.44	7	6.72	6.72	19.89
CB - GO F	0.3	0.04	3.1	2.9	3	8.68	8.12	8.4	8.40	60.61
CB – GO G	0.4	0.03	2.7	3.1	2.6	7.56	8.68	7.28	7.84	49.90
CB – GO H	0.4	0.04	2.1	2.4	2.1	5.88	6.72	5.88	6.16	17.78