Polymeric composite coatings with graphene and graphene oxide for the civil construction – A review

Revestimientos compuestos poliméricos con grafeno y óxido de grafeno para la construcción civil - Una revisión

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Abstract

Steel is one of the most used materials in civil construction and, although it exhibits a very satisfactory performance in terms of mechanical properties, it has the disadvantage of susceptibility to tribochemical mechanisms. Corrosion of steel of reinforced concrete structures (Standard NBR 7480 - CA50) can affect its structural integrity, decreasing its resistance to external stresses, affecting the service life and, therefore, the durability of the structure. The most common pathological manifestations in steel structures are mainly caused by the accumulation of moisture, deficient drainage of rainwater, and lack of protection against the corrosion process. Polymeric coatings with Graphene and Graphene oxide (GO) can be seen as a solution to these corrosion problems in carbon steel due to its chemical stability combined with its high properties such as the degree of hydrophobicity, impermeability to many types of salts and gases, in addition to its good conductivity, GO additions allow to obtain a coating with greater durability. This work aims to discuss the influence of GO on the improvement of anti-corrosion coatings on carbon steel. The literature points out that the introduction of GO concentration in the mass ratios of 0.1 to 5% w/w in coatings has the potential to improve the tribochemical properties of the coating on carbon steel. In this article, a bibliographical review was carried out about the use of GO applied to carbon steel in civil construction, its main methods of processing composites of a polymeric matrix reinforced with graphene oxide, as well as to check if there is an improvement in the main properties of that material.

Keywords: Coating; Carbon nanomaterials; Graphene oxide; Mechanical properties; Corrosion.

Resumen

El acero es uno de los materiales más utilizados en la construcción civil y, aunque presenta un comportamiento muy satisfactorio en cuanto a propiedades mecánicas, tiene el inconveniente de ser susceptible a los mecanismos triboquímicos. La corrosión del acero de las estructuras de hormigón armado (Norma NBR 7480 - CA50) puede afectar su integridad estructural, disminuyendo su resistencia a tensiones externas, afectando la vida útil y, por tanto, la durabilidad de la estructura. Las manifestaciones patológicas más comunes en las estructuras de acero son causadas principalmente por la acumulación de humedad, el drenaje deficiente del agua de lluvia y la falta de protección contra el proceso de corrosión. Los recubrimientos poliméricos con grafeno y óxido de grafeno (GO) pueden verse como una solución a estos problemas de corrosión en el acero al carbono debido a su estabilidad química combinada con sus altas propiedades como el grado de hidrofobicidad, impermeabilidad a muchos tipos de sales y gases, en Además de su buena conductividad, las adiciones GO permiten obtener un recubrimiento con mayor durabilidad. Este trabajo tiene como objetivo discutir la influencia de GO en la mejora de los recubrimientos anticorrosión en acero al carbono. La literatura señala que la introducción de la concentración de GO en las proporciones de masa de 0,1 a 5% p / p en revestimientos tiene el potencial de mejorar las propiedades

triboquímicas del revestimiento sobre acero al carbono. En este artículo se realizó una revisión bibliográfica sobre el uso de GO aplicado al acero al carbono en la construcción civil, sus principales métodos de procesamiento de composites de matriz polimérica reforzada con óxido de grafeno, así como comprobar si existe una mejora en el principales propiedades de ese material.

Palabras clave: Recubrimiento; nanomateriales de carbono; Óxido de grafeno; Propiedades mecánicas; Corrosión.

Introduction

In civil construction, the optimization of the use of metal structures accounts for a fundamental role in terms of mechanical performance, safety, and durability of the projects. The corrosion of structures in reinforced concrete is a cause of reducing its useful life due to the interaction of the metallic reinforcement with aggressive agents of the environment. This deterioration phenomenon occurs both in carbon steels (ferrous materials), and other non-ferrous metal alloys such as copper or aluminum used in construction when exposed to aggressive atmospheres (with or without atmospheric air) or comes into contact with aqueous media and vapors (SO_2,H^+,Cl^-) [1]. As steel is the most widely used metallic material in the form of sheets, plates, bars, and tubes in civil construction, they can have their useful life reduced when the water/cement ratio; the covering, the thickness of concrete between the internal face of the form and the reinforcement; or type of cement and its cure speed are not suitable for the environmental conditions imposed. To increase the useful life of concrete structures, in addition to adequate precautions on controlling aggressive agents and choosing a good quality concrete, it is also recommended to use coatings on the metallic structures to prevent or reduce the corrosion phenomena on those structures.

Recent studies [2] point out that organic or inorganic coatings, such as paint for the former and metallic or conversion coatings for the latter, are a tool used to protect against corrosion of metal structures in modern industry, significantly reducing the rate of deterioration. From specific steel coating techniques, deterioration can be interrupted or delayed. The use of industrial polymer coatings as barriers is the most economical way to protect metallic structures, increasing the useful life of the structure with the lowest costs over time. Films deposited on epoxy bases are among the most common due to their exceptional characteristics, superior adhesion to the substrate, dimensional stability, good chemical resistance, and low cost. However, this type of coating has fragility and low resistance to crack propagation. In this sense, the use of composite coatings, especially those reinforced with nanomaterials with allotropic forms of carbon, such as graphenes, nanotubes, fullerenes, DLC, etc, is a promising method to improve the corrosion resistance and mechanical properties of polymeric coatings, especially epoxy type [4].

A composite coating consists of two or more materials with different structures and chemical compositions that, when combined, aim to achieve properties superior to that of the individual components. The constituent phases must be chemically different and separated by a different interface. The properties of the composite material depend exclusively on the combination of the constituent materials. They can be completely different from those properties of the individual components, ideally combining the best properties of both. Vanguard techniques regarding steel reinforcement optimization use a coating with composites of a polymeric matrix with mechanical/chemical reinforcement of carbon material, such as graphenes. Those techniques consist of depositing the coating by painting, flame spraying, electrodeposition, or dip coating on the surface of the metal so that it is protected by a layer of paint or low-cost film, which was previously combined with new and more expensive graphene materials, presenting economic and performance advantages since the coating is mostly formed by thin layers of organic cheap material [4].

In addition, researches [5, 6, 7] state that the use of graphenes and graphene oxides (GO) can improve the corrosion resistance of organic coatings, inhibiting deterioration phenomena by preventing the migration of aggressive agents (H_2O, O_2, Cl^-, etc) due to the interposition of barriers by coating on the metallic surface, which also aim to stabilize the adhesion of the metal/coating interface, thereby improving the barrier properties of the polymer matrix with significant improvements in the resistance to corrosion and wear of the material, that is, its tribochemical properties.

The use of graphene and graphene oxide to protect the metal surfaces of metallic structures by interposing corrosion barriers has been widely studied worldwide. There are plausible characteristics of the coatings so that this material is pointed out as excellent anticorrosive barriers due to its high surface area, which can reach 2000m²/g, its high cohesion, or consistency within the polymer matrix increase the hardness and mechanical resistance of the film, and also act in the inhibition of the deterioration process, which reinforces its capacity to act as a physical barrier against corrosive species, having; therefore, reflexes in its impermeability for countless gases and salts, and finally, due to its excellent conductivity thermal or electrical does not generate residual thermal stresses in the entire film increasing the mechanical stability of the coating. The numerous hybrid nanocomposites of graphene and graphene oxide can effectively prevent the oxidation of underlying metals in oxidizing chemicals, water, or air over longer periods, thus having comparative advantages as active

inhibitors in protective coatings [8,9].

Corrosion brings several economic and quality impacts on processes: the loss of material efficiency, contamination of products, need for usage of higher safety factors on specifying materials, usage of more noble hence more expensive materials, the obligation of constant preventive maintenance such as paintings and coatings, disability of equipment or structures damaged by corrosion, among several other issues. In terms of physical properties, corrosion interferes with mechanical resistance, electrical and thermal conductivity. Corrosion monitoring is essential to avoid problems ranging from minor repairs to catastrophic disasters. It is relevant to highlight that the costs generated by corrosion problems can represent up to 5% of the countries' GDP, including on this estimative preventive investments and repair costs [4,9].

This work, through a bibliographic review, aims to verify the influence of the use of graphene and graphene oxide in polymeric nanocomposite coatings in the steel industry and civil construction and their particularities against metallic corrosion in metallic structures. In this work we consolidate the results of researches and experimental studies comparing results and identifying the benefits and employability of suggested methods as well as possible improvements of the addition of graphene and graphene oxide in the tribochemical properties of polymeric anticorrosive coatings for application in carbon steel.

In the first section, the introduction and the objective of the work are carried out. In the second section, the bibliographic review is presented, with the concepts used in this work, referring to corrosion in reinforced concrete reinforcements, graphene and graphene oxide and patents, and the use of nanocomposite coatings in polymeric matrices, main mechanical properties, and respective concentrations reported in the research bibliography using graphene and graphene oxide in aluminum and other metallic substrates and alloys. In the third section, we present the conclusion of the article.

Bibliographic review

In this section, we present different methods of processing techniques for obtaining polymeric nanocomposites of the epoxy type reinforced with graphene and graphene oxides available in literature. The focus is on the identification and quantification of the main increased tribochemical and mechanical properties, as well as the respective concentrations of reinforcement of graphene material in the composite polymeric coating applied in these studies.

Graphene and Graphene Oxide

Since its isolation in 2004, graphene has been the center of study and use in various applications in different industries, mainly as a reinforcement material in matrices. A layer of graphene is composed of carbon atoms arranged in a hexagonal network, where each atom is bound to three more neighboring carbon atoms in a hexagonal plane with sp^2 hybridization orbits [3,10].

Before the revolutionary discovery of graphene, it was known as an exclusively theoretical material, being cited only for the explanation of the formation of the different allotropic forms of carbon, illustrated below in Figure 1, because the scientists considered its structure as unstable [11,12].
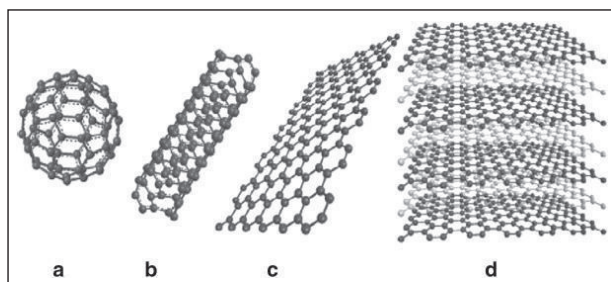

Figure 1: Forms of carbon bound by sp^2. (a) Fullerene (0D), (b) single-walled carbon nanotubes (1D), (c) graphene (2D), (d) graphite (3D).

The International Union for Pure and Applied Chemistry (IUPAC) characterizes graphene by a unique layer of graphite, having its composition by aromatized hydrocarbons of quasi-infinite size. This definition is not always followed in literature since four statements differ from the IUPAC definition [13].

1) A particle that has more than one layer does not meet the definition of a single layer.

2) When the width is in the order of tens of nanometers, the quasi-infinite parameter defined by IUPAC is damaged.

3) When graphene originates from the graphene oxide reduction method, the material obtained will comprise a high amount of oxygen groups on its surface.

4) Finally, there are carbonaceous materials that should be called amorphous carbon, as they have a large number of sp^3-type bonds, as well as defects and imperfections in their crystalline structure.

Graphene is one of the sheets that form the composition of graphite, as shown in Figure 2. In graphite, the interaction that occurs between graphene sheets is of the Wan der Waals type in 5.9 KJ.mol⁻¹, this force being too high to easily separate them [14].
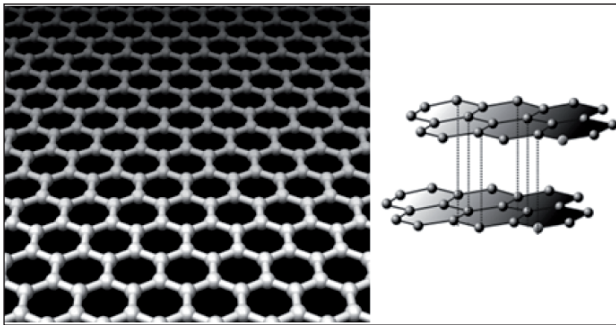
Figure 2: Graphene sheet demonstration.

The reduced graphene oxide (rGO) or graphene is a material similar to graphene oxide but its structure resembles a "Christmas tree" that contains several groups of oxygenated functional compounds in their composition. Using oxidation and reduction reactions is possible to obtain graphene oxide from graphene. This graphene is also called reduced graphene oxide or rGO and can be obtained through graphene oxide. The generated structure can get some oxygenated and functional groups that have a large number of defects. This chemical oxidation method is similar to the other method used to functionalize carbon nanotubes, thus also producing several functional groups through the nanotube [14].

Patents and the use of Graphene and Graphene Oxide in nanocomposite coatings

The use of graphene and graphene oxide has been widely deliberated about the possible improvement of the anti-corrosion and anti-fouling properties of the substrates [5,15] and its impact as an anti-corrosion protector of coated metal surfaces and as an anti-fouling protector used in boat hull paints.

It was addressed [5,7] that to improve the dispersion of graphene sheets in nanocomposites it is the use of its form in graphene oxide GO, which has functional groups including hydroxyls, epoxides, and carboxylic in its structure, to alter interactions, Van der Waals, facilitating its dispersion in the polymeric matrix. In addition, these functional groups are more compatible with the polymeric structure. In this sense, the functional groups of GO play an important role in the dispersion of GO in the polymeric matrix and the transfer of interfacial stresses in the composite. In addition, the processing technique influences the level of dispersion of the nano foil in the epoxy matrix and the property of the nanocomposites because the strong hydrogen bonds can be formed between the GO sheets dispersed in the polymeric matrix during drying. The two-dimensional structure presented by graphene allows it to show excellent performance in barrier coatings [3].

Applied Graphene Materials (AGM) is an innovative and leading company in the production and application of graphene in coatings, in addition to having developed and patented a unique graphene synthesis process. In a survey carried out [16] in partnership with AGM, they carried out work with industries specialized in the development of new materials to finalize the evaluation of graphene platelets produced by AGM in an epoxy coating. The company's goal is to demonstrate the effectiveness of an improved graphene coating in preventing corrosion. AGM evaluated two graphene platelet grades developed by them, A-GNP10 and A-GNP35 (T). Graphene A-GNP10 has a medium density with a rigid platelet structure and built-in oxygen functionality, which provides excellent dispersibility. Graphene A-GNP35 (T), on the other hand, is an ultra-low density material with a high flexible surface area and crumpled sheet morphology. The selection of these two materials was made because each of them has properties that can be useful in preventing corrosion.

Epoxy resins are widely applied as anti-corrosive coatings. They also can be used as an agglutination component in several industrial sectors, as they are classified as thermostable polymers that provide good adhesion on metal substrates, chemical, and dimensional stability, besides having easy applicability. Polymeric matrices of the thermo-rigid type are utilized in composite materials containing allotropic variations of carbon, one of the main matrices being epoxy resin. They have excellent mechanical properties combined with corrosion resistance, in addition to having a low cost. Its use in coatings is due to the factor of its low uncured molar mass that ensures high mobility of molecules during its application and in this way makes the resin to be easily spread on the surface of fibers used as reinforcement [5,17].

The graphene particles added in a polymeric matrix have the function of structural reinforcement, thus improving the mechanical, thermal, and electrical properties of the composite. For homogeneous dispersion of the graphene particles in the polymeric matrix, it is of utmost importance to optimize the means of adhesion and interaction between the reinforcement and its matrix [5,6,18].

Graphene particles will behave as a physical barrier between the metallic substrate and the corrosive environment, thus protecting the metal by filling micropores and possible flaws in the coating polymer matrix, in addition to generating increased adhesion to the substrate [5,19,20]

The dispersion of nanoparticles in polymeric matrices implies the modification of certain properties of this matrix because the polymer and the charges interact chemically [21]. These charges have a nanometric dimensioning on the scale of 1-500 nanometers and have a large surface area, thus contributing to an excellent dispersion in the polymer and the material to present a physical improvement of its characteristics, there must be homogeneity in the material. The addition of inorganic fillers in the polymeric matrices develops materials with high mechanical resistance, improves thermal stability, as well as good optical, electrical

or magnetic characteristics. In the case of epoxy-based coatings used as solvents and filled with graphene oxide (GO) nanosheets, studies [5,7] demonstrated their improvement in the protection against corrosion of carbon steel substrates. The results show that the dispersion of GO in the polymeric matrix is the main parameter that influences the execution of the coating. The viscosity of the polymeric matrix and the percentage of GO weight (% by weight) are principal characteristics for the quality of the GO dispersion.

For a coating to present a good performance is necessary a good adhesion to the substrate and also good resistance to friction to avoid a reduction in its protection [22]. As illustrated in Figure 3, there are four types of wear that can culminate in the deterioration of the metal: Adhesive wear, abrasive wear, fatigue wear, and lastly the erosion wear that occurs in corrosive media and together with the contact between the two surfaces generating a synergistic effect that results in corrosion faster than the individual action of these two factors: Corrosive environment and Contact. In general, this phenomenon is called tribochemical reactions. Being the factors that influence the protection of the substrate: roughness of the substrate, thickness, and the hardness ratio of the substrate and coating.
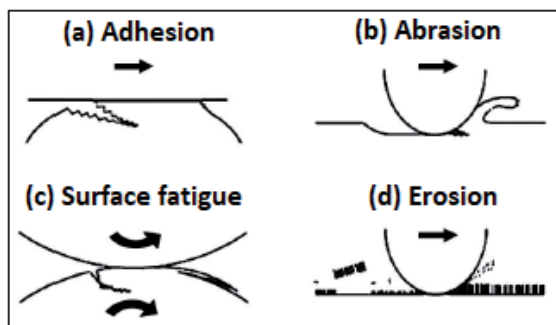

Figure 3: Types of wear mechanisms.

Electrochemical and mechanical properties

Corrosion resistance

Many studies have shown that the addition of graphene nanoparticles and graphene oxide to coatings can significantly increase corrosion resistance in metallic materials when compared to coatings without addition.

Nanocomposites of polymeric matrix of the epoxy type were prepared with different percentages in weight of OG (0.05, 0.1, 0.3 and 0.5), these were submitted to the salt spray test (salt spray test) for the analysis of the corrosion protection performance of the nanocomposite coating. Figure 4 shows images of the samples after 300 h of exposure to accelerated conditions of the salt spray chamber [7].

According to the results obtained [7], drastic corrosion points, rust, and bubbles were observed in the pure epoxy coating. The corrosion extends the risk and means that the pure epoxy coating has low resistance to corrosion (Figure 5). Nanocomposite coatings with different percentages by weight of graphene oxide have divergent behavior, although there is also rust (to a lesser extent) in coatings with 0.05% by weight of Oxide Graphene. There is less expansion of rust and corrosion products on substrates coated with traces of 0.5% by weight of Graphene Oxide. In contrast, nanocomposite coatings, including 0.1% and 0.3% by weight of Graphene Oxide, do not exhibit severe corrosion except for a few rust spots observed on them and corrosion around the scratch is not extended. The Salt Spray Test confirms that a percentage of Graphene Oxide by weight has a great effect on the corrosion resistance of nanocomposite coatings. And a nanocomposite with Graphene Oxide with 0.1% by weight shows the best corrosion protection performance in a NaCl electrolyte.
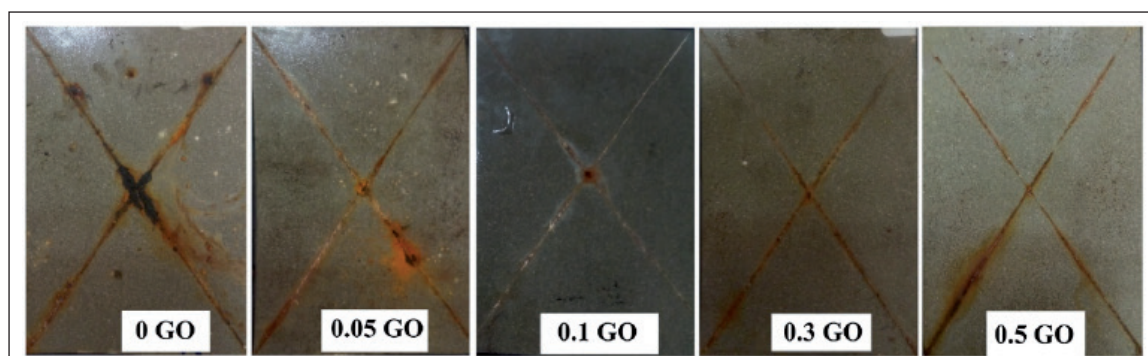

Figure 4: Images of epoxy coatings containing 0, 0.05, 0.1, 0.3 and 0.5% by weight of GO after 300 h of exposure to the salt spray test.
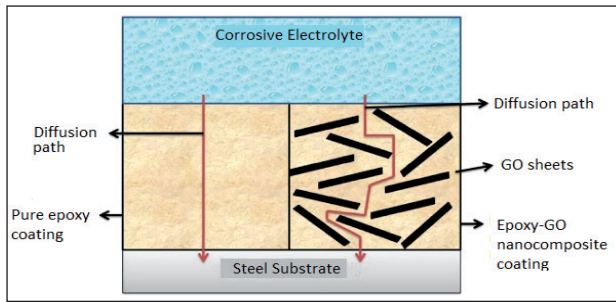
Figure 5: Schematic representation of the corrosion protection mechanism by epoxy-GO nanocomposite coatings on steel substrates.

The path of diffusion of water and oxygen from the coating to the substrate is obstructed due to the barrier effect of graphene oxide nano-foils that act as anticorrosive solutes as shown schematically in Figure 5, therefore, a smaller amount of corrosion products, rust and bubbles are formed. These properties are achieved if the Oxide Graphene nano-foils are well dispersed in the polymeric coating, as they increase the resistance of the coating against the diffusion of corrosive species (H_2O, O_2, and Cl^-), extending the life of the coating [7]. The results show that the GO nanoparticles disperse well in polymers with low viscosity. The Oxide Graphene sheets tend to agglomerate by increasing the percentage of Graphene Oxide by weight in a coating system. This effect occurs due to the tendency of oxygen functionalities to agglomerate and it also forms highly oxidized agglomerates surrounded by areas of crystalline graphene.
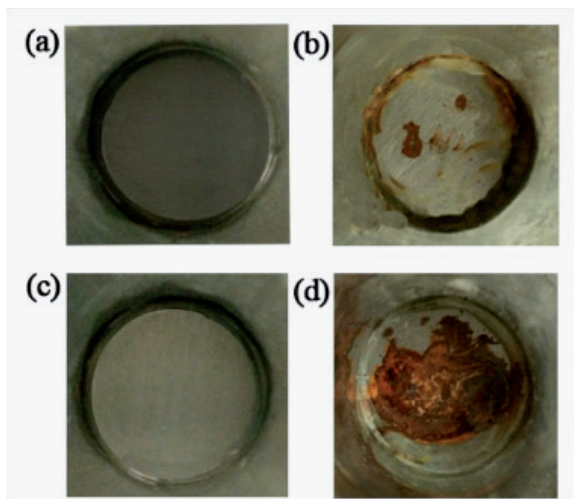

Figure 6: Steel coated with functionalized graphene (5%) (a) before and (b) after exposure for 480 h and mild steel coated with hydrolyzed APTES (c) before and (d) after exposure for 288 h.

In recent researches [8], authors investigated the barrier protection mechanism of graphene functionalized in steel panels using a hybrid film (APTES) composed of 3-trimethoxysilyl (aminopropyl), purchased from Alfa Aesar, which was hydrolyzed with acidified demineralized water with pH = 5 and used to chemically modify (functiona-

lized) different concentrations of graphene. The authors carried out electrochemical tests in which the coated panels were exposed to the test solution composed of 3.5% by weight of NaCl freely exposed to air, pH 5.5 at 25 ° C for long durations.

The results [8] illustrate the condition of 5% functionalized and hydrolyzed graphene surfaces, APTES coated systems, before and after the test is completed, are shown in Figure 6. The surface is severely damaged in the case of hydrolyzed APTES coated mild steel after 288 h of exposure. The damage is much less in the case of a 5% functionalized graphene-coated system, even after 480 h of exposure. The result indicates that even if the functionalized graphene coating delaminates at a certain point, most of the surface remains unchanged.

The company AGM, in partnership with other companies specialized in Paints and Coatings, such as the Paints Research Association, tests were carried out to evaluate the anticorrosive performance of epoxy coatings with the incorporation of graphene [16]. A two-component epoxy system, Epikote 828 with Epikure 3234 hardener, was used, which is widely used as epoxy primer systems to protect steel and aluminum structures. Graphene was dispersed directly in the resin, at concentration levels ranging from 0.1% by weight to 5% by weight for A-GNP10. A-GNP35 (T) was limited to a maximum concentration of only 1.0% by weight due to the very high surface area of this graphene type. The coatings were applied to steel panels for testing using an extraction method, and the thickness of the coatings was monitored before testing.

The steel panels submitted to the Salt Spray Test, where the samples were exposed using a repeated 60-minute cycle of diluted electrolytic fog (0.35% ammonium sulfate, 0% sodium chloride, 0.5%) at (24 ± 3) °C, followed by 60 minutes dry with the temperature rising to 35 ° C for a total of 1000 hours. The coated steel panels were named (A, B, C, D, E, and F) according to Table 1, and checked regularly to monitor the progression of corrosion [16].

Table 1: Steel panels coated with epoxy before (A, B, C) and after (D, E, F) 1000 hours of salt spray test.

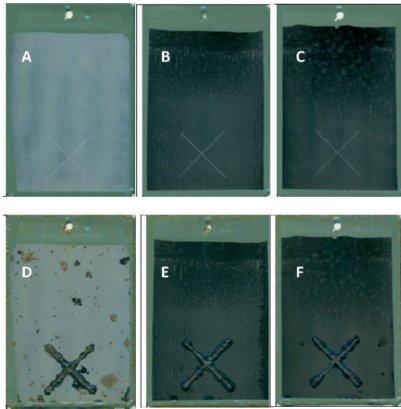| TIME	
0 hour	**1007 hours**
(A) 0% control of graphene Epikote 828	(D) 0% control of graphene Epikote 828.
(B) A-GNP35 of 0,5% (T)	(E) A-GNP35 of 0,5% (T) in Epikote 828
(C) 5,0% of A-GNP10	(F) A-GNP10 of 5,0% in Epikote 828

Figure 7: Steel panels coated with epoxy before (A, B, C) and after (D, E, F) 1000 hours of salt spray test.

According to the analysis of the results of the salt spray test presented in Figure 7, the addition of the lowest amount of graphene significantly increased the protection against corrosion of the epoxy coating. It was found that the control sample containing epoxy coating without graphene quickly showed rust spots and clear evidence of corrosion after just a few days of exposure, and the rust became quite severe during the test period [16]. The epoxy-coated samples loaded with graphene remained free of corrosion for up to 12 days and then showed only small localized stains. This localized corrosion appeared to be limited to regions where there were defects or corrosion in the coating. There was also an increase in the time it took for corrosion to start (appearance of black rust spots) with an increase in the graphene load. The best performance was achieved with the composite containing 5% A-GNP10 and 0.5% A-GNP35 (T).

According to the study carried out [16], AGM also carried out the immersion test in which the steel panels were prepared similarly and then subjected to total immersion in synthetic seawater, prepared to ASTM D1141 - "Standard practice for the preparation of substitute ocean water", at a temperature of 20 to 30 ° C for 30 days. After the immersion test was completed, the samples were cut and photographed by SEM (Table 2).

Table 2: Steel panels coated with epoxy before (A, B, C) and after (D, E, F) 30 days of synthetic seawater immersion test.

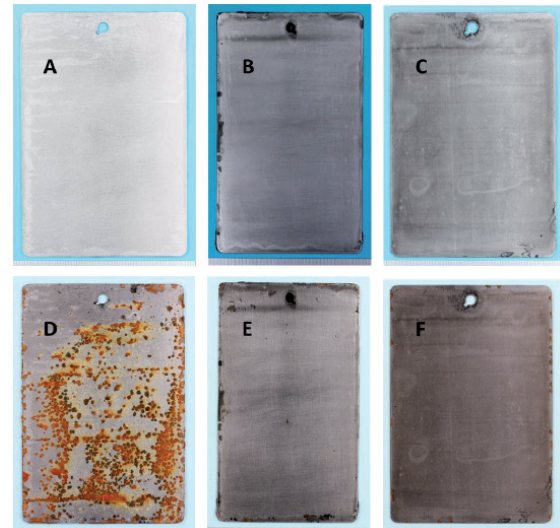| TIME	
0 days	**30 days**
(A) 0% control of graphene Epikote 828	(D) 0% control of graphene Epikote 828
(B) A-GNP35 (T) at 1,0% on Epikote 828	(E) A-GNP35 (T) at 1,0% on Epikote 828
(C) A-GNP10 at 1,0% on Epikote 828	(F) A-GNP10 at 1,0% on Epikote 828

Figure 8: Steel panels coated with epoxy before (A, B, C) and after (D, E, F) 30 days of synthetic seawater immersion test.

To complement the analysis of the results obtained in the immersion test, the authors [16] performed micrographs of the epoxy-coated panels in the SEM as shown in figure 8, where it is possible to observe the before and after the 30 days of immersion in synthetic seawater. Again the control epoxy without graphene suffers severe corrosion and rust, while the epoxy samples loaded with graphene are practically free from the corrosion process. Graphene significantly increased the corrosion mitigation of the epoxy coating, even at load levels as low as 0.1% by weight. Corrosion mitigation has improved as the level of graphene loading has been increased. Both A-GNP10 and A-GNP35 (T) offered better protection against corrosion compared to pure epoxy.
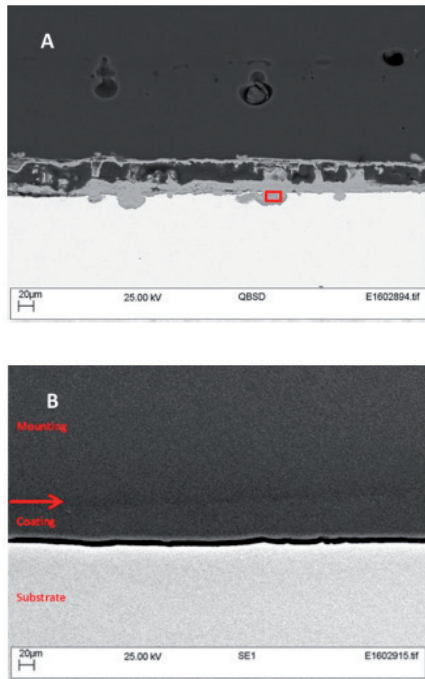
Figure 9: SEM micrographs of epoxy coated steel panels of cross-section after 1000 hours of salt fog test. (A) 0% control of graphene Epikote 828 showing growth of corrosion products under the epoxy coating. Inserting a red box marks the area examined using EDX. (B) A-GNP35 (T) 0.5% in Epikote 828 showing no corrosion of the steel substrate under the coating.

The SEM image of the panels characterizes the corrosion of the substrate under the epoxy coating, which is shown in Figure 9. The image on the left (A-D) is a cross-section of the panel coated with epoxy without graphene after 30 days of immersion. It can be seen that the seawater sneaked into the surface of the steel substrate causing it to corrode and show rust [16].

2.4.2 Wear Analysis

To perform the wear analysis by ball-on-plate test on substrates coated with composite film, the friction coefficient is measured in relation to the distance covered by the alumina sphere in the coating, thus, the measurement is interrupted when this friction coefficient on a quick change, that change is linked to the fracture of the lining. Using AA2024-T3 aluminum alloy substrates coated through

the Sol-Gel deposition process by a hybrid film formed according to the composition shown in Table 3 with and without the addition of graphene oxide particles, performed the ball-on-test plate to assess its wear behavior [22].

Table 3: Hybrid Film Composition.

Hybrid Film Composition	
Tetraethoxysilane TEOS of Sigma-Aldrich with 98% purity	4.2315 g
3-trimethoxysilyl-propyl-methacrylate (MAP) of Sigma-Aldrich with 98% purity	0.6365 g
Cerium nitrate (Ce(NO$_3$)) of Merck with 98.5% purity	0.0860 g
Ethanol (CH CH OH) of Aynth with P.A. purity	9.4608 g
Deionized water	2.8705 g

Varying concentrations of graphene oxide were added to the Si-1, Si-2, Si-3 and Si-u samples, which correspond to 1 g.L^{-1}, 0.5 g.L^{-1}, 0.25 g.L^{-1} and 0 g.L^{-1} respectively on Figure 10.
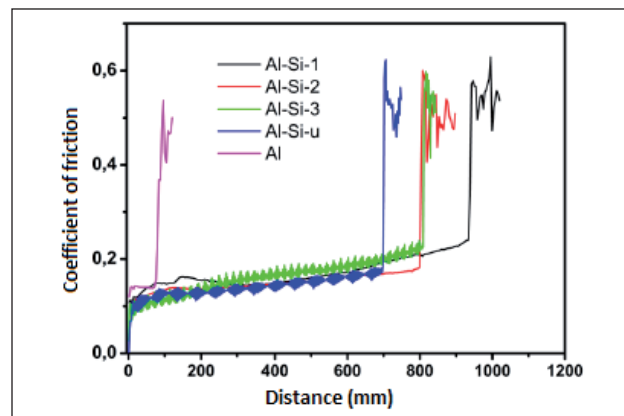

Figure 10: Graph of ball-on-plate analysis of substrates coated with composite film with and without GO.

The result of the wear analysis pointing to the graph suggests that the increase in GO particle concentration in the hybrid film causes an increase in wear resistance [22], as shown in Figure 10.

Mechanical Resistance

Studies conducted by our research group at CEFET-MG [23], demonstrated that epoxy composite materials reinfor-

Table 4: Results of mechanical tests of composites.

Number	Resin	Nanomaterial	Percentage (%)	Flexibility Modulus (Gpa)	Ultimate Tensile Strength (MPa)	Fatigue Limit (MPa)	Microhardness (HV 0.1)
1	Epoxy – LY 5032	-	0	2.95	31.57 ± 5.07	90.22 ± 16.35	17.60 ± 0.86
2	Epoxy – LY 5032	Graphene I	0.1	2.99	50.49 ± 5.42	70.00 ± 38.70	16.93 ± 0.35
3	Epoxy – LY 5032	Graphene I	0.3	3.00	49.65 ± 4.32	72.70 ± 24.28	19.47 ± 1.00
4	Epoxy – LY 5032	Graphene I	0.5	3.29	71.13 ± 1.31	99.76 ± 24.55	19.16 ± 1.17
5	Epoxy – LY 5032	Graphene II	0.1	2.52	60.65 ± 9.51	57.60 ± 11.27	18.43 ± 02.02
6	Epoxy – LY 5032	Graphene II	0.3	2.95	68.20 ± 5.67	93.88 ± 27.38	16.08 ± 1.14
7	Epoxy – LY 5032	Graphene II	0.5	3.18	74.73 ± 2.12	81.03 ± 21.78	17.97 ± 1.09
8	Epoxy – LY 5032	CNT I	0.1	4.30	54.35 ± 7.57	95.94 ± 20.28	18.38 ± 1.05
9	Epoxy – LY 5032	CNT I	0.3	3.28	55.95 ± 7.58	108.00 ± 9.88	16.53 ± 0.68
10	Epoxy – LY 5032	CNT I	0.5	3.58	44.41 ± 9.25	104.52 ± 55.52	16.53 ± 0.93

ced by carbon fibers (carbon allotropes) have shown much higher tensile and flexural strength values when compared to low-density metals widely used in the steel industry in special applications, reaching values higher than the order of 7 times for aluminum alloys and 1.5 times for titanium alloys. With promising results obtained by the usage of epoxy composite materials reinforced by carbon fibers, researches for improvement of its properties and application in various sectors have been subject of studies in a large scale.

Using epoxy resin composites with the addition of graphene and carbon nanotubes (CNT), our research group at CEFET-MG evaluated the behavior of specimens subjected to mechanical tests. Table 4 shows the analysis of the results obtained [24] and allows evaluating how the addition of nanomaterials (carbon nanotubes and graphene) can modify the structural behavior of the epoxy resin. In total, 15 substrates were produced for each composite, with 6 substrates submitted to the tensile test, another 6 submitted to the microhardness test, and 3 submitted to the flexion test. Analyzing the figure above, the author pointed out that composite 4 was superior to composite 7 in Flexion, reaching a value of 23%, and also superior to composite 1 (pure resin) by 10%. Regarding traction and the Elasticity Module, the difference between composites 4 and 7 was low, as shown in Table 4. It is worth noting that at low levels of nanoparticles by mass, composites 8 (0.1% CNT), 2 (0.1% graphene I), and 5 (0.1% graphene II) obtained very similar values in tensile, in the order of 70% above composite 1.
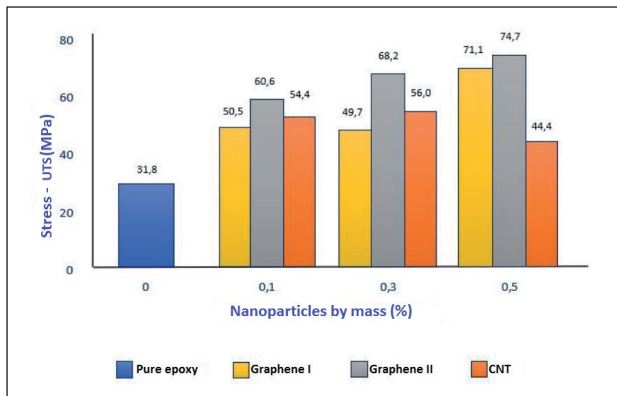

Figure 11: Variation of UTS as a function of the amount of nano-charge.

It points out that composites 4 and 7, epoxy resin with graphene I at 0.5% and graphene II at 0.5% by weight, respectively, stood out compared to the other composites from the structural point of view [24]. Both obtained an increase in the Tensile Strength Limit by more than 120% in relation to composite 1, as shown in Figure 11.
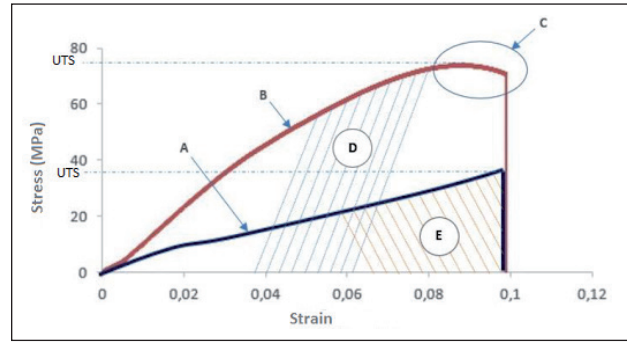

Figure 12: Stress-strain behavior of composites 1 and 7. A – Stress-deformation behavior of the composite 1; B – Stress-deformation behavior of the composite 7; C – Region showing plastic deformation; D – Area between curve B and horizontal axis; E – Area between curve A and horizontal axis; UTS – Ultimate Tensile Strenght (curves A e B).

The tests also showed a considerable increase in toughness, reaching more than 100%, to the point of modifying the performance of the material under stress, changing it from brittle (pure resin) to ductile [24], as shown in Figure 12.
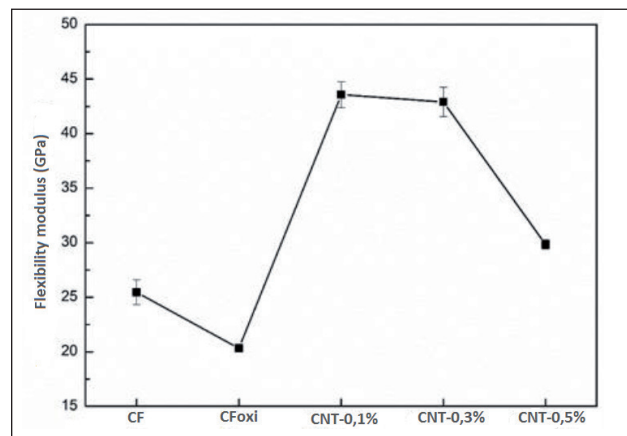

Figure 13: Flexibility modulus trend line in relation to carbon fiber treatment.

Using sizings of epoxy and carbon nanotubes (CNT) that consist of allotropic carbon material, it was found that when evaluating the trend line of the flexural modulus for surface treatment of the carbon fibers (CF) (Figure 13), the oxidation of the fibers causes a fall in the elastic modulus, while the deposition of 0.10% and 0.30% of CNT promoted a high increase in the modulus [23]. The deposition of CNT at 0.50% indicated an intermediate value of modulus, being higher than carbon fibers and oxidized carbon fiber (FCoxi) and lower than depositions of CNT at low levels. The results of mechanical resistance to flexion carried out in his study indicated that the oxidative surface treatment of the fibers caused a decrease in strength, while the sizing of CNT promotes an expressive gain in resistance to flexion.

Conclusion

As presented, coatings prepared by direct addition of 0.1% by weight of GO to the polymer matrix with lower viscosity show desirable GO dispersion quality, better adherence to the substrate, excellent barrier properties, and superior corrosion protection under NaCl electrolyte [7].

The permeation of water is an important parameter when evaluating anti-corrosion coatings. Substantial reduction in water intake and diffusion coefficient, as a function of graphene concentration, confirms graphene's ability to provide barrier protection [8].

The incorporation of graphene in the hybrid film on the substrate resulted in a dense network of graphene layers dispersed throughout the coating, explain the tremendous improvement in water permeation and corrosion attack.

The results [16] showed that the addition of very low charges of graphene A-GNP10 and graphene A-GNP35 (T) to epoxy coating systems can dramatically improve the corrosion mitigation of these coatings. Graphene offers a barrier to the diffusion of corrosive elements on the underlying surface. AGM believes that there is a potential in the usage of nanocomposite coatings that enable the removal or reduction of heavy metals and other anticorrosive pigments. The addition of the graphene particles A-GNP10 and A-GNP35 (T) from Applied Graphene Materials in epoxy coating formulations offers the chance to significantly increase the life of the coated parts

The ball-on-plate tests indicated an increase in wear resistance with an increase in the concentration of GO particles incorporated in the hybrid matrix film, wear-resistance, and abrasion properties are crucial for a good coating anti-corrosive [22].

In studies carried out by the CEFET-MG research group, we concluded that the composite material proved to be promising not only for structural composite applications but also on any exposed surface for various applications. It is up to a comparison study between alloys of metallic materials and CNT composite or even graphene/graphene oxide, which shows itself to be a material of very high mechanical resistance [23]. The results obtained in the mechanical tests of the samples of the various composites tested, of carbon nanotubes, graphene I, and graphene II inserted into the epoxy resin, confirm that the usage of graphene increases in the order of 70% the resistance of the composite compared to the pure resin, so that a significant improvement in the mechanical properties of the epoxy resin was identified with the addition of a small amount of nanomaterials [24].

Bibliographic researches prove the feasibility of using both graphene and graphene oxide in polymeric and hybrid coatings. The contents identified in research vary from 0.05% to 5.0% of addition on the weight of the coatings. Additions below 0.05% showed low efficiency in corrosion resistance, with the ideal content indicated in surveys above 0.1%.

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