



The influence of graphene oxide nanosheets on concrete properties on micro level

BY
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of the requirements for the degree of Masters in Civil Engineering

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AUTHORSHIP STATEMENT

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ABSTRACT

The thesis investigates the effects of graphene oxide (GO) as an additive in cementitious materials. This research aims to assess the benefits of employing graphene oxide as a reinforcement material on a nanoscale and primarily investigates how graphene oxide affects the microstructure of concrete. Although concrete is a fantastic material in compression, it is brittle and has low tensile and flexural strengths. Therefore, in the concrete research community, novel materials, particularly nanomaterials, capable of strengthening concrete and improving its properties on a nanoscale are of great interest. Graphene oxide nanosheets have demonstrated excellent qualities and promising outcomes in enhancing concrete's mechanical properties and microstructure. The first part of the thesis focuses on the literature review and previous discoveries in graphite-based materials. Then, studies about integrating graphene oxide into concrete materials and numerous previous test results are covered. The final section of this thesis focuses on experimental work. The impact of GO nanosheets on the microstructure of concrete samples containing GO at 0% and 0.03% by weight of cement and cured for 21 days will be thoroughly examined using nanoindentation test and SEM analysis. In addition, the experiment will investigate the mechanical parameters such as tensile strength and compressive strength of concrete samples cured for 28 days.

Keywords: graphene oxide, nanosheets, nanomaterials, nano-reinforcement, concrete reinforcement, concrete additives

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1. Introduction

In terms of volume, concrete is one of the most widely used building materials on earth. Due to its high compressive strength and widely available components such as aggregates, sand, cement, and water, concrete has been used in construction extensively. Strength and durability are the two most essential qualities of concrete when designing structures for load-bearing capacity and service life [1]. The strength of concrete is its capacity to withstand and resist compressive, flexural, tensile, and shear stresses and other external forces. The durability of concrete is its ability to resist aggressive environmental conditions during its service life [1]. Various factors affect the final properties of concrete, like the proportion of raw components, curing period, mixing process, and curing conditions [2]. Despite its remarkable compressive strength, concrete is weak in tension and has low strain capacity. Its tensile strength is approximately 10% of its compressive strength [3], ranging between 2-8 MPa [4]. As a result, concrete is brittle material when tensile forces are applied, leading to cracking and ultimately failure. Thus, its tensile strength properties are less considerable when designing structures.

For the past few decades, researchers have been coming up with several techniques for reinforcing the tensile strength of concrete. The steel bars and fibers are the most used materials in reinforced concrete structures [5]. Furthermore, over time, many additives and admixtures have been created to increase the performance of the concrete material. These reinforcing technologies can significantly increase concrete tensile strength and were the only way to reinforce concrete structures till recently. However, several limitations still exist with using these traditional reinforcing procedures. Corrosion in steel bars, for example, can develop due to chloride penetration through cracks and potentially compromise the load-bearing capacity. In

addition, studies show that large quantities of fiber reinforcement in fresh cement paste can significantly reduce its workability [6].

Another disadvantage of concrete material is that its primary component, cement, contributes to carbon dioxide pollution, owing to manufacturing waste and extensive water use and disposal. On average, cement accounts for 6 percent of global carbon dioxide emissions, with each ton of concrete containing between 100 and 300 kilograms of CO₂ [7, 8]. Moreover, with the new construction works developed every day to meet the world's rising population demand, the usage of concrete as the primary construction material is becoming unsustainable.

Therefore, there is a great need to explore new materials and technologies and adopt methods of concrete enhancement superior to existing ones. Traditional concrete reinforcing methods were focused on improving reinforcing materials, whereas possibilities of concrete's microstructure modification were somewhat neglected [5]. With the rapid development of diverse nanomaterials in recent years, numerous have been applied and tested in concrete technology. Researchers used different nanomaterials to reinforce concrete and improve its characteristics, including carbon nanotubes, silica nanoparticles, titanium dioxide, graphene, and graphene derivatives. [6]

Notably, the graphene oxide (GO) - particular graphene derivative holds excellent properties such as ultrahigh strength, flexibility, and large surface area, thus, tremendous potential for integration with cementitious materials. When mixed with water, GO disperses well compared to other nanomaterials due to many oxygen functional groups, creating a stable solution [6]. In many studies, a small percentage of graphene oxide addition significantly improved concrete's strength and durability [9]. "The Graphenano", a firm specialized in graphene industrial usage, claims that its graphene additive can reduce cement usage by 30%

without compromising the strength of concrete [10]. It is feasible to reduce the amount of concrete material required for building by improving the strength of concrete. In the future, if graphene oxide additive will be broadly used in the construction field, the benefits of utilizing this excellent material can provide savings on construction materials, transportation, labor, and working hours for a particular project. Also, it may considerably reduce carbon dioxide emissions, which in turn contributes to the sustainability of the industry in general.

The thesis will investigate graphene oxide (GO) as an additive in concrete material. Two concrete mix designs will be made in the experimental work, one with a 0.03% GO additive and the other with a plain concrete mix. SEM (Scanning Electron Microscopy) and nanoindentation test will be utilized to determine the impact of GO nanosheets on concrete microstructure. Also, the compressive and tensile strengths of the samples will be evaluated using a standard compressive test method and notched three-point bending test, respectively, after 28 days of curing.

2. Concrete technology

2.1 Reinforcing techniques in concrete technology

The researchers found the first traces of cementitious binding materials in southern Italy used during the Roman Empire in the second century BC [11]. However, modern Portland cement was not invented until the nineteenth century [12]. Because of its poor tensile strength, plain concrete was not generally employed in construction prior to the introduction of reinforcing materials. Jean-Louis Lambot utilized wire mesh and iron bars to construct concrete rowboats in 1848, which was the first practical application of reinforced concrete [13]. In 1867, Joseph Monier patented reinforced concrete material [2]. He used reinforced concrete to produce garden tubes and pots.

Steel bars are the most common type of concrete reinforcement. Because steel has a high tensile strength, a minimal amount is sufficient for reinforcing. Reinforcement, when properly applied, improves not only the tensile but also the compressive strength of concrete. Stirrups bars are commonly used to resist shear stresses. Ties, hoops, and spiral bars are employed in column reinforcement. Furthermore, because concrete and steel can form a perfect bonding, they can expand and shrink at roughly the same temperature while acting together to transfer the applied loads. [14]

Round steel bars are manufactured plain for stirrups and ties or with deformation used for main reinforcement. Deformed bars are designed that way to increase the mechanical bonding between steel and concrete. They are available in a variety of diameters and lengths. Also, steel reinforcements can be welded together as a mesh at a 90-degree angle, saving much time on the construction site. [2, 14]

Fiber-reinforced polymer (FRP) is another material that is commonly used to reinforce concrete. Microfibers come in various shapes and forms, including bars, cables, grids, sheets, and plates. The length of the fiber reinforcement ranges from 1 to 10 cm, while the diameter ranges from 0.1 to 1 mm [15]. The earliest fiber reinforced concrete (FRC) research began in the 1960s and continues today [4]. Fiber-reinforced polymers are often manufactured from glass, carbon, and aramid fibers. FRP in the shape of bars can be used in place of steel bars. They are composed of fibers embedded in resin to keep them together and form a bar shape. The significant feature of FRP bars is that, unlike steel bars, it is light in weight and does not corrode. As a result, engineers prefer to use them in bridges or chemical facilities where steel corrosion might happen. However, the fibers are usually oriented irregularly in the concrete material and do not withstand well tensile forces like steel bars [45]. Another disadvantage of FRP bars is that they are not as ductile as steel and fail abruptly once their ultimate tensile strength is reached [14].

Carbon fibers have an elastic modulus of over 200 GPa and tensile strength of 3.5 GPa. They are often used for retrofitting steel and concrete structures. Glass fibers have an elastic modulus of 72.4 GPa and tensile strength of 3.45 GPa, which improves cement composites' tensile and flexural strengths. In addition, studies have shown that microfibers can reduce large cracks by generating bundles of microcracks. However, fibers cannot prevent or lessen the number of cracks that emerge and have the disadvantage of entrapping air voids in concrete structures. [4]

2.2 Concrete additives and admixtures

Additives are chemical ingredients mixed into cement to change or improve its qualities during manufacturing. Researchers have developed many additives since the 1960s due to new and expanding high-strength concrete technologies. Silica fume, fly ash, blast furnace slag, and metakaolin are examples of mineral additives employed to improve cement properties [16, 4]. Other additives could be different chemicals serving different purposes. For example, accelerators shorten the time it takes for cement to set, whereas retarders, on the other hand, lengthen the time it takes for cement to set. Dispersants are used to reduce the viscosity of cement slurry, and a variety of fluid loss control agents are utilized to regulate water loss from the cement. [17]

Admixtures are substances added to concrete before or during the mixing process to improve its qualities. They are frequently used to improve concrete workability, reduce water content, boost strength and durability, and even manage the freezing point of water. Admixtures make up a small percentage of the total concrete mix, but they significantly impact the final structure's physical and chemical properties. Accelerators, anti-freezers, water reducers, air-entraining admixtures, and shrinkage compensating admixtures are all popular types of admixtures. Admixtures such as lignosulfonates, hydroxylated carboxylic acids, and salts of wood resins are used to decrease water content, while salts of wood resins and salts of petroleum acids are used to entrain air. [17, 18]

2.3 Nanomaterials in concrete technology

Nano-reinforcing materials range in size from 1-100 nm [15] (Fig.1) and are used to alter and restructure host material characteristics at the nanometer scale. The term "nano-concrete" refers

to concrete that contains nanoparticles with diameters smaller than 500 nanometers [16]. The purpose of using nanotechnology in concrete technology is to improve the microstructure of concrete to change the qualities and strength properties at the macroscale. Concrete may be modified at the nanoscale in both solid and liquid phases. [19]

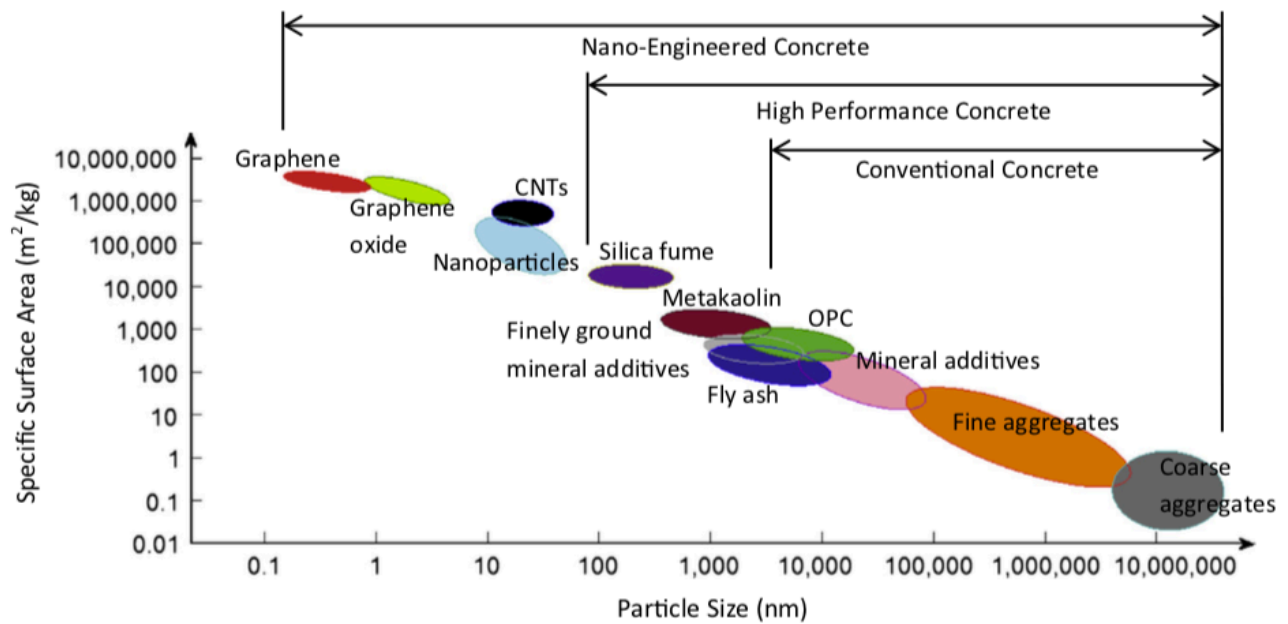


Figure 1. Size comparison of nanomaterials with other concrete components. [4]

Nanotechnology transforms traditional materials into new, superior materials that can self-sense, self-clean, and even self-control crack formation. Nanoparticles also act as fillers in the concrete mixture, filling the interfacial transition zone (ITZ) and resulting in a denser structure [16]. Even in small amounts, nanomaterials can significantly alter the characteristics of the host material [20].

Since its development, there has been much interest in using nanotechnology in concrete material. Nanomaterials such as nano-titanium oxide (nano-TiO₂), nano-silica (nano-SiO₂),

carbon nanotubes (CNTs), graphene sulfonate nanosheets, and graphene oxide nanosheets (GO) have all been investigated and tested as a concrete reinforcement [20]. Nanomaterials are classified into three types: 0D nanoparticles such as nano-silica, 1D nanofibers such as carbon nanotubes, and 2D nanosheets such as graphene oxide [4]. Researchers found that these nano-reinforcements can prevent microcracks from forming in the first place. They are more effective than traditional steel bar reinforcement because they prevent nanoscale cracks from becoming microcracks [21]. Also, because the spacing between the nanoparticles is minuscular compared to microfibers, they can be distributed more evenly and at a lower content [4].

Nano-silica improves concrete's strength, workability, and resistance to water penetration. Nano-titanium oxide helps concrete with self-cleaning properties and purifies the surrounding air. Also, some studies show that titanium dioxide helps concrete acquire its strength at an earlier age and increases its abrasion resistance. Carbon nanotubes are a possible substitute for tension reinforcement in cement-based materials due to their extremely high strength and high moduli of elasticity. Nanotubes have a long hollow structure formed by a one-atom-thick sheet of carbon. Nanotubes come in two forms, single-walled nanotubes (SWNT) and multi-walled nanotubes (MWNT). However, their application in reinforced concrete material is limited due to their high costs. [16, 19]

In general, there are two methods for producing nanomaterials (Fig.2), top-down and bottom-up methods. Larger particles are decreased in size to nanoscale using the top-down method without losing their initial qualities. For example, manufacturers use special milling machines for the milling technique. The disadvantage of this approach is that the end products are more likely to contain defects and inconsistent characteristics. Bottom-up engineering, also known as molecular nanotechnology, assembles atoms or molecular components. The size and

form of the nanoparticle can be modified in this manner to get the desired qualities. The disadvantage of this technology is the high cost of operation and the requirement for highly qualified personnel who can manipulate the material at the molecular level. As a result, researchers use this approach in more advanced applications such as electronics and biotechnology. [16]

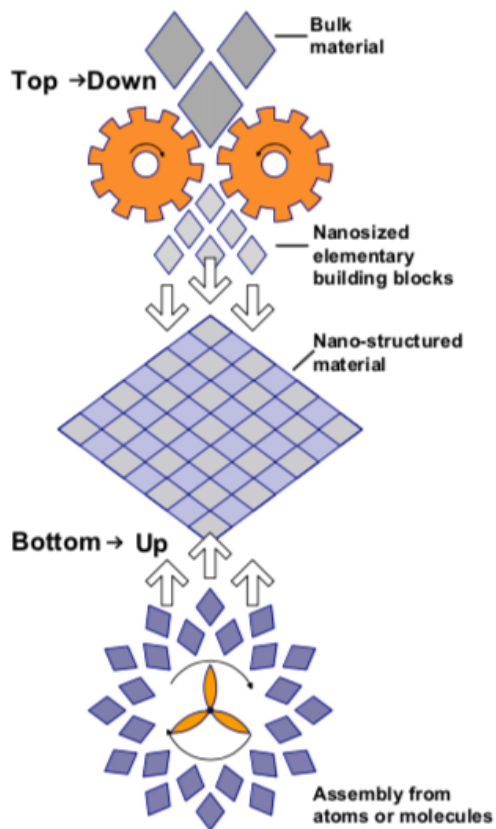


Figure 2. Top-down vs. bottom-up methods of synthesizing nanomaterials [19]

3. Graphite and its derivative graphene

3.1 Introduction

Graphite is one of three naturally occurring allotropes of carbon atoms, along with amorphous carbon and diamond. The term "allotrope" refers to an element where the atoms are the same, but their structural arrangement varies [22]. This mineral can be found all over the world in metamorphic rocks. The lattice bond structure of carbon atoms determines a material's strength and toughness. A diamond, for example, has four atoms connected by a single covalent bond, resulting in a three-dimensional structure. On the other hand, graphite atoms are organized in a two-dimensional pattern composed of thin layers of carbon atoms connected in a honeycomb lattice (Fig.3). [23, 24]

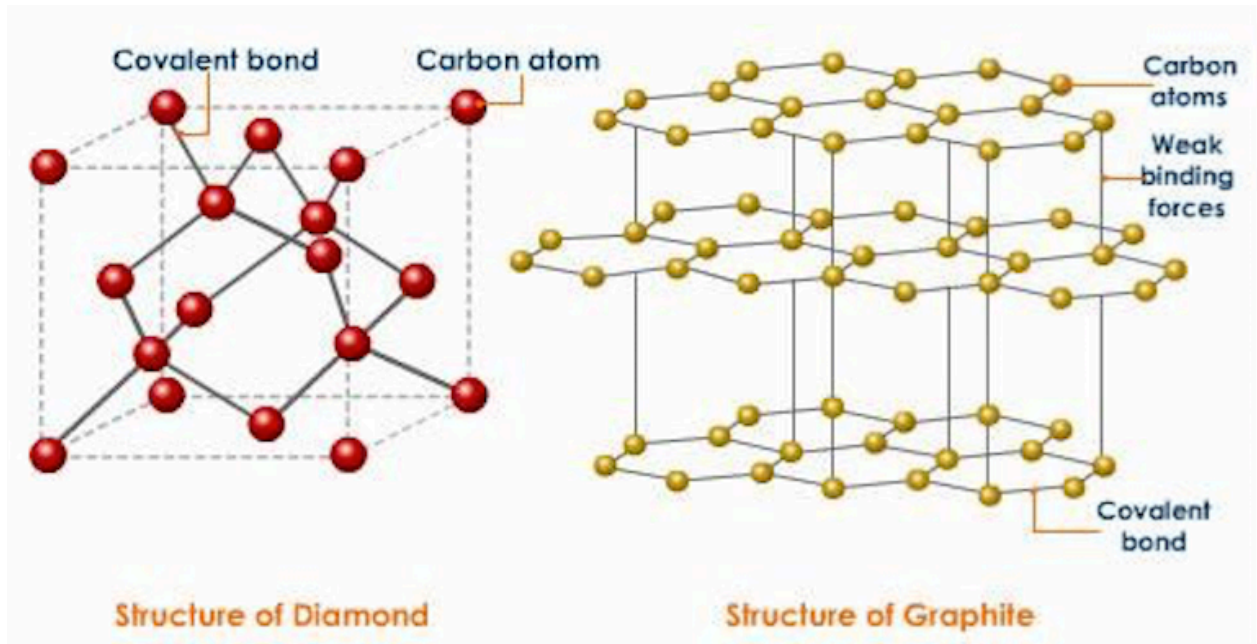


Figure 3. Atom arrangement of a diamond vs. a graphite [25]

Graphene is a single layer of graphite material. It is composed of carbon atoms organized in a hexagonal lattice to produce a single layer of a thin sheet (Fig.4). Researchers estimated around three million layers of graphene sheets in 1 mm thick graphite because one carbon atom has a diameter of approximately 0.33 nm [32]. These graphene sheets are available in various shapes (Fig.5), including 0D, 1D, and 2D [26].

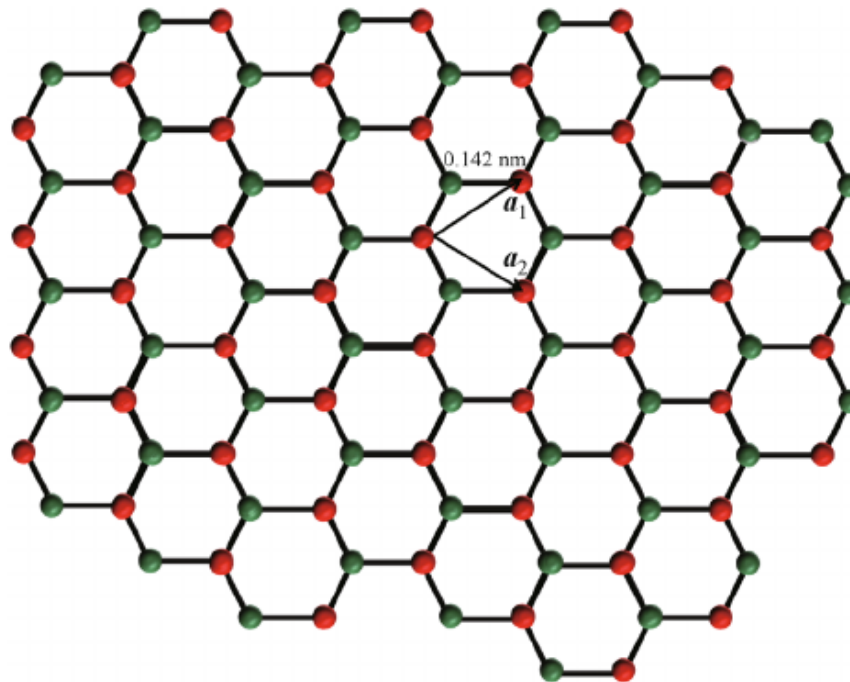


Figure 4. Atom arrangement of graphene [27]

Since the first successful separation of the graphene sheets, interest in graphene's usage in material science has grown significantly. Mechanical exfoliation, often known as the sticky tape technique, is one method for isolating graphene. However, the most efficient method is to employ the chemical vapor deposition (CVD) process. This method removes carbon atoms from a carbon source via a reduction process. [22, 28]

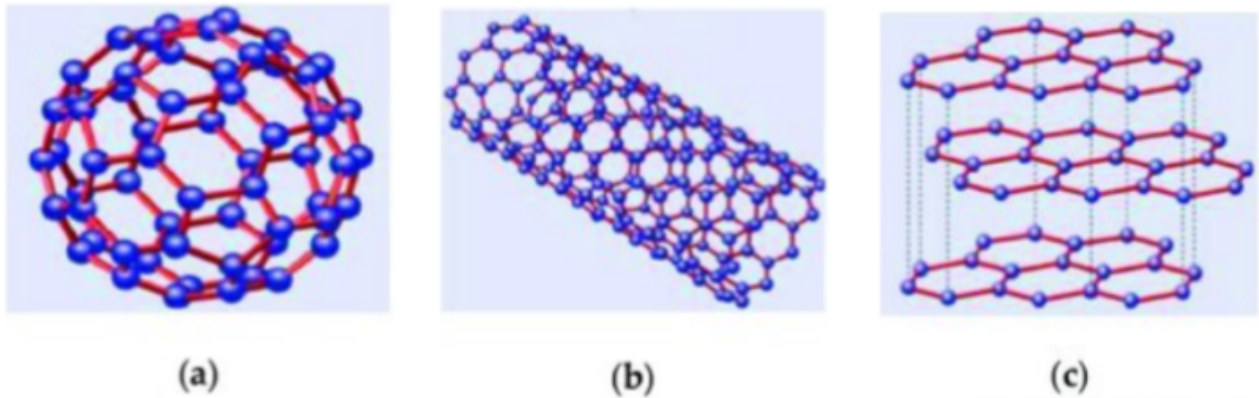


Figure 5. Different forms of graphene sheets: a) 0D graphene nanoparticle; b) 1D rolled graphene sheet; c) 2D graphene sheet. [29]

In 2004, Russian physicists Andre Geim and Konstantin Novoselov from the University of Manchester discovered graphene for the first time. To obtain the thinnest coating of graphene, they used the mechanical abrasion process, sometimes known colloquially as the "scotch-tape" method [31] or adhesive tape technique [23]. Two sticky tapes were used over graphite flakes in the process. They removed tapes one by one until only one layer of carbon atoms was left. [31]

The graphite layers have a weak van der Waals bond; thus, mechanical, chemical, or electrochemical forces can easily separate the bond. As mentioned before, there are two general ways to synthesize graphene sheets: one is by bottom-up method, and the other is top-down. The bottom-up method incorporates the growth of graphene from carbon-rich compounds [32] on silicon carbide [8] with control of its defects and layers. The top-down method comprises exfoliating graphite until a single graphene sheet is obtained. Both methods work well, but the bottom-up method is more costly and defect-free and primarily used in electronics or solar cells. The top-down method is an easier way to obtain graphene and can be used on an industrial scale, but the resulting graphene will be of lesser quality. [30]

One issue developers are now facing is the production of good-grade graphene in large quantities. The quality of the graphene sheets is essential because any impurities and defects can affect the final properties of the product [32]. Currently, high-quality graphene sheets are utilized in research facilities, while producers in electronics and sports equipment use lower-quality graphene flakes. Because graphene is a superb semiconductor and ultra-lightweight material, its application in electronics is quite appealing. [7] Graphene has been studied and utilized in several applications, including lithium battery replacement, usage in computer circuits, solar cells, and energy producers, to mention a few [22]. However, graphene's great strength and low weight are of great interest in the construction industry [7].

3.2 Properties of graphene

The properties of graphene sheets are summarized in Table 1. In general, graphene is the strongest material on earth, with the tensile strength of 130 GPA and Young's Modulus of 1 TPa, assuming a thickness of 0.335 nm [32, 33]. According to Berkeley Laboratory experts, graphene is 200 times stronger than steel, weighs less than paper [7], and acts as a molecular barrier [34]. The excellent mechanical properties of graphene are associated with its in-plane strong sp^2 covalent bond and its atomic thickness [30]. Furthermore, the thin graphene sheets are flexible, translucent, water-impermeable, and conduct electricity better than most metals. For example, its electric conductivity is 6500 s m^{-1} , which is thirteen times better than copper metal [32, 34].

According to research, semi-conductive polymers conduct electricity better when put on top of graphene rather than a typical silicon material [35]. In addition, the electron mobility of graphene is $25 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, and fracture toughness is 4 MPa [32, 34]. On top of that, graphene is a

perfect material for thermal conductivity with $3000-5000 \text{ W m}^{-1}\text{K}^{-1}$, making graphene one of the highest thermal conductive materials known [34].

Because graphene has a 2D planar structure, it attaches perfectly from both sides to the material with which it is used. The theoretical specific surface area of graphene is $2630 \text{ m}^2/\text{g}$. In principle, a larger surface area will be advantageous in terms of better bonding with other materials. [6]

Also, according to studies [30], graphene sheets are highly impermeable and can act as a physical barrier. It does not allow even the smallest molecules of helium to pass through. Due to this quality, researchers used graphene to create composite materials like anti-corrosion epoxies.

Table 1. Properties of a single sheet of graphene

Thickness	0.335 nm
Young's modulus	1 TPa
Tensile strength	130 GPa
Fracture toughness	4 MPa
Surface area	$2630 \text{ m}^2/\text{g}$
Electrical conductivity	6500 s/m
Thermal conductivity	$3000-5000 \text{ W/m.K}$
Electron mobility	$25 \text{ m}^2/\text{V.s}$

3.3 Application in concrete technology

Graphene can be used as a concrete additive. The addition can be used in building construction and bridge, tunnel, and harbor designs due to its excellent resistance to water penetration. Also, the additive increases the durability of concrete by making it more resistant to carbonation,

chlorides, and sulfates attacks. The graphene additive developed by the Graphenano company is expected to enhance concrete durability qualities and extend the service life of buildings by 30 years. [10]

Researchers at the University of Exeter in the United Kingdom used graphene flakes as a nano additive in the concrete mixture. As a result, they discovered that concrete's compressive strength improved by 146%, flexural strength climbed by 79.5%, and water resistance increased by roughly 400%. Furthermore, Concrete Technology claims that its graphene addition boosts concrete compressive strength by 40% and flexural strength by 70%, implying that less steel reinforcement is required. As a result, researchers believe reducing one cubic meter of regular concrete to 0.85 cubic meters of graphene-enhanced concrete is possible. Also, studies show that graphene particles fill up porous structures in concrete, lowering overall porosity and cutting water permeability by about 300%. These advantages of graphene additive can potentially impact future construction quality and costs. [9, 33]

3.3.1 Thermal and electric conductive concrete

Researchers discovered that one of the advantages of graphene-reinforced concrete is the ability to conduct electricity. According to tests [31], graphene conducts electricity 100 times faster than conventional silicon, and also it is a better heat conductor than most metals. Electrically conductive concrete will have many applications in the future, like heating living spaces, melting ice and snow on the pavement, and so on. Another application could be using the conductive property to monitor the structure itself. For example, self-sensing monitors could be installed in graphene-enhanced structures to measure the amount of strains, deformation, and cracking in the concrete during its lifetime.

In February 2019, the Italcementi company presented a new floor heating system (Fig.6) with a thin layer of graphene-concrete between the screed and the surface. The concrete produces heat by transforming the electric energy into thermal. This technology can be used in the same way for heating the outside pavements during winter times. [31]

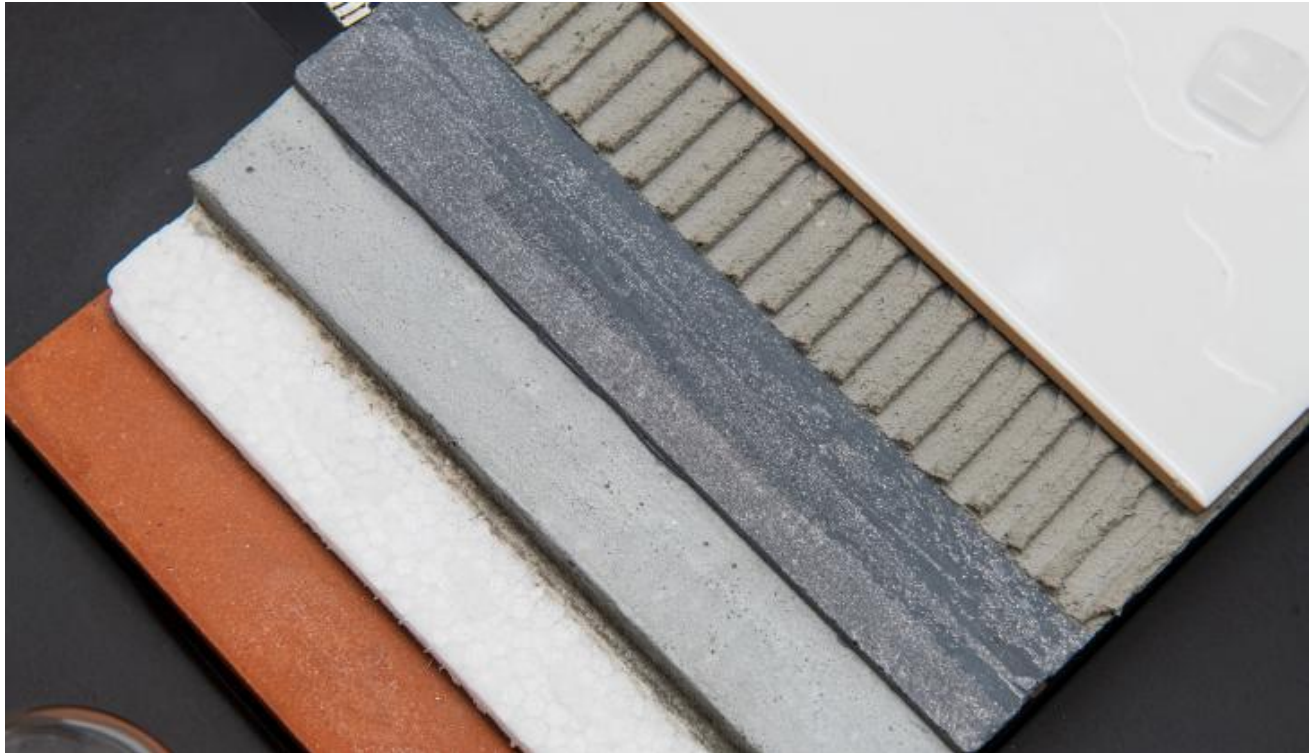


Figure 6. Italcementi's floor heating system using graphene-enhanced concrete. [31]

Researchers at Talga Resources Ltd. achieved electric conductivity in graphene concrete of about 0.05 ohm-cm volume, where ohm measures the resistivity of a material to conduct electricity. In comparison, ordinary mortar has a resistance of around 1,000,000 ohm-cm. Talga hopes to replace the traditional water-pumped heating system with electrically conductive

concrete floors with these discoveries. Also, they are investigating ways for making wireless charging technologies for electric cars while driving and during parking. [36]

3.3.2. Self- sensing concrete technology

Self-sensing technology has become an integral structural element, as significant budgets are spent on repair and maintenance each year. Self-sensing and self-monitoring concrete implies that it can keep track of the harm it has sustained. The capacity of a material to self-sense is dependent on its electrical resistivity. Electrical resistivity is a property of materials that indicates how much electricity may flow through them. The resistivity of concrete materials is dependent on the water-cement ratio, aggregates, additives used, and the material's age. Concrete acts as an electrolyte while wet but almost does not carry electricity when dry. [8]

When a particular quantity of functional fillers is applied, it creates a continuous route for current to travel through the concrete. Several forms of functional fillers, including steel, carbon fibers, graphite powder, and graphene oxide, were utilized and evaluated for this purpose. Graphene oxide as an additive has demonstrated significant potential for usage in self-sensing applications. Current flowing through the material can be utilized to assess the type of damage produced by cyclic loads. The idea behind this is, if a crack forms, a continuous electric current will be broken, and a signal of damage can be sent to the monitoring equipment and repaired on time. [8]

4. Graphene Oxide

4.1 Introduction

Nanomaterials, in general as reinforcement material in concrete, have several drawbacks: they do not disperse properly in the cement matrix. Graphene is not an exception. In addition, other disadvantages of graphene include its bottom-up production and tendency to agglomerate in a solution. So instead, researchers developed graphene oxide using an oxidation process from graphite or other carbon sources (Fig. 7). In 1859, British chemist Benjamin C. Brodie discovered graphene oxide almost accidentally by exposing graphite to strong acids [32, 37]. Later, Staudenmaier and Hummers devised a safer approach for producing high-quality GO from graphite flakes [38].

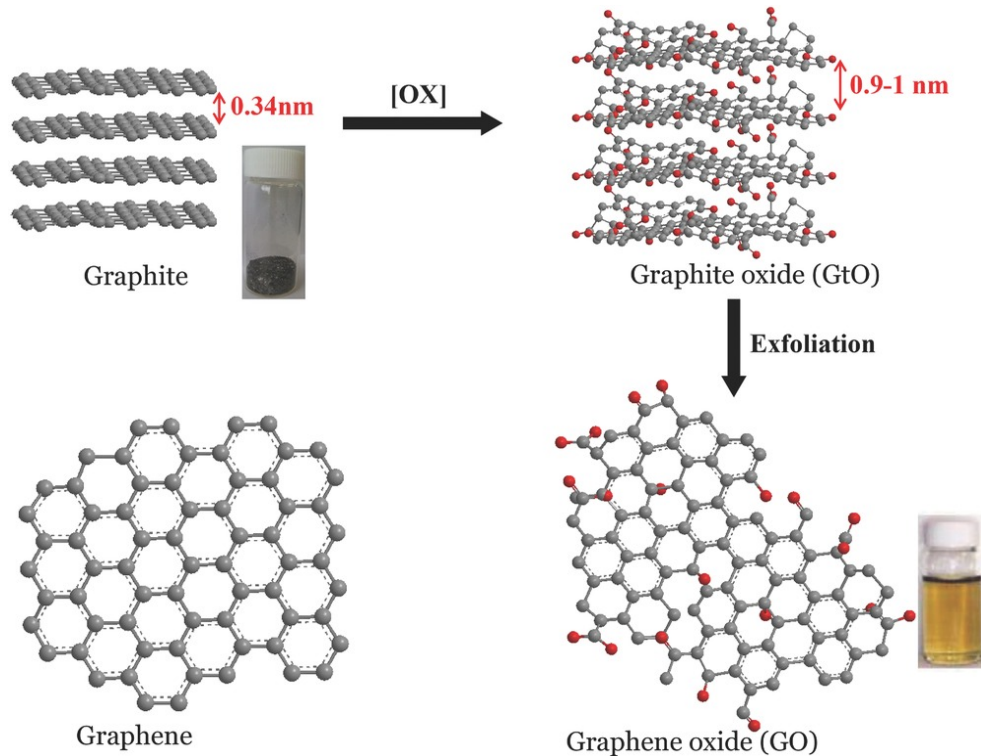


Figure 7. Oxidation process of GO from graphite [5]

Graphite is first oxidized to form graphite oxide, then exfoliated to produce single graphene oxide layers ($C_{54}H_{17}+O+(OH)_3+COOH$) [1]. The van der Waals forces between the sheets are changed because oxidative functional groups are connected to GO sheets' basal planes and edges. During the oxidation process, the interlayer distance of graphite layers widens from 0.335 nm to 0.65 nm graphene oxide layers. Also, the addition of functional groups makes GO extremely hydrophilic and easily exfoliated in water, resulting in a stable dispersion of single-layered sheets. The effect of oxygen content on GO dispersion is self-evident; dispersion improves as oxygen levels rise. However, the structural defects increase as the oxygen content increases. Thus, regulating the number of functional groups is important to attain good quality GO sheets. Also, small amounts of silica fume nanoparticles could be added to the cement mixture to improve graphene oxide dispersion properties. [6, 21, 34, 37, 38, 57]

Graphene oxide consists of monolayer sheets of sp^2 and sp^3 hybridized carbon atoms with a hexagonal carbon network. The carbon atoms are covalently linked to various functional groups, such as hydroxyl (-OH), alkoxy (C-O-C), carbonyl (C=O), and carboxylic acid (-COOH) (Fig.8). [30, 34, 39]

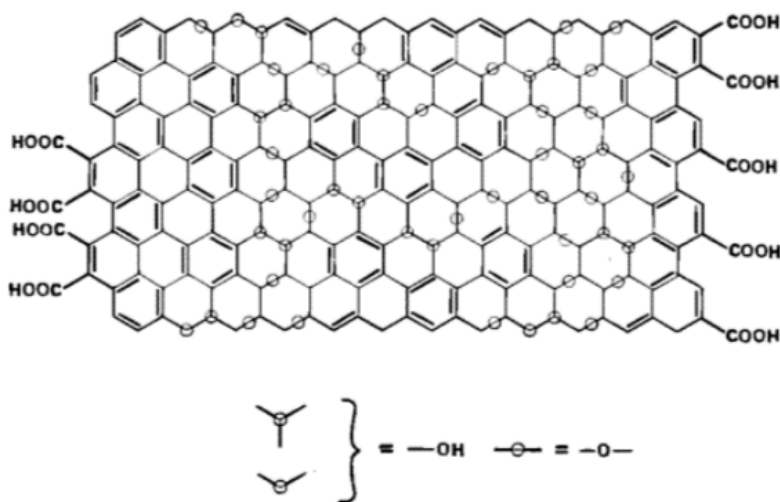


Figure 8. Oxygen, hydroxyl and carboxyl groups in graphene oxide [6]

The biggest downside of adding graphene oxide into concrete is that its relatively high surface area hinders the workability of fresh cement paste. Nonetheless, investigations show that even a tiny amount of 0.01 percent to 0.05 percent GO content by weight of cement can significantly boost the mechanical strengths of concrete. Also, researchers showed that GO nanosheets could affect the microstructural morphology of the concrete phases and increase the formation of main hydration products. [20, 40, 41]

4.2 Properties of graphene oxide

During the fabrication process and introduction of functional groups, the sp^2 bonding orbitals of graphene get disrupted, and GO loses some of the superb properties of graphene. Due to this, unlike graphene, GO is electrically resistive ($1.64 \times 10^4 \Omega \text{ m}$) and has low thermal conductivity ($0.5\text{-}1 \text{ W m}^{-1}\text{K}^{-1}$). The low thermal conductivity properties of GO were tested in the usage of fillers in flame retardants and shown to improve flame retardant properties. [32,34]

Also, the functional groups degrade the mechanical properties of graphene, and GO exhibits lower elastic modulus and tensile strength than graphene. Chuah et al. [4] found that the elastic modulus of GO was between 23-42 GPa, with a tensile strength of 0.13 GPa, and a surface area between 700-1500 m^2/g . Smith et al. [34] estimated the Young's modulus of GO to be around 207.6 ± 24.3 GPa. According to the studies in [43], the theoretical Young's modulus can range from 290-470 GPa, and the tensile strength can range from 30-60 GPa. The GO properties' variation depends on the number of surface groups, the thickness of GO sheets, defects from the manufacturing processes, and the layout of its structure (ordered or amorphous) [34, 43]. As

coverage increases, tensile strength and Young's modulus decrease due to the breakdown of the sp^2 carbon structure. Also, researchers discovered that the Young's modulus of a monolayer GO sheet was significantly greater than that of a thick GO sheet.

4.3 Synthesis of graphene oxide

In the present day, the only way to mass-produce GO for large-scale applications is to use a chemical oxidation process. Brodie used potassium chlorate ($KClO_3$) to mix with graphite in nitric acid (HNO_3); however, the by-product was difficult to purify. Later, Staudenmaier modified Brodie's approach and added $KClO_3$, H_2SO_4 , which minimized the explosion risk but still generated toxic ClO_2 gas. However, in 1958, Hummers and Offeman came up with a further modified method, a safer and more scalable way of oxidizing graphite, which is now known as the Hummer's method. [34, 57]

In brief, Hummer's method is a top-down approach and includes three steps: oxidation, purification, and exfoliation. First, functional oxygen groups are introduced by oxidizing graphite, converting graphite into hydrophilic graphite oxide, and increasing the distance between its interlayers. A mixture of concentrated sulfuric acid (H_2SO_4), sodium nitrate ($NaNO_3$), and potassium permanganate ($KMnO_4$) are used in the oxidation process. Graphite oxide is purified using hydrochloric acid to eliminate any remaining ions (such as K^+ , H^+ , Mn^{2+} , N^+ , NO_3^- , SO_4^{2-}) and contaminants. The unexfoliated graphite oxide, present in minute proportions, is removed by centrifugation. After that, dialysis is employed to remove any remaining salts or acids from the graphite oxide. At last, graphite oxide layers are reduced to GO sheets by the exfoliation process. [4, 30, 34, 57]

All of these methods of oxidizing generate toxic gases in small amounts, such as NO_2 , N_2O_4 , ClO_2 , and form an exothermic reaction that has a risk of exploding. Thus, researchers are coming up with new ways to improve the Hummers' method further and reduce the side effects of the chemical oxidation process. Any other methods that improve Hummers' method are referred to as "modified Hummers' method". [34, 57]

4.4. Dispersion of graphene oxide

Some studies [4] show that GO does not require additional surfactants for dispersion. Because of its functional groups, it disperses well in water. However, a large number of ions (Na^+ , K^+ , OH^- , Ca^{2+} et.) [44] present in fresh cement paste and the van der Waals forces between the nanosheets can affect the efficacy of GO dispersion [39]. The excellent dispersion is essential for GO to work well as a reinforcing material. Ultrasonication, stirring, calendaring, ball milling, shear mixing, and extrusion are the mechanical processes that researchers often use. The most common method for dispersing GO in liquid solutions is using ultrasonication. It uses an ultrasonic probe to generate excitation energy that breaks apart nano clumps. [4] However, some studies have shown that ultrasonication and other mechanical methods were more effective in dispersing GO in water and failed to do so in the Ca^{2+} of cement matrix [44]. Thus, different methods should be used along with mechanical processes.

Adding various surfactants is another technique to optimize nanomaterial dispersion. Surfactants function by decreasing the surface energy of nanofillers. However, some surfactants can have an adverse effect on the hydration products of concrete; thus, they have to be used with care [44]. According to many studies, Polycarboxylate (PCE) based water-reducing admixture is the most effective among the several types of chemical admixtures tested [4]. Because the PCE

has a comb-like molecular structure, it better adsorbs on the GO surface [44]. Also, Korayem et al. [42] and Zhao et al. [44] found that silica fume (SF) and metakaolin (MK) can aid in some way the dispersion of GO nanosheets as well as contribute to the compressive strength of tested composites.

In general, researchers recommend using the combined methods of ultrasonication and the addition of PCE for the most effective GO dispersal. The dose of PCE and the sequence of combining PCE and GO with water and cement are critical for them to work. Most studies suggest PCE and GO to be combined with water first, then mixed with cement, not vice versa. When PCE is added after combining GO with cement, it can no longer disseminate GO particles because GO and calcium ions already create a rapid chemical reaction when mixed. [44]

4.5 Field experiments and tests

4.5.1 GO effects on hydration of cement

A large number of chemical reactions occur during the mixing of cement with water, and this process is known as cement hydration. The cement mainly consists of tricalcium silicate C_3S (Ca_3SiO_5), dicalcium silicate C_2S (Ca_2SiO_4), tricalcium aluminate C_3A ($Ca_3Al_2O_6$), tetracalcium aluminoferrite C_4AF ($Ca_4Al_nFe_{2-n}O_7$), clinker sulfate (Na_2SO_4 , K_2SO_4), and gypsum ($CaSO_4 \cdot 2H_2O$). Upon adding water four types of minerals that are alite (C_3S), belite (C_2S), aluminate (C_3A) and ferrite (C_4AF) will carry out an intricate hydration reaction that forms ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$, AFt), $Ca_4Al_2(OH)_2 \cdot SO_4 \cdot H_2O$, AFm), calcium silicate hydrate ($3CaO \cdot 2SiO_2 \cdot 4H_2O$, C-S-H) gel, and calcium hydroxide ($Ca(OH)_2$, CH). In other words, the resultant matrix will consist of CH (Portlandite), unhydrated clinker, small amount of

capillary pores, and the main binding C-S-H gel (Calcium-Silicate-Hydrates), which will account for up to 60-80% of the total volume. The density and crystal structure of this C-S-H gel is critical for forming the final mechanical characteristics of the concrete. As a result, it is vital to understand the structure of C-S-H and look for methods to enhance its formation. [4-6, 15]

Researchers found that nanoparticles have pozzolanic capabilities, producing C-S-H from non-strength contributing CH (calcium hydroxide) crystals [4]. According to studies [5, 44, 45], GO additive can improve the degree of hydration of calcium hydroxide (CH) and calcium silicate hydrate (C-S-H) during the development stage by filling pores and having a bridging effect [39]. Furthermore, the large specific surface area of GO has been demonstrated to offer nucleation sites for hydration products and a seeding action that promotes the growth of hydration products on the surface. [4, 44, 45]

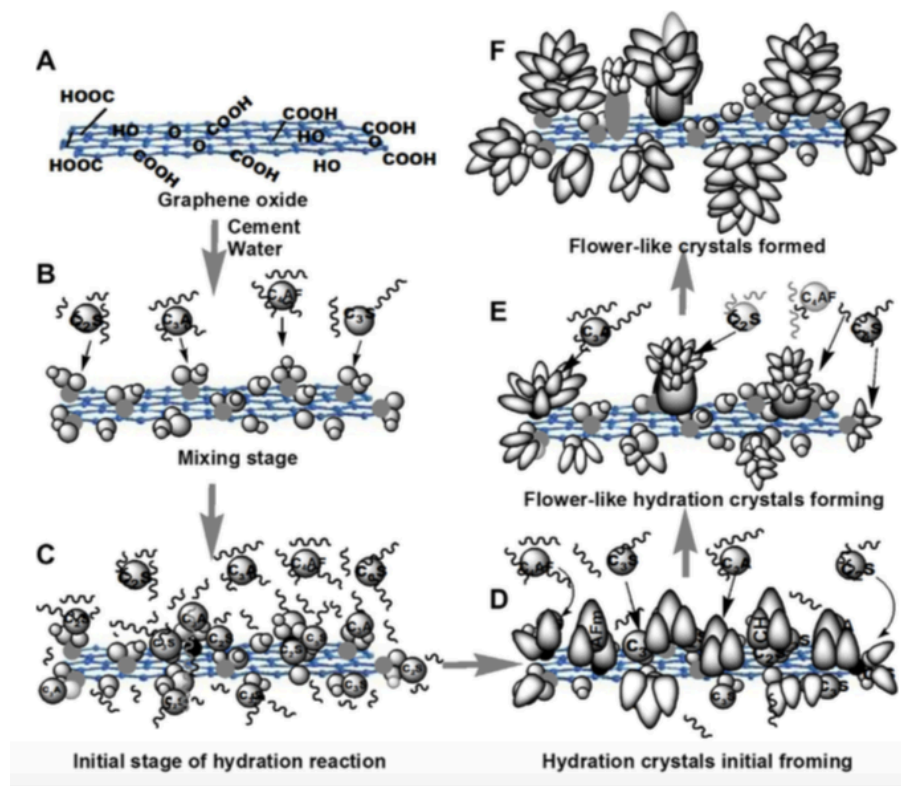


Figure 9. A cement hydration process in concrete with GO nanosheets. [5]

In (Fig.9) hypothetical reaction sequence shows how the addition of GO affects the hydration process. In a) GO surface has oxygen functional groups, primarily -OH, -COOH, and -SO₃H, which react chemically with b) C₃S, C₂S, and C₃A, in c,d) hydration reaction occurs, and in e,f) more round-shaped hydration products begin to form on the GO surface. The generated round-shaped crystals fill the pores in the cement composite and act as a connecting bridge, considerably increasing the concrete's mechanical properties. [5]

4.5.2 Effects on workability of fresh cement paste

Concrete must be workable to be transported and compacted properly on the construction site. Fewer air voids get trapped in the concrete mixture with thorough compaction, influencing its mechanical qualities. Several studies indicate that GO has a negative impact on the workability of cement composites. The large surface area of GO nanosheets and hydrophilicity of the 2D flat surface requires more water to saturate a large surface and, in return, decreases the amount of available water in the fresh concrete mixture [4, 37, 39]. Polycarboxylate ether-based superplasticizer or fly ash might be used in the mixture to remedy this problem partially [4, 46]. In addition, researchers found that PCE helps release the entrapped water in the cement mixture and disperse cement grains that could increase water content to wet GO nanosheets [44]. However, completely eliminating the impacts of GO on the workability of the cement composite is difficult.

In an experiment conducted by Kjaernsmo et al. [47] compared to a reference plain concrete mix, the diameter of fresh mortar was reduced by 5.5% for GO 0.03wt% content, 18.9% for GO 0.05wt%, and 60.6% for GO 0.2wt% in a mini-slump test. Pan et al. [21] found that with GO content of 0.05% in the mini-slump test, the workability was decreased by 41.7%. In another

experiment by Gong et al. [45], the workability of a cement mixture containing 0.03% GO by weight of cement was lowered by 34.6%. The workability of four samples with varying GO dosages declined as the GO level increased in a study by Devi and Khan [37]. Similar results were found by Wu et al. [46] for all samples with varying percentages of GO 0.02%, 0.03%, 0.04%, 0.06%, and 0.08% had reduced slump of concrete (Fig.10), with 0.08% being the greatest.

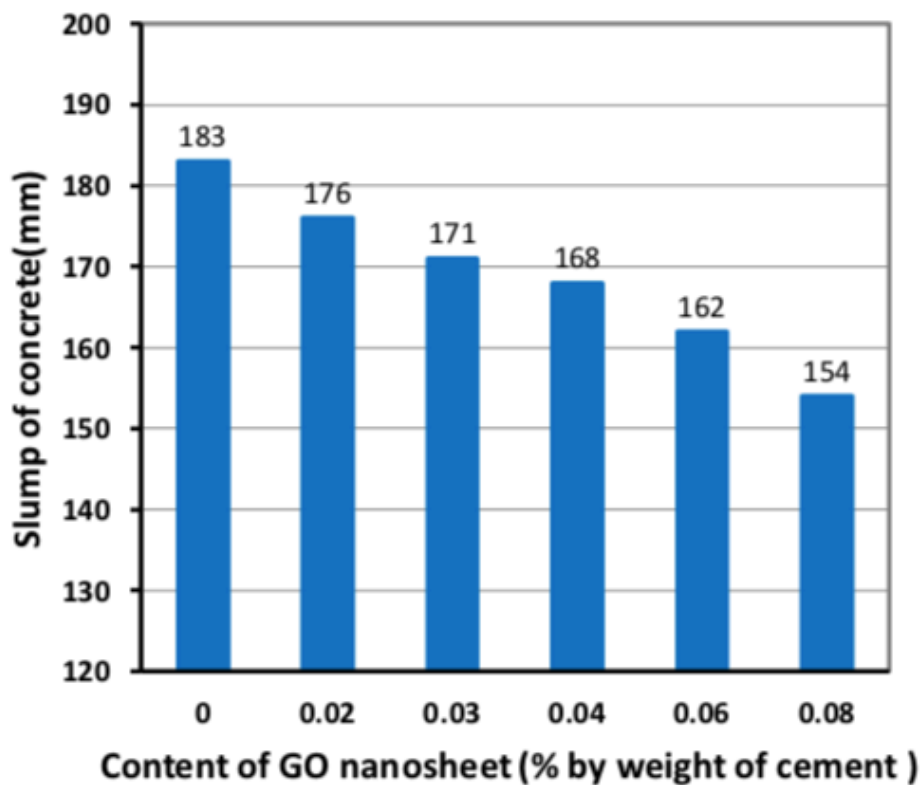


Figure 10. Comparison of slump degree of concrete samples with different GO contents and reference concrete sample. [46]

It is reasonable to conclude that the more GO nanosheets added to the cement composite, the more water is required to wet those nanosheets, decreasing water availability. However, in specific studies [48], when the dosage was 0.03%, the mini-slump width was reduced

considerably by 21%, whereas there was no significant difference at higher or lower dosages. Similarly, when 0.03% GO was added to cement paste in a study by Wang et al. [49], the viscosity increased significantly, and the setting time decreased. The above studies suggest that rising doses have a more apparent effect on workability, and 0.03% GO concentration is the dosage that causes the most significant change in the fresh cement paste.

4.5.3 Influence on mechanical strengths

4.5.3.1 Compressive strength

The compressive strength of concrete samples with GO nanosheets was substantially higher than that of plain concrete samples. For example, in a study by Gong et al. [45], the compressive strength of samples containing 0.03% GO improved by 46% at 28 days of curing. Furthermore, in the experiment by Pan et al. [21], samples with a dosage of 0.05% GO by weight of cement exhibited a compressive strength improvement of 15-33%. Other studies [5, 20, 46, 50-52] had similar results and found a considerable increase in compressive strength of concrete samples with GO addition. Also, due to the ongoing hydration process, the age of concrete affects the strength of the material. The compressive strengths of samples were measured at different curing days by Pan et al. [21]. Results (Fig.11) indicate that the GO-containing samples had a higher increase in mechanical strength at all ages.

Another interesting finding was that when the GO dosage reached a particular percentage, the compressive strength improved the most, and as the dosage increased further, the compressive strength declined. For example, Lv et al. investigated [53] samples with GO concentrations of 0.03%, 0.05%, and 0.07% by weight of cement, the sample with 0.05% GO exhibited the largest

increase of 64.9%. In a study by Kang et al. [52], the compressive strength was enhanced by 32% with a GO concentration of 0.05% and then dropped as the GO content grew to 0.25% and 1.0%. The compressive strength was maximum at 0.05% dose and increased by 47.9% from Lv et al.'s study [5] out of 5 distinct GO containing samples with 0.01%, 0.02%, 0.03%, 0.04%, and 0.05% dosages. The decrease of reinforcing mechanisms of GO at higher dosages may be due to the tendency of GO sheets to aggregate. As the dosage increases, the sheets tend to overlap each other and disperse unevenly [44]. According to these investigations, the best GO percentage for reinforcing cementitious materials is between 0.03% and 0.05% by weight of cement.

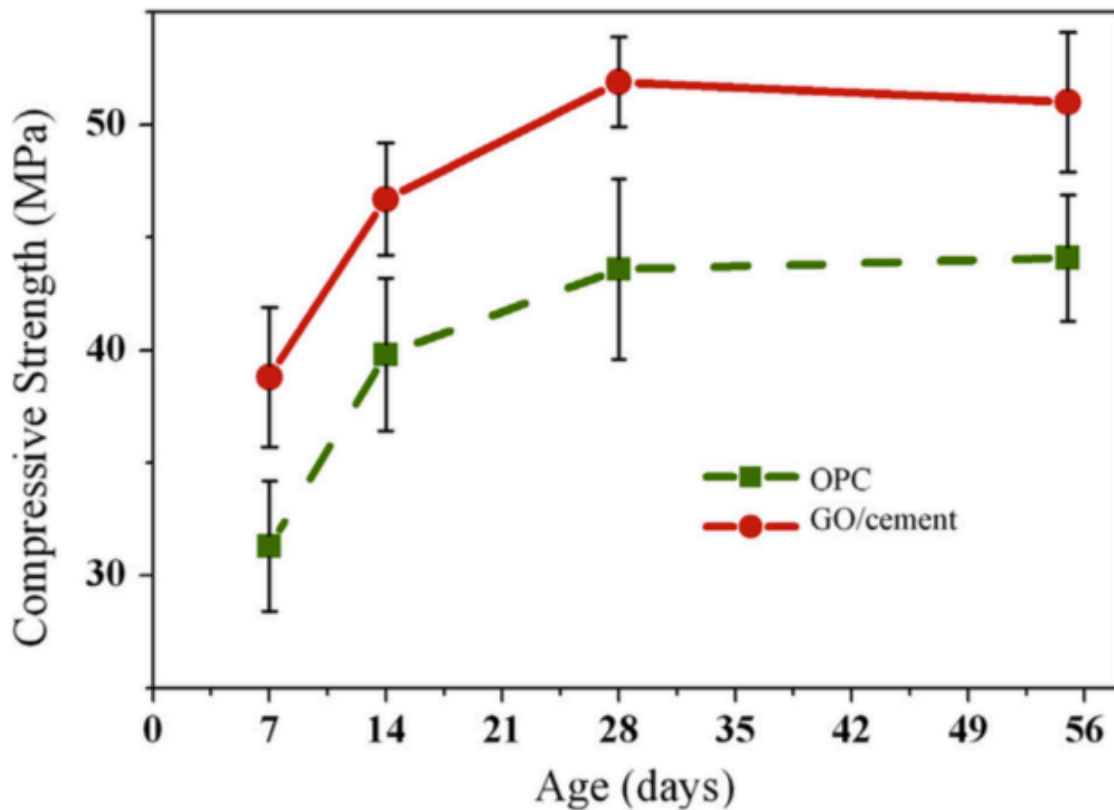


Figure 11. The influence of concrete curing age on mechanical strengths [21]

4.5.3.2 Flexural strength

Flexural strength of GO-containing samples increased in all studies, similar to compressive strength. Flexural strength improved significantly in several trials [5, 21, 51, 53]. The concrete samples containing GO 0.05% by weight of cement demonstrated a 41-59% growth in flexural strength in [21] and by 39.62% in [51] with 0.03% GO addition. Also, in a study by Lv et al. [5], the flexural strength of concrete samples was improved the highest by 60.7% at 0.03% GO content, out of 5 different GO samples with 0.01%, 0.02%, 0.03%, 0.04%, and 0.05% dosages. In [53], out of the 0.03%, 0.05%, and 0.07% GO dosages tested by Lv et al., the 0.05% samples improved more than other samples by 149.73%.

However, GO addition did not influence concrete flexural strength that much in some other studies. For example, in a study by Wu et al. [46], at a w/c ratio of 0.5 and a higher dosage of 0.08% GO, the flexural strength increased slightly by 15.6%. On the other hand, similar results were found by Lu et al. [50] the flexural strength increased by only 16.2% with a GO of 0.05%. According to these investigations, the best dosage for the most significant improvement in flexural strength is from 0.03% to 0.05% GO addition.

4.5.3.3 Tensile strength

In most investigations, split tensile tests were employed instead of direct tensile strength tests. The tensile strength of 0.03% GO-containing samples was improved by 50% by the age of 28 days in an experiment by Gong et al. [45]. Likewise, tensile strength was enhanced by roughly 53.8% in a study by Wang et al. [51] with GO 0.03%. Lv et al. [5] found that the tensile strength improved the greatest at 0.03% GO and by 78.6% out of five samples with GO 0.01%, 0.02%, 0.03%, 0.04%, and 0.05% doses.

According to the researchers, the improved mechanical strength is attributed to GO nanosheets' pore-filling action and the influence of GO on the ability to hinder crack propagation at the formation stage and the superior mechanical properties of GO itself [44,45,50]. A substantial disparity in test results is dependent on various factors. The reinforcing efficacy of GO nanosheets is strongly reliant on GO properties such as sheet size, oxygen content, sheet thickness, and qualities such as Young's modulus and tensile strength [44]. Concrete ingredients such as the type and amount of superplasticizers employed, the type of cement utilized, the w/c ratio, curing age, and curing conditions impact the ultimate mechanical strength [44]. Moreover, the GO nanosheets' size influenced the cement mixture's mechanical properties. Composites with GO sheets ranging in thickness from 14 nm to 900 nm improved compressive strength by up to 63% on average, whereas sheets ranging in thickness from 3 nm to 100 nm improved compressive strength by up to 86% [30]. In addition, in most investigations, along with increases in compressive, flexural, and tensile strengths, GO addition has improved other properties of concrete such as toughness, Young's modulus, energy absorption, and dynamic mechanical properties [44].

4.5.4 Influence on durability of concrete

Structural durability is crucial in lowering maintenance costs and ensuring that the structure will operate for its intended service life. Unfortunately, concrete structures are vulnerable to various environmental problems, which can cause considerable damage to the structure. The chemical corrosion from CO₂, SO₂-4, Cl⁻, alkali-silica reaction (ASR), calcium leaching, bacterial assault, wetting-drying cycles, freezing-thawing cycles, and thermal changes all have an impact on the longevity of concrete material [30, 44,]. The main routes for aggressive substances to pass

through are pores, cracks, and the permeability quality of concrete [30, 44].

The carbonation in concrete structures causes a considerable reduction in pH and corrosion of steel reinforcement. Researchers discovered that carbon-based nanomaterials might be employed to alter the pore structure of the cement matrix, making it more resistant to fluid penetration and chemical attack. Zhao et al. [44] and Mohammed et al. [1] investigated the carbonation degree of GO-containing concrete samples. The samples with GO sheets had lower carbonation depth because the GO nanofillers reduced porosity and made the structure denser.

Also, according to Mohammed et al. [1], GO nanosheets can act as a strong barrier against Cl⁻ penetration into concrete structures. In their experiment, the mortars containing 0.01% GO by weight of cement had a chloride penetration depth of 5 mm, which was much lower than a reference plain mortar with a depth of 26 mm (Fig.12).

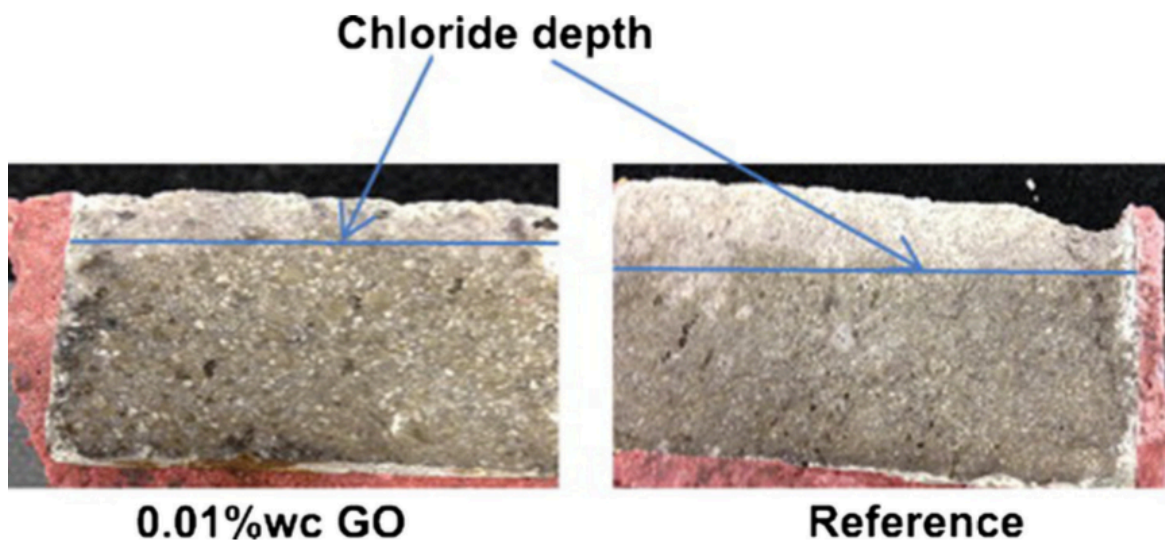


Figure 12. Comparison of chloride penetration depth, left: concrete with GO additive, right: plain concrete [30]

Devi and Khan [37] tested the sorptivity of concrete samples with varying GO percentages. For the samples containing 0.08% GO and cured for 90 days, the water absorption was reduced by 46% compared to plain concrete. Furthermore, Tong et al. [54] exposed GO samples to 300 freeze-thaw cycles to test frost resistance, and GO samples had the best results, with the least change in length and weight. Thus, GO addition can positively influence the durability properties of concrete material.

4.5.5 Porosity of concrete

The dried concrete material has a porous structure consisting of around 10-15% pores [59] of the total volume. Pores form from the air voids that were not well compacted during concrete placement and water evaporation. The size and volume of pores in hardened concrete material influence its mechanical and durability properties. Capillary pores are divided into three types: large pores (from 50 to 10000 nm), medium pores (from 10 to 50 nm), and small pores (from 2.5 to 10 nm). In previous studies, researchers used Mercury Intrusion Porosimetry (MIP), gas absorption method, water sorptivity, and nanoindentation tests to explore the influence of GO addition on the size and quantity of pores in concrete samples. All of the studies discovered a decrease in total porosity and a decrease in macro-sized pores in concrete. This action could be attributed to the pore filling effect of GO nanosheets and the seeding effect of GO nanosheets, which enhances hydration products and fills unoccupied spaces. [4, 44, 49] For example, in an experiment performed by Gong et al. [45], more calcium-silicate-hydrate gels were produced in GO-enhanced concrete samples with 0.03% GO addition by weight of cement, leading to reduced total porosity of 13.5% compared to plain concrete samples. Furthermore, the number of gel pores $d < 10$ nm was 100% higher than the reference samples.

4.5.6 Effects on the microstructure of concrete

The precise impacts of GO nanofillers on concrete microstructure are somewhat inconsistent. SEM (Scanning Electron Microscope) photographs of the microstructure of concrete samples containing GO (Fig.13, Fig.14) show that the GO additive can significantly alter the shape of hydration crystals in concrete. As the GO dosage increases, the crystal structure of hydration product C-S-H becomes denser and more spherical shaped. The more significant the shift in crystal formations into flower-like or polyhedron-like structures, the greater the mechanical strength of concrete [5]. Similar results were obtained in [49, 51, 55].

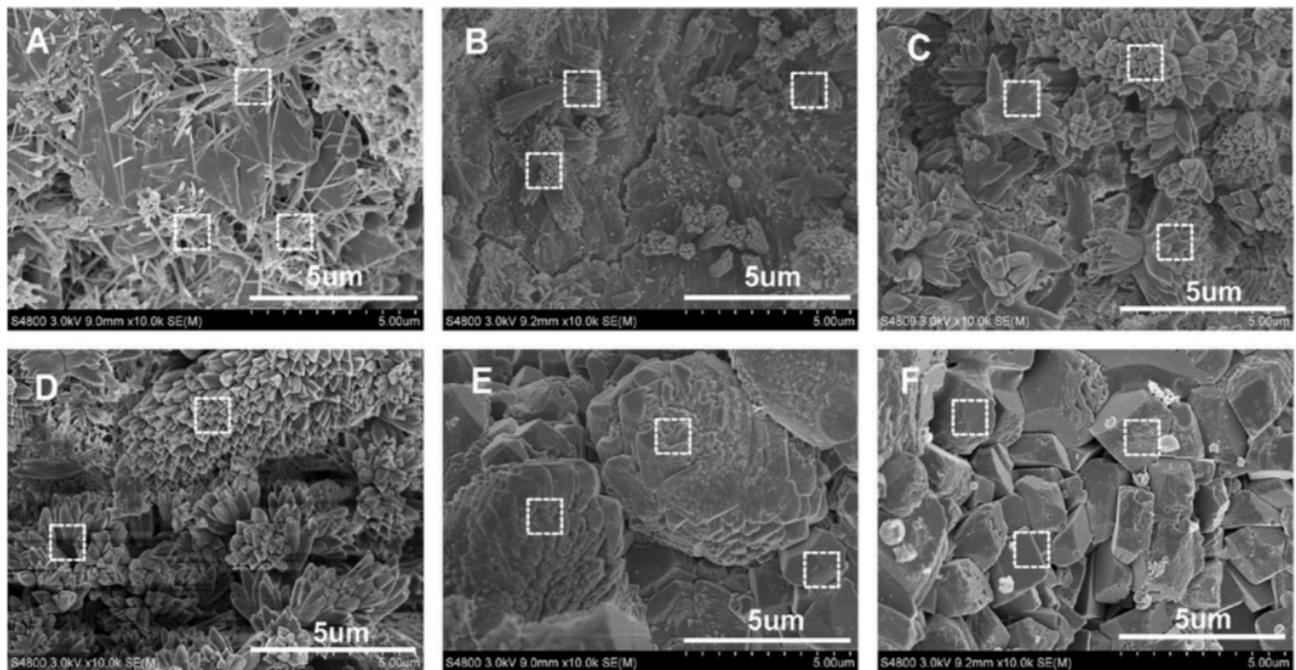


Figure 13. Concrete microstructure at A) no GO; B) GO content 0.01%; C) 0.02%; D) 0.03%; E) 0.04%; F) 0.05%. [5]

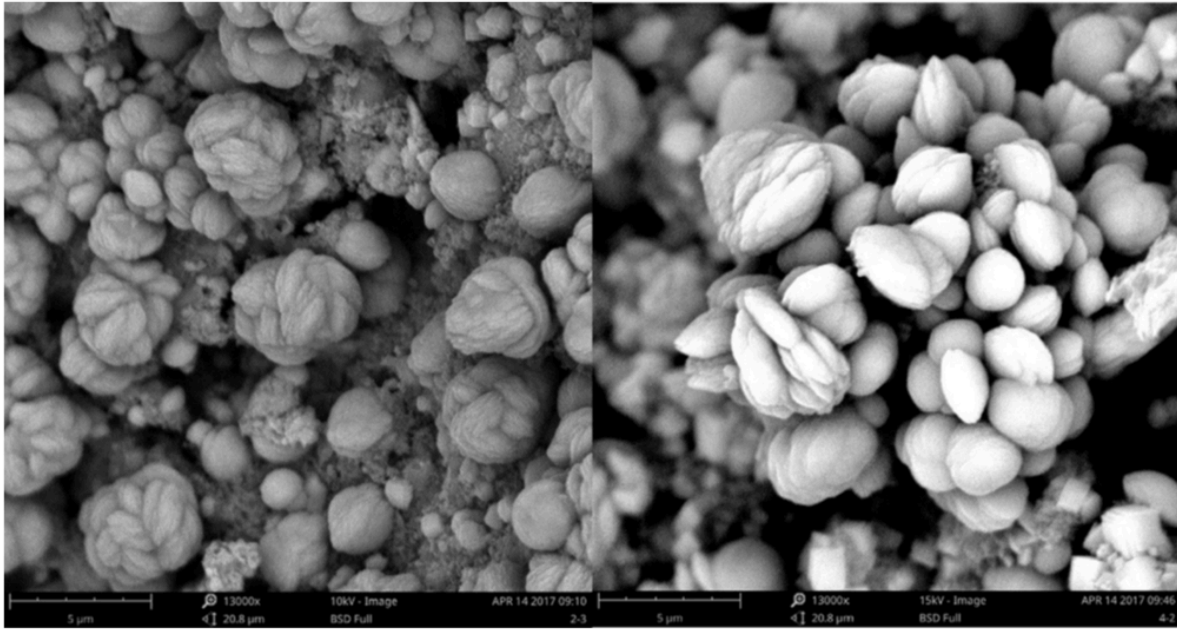


Figure 14. Cement hydration products formed in flower-like shapes [55]

However, Cui et al. [64] discovered that the flower-like crystals are calcium carbonates rather than modified hydration products, and the crystals were calcium carbonate (CaCO_3). Other investigations [44,51,60,63] found that adding GO to the cement matrix did not influence the morphology of the hydration products. In an experiment conducted by Horszczaruk et al. [63], despite the enhanced Young's modulus of GO-samples with 3wt% dosage, the samples had essentially identical microstructure to plain concrete samples evaluated by SEM. As a result, more research is needed to determine the precise impact of GO nanosheets on cement matrix morphology.

Pan et al. [21] also looked into the influence of GO sheets on the formation of fractures in concrete samples. Researchers discovered that GO nanosheets reduced the propagation of cracks and changed the fracture path. Simple concrete fractures, for example, appear to form and

expand in a straight-through pattern in SEM images (Fig.15), but cracks in GO reinforced samples are more dispersed and refined in size. This is because nanoscale cracks come into contact with nanosheets when they form and propagate, and the nanosheets act as a barrier, causing the cracks to spread radially and reduce in size.

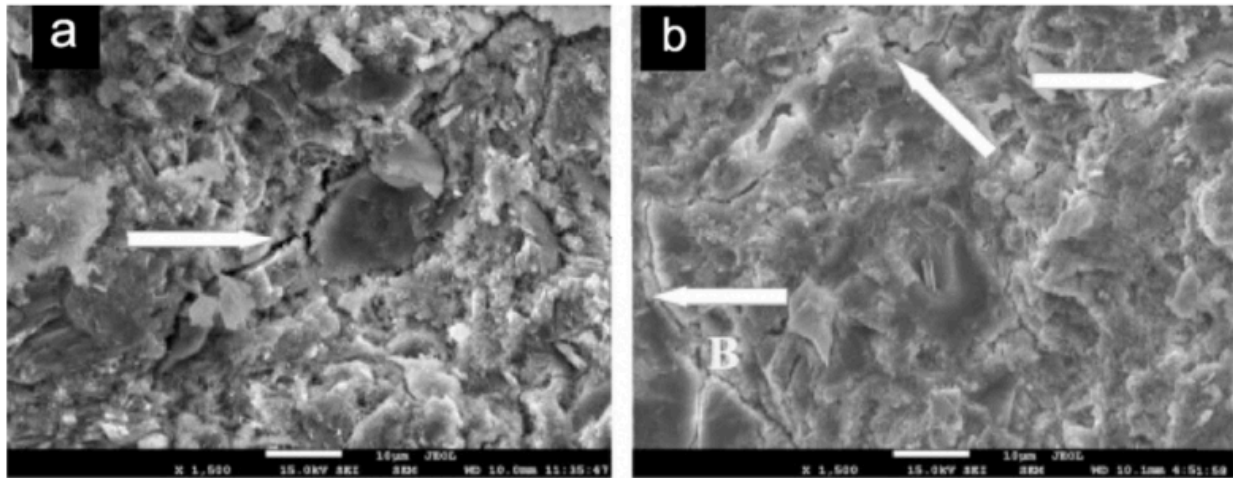


Figure 15. SEM image of a) plain paste with straight crack formation b) GO enhanced mixture with microcracks. [21]

4.5.7 GO used for surface treatment of concrete

Decreasing the high costs associated with maintenance and repair works of concrete structures is a predominant issue in the industry. High-performance concrete and a low water-cement ratio, admixtures, stainless steel, and corrosion inhibitors can all extend the life of a structure. Another method for extending the life of new and existing buildings is to utilize surface-protecting materials that are hydrophobic and function as a barrier.

There are a variety of ways and coating treatments on the market for protecting concrete structures from aggressive agents that cause the material to deteriorate faster. There are three different types of concrete surface protection techniques: a) coating the surface with a thin film; b) impregnation technique, in which the product interacts with some soluble concrete materials to form an insoluble layer; c) hydrophobic impregnation method, in which the outer concrete layer repels water (Fig.16) [42]. Unfortunately, there is no one-size-fits-all solution for surface protection available today. The used surface treatment method, barrier material, and concrete properties all determine the protection's degree of efficacy.

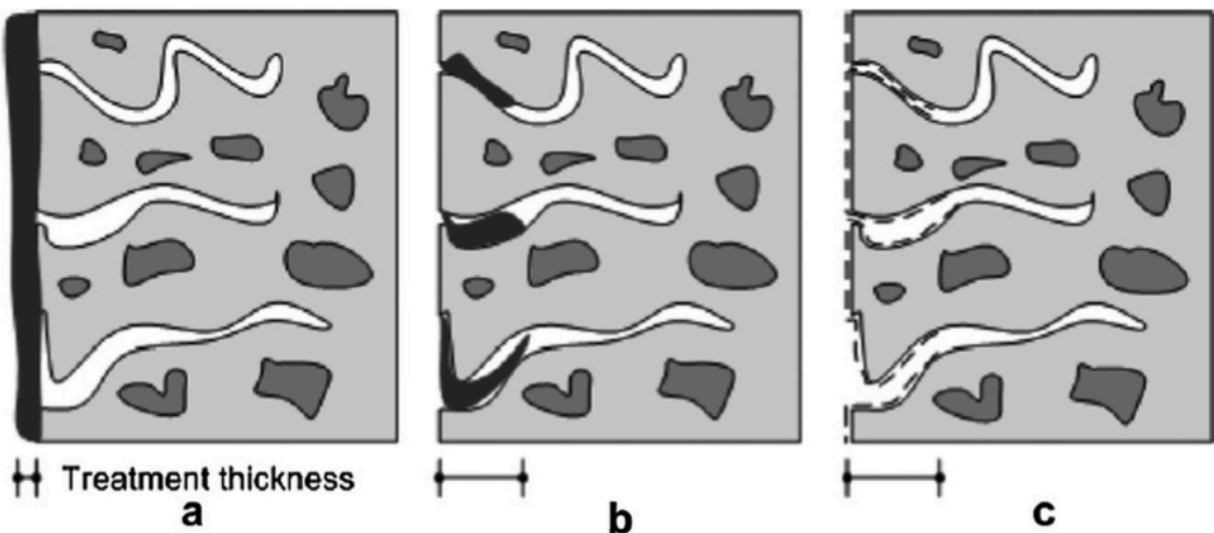


Figure 16. Types of surface treatment of concrete: a) surface coating b) impregnation method c) hydrophobic impregnation. [42]

Graphene oxide application as a concrete coating has also been tested recently in some studies. Researchers coated several concrete samples with a 9 mg graphene oxide coating in one investigation. They tried three methods of applying graphene oxide: spraying, brushing, and immersing the concrete in the substance. After 90 days, researchers tested the samples for water

absorption and vapor transfer properties. Results show that graphene oxide increased the concrete sample's ability to withstand capillary and volumetric water penetration by 57% and 40%, respectively. Furthermore, the coating reduced chloride ion penetration by around 25% while maintaining vapor permeability. [40] Thus, GO has great potentials for use as a surface treatment material for concrete structures in the future.

4.6 Challenges of using nanomaterials in concrete technology

Nanomaterials have few drawbacks when used in cementitious materials despite their numerous benefits. Nanofillers tend to clump together because of the strong van der Waals forces between the particles, making it difficult to distribute them in the mixture. As a result, additional dispersion-increasing agents must be used in tandem. Even though graphene oxide nanosheets establish a strong bond with cement particles due to their 2D structure, most other 0D and 1D nanomaterials lack similar bonding utilities.

Another drawback of nanomaterial is the high cost of its production. Thus, its currently utilized in more specialized industries in smaller quantities or used in laboratory experiments [19, 30, 41]. In order to integrate graphene oxides in widely used materials like concrete, less expensive mass-production methods must be developed.

Quality control, large-scale production, and environmental challenges relating to manufacturing methods are some of the issues surrounding the use of graphene oxide. Graphene oxide synthesized in a laboratory-controlled setting utilizing a bottom-up technique is employed sparingly at the moment. In practice, commercially available graphene oxide is produced via a top-down technique, which results in a high probability of flaws and poor mechanical properties.

Furthermore, KMnO_4 is utilized in the chemical exfoliation of graphite, which could harm the environment. Also, when KMnO_4 and H_2SO_4 react chemically, Mn_2O_7 is formed, which should be handled with caution because it can explode at temperatures above 95 degrees Celsius. Another concern would be the post-treatment wastewater from the GO purification stage containing high quantities of salts and acids. Despite these obstacles, the researchers are developing new 'modified Hummers' methods for synthesizing GO from graphite that is both safer and environmentally friendlier. Several companies are now producing GO in a ready-to-use form at lower prices. As a result, GO is expected to become more frequently employed in the construction industry in the future. [30]

5. Experimental Work

5.1 Materials and chemicals

Ordinary Portland Cement (OPC) type CEM I 42.5R, tap water, and GO liquid dispersion were used in this experiment. Also, polycarboxylate based superplasticizer (STACHEMENT S 33 FM) was added to improve the fluidity of samples. The chemical composition of OPC is listed in Table 2.

Table 2. Chemical composition of cement type CEM I 42.5R

Component	Percentage (%)
SiO ₂	20.51
CaO	63.77
Al ₂ O ₃	4.74
Fe ₂ O ₃	3.30
MgO	1.05
SO ₃	3.07
K ₂ O	0.95
Na ₂ O	0.15
MnO	0.09

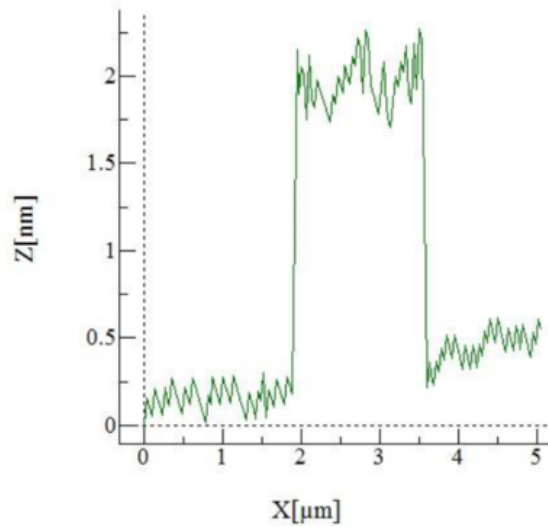
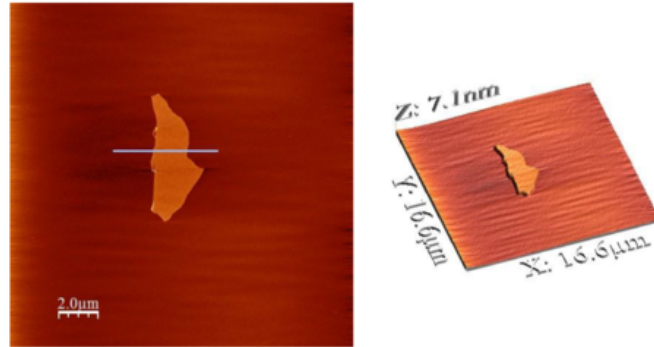
5.2 Characteristics of graphene oxide nanosheets

Graphene oxide was provided by GoGraphene (go-graphene.com). The aqueous dispersion is at 1% concentration equivalent to 10mg/ml of graphene oxide. The chemical composition of GO is shown in Table 3.

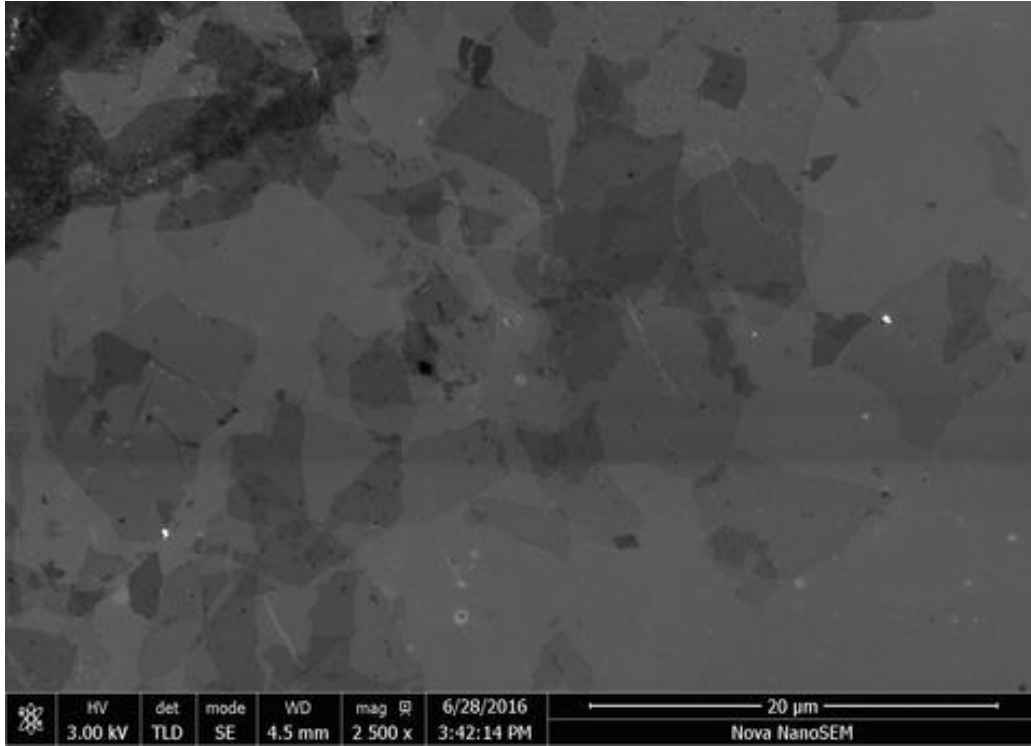
Table 3. The composition of graphene oxide [56]

Element	Percentage (%)
Carbon	60-70
Oxygen	> 30
Nitrogen	< 1
Sulfur	< 2
Trace Metals	< 0.1

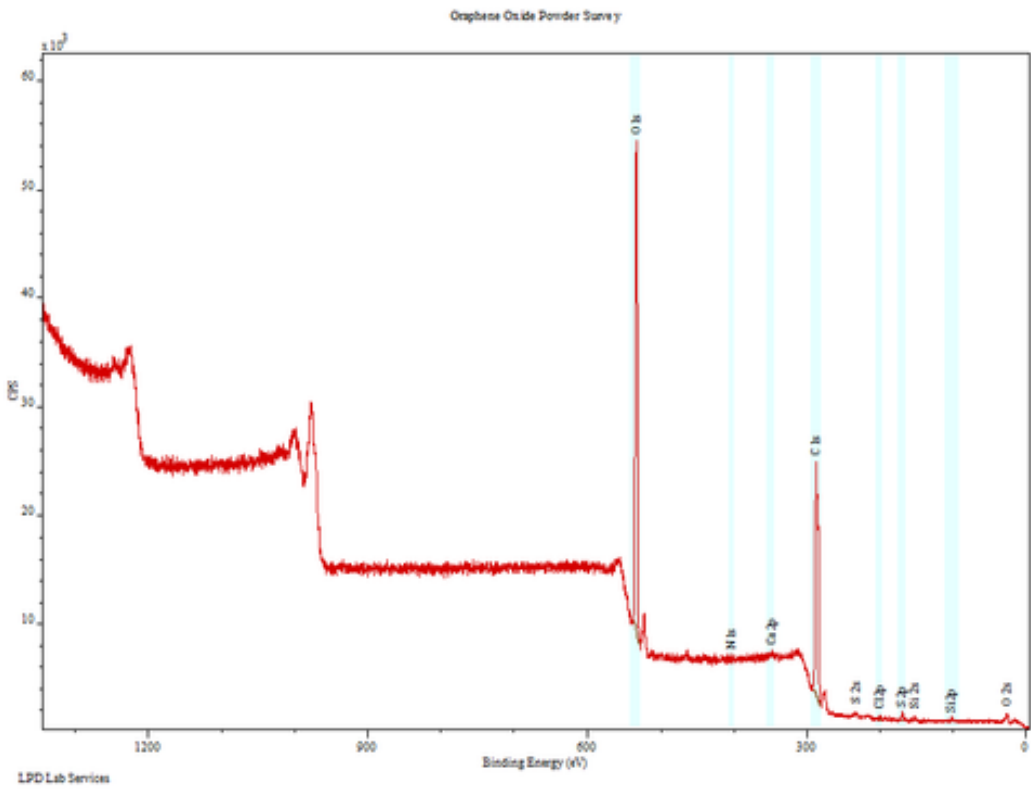
AFM (atomic force microscopy) (Fig.17a) and SEM (scanning electron microscopy) (Fig.17b) results show that at least one lateral dimension of sheets is higher than 5 microns and the sheet depth is less than 2 nm, indicating that GO is not more than two sheets thick (one GO sheet thickness is around 1 nm). Small white spots in SEM images are metal impurities that present less than 0.1%. The XPS (X-ray photoelectron spectroscopy) (Fig.17c) is used to determine the composition of GO in (Table 3). The presence of functional groups can be seen from the FTIR-ATR analysis (Fourier Transform Infrared Attenuated Total Reflectance) (Fig.17d, Table 4). [56]



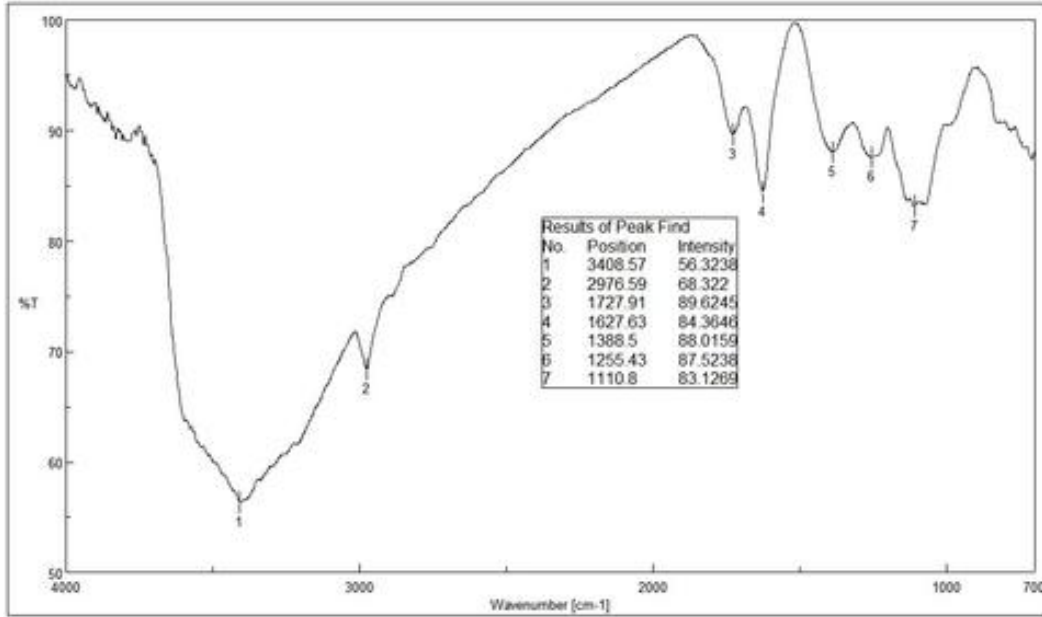
(a)



(b)



(c)



(d)

Figure 17. a) AFM analysis, b) SEM image, c) XPS analysis, d) FTIR-ATR analysis. [56]

Table 4. Chemical bonding in GO sheets by FTIR spectroscopy (Fig. 17d). [56]

Wave number	Possible bond identification
3408.57	O-H
2976.59	Aliphatic C-H
1727.91	C=O Carboxyl vibration
1627.63	C=C
1388.5	C-O
1255.43	C-O
1110.8	C-O

5.3 Preparation of samples

Two concrete mixes with a water-cement (w/c) ratio of 0.4 were made. GO dispersion was added to one mix at a dosage of 0.03% by weight of cement. The other mix was a plain concrete mixture that was used as a reference sample. The PC superplasticizer was added at 0.5% by weight of cement in the manufacturer's recommended range. Table 5 shows the mix proportions.

Table 5. Mix proportions of concrete samples.

Sample name	GO [%]	Cement [g]	GO [mg]	Water with GO 10 mg/ml [ml]	PC [ml]	Water [ml]
PLS	0	3000	0	0	14.2	1185.8
GOS	0.03	3000	900	90	14.2	1095.8

Molds for concrete samples (Fig.18) were created utilizing the ORIGINAL PRUSA i3 MK3 3D Printing Machine (Fig.19). The molds for three-point bending test and compressive strength test were prism shapes with dimensions of 40 mm x 40 mm x 160 mm. The molds for microstructural study were produced in a specific rectangular shape with an opening to cause an intentional fracture during testing, and their dimensions were 3 mm x 30 mm x 30 mm.



Figure 18. Molds for concrete samples.



Figure 19. 3D printers from ORIGINAL PRUSA i3 MK3.

5.4 Mixing and curing process

As recommended in other studies, the PC superplasticizer was first added to the water and combined for 2 minutes at a moderate speed in an electric mixer. After that, the graphene oxide dispersion was gradually added to the liquid mixture while the mixer was switched on and mixed at high speed for 3 minutes. The cement was added last, and it was mixed for 2 minutes at medium speed, then 3 minutes at high speed. After mixing, the freshly mixed concrete was poured into the molds and vibrated to ensure proper compaction. Next, the samples were wrapped in polyethylene sheets to prevent moisture evaporation and cured for 24 hours. After that, the cover sheets were removed, and the specimens for microstructural analysis were cured for 21 days. The samples for mechanical tests were cured for 28 days at room temperature.

5.5 Microstructural analysis

5.5.1 Sample preparation for microstructural analysis

The samples for phase observation, for fracture surface analysis, and later for nanoindentation test were molded in a shape of 30 mm x 30 mm and 3 mm thickness (Fig.20a) using a 3D printer (Fig.20). Prior to testing, the samples were de-molded and oven-dried for 24 hours at 50°C degree. Because the surface of the samples for the nanoindentation test should have low roughness, the samples were prepared using a series of silicon carbide (SiC) papers in the following order: 1) polished using paper grit size #320, 2) SiC #1200, 3) SiC #2000, 4) and at last with even smaller grit size #4000. After each polishing step, the samples were put into an alcohol, and residues were removed using an ultrasonic cleaner. Next, the samples were polished with diamond spray DP-Spray P 0.25 μm on a soft cloth and the surface smoothness was checked by AFM.

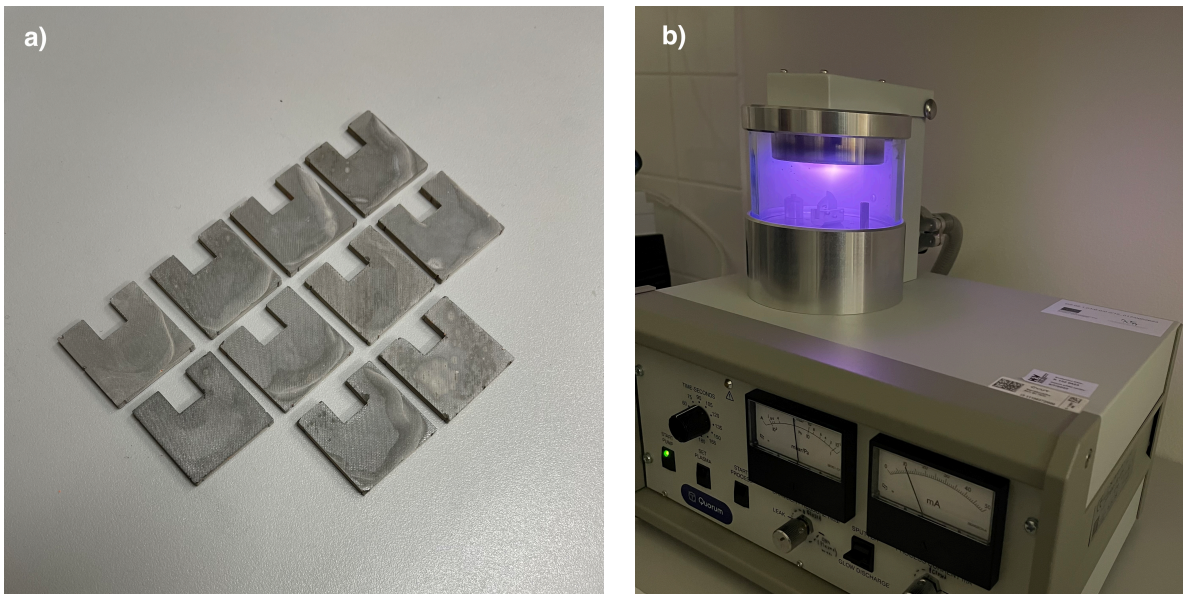


Figure 20. a) samples for microstructural analysis, b) coating of fractured surfaces

In addition, the samples for fracture surface analysis by SEM were intentionally fractured in between, and before testing the fractured side was sputter-coated with gold-palladium (Au/Pd) layer mounted on the samples stubs (Fig.20b) to enhance its conductivity.

5.5.2 SEM analysis

The Scanning Electron Microscope Phenom XL (desktop scanning electron microscope) was used to compare the morphology of the plain concrete samples (PLS) and GO-containing samples (GOS), and quantify the volume of formed phases. First, SEM images were taken on fractured surfaces (Fig.21) of two different concrete samples to closely observe the effects of GO nanosheets on the cement hydration products, specifically C-S-H gels. The magnification was 5000x with spot size 10 μm , and SEM was in BSE mode.

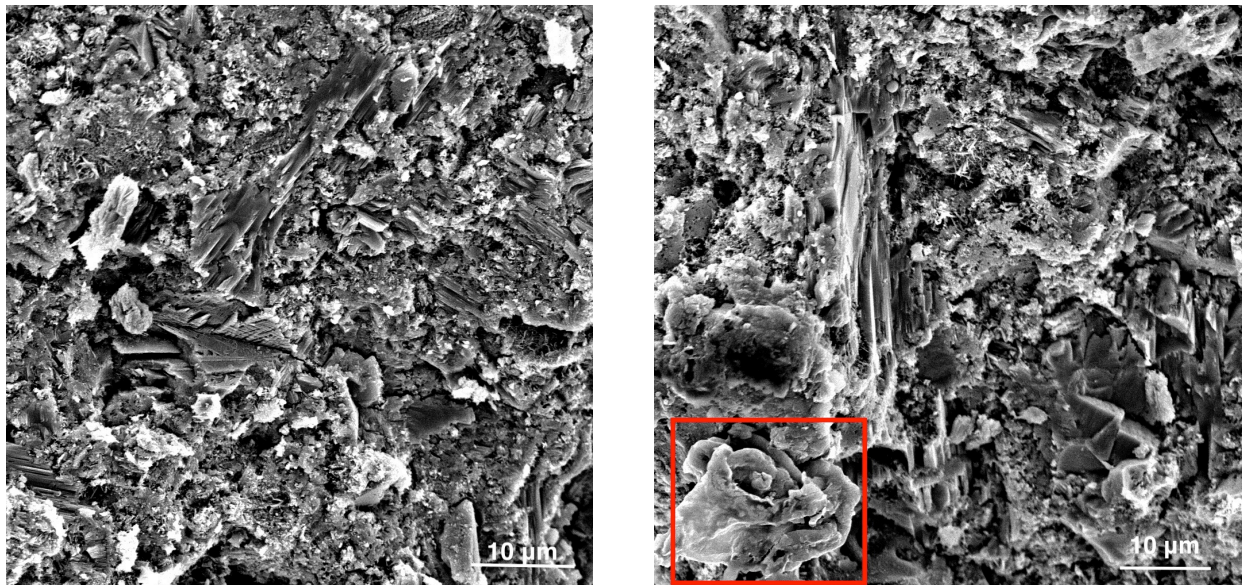


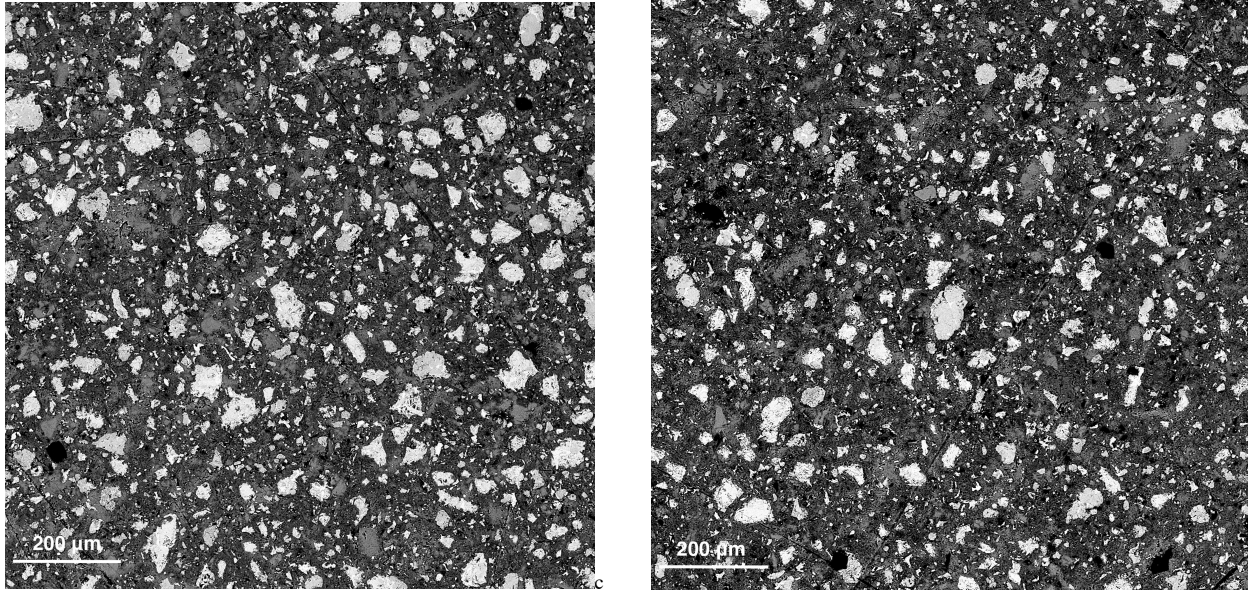
Figure 21. Magnification 5000x, left: PLS , right: GOS

The surface morphology of the concrete samples was also analyzed and contrasted using polished concrete samples. Figure 22 depicts some examples of SEM images acquired from the flat polished side of the materials. The approximate phase composition of samples with a magnification of 350x and spot sizes of 200 μm is compared in (Fig.23a). Furthermore, the phase composition and volume content are more clearly evident in (Fig.23b) samples magnified to 900x and with a spot size of 80 μm . C-S-H (low density) and HD (high density) C-S-H are both included in the C-S-H approximation.

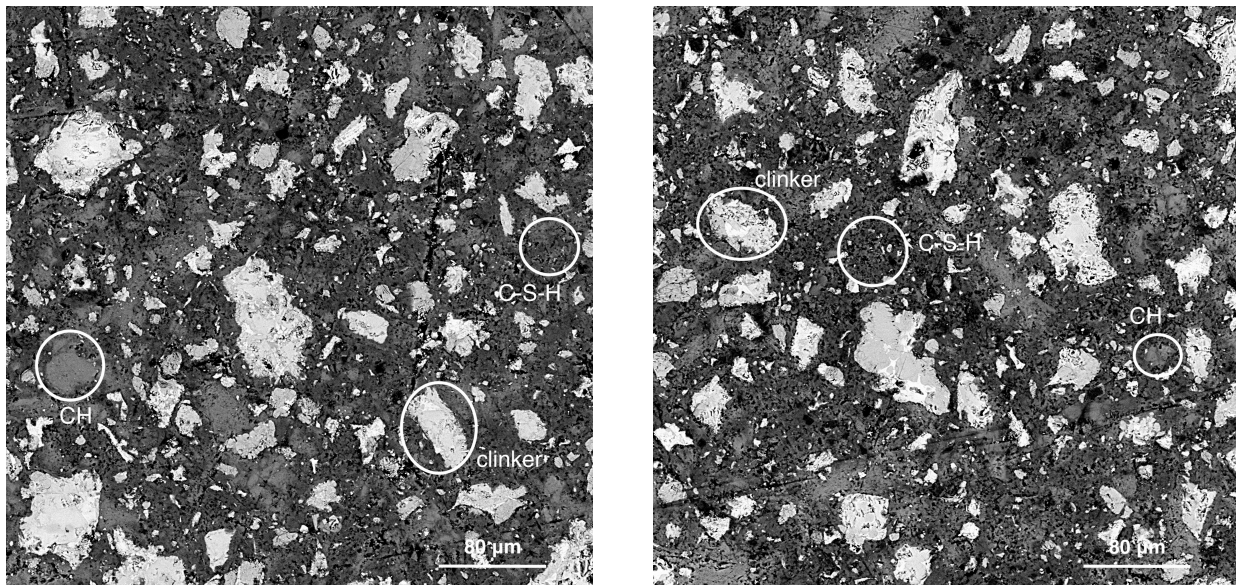
The differences in volume between the individual hydration phases are difficult to see in SEM images. As a result, a simplified analysis was carried out to quantify the volume of phases by estimating the percentage of each phase using pixel color thresholding, and approximating each phase by color. Individual phase volume percentages for each mix design were computed using the SEM images from the polished surfaces and their weighted average presented in Table 6.

Table 6. An approximation of phase volume from SEM images.

Sample name	C-S-H gel %	CH %	Clinker %	Pores %
PLS	56.3	15.6	19.4	8.8
GOS	64.5	11.9	17.0	6.7



a. Magnification 350x , left: plain concrete (PLS), right: graphene oxide concrete (GOS)



b. Magnification 900x, left: PLS, right: GOS, showing individual phases

Figure 22. SEM images of concrete phases

5.5.3 SEM results and discussion

There are no obvious indications that GO nanosheets impacted the shape of cement hydrates based on the fracture surface study in Fig.21. Chemically, the hydration products did not interact with the GO sheets. Furthermore, no hydration crystal modifications have been seen, such as transforming crystals into flower-shaped crystals. Due to their low dose, flat shape, and small size, GO sheets are difficult to notice in these photos. According to Kjaernsmo et al. [47], the GO sheets are visible in concrete morphology when their dose increases from 0.05wt% and above. On the SEM image of GO-enhanced concrete, a potential aggregation of GO nanosheet can be seen in the left corner marked with a red square. However, as Cui et al. [64] explored, it could be a calcium carbonate production (CaCO_3). As a result, additional EDS analysis is required to identify whether the GO sheets were agglomerated.

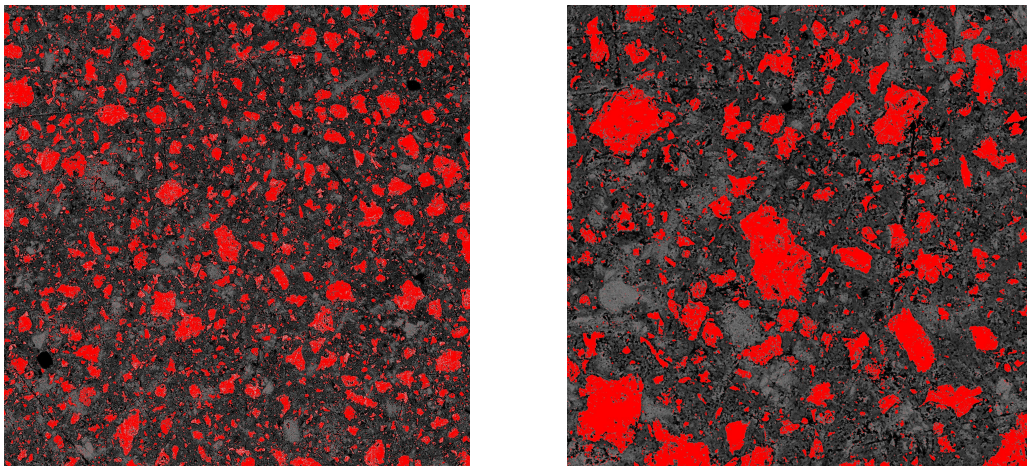


Figure 23. Clinker volume representation by color thresholding.

In addition, surface morphology observations and phase volume estimation were performed using SEM images from Figure 22. The images show the development of the

principal phases, C-S-H gels, CH (Calcium Hydroxide), anhydrous clinker, and pores in the concrete microstructure. From Table 6, based on the volume estimation, no significant differences in the main phase formations in the two concrete samples are seen. The main hydration product C-S-H shows a slight increase in GO-reinforced samples compared to plain concrete. Also, the GO additive reduced the total volume of pores, albeit not dramatically. Furthermore, because the samples were examined at 21 days and are still in the early curing stages, the CH (Portlandite) and un-hydrated clinker percentages are high. Clinker is often present in concrete samples at a rate of 2-5 %, while CH is present at 10 % [59]. The hydration process would continue if cured for a long time. Therefore, a significant amount of un-hydrated clinker is seen in Figure 23.

5.5.4 Nanoindentation test method

The nanoindentation test is a method of determining heterogeneous material's elastic characteristics and hardness at the nanoscale. It operates by inserting a tip usually a diamond tip into the tested specimens and measuring the material's local response. The load is kept constant for a few seconds before being steadily withdrawn to eliminate creep. The Oliver and Pharr method is commonly used to assess indentation modulus M , hardness H , and creep compliance C in cement-based materials. Indentations are usually made in a grid pattern in heterogeneous materials, and many indents are required to cover all phases of the concrete. A three-sided pyramid-shaped Berkovich tip is widely used to study cementitious materials. A load-depth curve is recorded during each indentation (Fig.24a). [59,61,62]

The initial slope of elastic unloading can be used to calculate the two mechanical parameters M and H . The following equations are used to calculate M and H :

$$M = \frac{1}{2} \left(\frac{dp}{dh} \sqrt{\frac{\pi}{A}} \right) \Big|_{h=h_{\max}} \quad (1) \quad H = \left(\frac{p}{A} \right) \Big|_{h=h_{\max}} \quad (2)$$

where h is the indentation depth, h_{\max} is maximum indentation depth, and p is the indentation load, A is the projected contact area. [61]

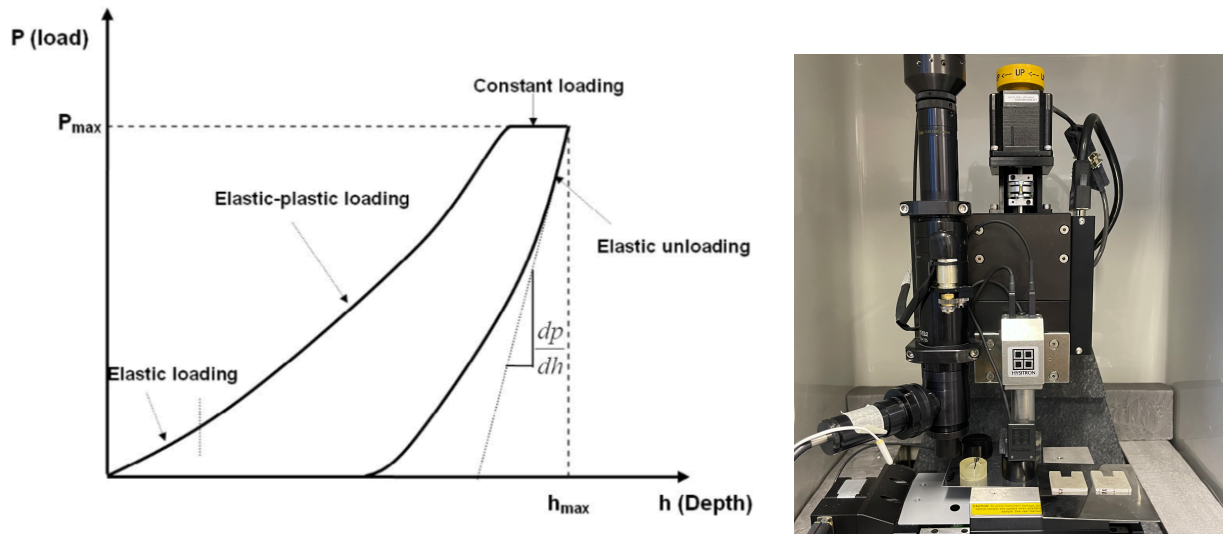


Figure 24. left: a) typical load-depth curve from nanoindentation test [61]; right: b) Hysitron TI-700

The measurements were taken with a Hysitron TI-700 (Fig.24b) using a Berkovich tip. The samples were indented to a depth of approximately 200 nm with a maximum loading force of 3 mN. The loading period was set to 3 s, the holding time was 20 s, and unloading period was 3s. In total, 400 indentations with a 10x40 μm grid area spaced 10 μm were made on each sample to cover all essential phases of heterogeneous material statistically. The nanoindentation test was carried out in standard room conditions with a temperature of 22°C and relative

humidity of 40-60%. M and H were measured from each indentation point, and the indentation modulus M was used to derive the material's Young's modulus-E value at that point. The following formula was used to calculate E:

$$\frac{1}{M} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_{tip}^2}{E_{tip}} \quad (3)$$

where: M is obtained from the nanoindentation results, ν is a Poisson's ratio of concrete $\nu=0.2$, ν_{tip} is Poisson's ratio of the indenter tip $\nu_{tip}=0.07$, and E_{tip} is Young's modulus of diamond tip $E_{tip}=1141$ GPa.

5.5.5 Nanoindentation test results and discussion

An example of the obtained load-depth curve for each individual phase is shown in (Fig.25).

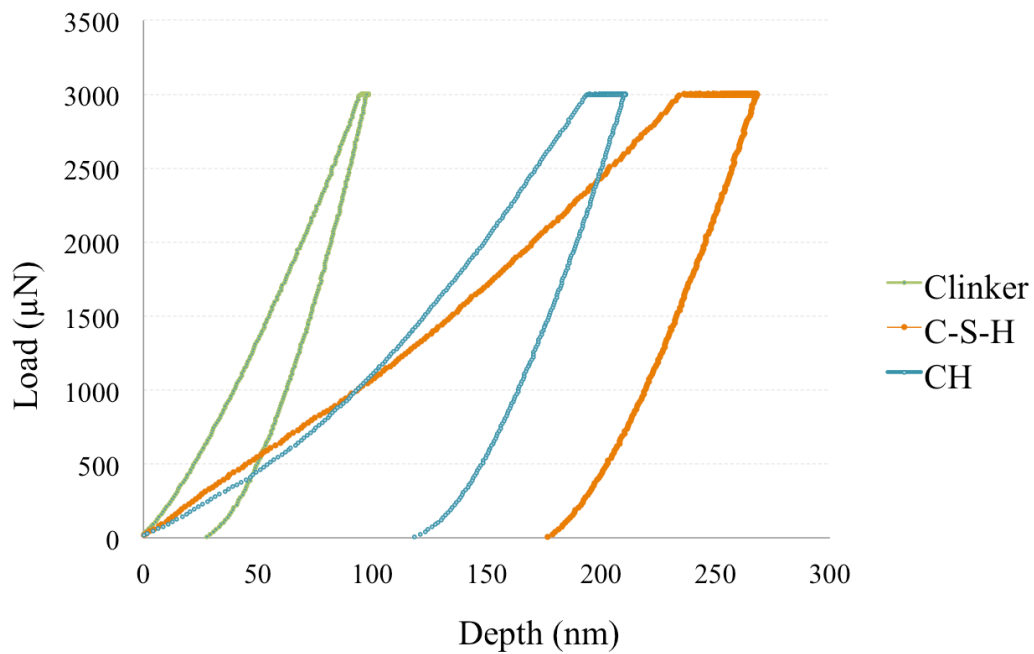


Figure 25. Indentation curves for each phase.

From 400 indentations on each sample wide range of Young's modulus values from 9-136 GPa and hardness values from 0.07-12 GPa were obtained. Furthermore, a frequency density plot (Fig.26) shows obtained Young's modulus of plain concrete samples (PLS) and GP-containing samples (GOS). To further investigate the mechanical properties of C-S-H, CH, and clinker, their properties can be averaged from the frequency density graphs using a deconvolution method. A statistical deconvolution tool is a helpful method in obtaining properties of multiple phases in heterogeneous material [58]. The obtained deconvolution graphs are shown in Fig. 27, and respective mean values of Young's modulus of each phase are summarized in Table 7.

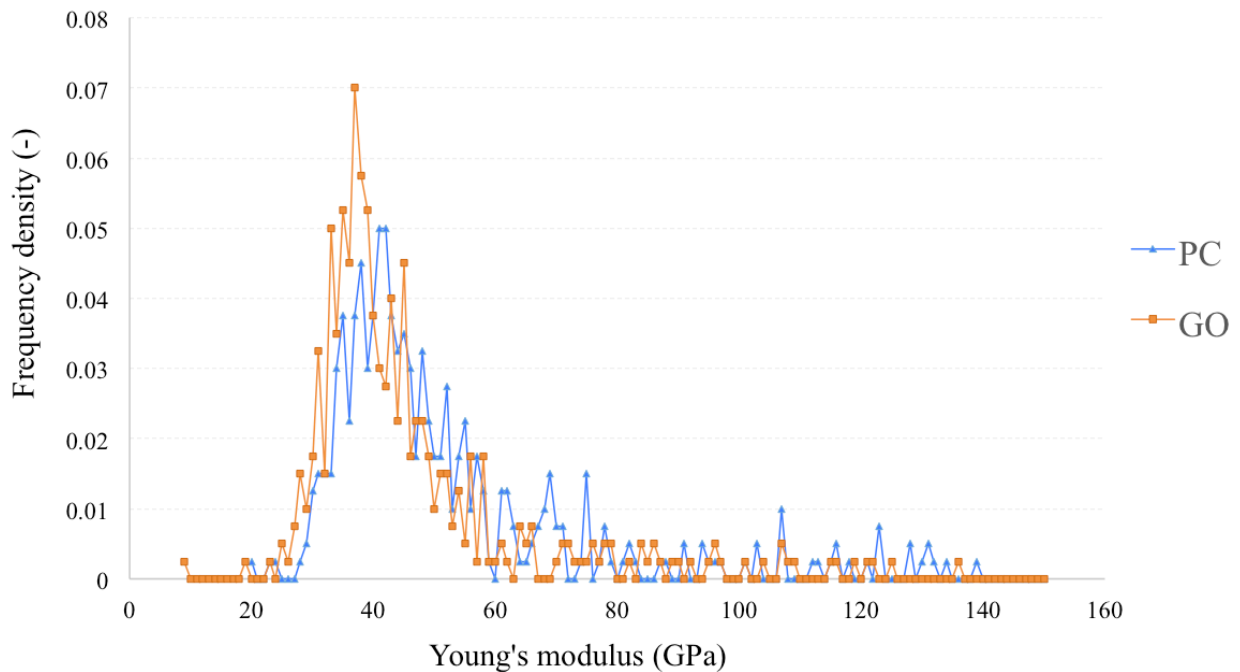
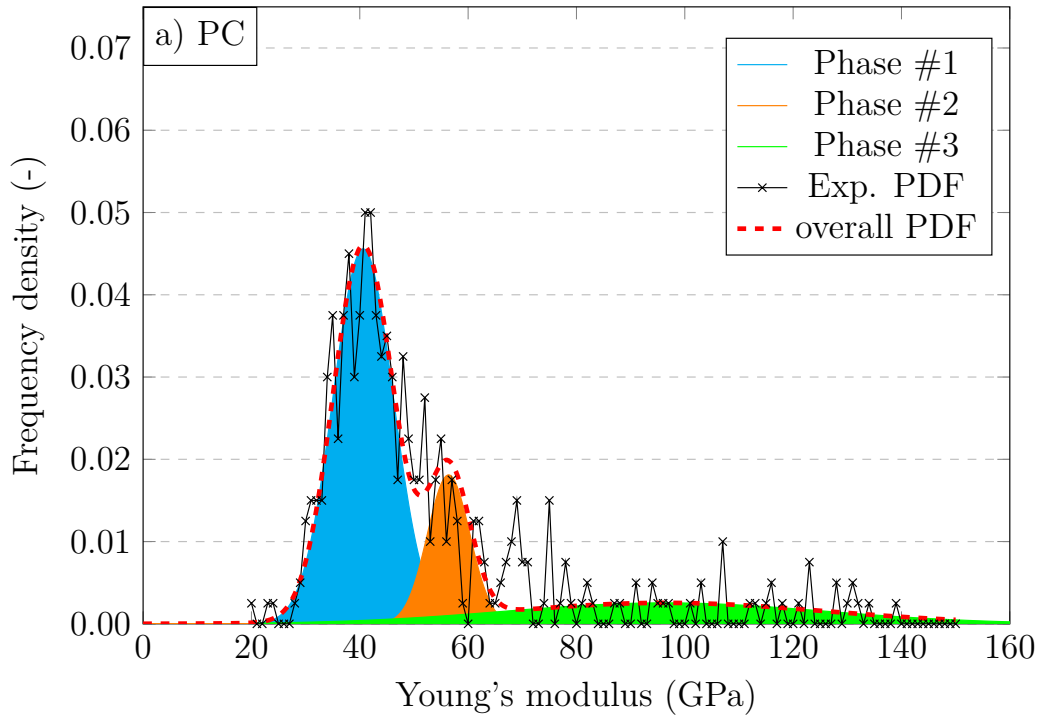
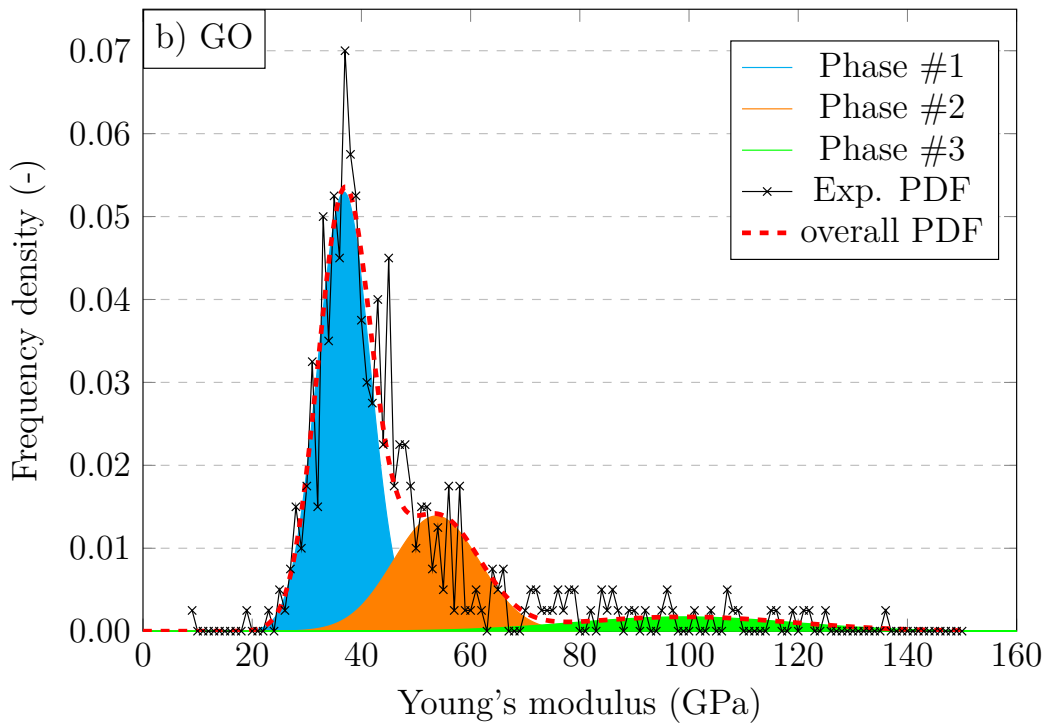


Figure 26. Frequency plot from nanoindentation points.



a) Plain concrete samples



b) GO-containing samples

Figure 27. Result of individual phase analysis using statistical deconvolution

Table 7. Mean Young's modulus values and fraction of each phase

Sample name	PLS			GOS		
Phase #	1	2	3	1	2	3
Name of phase	C-S-H + CH	small Clinkers	large Clinker	C-S-H + CH	small Clinkers	large Clinker
Mean E [GPa]	40.6	56.4	96.4	36.9	53.7	99.1
Standard deviation	5.6	3.9	29.4	4.9	7.9	20.1
Volume fraction	0.64	0.18	0.18	0.64	0.27	0.09

In the frequency plots from Fig.27, three peaks are seen. Thus, three Gaussian distributions are assumed. Individual mechanical phases were split using statistical deconvolution based on distinctive peaks in modulus of elasticity histograms, and each phase was assigned the chemical composition with the highest probability. The primary hydrate products C-S-H plus CH are shown in cyan in the deconvolution plot (phase 1), while small clinkers are shown in orange (phase 2) and large clinkers are shown in green (phase 3). From Table 7, the volume fraction of hydration products and elastic modulus values differ little between the two samples. In plain cement samples (PLS), the mean modulus of elasticity of hydration products is around 40.6 GPa and in GO reinforced samples (GOS) it is 36.9 GPa and their volume fraction is the same 64%. In addition, other phases of two samples exhibit similar mechanical response. According to these results, GO nanosheets had little to no effects on the concrete hydration products and this is supported also by SEM analysis.

5.6 Mechanical strength tests

5.6.1 Tensile strength test method

Tensile strength of concrete samples at failure was measured using a notched three-point bending test (Fig.28) on prismatic specimens 40 mm x 40 mm x 160 mm in size (Fig.29). Six prisms for each concrete mix design were made and tested for the accuracy of the test results.

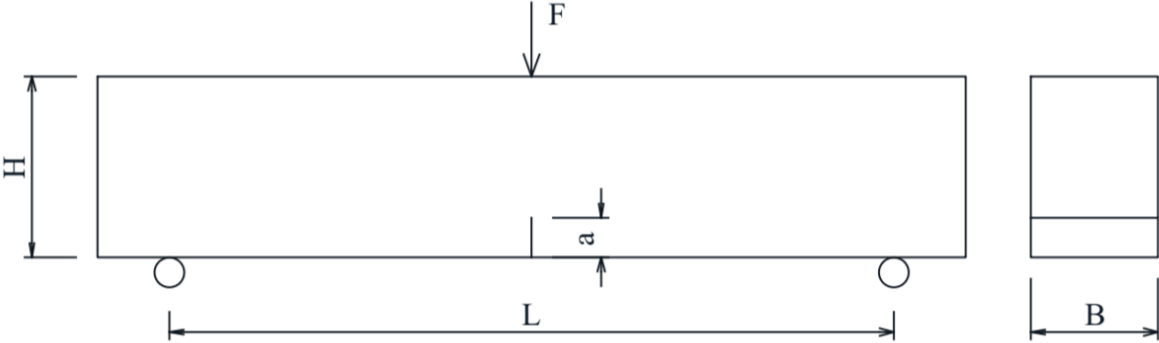


Figure 28. Notched three-point bending test



Figure 29. Samples for tensile and compressive strength tests.

A typical load-displacement graph of mortar samples is shown in Figure 30. In the graph, three separate stages of activity can be seen. First stage, as the load increases, the deflection increases linearly without crack development; second stage, as the line becomes curved, cracks appear and propagate; and third stage, as the graph lowers, the crack propagates fast until failure [65].

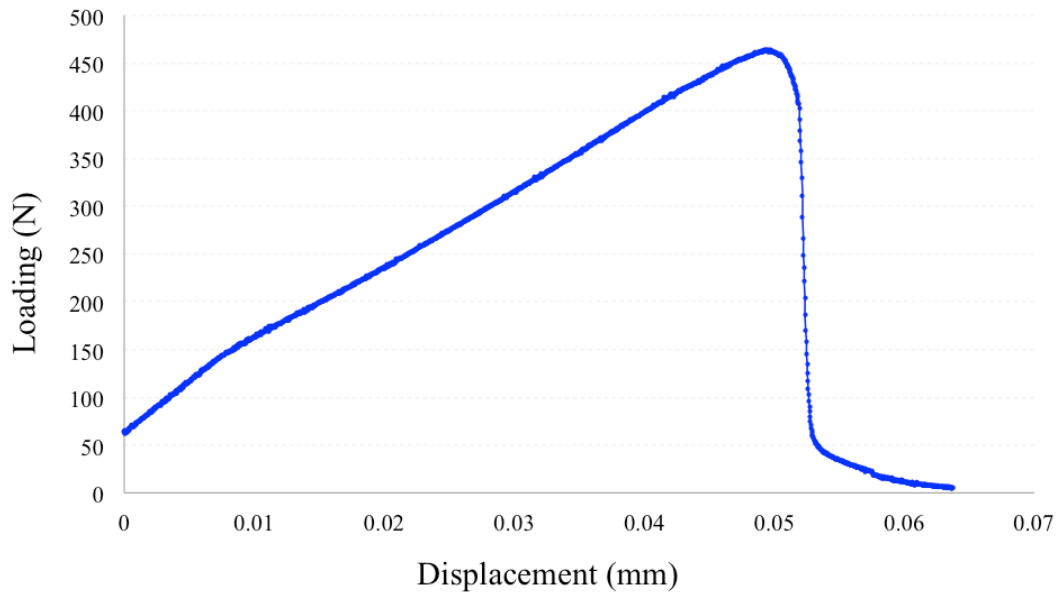


Figure 30. Load-displacement curve for tested specimens.

The maximum tensile stress was calculated using the following formula [65]:

$$f_t = \frac{3P_{\max} l}{2b(d - a)^2}$$

where: P_{\max} is maximum force, b is the specimen width, l is the span, d is the height, a is a notch depth.

5.6.2 Compressive strength test method

After the three-point bending test, the prism halves were used to measure the compressive strength on the MTS Criterion testing machine (Fig.31).

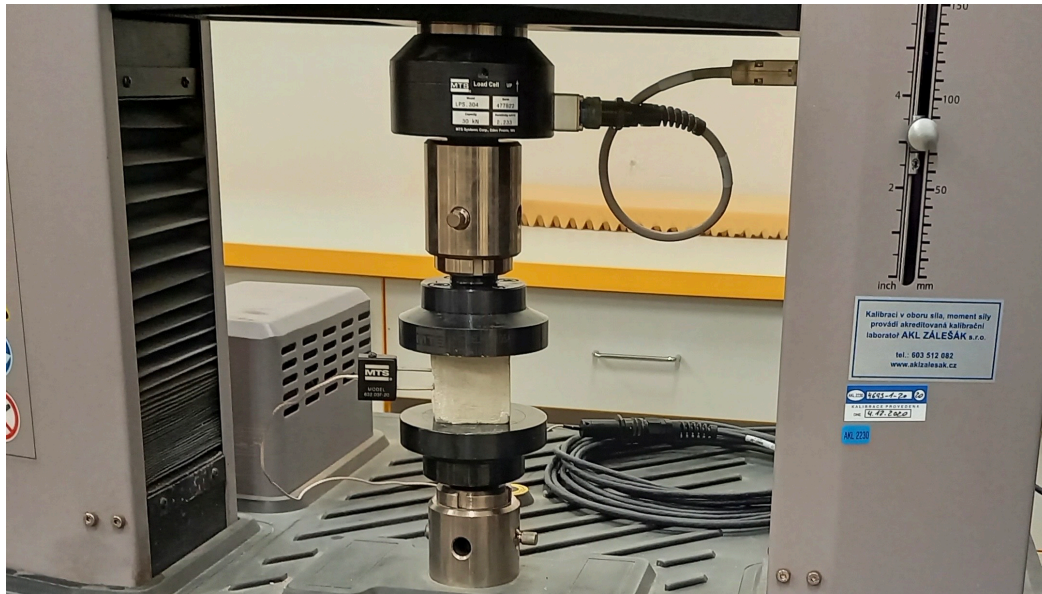


Figure 31. Compressive strength test set up

5.6.3 Mechanical strength tests results and discussion

The results of the tensile strength test are shown in Table 8. Also, the compressive strength test results are shown in Table 9. Finally, in Fig. 32, the average results of mechanical strengths of plain concrete samples (PLS) and GO-containing samples (GOS) are summarized.

Table 8. Tensile strenght of the samples.

Sample	Trial	Dimensions				Force _{max}	Tensile stress f _t	Average f _t
		Width	Height	Height _{effect.}	Notch			
		mm	mm	mm	mm			
PLS	1	39.1	37.8	35	2.8	463.69	2.3	3.0
	2	39.7	37.8	35	2.8	853.78	4.2	
	3	40	37.8	36.3	1.5	680.57	3.1	
	4	39	38	36	2	606.08	2.9	
	5	38.5	38	34.3	3.7	459.9	2.4	
	6	38.7	37.8	34.3	3.5	526.84	2.8	
GOS	1	38.6	37.8	36.8	1	651.35	3.0	3.7
	2	38.9	37.7	36.2	1.5	828.64	3.9	
	3	39.3	37.8	36.1	1.7	720.67	3.4	
	4	39.3	37.8	36.3	1.5	830.02	3.8	
	5	39	38.2	35.5	2.7	746.72	3.6	
	6	39	38	36.1	1.9	959.57	4.5	

Table 9. Compressive strength of the samples.

Sample	Trial	Dimensions				Forcemax	Comp.stress	Average ft
		Width	Height	Height eff.	Notch			
		mm	mm	mm	mm			
PCS	1	39.1	37.8	35	2.8	138	88.2	75.2
	2	39.7	37.8	35	2.8	111	69.9	
	3	40	37.8	36.3	1.5	116	72.5	
	4	39	38	36	2	116	74.4	
	5	38.5	38	34.3	3.7	100	64.9	
	6	38.7	37.8	34.3	3.5	126	81.4	
GOS	1	38.6	37.8	36.8	1	134	86.8	75.3
	2	38.9	37.7	36.2	1.5	117	75.2	
	3	39.3	37.8	36.1	1.7	127	80.8	
	4	39.3	37.8	36.3	1.5	114	72.5	
	5	39	38.2	35.5	2.7	101	64.7	
	6	39	38	36.1	1.9	112	71.8	

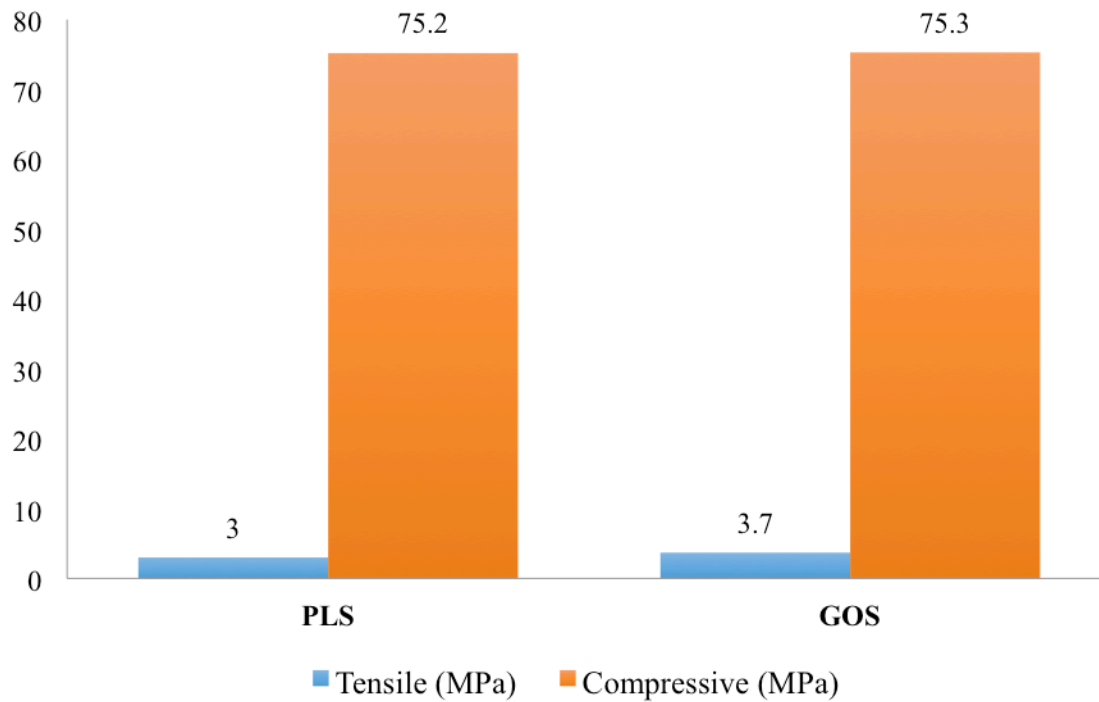


Figure 32. Mechanical strengths test results.

From the results, the average tensile strength of plain concrete samples (PLS) is 3.0 MPa, and for the GO-containing samples (GOS), it is 3.7 MPa. Thus, GO reinforced samples showed a 23% increase in tensile strength at 28 days of curing. On the other hand, the average compressive strength measured from 6 samples is practically the same for the compressive strength test.

6. Conclusions

Graphene oxide nanomaterial is derived from graphite and holds remarkable physical and chemical properties. GO is unique due to its 2D sheet structure, huge surface area, high tensile qualities, and good dispersibility. Although scientists were able to generate it in its pure form only in the last few decades and continuous studies are being conducted, the potential utilization of graphene oxide in various industries is enormous. This thesis demonstrates and thoroughly evaluates the effects of graphene oxide nanosheets as a reinforcement additive in cementitious materials.

From a number of previous investigations by researchers, GO is an excellent material for usage as a reinforcement material in concrete. Concrete's mechanical strength and durability can be significantly improved by a small addition of 0.03 percent to 0.05 percent GO by weight of cement. Several studies have demonstrated that adding GO to cement can improve the hydration process, reduce porosity by filling them, and boost resilience to corrosion and other hostile chemical agents. However, not all researchers have found GO reinforcement to be beneficial. There is still much variance between reports and actual results.

In the experimental work, synergetic analysis was performed utilizing SEM analysis, nanoindentation test, and mechanical strength testing to investigate the reinforcing effects of GO nanosheets in cement composites. According to SEM and nanoindentation investigations, GO nanosheets did not affect cement hydration products or microstructure regulation. Other researchers observed comparable outcomes in [44, 51, 60, 63] studies.

The tensile strength of GO-reinforced samples was increased by 23% compared to ordinary concrete samples in mechanical strength tests. The compressive strength, on the other

hand, was unaffected. Similarly, Kjaernsmo et al. [47] discovered GO nanosheets increased concrete mechanical strength at early curing stages but had little effect beyond 28 days.

Many factors could have influenced the results of this experiment. The most important reason might be the reduced workability of GO-containing samples. During the mixing process, the workability of the cement mix with 0.03% GO dosage was significantly reduced. As a result, more PC superplasticizer is required to compensate for the lower water content. Another possible problem could be an agglomeration of GO nanosheets.

The increased tensile strength could be attributed to GO nanosheets having a 2D structure and large surface area that bond well with cement hydration products. Moreover, due to the high tensile strength of GO nanosheets themselves, when the flexural force was applied, nanosheets helped concrete to exhibit ductile behavior. The fracture bridging action of GO nanosheets could also explain the enhanced tensile strength. When nanoscale cracks first appeared and collided with GO sheets, crack propagation was more likely to be diverted radially than in a straight-trough manner.

According to the experiment and earlier investigations, the GO reinforcing effects in concrete still have much space for development. Future studies should concentrate on identifying the best technique to disperse nanosheets, the optimal quantity of GO concentration, ways for compensating for poor workability, lowering production costs, and, most importantly, maintaining GO sheet quality. Nonetheless, graphene oxide is a promising next-generation material with much potential for future usage in concrete technology.

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