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Optimizing content graphene oxide in high strength concrete

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Summary
This paper describes research advances in the field of nanomaterials, which represents a valuable opportunity for developing compounds nanoscale materials, such as graphene oxide, the effect of the incorporation of nanomaterials disclosed in low doses for increased resistance in the concrete, better hydration and improve the microstructure and mechanical properties of the concrete

Keywords: graphene oxide, dispersion, hydration, porosity, mechanical properties.

I. Introduction

The factors affecting the mechanical properties of concrete require level investigations microstructure between the reactive paste (cement and water) and inert aggregates (gravel and sand), concrete is a porous material composed of reactive material and aggregates inert, is permeable to air and water properties and this has great influence on the strength and durability of concrete structures, which traditionally has studied it from this perspective, water to the concrete mix is added to increase workability and to facilitate the process of hydration reaction of cement with water, more water more pores are formed in the concrete, leading to reduction in strength and deterioration thereof, the mechanical properties of concrete are determined by the porosity generated during the hydration process the amount of water added to the mixture.

The graphene oxide is chemically conoicido as (r-GO), atomically composite carbon, oxygen and hydrogen, a three-dimensional structure composed of millions of layers of graphite; existing in all body cast plain concrete or reinforced and which is possible to peel in the water, creating highly resistant layers in the material in which you are dispersed.

Laboratory tests indicate that when mixtures of Portland cement are performed, including controllably graphitic material agragados and steel reinforcement, the mechanical properties, físiscas and concrete strength are improved to obtain the dispersion of oxide layers graphene by the water used.

There has been much research on the effects of water-cement ratio and the correlation between the strength and porosity of a solid relationship, we can say that there is an inverse relationship between porosity and mechanical strength, it can be stated that the volume of the capillary pores decreases with increasing the degree of hydration and the decrease in water-cement ratio. This is confirmed by Figure 1, in which the effect of the water-cement ratio is shown.

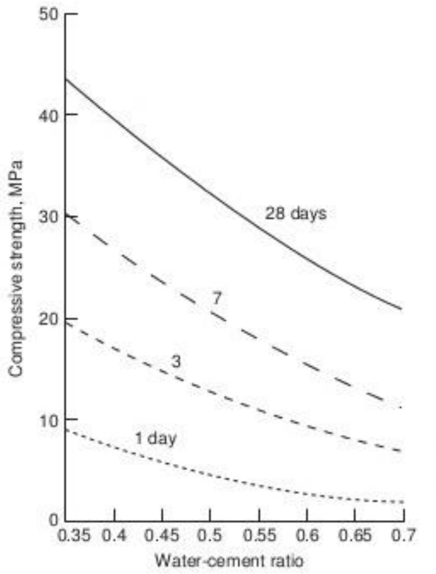


Fig 1. Effect of water / cement ratio on the strength of concrete [6].

The effect of water cement ratio in the compressive strength of concrete is visible considering Figure 1 for an age of curing constant, higher water cement ratio means lower compressive strength at 28 days of curing.

The macropores (above 50 nm) are most influential in determining the strength and durability of the concrete and therefore the appearance of the structures, while the micropores, the lower hollow 50 nm play an important role in contraction drying and creep of concrete, the size of these holes is so small that are in the range of action of the van der Waals force and water absorbed in the pores is maintained by hydrogen bonds.

Pores, due to its size adversely affect the forces on the solid surface of the hydrated product in which water loss is responsible for concrete shrinkage.

Graphene oxide has generated interest as a supplement in the concrete mixture as a precursor for increasing the strength and other characteristics, allowing the possibility of controlling the properties of concrete as structural and architectural element. The graphene oxide can be used as raw material for the synthesis of nanoparticles of composite material.

The graphene oxide, also used as an additive to reinforce composite materials of cement (cement paste, mortar and concrete), recently, there have been several patents [1], [2] and several studies showing an increase in compressive strength and resistance to bending, raising interest in the development and the significance in the cement industry, concrete and construction, this research seeks to overcome resistance before achieved.

The mechanism for this improvement in mechanical properties has been developed in part by Shengua et al. [3], who he proposed a regulatory mechanism graphene oxide in cement hydration products.

This work is the preliminary result of an ongoing investigation whose purpose is the analysis of the most appropriate for the particular high higher than those presented in previous studies resistance proportions. It intends to identify the best techniques for the characterization of graphene oxide and to understand the mechanism that produces improved performance of concrete, especially concrete that usually consists of sand, coarse aggregate, fine aggregate, water and chemical additives (accelerations, plasticizers, etc.).

There have been many investigations to increase the strength of concrete by manipulating the properties of materials and quantities, for example by adding minerals such as fly ash, silica fume, supplementary cementitious materials, reinforcing clay particles and micro fibers. In recent years, research is moving towards the nanorefuerzo to generate high-strength concrete.

Cementitious material

Cement is a fine powder, when mixed with water, resulting in a paste that eventually hardens in [4] defines a cementitious material as "an inorganic material or a mixture of inorganic materials that develops strength by reacting chemical with water "used in the production of mortar (mixture of cement, sand and water) and concrete is a mixture of inert material with cementitious material, a combination of cement and aggregate to form a building material whose microstructure is shown in Figure 2 [5].

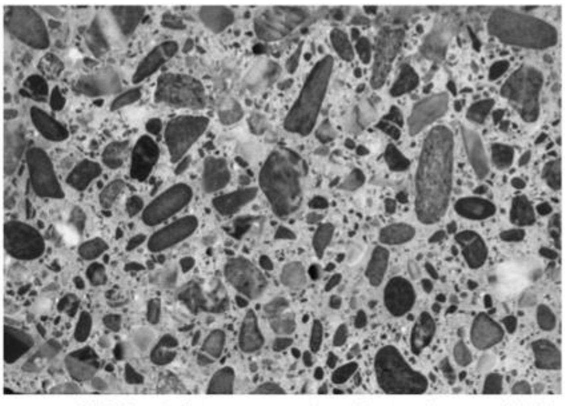


Fig 2. Concrete Microestructue [5]

Today concrete structures such as dams, folders bearing on highways, runways, sidewalks etc. are constructed with concrete, cement is produced by spraying clinker consisting essentially of hydraulic calcium silicates crystal. Production cycles of Portland cement is characterized by distinct stages:

1. The grinding and mixing of natural or artificial materials such as clay, limestone (a source of calcium) and another component to control the content of metal oxide in the mixture (bauxite, siliceous materials, iron oxide, etc.). After obtaining a homogeneous mixture is heated in a rotary kiln at high temperature is cooled for obtaining Clinker.

2. The next step consists in grinding the clinker with a small amount of gypsum as a source of sulphates and other additives water is added to obtain a cement paste [6].

Factors influencing the mechanical properties

The source of the mechanical properties of the concrete, is composed of a porous microstructure of the cement paste and the pulping and coarse aggregate. Cement paste, as a porous material, is permeable to air and water properties and this has influences resistance and durability.

II. Research Methodology

The concrete mix should be designed to define the compressive strength and flexural and dosed to improve the durability of the structures, we identify two different methodologies for improving concrete strength:

1. The inclusion of inert materials having higher compressive strength, which contributes to increased mechanical strength of the concrete.

2. The use of additives, which are chemicals that modifies the properties of the cement paste that lead to a better concrete strength, is common to use chemical additives, as water reducers reducing the amount of water be added to the mixture, without losing the ability to work, this mixture has a low water-cement resulting in a concrete of higher quality, Another type of chemical used are mineral additives, such as pozzolanic materials, ash or silica fume, which provides an improvement in compression strength and durability of concrete, products pozzolanic reaction occupy the pores of the structure driving a better distribution of pore size dough concrete [6].

The methodology for improving the strength of concrete can be divided considering the dimensions of the material used by:

1. Macroscopically: use steel rebar, which is placed inside the concrete in the areas that are expected to be in tension or compression, the concrete supports compression loads and steel bars supports the tension there are some problems associated with the reinforcing bars, as corrosion

by chloride ions which are more easily diffuse through the cement mixture reaching the steel induced.

2. Microscopically: using microfibers (carbon, glass or polymer) and microparticles (silica fume, fly ash) to control the nucleation and growth of cracks at the microscale and induction of change in the microscopic level [6].

3. A nanoscopic level: the use of nanomaterials such as nanoparticles and nanofibers that produce a higher degree of hydration due to the total surface area and can provide a chemical modification at the nanoscale, which has a potential to improve the mechanical properties concrete. Some of these are nano-silica (SiO2) [7], nano-alumina (Al2O3), nano-iron (Fe2O3) [8], nano-titanium oxide (TiO2), nano-clay nano-calcium particles carbonate (CaCO3) [9] or also carbon nanotubes [10] and graphene oxide [11].

The methodology adopted in this work is the number 3

III Development

The graphene oxide fiber in concrete on the use of graphene begins in the late 60's and continue today [11], [12], [13]. Currently, it is used in the construction of bridges, resistant to earthquakes and precast concrete structures.

The main fibers used as reinforcement for concrete are:

1. - steel fibers and microfibers of different shapes and dimensions which are used to control cracks related to the expansion caused by the reaction of silica and alkaline corrosion of the reinforcing bars.

2. Glass fibers of more than 70 GPa of elastic modulus of more than 3 MPa of tensile strength.

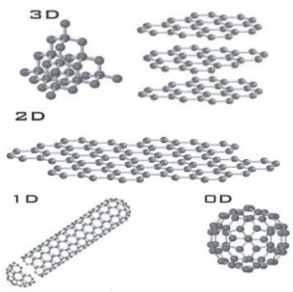
3. Synthetic fibers: polypropylene, polyethylene and polyolefin, polyvinyl, polyacrylonitrile.

4. Carbon fibers having a modulus greater than 200 MPa of tensile strength and more than 3 GPa of elasticity.

K. L. Lin [14] studied the effect of nano-silica cement mortars, reaching the same conclusion Jo Byung-Wan, the increase in compressive strength and decrease in setting time. Hui Li [15] these studies demonstrate the improvement in resistance due to the current proportion of nano-silica nanoparticles and nano-iron, resulting in a more compact and homogeneous structure.

Graphene and graphene oxide can produce composite cement high performance, but the inherent limitation of highly brittle materials, associated with the cement paste, are unchanged with the possibility of regulating the microstructure of the cement, the oxide graphene is an opportunity to solve this problem.

Physical and chemical properties of graphene oxide.
Graphene is one of the allotropes of carbon represent the basic structural unit of graphite (layer stack graphene), carbon nanotubes (graphene layers rolled into a cylinder) and fullerenes (graphene sheet wrapped with the introduction of pentanes in hexaoxido network grafenonal, graphene is a flat sheet of thickness atom characterized by hexaoxido network grafenonal wherein each carbon atom form a layer of allotrope carbon, graphite and carbon nanotubes and fullerenes [16], the electron network offer a very high mobility, this high mobility of charge carriers determines the electrical and thermal properties combined with mechanical strength.



a) b)

Fig 3 a) allotropic forms of carbon. Diamond and graphite (3D); graphene (2D); nanotubes (1D); fullerenes (0D) b) graphene

The properties of graphene are influenced by the presence of the carbon structure that disrupt conjugation system, acting as a limitation to the trajectory of electrons and mobility, graphene can be characterized by pentaoxide grafenonos I heptáoxido of grafenonos. Intrinsic corrugation of graphene planes has been studied and simulated with the Monte Carlo technique [18], there are several techniques for the production of graphene, the most used are:

1.-The micromechanical cleavage method [19].

2. The method of chemical vapor deposition with various substrates (Ni (111), Cu, SiC) and feeding a source gas containing carbon atoms such as methane or ethane, adequate [20] temperature.

3. The method of exfoliation liquid phase, with controlled shear forces associated hydrodynamic cavitation process, allowing exfoliation of graphite by chemical dispersion followed by sonication in water and organic solvents [21].

4. The method of reduction of graphite oxide consisting chemical or heat treatment to decrease the oxidation state of graphite oxide and restore electrical and thermal conductivity, include treatment with hydrazine [22], and dehydration [23] or thermal reduction [24], [25].

The last production technique can be considered as precursor materials for large-scale production of graphene and chemically modified materials covalently with various polymers, biomolecules and nanoparticles allowing self-repair structures [26].

Graphene oxide : Graphene oxide is formed by a graphene layer with different functionalities oxygen, mostly in the form of hydroxyl and epoxy groups, with small amounts of carboxyl, carbonyl, occurs through chemical oxidation of graphite, with dispersion and exfoliation in water or organic solvents, due to the stoichiometric composition of graphene oxide, their amorphous character and the inhomogeneous distribution of the groups oxygen, atomic precise structure is still unclear, in recent years have been proposed various models structural.

In 1939, Hofmann and Holst [27] proposed the first simple model of graphene oxide, Reuss [28] proposed a variation model of Hofmann and proposes the incorporation of hydroxyl and ether oxygen, randomly distributed in the carbon structure Reuss [29] in order to explain the acidic properties of graphite oxide, reexamined structure incorporating hydroxyl and carbonyl groups, Scholz and Boehm [30] proposed a new structure with the carbon molecule and carbonyl groups and hydroxyl, Nakajima et al. [31], [32] propose a model in which graphene oxide has two carbon layers bonded together by carbon-carbon bonds, The best-known model is the one proposed by Lerf and Klinowski [33] with benzene rings unoxidized and regions alicyclic hydroxyl bearing, Szabo et al. [34] have proposed a new structural model consisting of a network of carbon and two types of regions hexáoxido of grafenonos planes with C = C bonds cyclohexane-trans linked and functional groups such as hydroxyl compounds, ether, carbonyl and phenolics.

Graphite oxide was synthesized in 1859 by the British chemist B. C. Brodie [35]: it was investigating the graphite structure by observing the reactivity of graphite flakes. They were carried out several reactions and one with addition of potassium chlorate ($KClO_3$) to a suspension of graphite low nitric acid (HNO_3). The material obtained is composed of carbon, hydrogen and oxygen, oxidative treatments successive determined an additional increase in the oxygen content, Staudenmaier developed an alternative process for the oxidation of graphite it involves a mixture of sodium nitrate ($NaNO_3$), achieving levels similar to those obtained with the above method more economical oxidation.

Characterization of graphene oxide

In order to study the structural characteristics of graphene, they have been used various techniques, one of the easiest is the XRD, where several authors [36], [37], [38] used the distance between layers of nanoplatelets to determine the characteristics of graphene oxide. Raman spectroscopy becomes one of the most powerful techniques for graphene and related materials is mainly used to observe the degree of order or disorder in the crystal structure [39], [40], [41], [42].

IV Results Achieved

Mechanical characteristics

To date the average compressive strength obtained in this investigation for concrete samples with the dosage base reference (fc = 350kg / cm2) shown in Table 1.

Table 1. average compressive strength

1 Mpa = 10.197 Kg/cm^2

	7 days		14 days		28 days	
Graphene oxide in %	**Mpa**	**Kg/cm^2**	**Mpa**	**Kg/cm^2**	**Mpa**	**Kg/cm^2**
0.00 (f´c=350kg/cm^2)	19.00	193.74	22.00	224.33	34.32	349.96
2.00	27.11	276.44	40.11	409.00	53.81	**548.70**
4.00	26.31	268.28	42.01	428.38	51.51	525.25
6.00	29.11	296.83	40.41	412.06	51.21	522.19

The control sample was tested without the addition of graphene oxide at 7, 14 and 28 days, in a controlled humidity and temperature, in addition to the respective curing, as shown in Table 1 and in Figure 4, also show micrographs of samples.

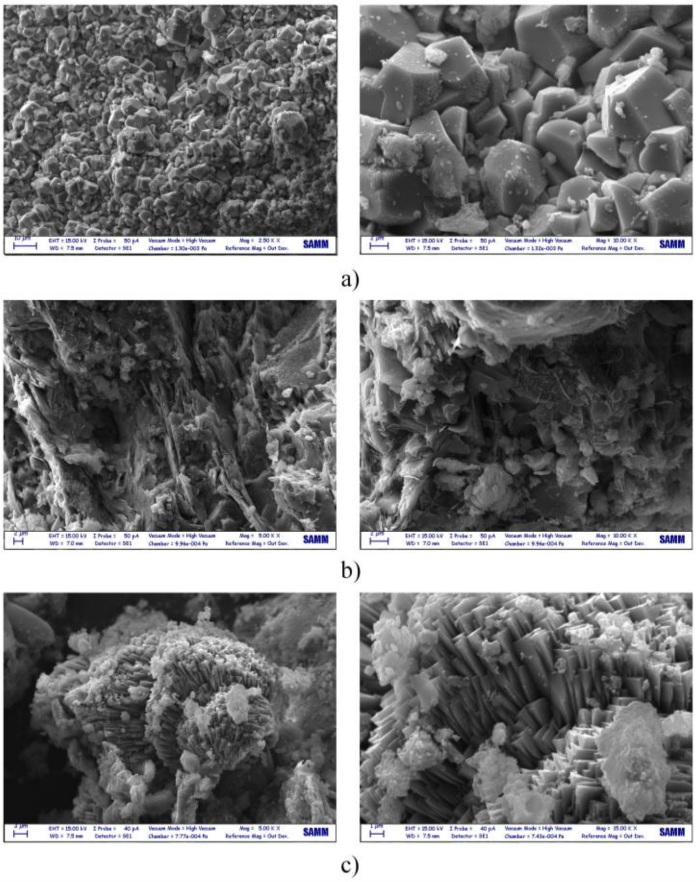


Fig 4. Micrographs of concrete samples: a) 7 days; b) 14 days; c) 28 days [35].

It was also observed that the graphene oxide does not influence the hydration of the concrete and thus in the formation of crystals, so no interaction between the graphene oxide and cement.

The compressive strength increases with increasing the content of graphene oxide, to a maximum of 2%, with a maximum increase of 57% at 28 days, after which decreases with further increases in the content of graphene oxide compared to the control sample (fc = 350kg / cm2) at 28 days.

Analysis of Energy Dispersive Spectroscopy

Energy dispersive spectroscopy, Energy Dispersive Spectroscopy (EDS for its acronym in English), is an analytical technique used for elemental analysis and chemical characterization. EDS was used to obtain the distribution, homogeneity and distribution of carbon in samples of concrete.

Reinforced Concrete nanoparticles

Nanoparticles show unique physical and chemical properties due to their size (10-70 nm), the nanoparticles have the ability to fill the pores of the concrete structure allowing increased compressive strength.

In Figure 5 the image of the nano-silica particles shown in Figure 6 and concrete with and without nanoparticles.

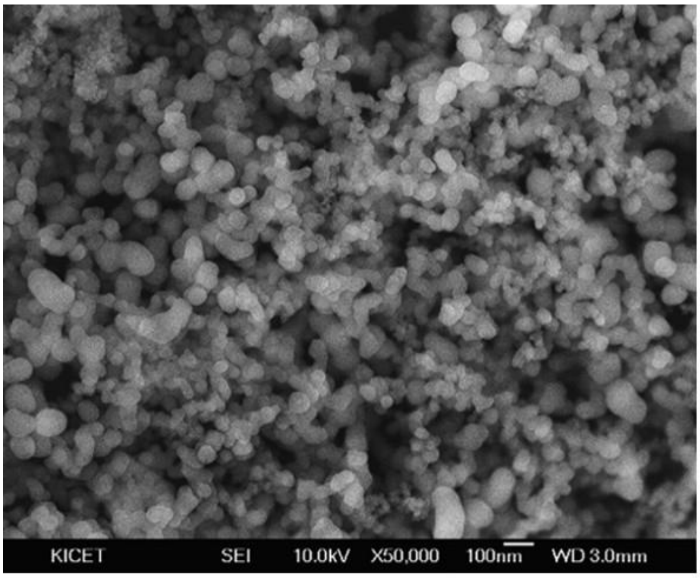


Fig 5. Micrograph of a particle nano-silica [35].

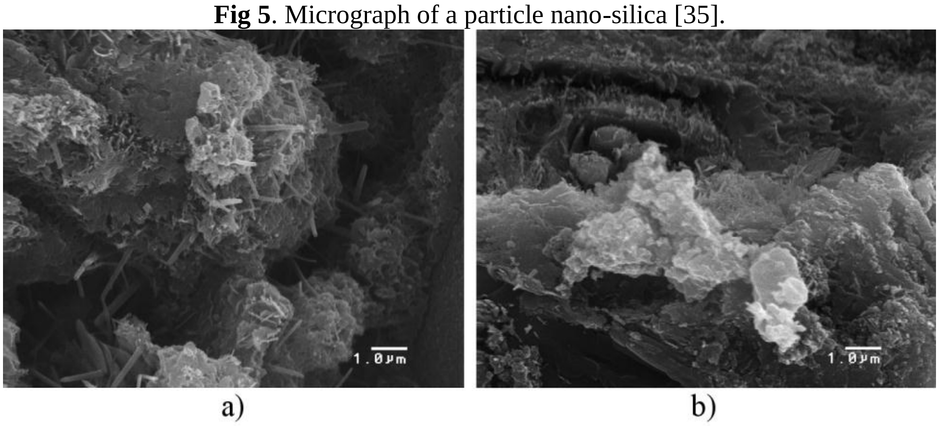


Fig 6. Micrograph: a) control sample of concrete, b) sample with nanoparticles [35].

It was evaluated the compressive strength of concrete at 7, 14 and 28 days, samples with particles noticing a high resistance to compression, this difference in resistance is caused by the pozzolanic reaction with particles of nano-silica and evaluated higher amount of cement-Silica-Water.

It was found that the compressive strength tends to increase as the content increases from 3% to 12%, the use of a high content of nanoparticles must be accompanied by adjustments in the dosage of water and superplasticizer additive, in order to ensure that specimens do not suffer cracking and low workability.

V. Partial Conclusions

Nanoparticles graphene oxide improves the mechanical properties of the concrete, both compression and flexural strength, concrete samples were tested with graphene oxide in percentage of 2% to 6% by weight to obtain high strengths.

Graphene oxide is formulated in a liquid base, so it keeps the color of concrete intact and does not interfere in the construction process.

The compressive strength increases with increasing graphene oxide content, up to a maximum of 5%, with a maximum increase of 57.4% at 28 days compared to the control sample (fc = 350kg / cm2 = 34.32 Mpa.).

The flexural strength increases as the content of graphene oxide, peaking 4%, after which decreases with further increases in the content of graphene oxide, the maximum increase was 65.2% relative to the sample control at 28 days, it was determined that the flexural strength and compressive strength does not influence the size of the size of nanoparticles.

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