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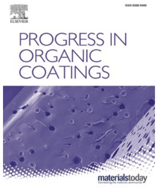

Review

State of the art and current trends on layered inorganic-polymer nanocomposite coatings for anticorrosion and multi-functional applications

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ABSTRACT

This review highlights the most important advances in the development and manufacture of advanced hybrid polymer-inorganic layered anticorrosion coatings for marine applications. These newly hybrid anticorrosion systems are gaining importance with the premise to improve the efficiency of the widely employed pure organic coatings, while widening the available types of polymeric materials employed. These could give rise to innovative high protective coatings with improved characteristics (mechanical strength, conductivity, biodegradability) or secondary functionalities (self-healing, anti-fouling). Through this document, four aspects are mainly overviewed, first, the use of 2D-layered inorganic fillers in coatings based on a barrier-type protection anticorrosion mechanism, with a special focus on graphene and its derivatives. Second, different modification strategies are presented, including covalent and non-covalent, always aiming to increase the compatibility between filler and matrix that would give as a result more efficient systems, due to 2D-layered fillers biggest drawback, their tendency to agglomerate. Third, different multi-functionalizing opportunities that graphene and its derivatives have to offer when introduced to these systems are reviewed, presenting some of the latest works reported in the past 2 to 3 years, while reviewing alternative layered structures such as natural clays or layered double hydroxides with their modifications. Fourth, different possibilities for multifunctioning these systems and their compatibility with graphene-like fillers are discussed. Finally, the conclusions and future perspectives on graphene-based anticorrosion nanocomposites are presented.

1. Introduction

Since metallic materials became mainstream in the building of marine transportations, warships and all kinds of offshore infrastructures, the fight against corrosion has been a major issue to enhance the stability and durability of these materials. Seawater is a complex, highly aggressive media, always exerting a corrosive effect on any material in contact with. Recently, the study by the National Association for Corrosion Engineers (NACE), a worldwide authority for corrosion control, has quantified the global annual cost in the fight against corrosion on US$ 2.5 trillion dollars, which represents a 3.4% of the global GDP. A widespread implementation of optimized corrosion prevention methods could mean savings between 15 and 35% (US$ 375–875 billions) [1].

Sea-water chemical properties must be carefully considered for selecting materials that are able to withstand no less than 25 years of lifetime operational periods. The corrosive potential of seawater is a function of a series of interdependent parameters including chemical (salinity, oxygen concentration, temperature and pH) [2], biological and mechanical factors. Corrosion and pollution are perniciously interrelated processes that affect the environment and the durability of marine structure materials [3]. Although different metallic materials and their alloys can be used for marine infrastructures, carbon steels, being inexpensive while offering good mechanical properties, are massively produced and used ($\approx 1.8 \times 10^9$ tons worldwide in 2018) [4]. These materials mainly suffer from uniform corrosion, allowing the modeling of the process to accurately predict short and long-term behaviors as

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well as their lifespan when immersed in seawater. The corrosion model proposed by Melchers et al. [5], comprises three phases where the first and second phases are controlled by O_2 concentration and diffusion, respectively. Thus, preventing the access of aggressive species to the metallic surface is known to be an excellent methodology to protect a material from environmental damage. A common way to achieve this effect is the application of anticorrosion coatings in barrier-type protections, which has become the most used approach and is the main focus of the present review.

Epoxy resins and polyurethane based coatings, acting as artificial barriers to separate the steel from the corrosive environment, are some of the most commonly employed materials as corrosion protection systems with applicability in a wide range of marine transports and infrastructures [6]. These protection systems may contain chemicals like binding agents, pigments or colorants for, among others, naval traffic security reasons [7]. These organic components are susceptible of being released from the coatings upon contact with seawater through leaching or weathering processes or material losses [8]. For a specific coating product, several factors, such as their concentration/viscosity, how the coating is applied, salinity of seawater, exposure to sunlight, stress corrosion cracking processes, *etc.*, determine their released quantity [8]. Thus, developing new forms of protection against corrosion based on eco-friendlier materials, with intrinsic durability, good substrate adhesion and adequate mechanical properties is key in order to withstand external stresses, mechanical solicitation or weathering [9], while minimizing the release of toxic substances during their application and operation times [10].

Thus, this review focuses on hybrid organic-inorganic corrosion protection systems, using eco-friendly 2D-layered inorganic fillers such as natural clays or layered double hydroxides (LDHs), traditionally employed, or more recently graphene (GR) and its derivatives graphene oxide (GO) and reduced graphene oxide (rGO). These late materials have started to display exceptional anticorrosion barrier properties for which they are generating an important research effort around them. This is evidenced by the continuously increasing number of publications (Fig. 1).

This document provides an overview on the uses of these inorganic components in nanocomposite anticorrosion coating systems, as it has been a recently explored strategy [11]. First, it presents its state-of-art and discusses its limitations and possible improvements. Then, it states the potential of 2D-layered inorganic-polymer nanocomposite multifunctional coatings, in particular, those based on GR and its main derivatives, as tools in the fight against corrosion of all kind of metallic tools and infrastructures. In a subsequent section, it presents the different possibilities for the functionalization of GR or its main derivatives, including both covalent and non-covalent approaches. Then, some alternative 2D-layered inorganic fillers will be reviewed, focusing on the specific applicability that each family of fillers may provide. Finally, it reviews the multi-functionalizing opportunities in graphene-polymeric anticorrosion coatings, such as, self-healing, antifouling, early-sensing or fire-retardant systems, giving examples shown in recently published research articles and covering all the possibilities that this technology of multi-functionalization can offer.

2. Barrier-type coatings: components, efficiency, limitations and environmental concerns

Regardless of the specific mechanism, the overall objective is to slow down or completely inhibit the electrochemical processes that contribute to corrosion [12]. Barrier coatings mechanism of action is based on preventing the accessibility of corroding chemical species to the aqueous-metallic interphase. Corrosive species are transported either by discrete low-resistance routes present within the coating or through hydrophilic regions in the coating matrix to the coating-steel interphase [9]. Thus, the overall protection is highly dependent on the impermeability and hydrophobicity of these coatings and increasing them are two fundamental strategies followed when designing these protection systems [13]. Over the past decades chromate-rich pigments, that have been restricted due to the toxicity and carcinogenicity of the potential hexavalent chromium release during their operational time [14] were a common strategy. Although pure polymeric systems have been an initial approach to substitute them, the use of other hazardous air pollutants and/or volatile organic compounds during their synthesis and preparations has also been severely restricted [15]. However, some interesting studies have been still developed in recent years for organic coatings such as the one by Poorteman et al. [16]. In this work, some improvements over commercial epoxy coatings were reported by employing novel para-phenylenediamine benzoxazine barrier coatings over 1050 aluminum alloys, observing a greater geometrical stability while UV-curing, efficiently maintaining their shape without contraction over the coated substrate and a highly reduced water uptake during saline tests, that could lead to improved anticorrosion protection.

Together with the mentioned restrictions, the major drawbacks of these systems, their potential failures due to the presence of defects such as pinholes, air bubble inclusions, poor adhesion between pigments or mechanical damages [17] have evidenced the need for further research in new more efficient and less pollutant solutions. As a consequence, a new and wide landscape of composite materials has appeared, aiming to expand the available options, while improving the overall efficiency. Some examples include conductive or engineered polymers, metal oxides, polysiloxanes, thermally sprayed cements, systems containing encapsulated monomers [18] and sol-gel coatings [19].

In order to overcome the drawbacks of inorganic or organic coatings on their own and inspired by the advances in the field of nanomaterials, hybrid inorganic-polymeric systems started to gather attention in the past decade. This new tendency aims at unifying multiple mechanisms of

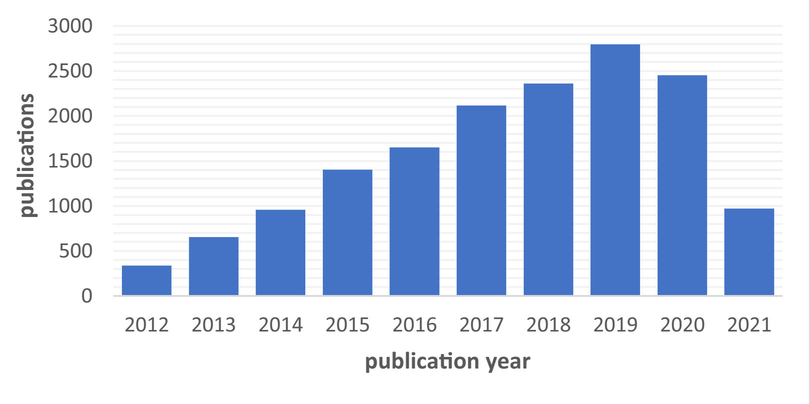

Fig. 1. Number of publications per year (2012–2021) with “graphene oxide” and “coating” in their titles. (Source: Web of Science, accessed 30th June 2021).

anticorrosion protection in a synergetic way in unique systems, increasing the lifetime of the protected components even on harsh corrosive environments [12]. The explored strategies have allowed the design of a wide range of coatings [20], including advanced amorphous metallic alloys [21], molecularly structured sol–gel coatings [15], engineered polymers [22], and multicomponent composite coatings [23].

Among hybrid polymer-nanoparticulated inorganic barriers, many are the possible fillers to be employed, for example, carbonaceous materials such as carbon nanotubes wraped in polydopamine that improve the anticorrosion properties of polyurethane coatings taking their electrochemical impedance from $6.83 \times 10^4\ \Omega\cdot cm^2$ to $1.01 \times 10^7\ \Omega\cdot cm^2$ after 7 ageing cycles tests [24]. Superhydrophobic silica nanoparticles may also be introduced in a polymethylmethacrylate matrix for obtaining a superhydrophobic coating (water contact angle = 158° and sliding angle = 2°) [25] by simply spraying over a steel surface, granting antiicing and remarkable anticorrosion properties. Metalic nanopowders (Zn, Al, Ti…) are also an option, with higher negative corrosion potential than the steel substrates, providing a cathodic protection mechanism against corrosion [26]. Furthermore, many different metal oxides can also be included with different effects for each one. As it has been reported by Shi et al. [27], the inclussion of SiO_2 nanoparticles into an epoxy coating can improve the Young's modulus of the coating through the improvement of its microstructure and thus, the anticorrosion performance. In another work, the addition of TiO_2 nanoparticles was proven to induce an anodic passivation mechanism [28] leading to the improvement of the barrier effect and the coating anticorrosion barrier performance. In the same way, ZnO nanoparticles may be used to fill up the interstitial spaces of acrylated epoxy coatings increasing the hydrophobicity and the overall corrosion protection [29].

Among all the 2D-layered inorganic materials, main focus of this review, some families, due to their high surface area and impermeability, together with other properties, have become relevant in the manufacturing of barrier-type anticorrosion coatings. These 2D-layered inorganic fillers include natural nanoclays (NC), layered double hydroxides (LDHs) [30] and more lately metal organic frameworks (MOFs) [31], nitrides or carbides with layered structures, such as boron nitride (BN) [32], *SiC* [33] or B_4C [34] and graphene-family products [35]. Aside from the impermeability, anticorrosion systems containing 2D-layered inorganic fillers are also preferred as they usually offer capabilities for multi-functionalitation. Natural layered nano-clays display the capability of encapsulation and releasing for self-healing applications [36]. Some metal-organic frameworks (MOFs) display an increase in hydrophobicity [37]. LDHs have additional anticorrosion capabilities due to their ability to contain anions in their interlaminar space [38]. These anions can be corrosion inhibitors [39] that can be released on demand and, in some cases, exchanged with corrosive species, such as chloride anions [40], acting both as controlled release systems and nanotraps. Graphene-family fillers offer the possibility of a high range of chemical modifications through both covalent or non-covalent interactions [41] which may improve the interfacial affinity and dispersibility of the fillers in polymeric matrixes [42], a key factor for taking full advantage of these fillers in anticorrosion hybrid systems.

3. Preparation and anticorrosion effect of layered inorganic-polymer nanocomposite coatings

2D-layered inorganic-organic coating structure is usually bioinspired in a “brick-and-mortar” structural concept, the one present in nacre on some bivalves mollusks shells, in which stiff aragonites act as fillers (or bricks) and are glued together with a soft polymeric matrix (or mortar) [43]. Strong interaction occurring in filler-matrix interfaces in such coatings can provide them with an orderly layered structure. These structures exhibit improved adhesion and integrality [44]. Meanwhile, diminishing the natural nano-capillarity existing within the filler laminates and interphases, *via* modification of the fillers or the crosslinking of the organic matrix, would, in principle, hinder the transport of O_2 and H_2O molecules through them. Fig. 2 shows the differential diffusion pathways of corrosive electrolytes through composite 2D-layered-organic coatings without (Fig. 2.a) and with (Fig. 2.b-d) a 2D-layered filler as graphene oxide. In Fig. 2, it is also appreciable the dependence on optimal loaded amount of the fillers and their homogeneous dispersions, avoiding low tortuosity paths (Fig. 2.b) or the appearance of microcracks in inhomogeneous dispersions (Fig. 2.c), to achieve efficient anticorrosion systems (Fig. 2.d).

When constructing efficient inorganic-organic nanocomposites, aside from the adequate dispersion of the fillers that could improve the stiffness, ductility and fracture toughness of the final material [46], maximizing their active surface area needs to be considered. However, high surface areas promote interactions between nanoparticles causing them to agglomerate [47], increasing the difficulty of some preparation processes. Among the different methodologies employed in the preparation of organic-inorganic nanocomposite materials [48,49], some become more relevant in order to make the composite slurry containing polymer and 2D-layered fillers easy to be deposited on substrates. The possible scalability of the process, the layered structure of the inorganic fillers, the rheological behavior of the mixture and the overall costs need to be considered. Thus, mechanical mixing, solution intercalation and *in-situ* polymerizations are some of the most employed methodologies.

In mechanical mixing, it is important to consider the time and speed of stirring [46]. For a procedure based on this inexpensive and easy methodology, the filling materials need to be carefully chosen or designed. Fillers would require an adequate functionalization for an optimal interaction with the matrix and, according to the Derjaguin-Landau-Verwey-Overbeek theory [50], enough surface charge (ζ potential) to achieve meta-stable dispersions within each specific matrix. Solution intercalation relies on the ability of the filler to be disaggregated in thinner sheets allowing the polymeric chains intercalation between them, thus, maximizing the interphase filler-matrix. These processes may be assisted by ultrasound bath immersion or ultrasound processing [51], in which case, the output energy, duration and temperature control need to be controlled to avoid undesired early curing processes [46]. Both methodologies are easily scalable as they rely only on relatively non-expensive instruments, such as a magnetic stirring plate, an ultrasound bath or an ultrasound processor.

In *in-situ* polymerizations, monomers or prepolymers/oligomers, plasticizers (not in every case) and the 2D-layered fillers are firstly mixed to subsequently produce the polymerization of the system by adding the corresponding initiators and external stimuli (heat, UV radiation, …), if required [52]. The *in-situ* polymerization methodology usually simplifies the composites preparation processes while ensuring high interfacial stability and compatibility among the different components [53]. A wide range of types of polymerization reactions are adequate for *in-situ* conditions, including radical, cationic or anionic [54], among others. Thus, *in-situ* polymerization technique is ideal for achieving composites with 2D-layered fillers covalently connected to a polymeric matrix, producing latexes with high colloidal stability, decreasing fillers aggregation and allowing highly uniform dispersions during coating/film formation processes [55].

As has been mentioned, the maximizing of layered fillers dispersibility and active surface area are two of the most employed strategies. Surface grafting through covalent interactions and self-assembly processes mainly based on physical interactions.

The covalent modification approach is a state-of-the-art procedure that can be applied to all kinds of layered structures. An improvement in the fire-retardant capabilities of LDHs can be achieved when modified with *Zanthoxylum bungeanum* seed oil, by improving its dispersibility when added during the processing of leather [56]. This approach is applicable to nanoclays, as in the work by El-Fattah et al. [57]. In this work, an organic modification with octadecylamine improved nanoclay dispersion in a polyurethane matrix enhancing final material corrosion protection, thermal stability, flame retardant capacities and mechanical

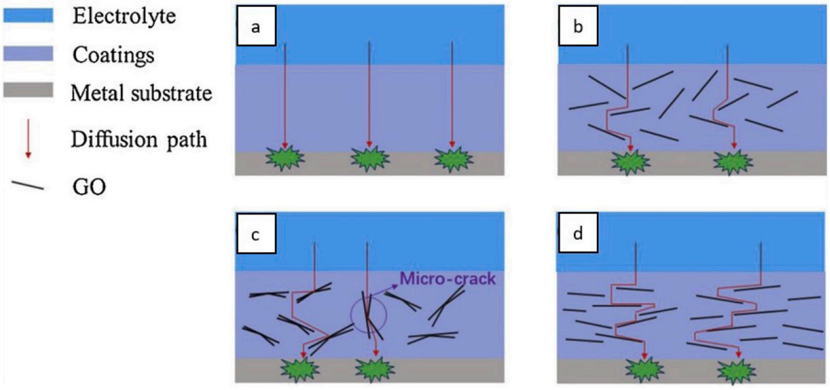

Fig. 2. Schematics of a 2D-layered inorganic (GO)/polymer composite anticorrosion coating with elongated pathways for corrosive species. (a) Pristine coating. (b) Coating with insufficient filler load, (c) Coating with optimal filler load but poor dispersion, appearance of microcracks. (d) Coating with optimal filler load and homogeneous dispersibility. (Reprinted with permission of Wang et al. [45]. Copyright 2012, Elsevier).

properties. With graphene-family fillers, the covalent approach is usually employed with GO due to its convenient functionalization. The applicability of covalently modified GO is being studied not only in anticorrosion materials [58–61], but also in a wide range of other applications [62–64]. Meanwhile, self-assembly approaches can be found with both GO and GR in the improvement of anticorrosion capabilities of modified lignin/graphene/waterborne epoxy coatings [65], as part of promising oil/water separation membranes [66] or as biosensor [67]. The stated examples evidence the increasing interest focusing on the *ad-hoc* modification of inorganic 2D-layered fillers for, the improvement of existing or the construction of novel, multifunctionalized coating nanocomposites.

4. Graphene and its derivatives in polymer nanocomposites anticorrosion coatings: description, dispersion and applications

Graphene, discovered by Geim and Novoselov in 2004 [68], is a one-atom-thick planar sheet of sp^2-bonded carbon atoms, densely packed in a honeycomb crystal lattice (Fig. 3.b). Graphene sheets can be obtained by mechanical exfoliation of graphite (Fig. 3.a), among other techniques. Graphene high strength (Young's modulus 1 TPa) [69], high thermal conductivity (5300 W/m/K) [70], optical transmittance make this material a promising candidate for a broad range of possible applications [68,71]. Furthermore, the research effort focused on graphene evidenced the potential of this novel material in corrosion protection systems. Since their discovery and develop of knowledge, graphene and its derivatives, graphene oxide (GO) and reduced graphene oxide (rGO) (Figs. 3.c, 3.d) have been considered ideal candidates for the construction of protective anticorrosion layers, due to Its high current density,

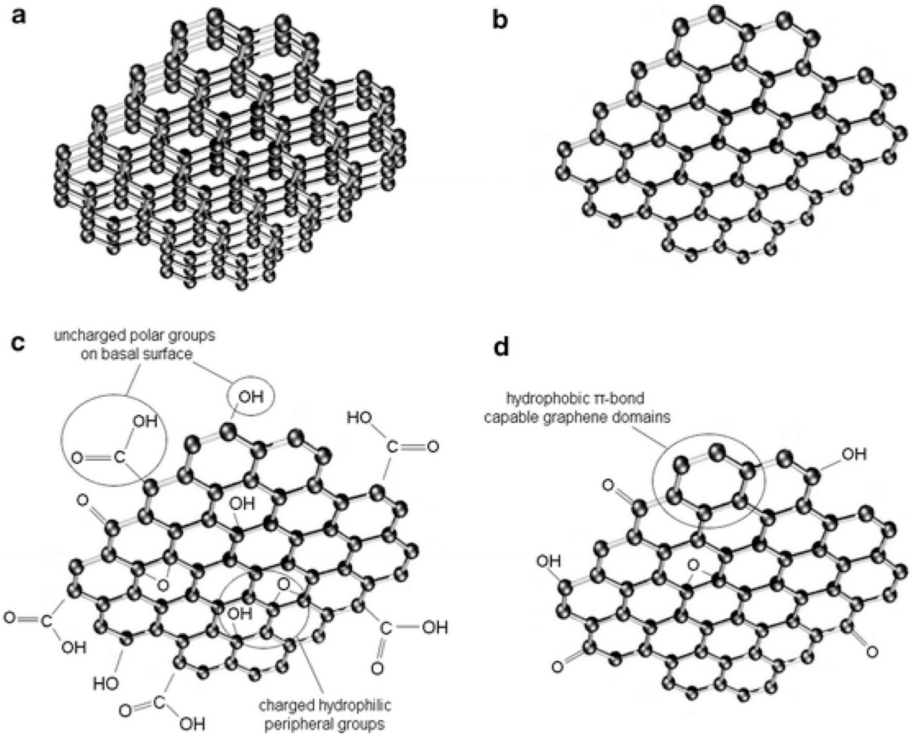

Fig. 3. a) Graphite, b) graphene and its main derivatives: c) graphene oxide and d) reduced graphene oxide. (Reprinted with permission of Jastrzębska et al. [74]. Copyright 2012, Springer).

high surface area (2630 m^2/g) [72], chemical inertness, environmental friendliness, super-hydrophobicity at nanometric scale and impermeability [11]. Graphene properties vary whether it is 1–2 layered, multilayered or presenting alternative structures such as carbon nanotubes or fullerenes. Among them, sheets of mono/bi-layered graphene to graphene with up to 10 layers are the most adequate for anticorrosion applications due to their large active surface area being taken as an advantage, while avoiding an excessive defects and pore densities typical of 3D graphene [73] that could accelerate corrosion processes.

Several attempts for graphene and its derivatives utilization as part of this kind of coatings have been lately focusing research efforts [75]. Examples of anticorrosion systems contining graphene family fillers were reported by Yu et al. [76] in which polystyrene (PS)/modified-graphene oxide (GO) nanocomposites were successfully prepared using *in-situ* miniemulsion polymerization. These nanocomposites showed an increased corrosion protection efficiency from 37.9% of pure PS to 99.53% with the incoporation of 2 wt% modified GO, as well as improved thermal stability (decomposition temperature from 73 to 372 °C) and storage modulus (from 1808.76 to 2802.36 MPa). Another example of graphene-based composites was reported by Yang et al. [77] In their study, fluorographene was used to modify a superhydrophobic epoxy coating synergistically coupling the protection function of both superhydrophobic surface with organic coating, granting it with anticorrosion and self-cleaning properties.

Structurally complete graphene in its ideal honeycomb lattice and two-dimensional structure is, in principle, impermeable, an important property to be considered when designing anticorrosion barrier type coatings. Furthermore, coatings based on these materials have already proven their efficiency inhibiting the corrosion of different metallic surfaces such as copper [78], nickel [79], aluminum [80] and iron [81]. The efficiency of graphene as anticorrosion additive is mainly based on its impermeability [82] and highly relies on its uniform dispersion, a correct orientation, parallel to the metal surface and an adequate adhesion strength between the coating and the protected substrate [83]. Unfortunately, graphene inertness and lack of functional groups on its 2-D lattice [84] results in poor adhesion strengths and dispersibility in polymeric matrixes with graphene sheets tending to agglomerate [85]. With the premise that oxygen-containing groups on GO surface (hydroxyls, epoxides and carbonyls) could improve the interactions with the polymer matrix improving both dispersibility and adhesion, these graphene derivatives gain prominence in the overall research effort. Fig. 4 shows how a single graphene oxide sheet could be combined with either nanoparticles, mainly interacting with oxygen containing groups or polymeric fillers, which usually would prefer to interact with the hydrophobic regions.

4.1. Graphene oxide

Graphene oxide is obtained from natural graphite by chemical exfoliation [87] or by the Hummers method [88] involving the oxidation of graphene with $KMnO_4$ in highly concentrated H_2SO_4. The 2D lattice of graphene oxide sheets is decorated with oxygen-containing functional groups (epoxy, hydroxyl, carbonyl, carboxylic) that improve its chemical reactivity and dispersibility in water or other polar solvents [89]. However, graphene oxide sheets are not flat but rather rough (surface roughness ≈ 0.6–0.8 nm [90,91]) with a predominantly amorphous structure. GO is usually characterized by its chemical compositions, usually its C/O ratio, depending on the initial graphitic material and its synthesis conditions [92]. Introduction of hydroxyl groups also makes GO hydrophilic, whereas graphene is strongly hydrophobic [93]. The most commonly used method to obtain few layered graphene oxide sheets is to produce its exfoliation *via* sonication process of aqueous dispersions. Among its multiple applicability and due to its biocompatibility, ultrahigh drug loading capability, and ease of surface functionalization, graphene oxide displays a great interest for biomedical applications [94,95].

One of GO most important advantages is its compatibility with a wide variety of polymeric matrixes, among which, good alternatives for using more ecological friendly polymers can be found. This represents a much-desired fact for marine contamination control agencies. Examples of eco-friendly polymers compatible with GO with their applicability aimed at anticorrosion systems include waterborne synthetic polymers, such as polyvinyl alcohol (PVA) [96] or waterborne polyurethanes (WPU) [97] and biopolymers, such as, alginate (ALG) [98], chitosan (CHI) [99], carboxymethyl cellulose (CMC) or xanthan gum [100], among others. Furthermore, in biopolymers, the presence of multiple adsorption centers in which hydrogen bond interactions between GO fillers and their correspondent matrixes functionalities are promoted, granting them part of their interest [100]. Physical adsorption through hydrogen bonding is a well-known strategy to provide acceptable mechanical properties, through non-covalent crosslinking, usually leading to strengthened particle-particle interphases [101]. This combination of GO with biopolymers usually allow full waterborne systems with an excellent film forming capability by simple evaporation of bulk water, followed by an interfacial tension-induced deformation of the colloidal polymer particles and finally the interpenetration of the polymer molecules across the particle–particle interface [102]. Water soluble polymers have been already explored to obtain application-specific composite coatings for a wide range of substrates by easily scalable techniques such as, solvent evaporation [103], layer-by-layer assembly [104] or vacuum filtration [105].

4.2. Reduced graphene oxide

Reduced graphene oxide can be obtained employing several reducing agents [106] or by thermal reduction [93]. The removal of functional groups during the reduction of GO increases the C/O ratio which translates into the curing of structural defects, reducing the

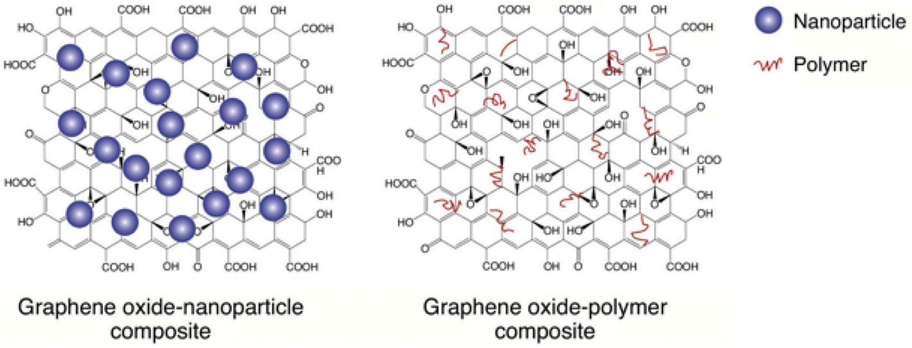

Fig. 4. Schematics of the functionalization of a graphene oxide sheet with nanoparticles or polymeric components. (Reprinted with permission of Zhao et al. [86]. Copyright 2017, Elsevier).

nanopores generated in the laminar structure by these groups [107] (Fig. 5). These reduction process also regenerates part of the π conjugated system, thus creating alternate pathways for electrons, stopping them from reaching cathodic areas and slowing the corrosion cycle. In De and Lutkenhaus [108] and Chu et al. [109] the results highlighted the need of a good balance between GO/rGO and PVA to obtain good barrier and electronic properties while resisting swelling effects. Meanwhile, rGO has also been employed in combination with synthetic waterborne polymeric matrixes, such as polyesteramides [110] or polyurethanes [111] obtaining rGO reinforced composite coatings with superior anticorrosion performances.

4.3. State of the art in anticorrosion coatings containing graphene-family fillers

During 2010s decade several scientific works started to assess the compatibility of graphene products with some of the most employed polymeric matrixes in the coatings industry, as epoxy resins [112,113] or polyurethanes [114]. Many of these works also stated the improvement in anticorrosion efficiency of these novel graphene containing coatings when compared with their pristine counterparts [115–117]. Supported by these early works several companies started to develop their own formulations and have already made commercially available graphene-based anticorrosion painting. Among these companies Applied Graphene Materials (UK), Electro Conductive Products (UK), Sherwin-Williams Protective and Marine Coatings (US), The Sixth Element Materials (China) and GrapheneStone (Spain) which have developed ecological, more-durable paints combining lime with graphene technology, are worth mentioning [118].

Despite these promising beginnings, to date, commercially available paints containing graphene products offer a limited increase factor of 2 to the anticorrosion protection. Furthermore, these commercial coatings are still bind to the use of potentially environmentally dangerous products, solvents or additives, as zinc (highly toxic for aquatic life), in most formulations or the evolution of toxic species during their operational time. Besides, under the new ISO 12944-2018 for marine environments, the duration of the performance evaluation tests has been extended to several 4200-h runs of how coatings behave under different temperatures, humidity and immersion levels [119]. With these challenges to overcome, a considerable number of publications, some reviewed in the following sections, evidence plenty of room for improvement. This technology needs to start addressing problems such as the optimization of the right amount of filler to employ, the improvement in the different methods and chemical strategies to improve the dispersion, the multi-functionalization of the final products, for example with a self-healing ability and the employment of alternative more ecological friendly products.

4.4. Improvement of graphene-like fillers properties in organic matrixes

Despite the advances made in graphene-based nanocomposites during the last few years, some challenges still need to be addressed for these materials to reach their maximum expectations. Among these challenges, the control of the alignment and spatial organization of the graphene-based fillers, the poor interfacial adhesion with the absence of covalent interactions and the exploration of less risky synthetic routes with less solvent wastes, are the most important [75].

When employing GR or GO sheets as fillers one of the most challenging aspects is its concentration. In graphene, due to the promoting of π-π interactions between sheets [120], as well as in graphene oxide, due to the affinity between different oxygen containing groups through hydrogen bonds or other electrostatic interactions [121,122] the stacking of different layers is favored, producing their self-aggregation [123]. As it has been reported, the water barrier and mechanical properties of GO-polymer composites starts to be enhanced with the addition of 0.04–0.08 wt% GO [124]. Employing higher GO concentrations may cause the aggregation of GO, leading to the reduction of its active surface area, which actively block the diffusion of corrosive species. This aggregation phenomenon always has negative effects on barrier-type coatings performances. First, the total active surface of graphene and its derivatives is considerably reduced, thus shortening the permeation paths for corrosive species to travel through the coating [125]. Second, due to these interactions between layers, the dispersibility of these species is difficult even in solvents with affinity, resulting in an increased viscosity of the coating mixture, making its deposition step difficult [126]. Additionally, these self-aggregation phenomena leads to inhomogeneities in the materials and induces defects that hinder its mechanical properties by reducing the intimate union between matrix and fillers [127] which would, in addition, favor the corrosive species migration.

To date, many research works have been developed with the aim of obtaining homogeneously dispersed graphene/polymer systems through four main approaches: unmodified simple mechanical dispersion, unmodified wet transfer dispersion, chemical covalent modification and dispersion and non-covalent physical adsorption and dispersion [125], evidencing some of its limitations. Unmodified strategies, based on the principles of similarity and inter-miscibility of materials, presented problems as long-time complicated operations, unstable dispersions and environmental issues regarding the aqueous phase waste liquid when their scalability to high-volume industrial productions was evaluated. Modifications approaches could help by improving these fillers affinity with the matrix, and, in turn, produce an increase in their dispersibility and homogeneity, thus reducing the effect of the stated issues [128]. However, the drawbacks for each specific modification strategy need to be considered. While covalent interactions would offer better mechanical properties, the cleavage of some chemical bonds during grafting reactions could introduce structural damage. For physical modifications/adsorptions, based on non-covalent interactions (electrostatic, electron orbital conjugation or hydrogen bonding), it can guarantee a more intact structure of each individual sheet, but the whole system would probably lack the superior mechanical properties of covalent modified systems [125].

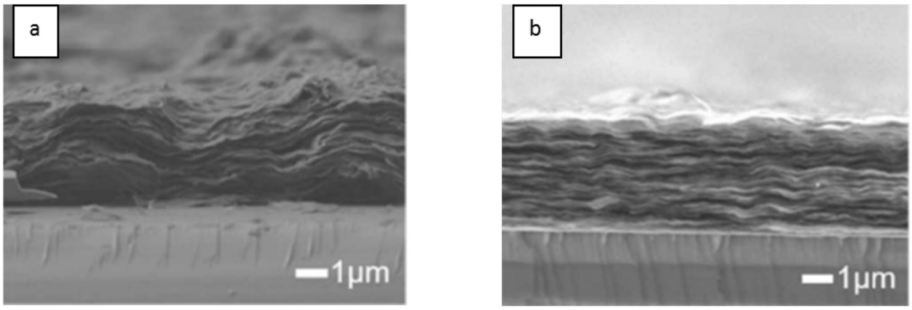

Fig. 5. Cross-sectional SEM images of PVA/GO-coated silicon coating over aluminum alloy substrates before (a) and after (b) 8 min reduction process with HI. (Reprinted with permission of De et al. [108]. Copyright 2018, RSC)

The covalent modification of graphene aims to maintain the fillers chemical stability and the whole coating mechanical properties [129]. These kinds of modifications involve the surface grafting of amphiphilic molecules, with a hydrophilic part able to interact with the filler and a hydrophobic part that would increase the compatibility between filler and matrix. The most followed approaches at this regard include the bonding of polymer chains, small molecules or nanoparticles [76,130,131]. By employing this methodology, the filler may adopt the characteristics of the polymeric matrix and improve the overall performance of the coating [132]. This state of the art strategy is present in many published works, such as the work reported by An et al. [133] where covalently modified graphene oxide was achieved by grafting 4,4′-methylenebis(phenyl isocyanate) (MDI) (Fig. 6). The followed approach was the grafting of isocyanate containing molecules by reaction with the hydroxyl groups to graphene oxide surface. Reported researches following this strategy have already proven a decrease in the hydrophilicity [134] and the antistacking effect of the individual sheets [135] whilst increasing the total active surface area [136]. Back on the work by An et al., they successfully obtained the modified MDI-GO achieving a nanocomposite material with enhanced thermal stability and electrochemical properties when compared with pure GO. The obtained results allowed the design of a new scalable and economical way for GO modification that could improve the anticorrosion performance of polystyrene coatings by enhancing its barrier mechanism efficiency.

Other reported covalent modification strategies include the work by Haghdadeh et al. [137]. In an attempt to improve the anticorrosion and mechanical properties of polyurethane (PU) coatings, graphene oxide sheets covalently functionalized (fGO) with (3-glycidyloxypropyl) trimethoxysilane were introduced into the matrix. The results obtained after the characterization process evidenced a tensile stress, energy at break, loss factor and storage modulus significantly higher, while improving the fGO stability and dispersion when compared to unmodified GO/PU coatings. The interfacial bonds between the PU-fGO nanosheets were significantly enhanced. This last result was also assessed *via* theoretical quantum mechanics approaches to examine the interactions of trimethoxy silane with polyurethane and GO surface.

An additional example of the covalent approach was reported by Li et al. [138]. In their first published paper devoted to this study, the researchers provided a new methodology for microwave-assisted simultaneous reduction and titanate treatment of graphene oxide. Titanate coupling agent was used for this functionalization (Fig. 7) with results proving its covalently bonding to the graphene oxide surface. Meanwhile, the hydrophilicity of graphene oxide was maintained after the simultaneous reducing process using hydrazine hydrate as reducing agent, while restoring some of graphene conductivity. Finally, the researchers successfully obtained a polyurethane with modified reduced graphene oxide nanocomposite coating by mixing a 2 mg/mL of the modified GO solution into the waterborne polymeric matrix. The increased anticorrosion properties of PU composite coatings were evaluated in the late published paper at this regard [111] by electrochemical impedance spectroscopy. The results evidenced an increase of the anticorrosion efficiency achieved when adding 0.2 wt% of the previously prepared filler. Furthermore, the results proved that with a filler concentration of 0.4 wt% the self-alignment of the sheets, parallel to the substrate, could be driven by the reduction of the total excluded volume. This procedure allowed the full utilization of its high surface area, further preventing the permeation of electrolytes and improving the performance of the coating.

In a recent explored strategy, the covalent functionalization of GO can be performed employing conducting polymers such as polyaniline, polypyrrole or polyacetylene with unique electrochemical properties that have, recently, granted them a considerable attention. These polymers can effectively protect the metals from corrosion through a passivation mechanism, as it has been reported in previous reviews [139,140] and in the work presented by Baldissera et al. [141], in which different forms of polyaniline (PANI), undopped-PANI, sulfonated-PANI and PANI fibers were introduced in epoxy coatings achieving increased anticorrosion performances in every case.

Non-covalent modification of these inorganic fillers occurs mainly *via* the interaction of π-π bonds, hydrogen bonds and/or ionic bonds [142], and it is usually aimed at facilitating the conductivity of the coating or achieving an ultra-high specific surface area of the filler [129]. A graphene non-covalent modification strategy was presented by Chen et al. [142], where poly (2-butylaniline) (P2BA) was employed as dispersing agent (Fig. 8) *via* π-π interactions with graphene nanosheets. The functionalized graphene sheets were incorporated in an epoxy resin coating remarkably improving its corrosion and wear resistance properties that could be attributed to the synergistic effects of the redox catalytic capability of P2BA, and the high mechanical and barrier properties of well-dispersed graphene nanosheets (0.5–1 wt%) in the epoxy matrix.

A novel eco-friendly approach has already been described by Cui et al. [143], and in their work, polycarbodiimide (PCD), a crosslinking agent of water-borne PU, was selected to modify GO. By varying the PCD/GO ratio, three different conformations of functionalized graphene were generated. Molecular dynamics simulations were carried out to study the correlations between the PCD/GO ratio, the conformations of functionalized graphene and dispersion state of graphene layers. The results of electrochemical impedance spectroscopy, after 120 days immersion time, evidenced the best anticorrosion efficiency being when

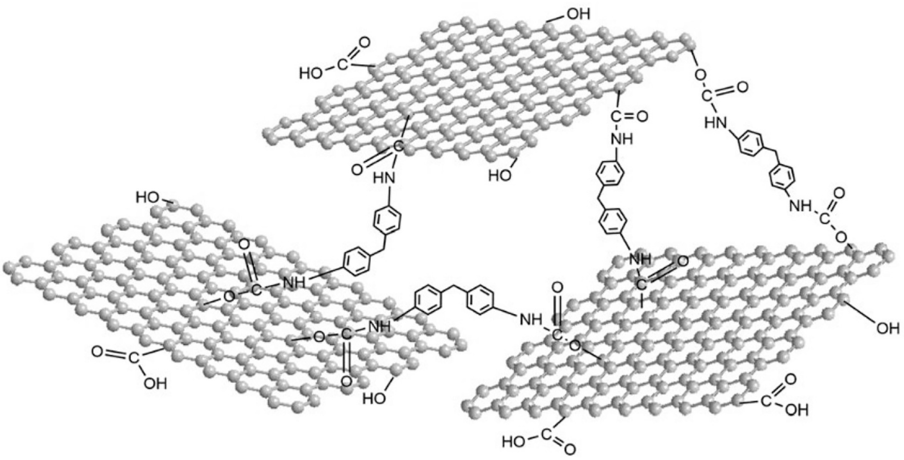

Fig. 6. Covalent modified graphene oxide with 4,4′-methylenebis(phenyl isocyanate) chemical structure. (Reprinted with permission of An et al. [133]. Copyright 2019, Springer).

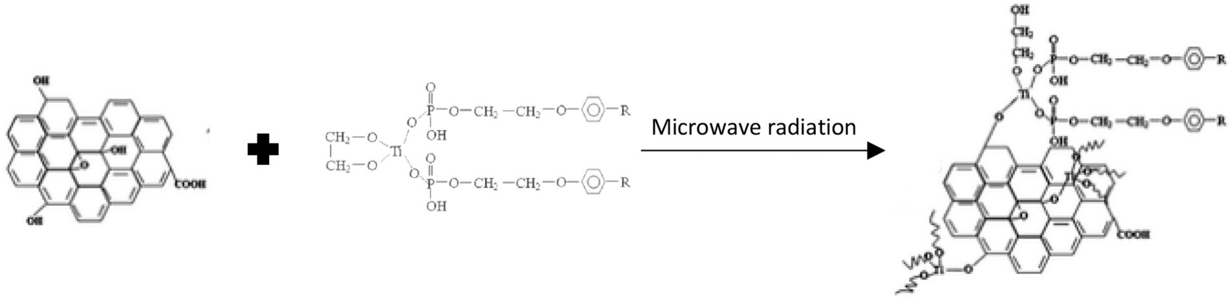

Fig. 7. Schematics of the reaction between GO and titanate coupling agent. (−R represented for carbon chain). (Reprinted with permission of Li et al., *J. Mater. Chem. A*, copyright 2012, RSC) [138].

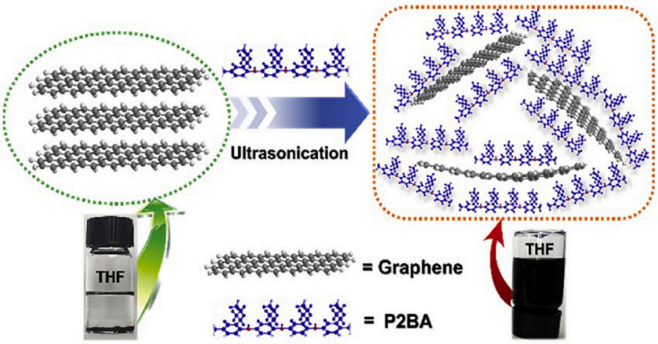

Fig. 8. Dispersion of graphene in organic solvent using P2BA as dispersing agent. (Reprinted with permission of Javidparvar et al. [142]. Copyright 2019, Elsevier).

0.2 wt% functionalized crosslinkable GO was added, with a PCD/GO mass ratio over 8.75 favoring the tail conformation over grape-cluster or network conformations. Another example of the eco-friendly approach is presented in Ionita et al. [144], where they obtained composite alginate-GO films presenting a 300% improved Young's modulus in comparison with pure alginate films, when up to 6 wt% of GO was added. Furthermore, the combination of graphene and its derivatives with biopolymers opens up the possibility of further introducing additional chemical crosslinking *via* different methodologies thanks to these polymeric systems convenient functionalization and well-known structures. Among these strategies, the methacrylation of polysaccharides [145,146] enables them for UV-curing (photopolymerization) processes or different environmentally friendly external crosslinking agents such as citric acid [147], appear as promising alternatives.

One recent and remarkable work in which the best of both covalent and non-covalent modifications is brought together was reported by He et al. [148]. In this work, graphene (GR) was initially modified through π-π interactions with tannic acid (TA) and γ-(2, 3-epoxypropoxy) propytrimethoxysilane (KH560) was then used to modify the graphene-tannic acid hybrids, which greatly improved its dispersibility in an epoxydic matrix (Fig. 9). These hybrid covalent/non-covalent coatings displayed an improved anticorrosion performance when compared with pristine epoxy or epoxy/GR-TA coatings (Fig. 12.a), with greatly reduced corrosion byproducts detected during the first 100 h and 200 h of service, as well as higher water contact angle 82.4° ± 0.82° for the GR-TA-KH560/epoxy (0.7 wt%) system (Fig. 12.b).

As important as the modification of GR and its derivatives towards achieving an adequate dispersion, is the availability of one or several techniques to evaluate it. Initially the dispersibility of modified graphene-like products is usually studied in aqueous dispersions, prior to their incorporation to the polymeric matrixes. This can be performed by measuring their zeta potential and average size [149]. An easy way to obtain these results is by means of dynamic light scattering (DLS). More negative potentials ($\zeta < -30$ mV) and smaller sizes, would hint to, in principle, more homogeneous dispersions [150]. Once the fillers are introduced in the polymeric matrixes, microscopy techniques, as scanning electron microscopy (SEM), transmission electron microscopy (TEM) or atomic force microscopy (AFM) are usually employed for the assessment of an optimal dispersion state, as well as for determining their sizes and morphologies [151]. Additionally, spectroscopy techniques as Fourier transform infrared spectroscopy (FTIR) or UV–Vis spectroscopy, may allow to obtain information over the different interactions present among components before and after the obtention of the coatable mixtures and the final coatings/films. Furthermore, when employing graphene products, Raman spectroscopy would provide information over the defects induced on them by the variation on the Csp$_2$/Csp$_3$ hybridized carbons proportion [152] due to the various chemical modifications. X-ray diffraction (XRD) may be also of use for studying the relative orientation of the nanoplatelets when comparing different pole-figures obtained with the sample being irradiated from different angles.

Published works [153] include a number of examples on the

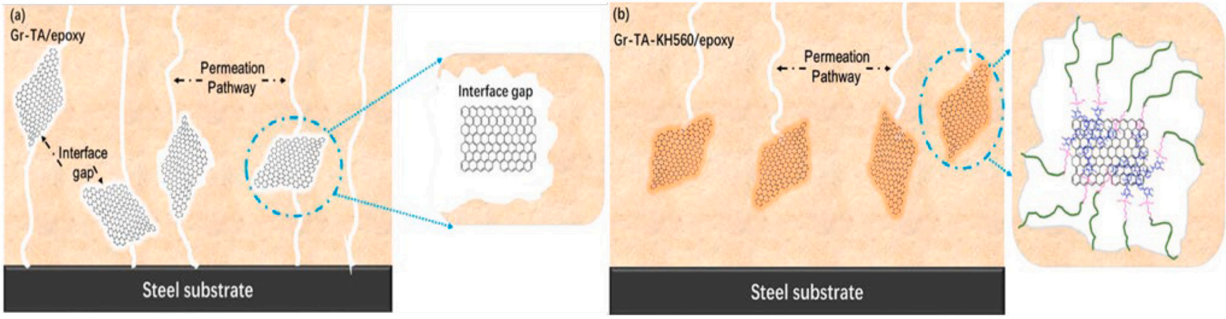

Fig. 9. Anticorrosion barrier-type protection mechanism of hybrid tannic acid-graphene/epoxy coatings (a) with unblocked interfacial gaps favoring the permeation of corrosive species *vs.* KH560 modified tannic acid-graphene/epoxy coatings (b) with antipermeating crosslinked interfaces. (Reprinted with permission of He et al. [148]. Copyright 2019, Elsevier).

employment of mentioned techniques to study the dispersibility and morphology of different 2D-layered inorganic fillers in nanocomposite anticorrosion systems. In Li et al. [153] UV–Vis and Raman where employed to analyze the interactions filler-stabilizing agent-matrix while TEM was employed to analyze dispersion (Fig. 10.a) and morphology, the latter supported by SEM and AFM (Fig. 10.b) as well.

These techniques are available for any kind of layered structure as in Cui et al. [32] with hexagonal boron nitride (h-BN) sheets as fillers in an epoxy resin (EP) matrix (Fig. 11.a-c).

Although TEM and AFM are more restricted techniques not at the disposal of every research team, SEM, a relative instrumentally cheaper technique is adequate for the study of fillers dispersion. Investigating the fracture surface morphology is a common methodology for studying the dispersion state of particles in the coating matrix. The morphology of the fractured area and the way cracks propagate give information over the interfacial particles/matrix interactions state [154]. In a work by Ganjaee et al. [155], a field emission scanning electron microscope (FE-SEM) was employed to study the dispersion of both GO and nanoclay (NC) sheets and their colloidal stability introduced in epoxy-phenolic hybrid matrixes. The FE-SEM micrographs obtained (Fig. 12.a-b) allowed the determination of the optimal proportion GO/NC set finally in 34:66 to obtain the most homogeneous dispersion, improved mechanical properties and the highest anticorrosion protection capacities.

A good example on the use of Raman spectroscopy is the one presented by Jiang et al. [156] where Raman mapping was employed to study the distribution of GO sheets with different aspect ratios in epoxy resin matrixes. This was achieved by measuring the relative intensity ratio of the GO-D characteristic Raman band (1350 cm^{-1}) and the characteristic epoxy Raman band (1100 cm^{-1}) over a surface of 100μm^2. This technique clearly revealed the uniform dispersion of different aspect ratio GOs, without presenting severe aggregation as shown in Fig. 13.a-c.

Despite all these important efforts to develop new graphene-based anticorrosion coatings, additional problems derived from graphene production method in large quantities, mainly during the reduction of graphene oxide, arose. The oxygen containing groups in GO cause nanopores in the two-dimensional sheets that do not completely disappear during the reduction process, thus hindering their impenetrability and potential protection [157]. This drawback produces an important challenge in the research effort which has led to the use of graphene and its derivatives as fillers on graphene modified organic nanocomposite coatings, rather than the use of reduced graphene made by chemical vapor deposition. The different polymeric matrixes could help solving this graphene inherent defectology issue. Table 1 includes a summary of all the systems described in the reviewed literature and their most important achievements.

5. Alternative layered fillers to be used in anticorrosion composite coatings

When designing and developing efficient anticorrosion systems, there have been other significant approaches and strategies followed during the last years. Before the development of knowledge around graphene and its derivatives, which have focused the attention in the last years, some alternative materials were used as impermeabilizing inorganic fillers in organic matrixes, such as natural clays and LDHs. Furthermore, MOFs have also started to attract some attentions. These alternative fillers display some unique properties that will be overviewed in this section, making them suitable candidates for some specific applications.

5.1. *Natural nanoclays*

Clay minerals are phyllosilicates which provide plasticity to natural clays and allow them to harden upon drying or firing [161]. The adequacy of these nanoclays as fillers in anticorrosion hybrid coatings is based on their large surface area and low toxicity [162], together with the adsorption and cation exchange capacity and good solubility and rheological properties [163]. Among many mineral families, two of the more employed nanometric clays used to be dispersed in polymeric matrixes are based on their structures such as montmorillonite (MMT), a hydrated swellable, smectite-type clay with general formula $(Na, Ca)(AlMg)_6(Si_4O_{10})_3(OH)_6XH_2O$ [164], with silica and alumina as essential components. An alternative to MMT is those with a sepiolite-like (Sep) structure formed by two silica tetrahedral sheets around one central magnesia octahedral sheet with $Si_{12}O_{30}Mg_8(OH, F)_4(H_2O)_{4.8}H_2O$ [165] as their unit cell formula.

The layered structure of montmorillonite type clays makes them perfect candidates for brick and mortar type composite coatings as evidenced in many research works, and among the recently published ones, it is worth mentioning the research by Mehrabian et al. [164]. The researchers studied the effect of 2-benzylbenzimidazole as surface modifier of Na^+-MMT nanoparticles for improving their dispersibility, and so their anticorrosion performance, in epoxy-based coatings. With the addition of 3 wt% of modified nano-clay particles, it was accomplished the fabrication of a polymer-clay nanocomposite coating (2-BBI-(Na^+-MMT/epoxy) with improved interlayers separation and a more homogeneity distribution. These systems presented a greatly decreased water absorption capability and an improved substrate adhesion when compared to unmodified Na^+-MMT/epoxy coatings, as shown in the results of swelling degree analysis and pull of tests (Fig. 14), and an overall improvement of its anticorrosion barrier characteristics as evidenced by the electrochemical impedance spectroscopy (EIS) results.

Another recent example of similar montmorillonite employing systems is shown in the work by Schindelholz et al. [166]. These nanoclays are presented as alternatives to costlier, more toxic, and less scalable thin film materials, such as graphene, hexavalent chromium, or atomic layer deposited metal oxides. Within their work, the researchers developed a layer by layer assembled nanocomposite by a sequential deposition *via* dip coating of a quad-layer (QL) of cationic branched polyethyleneimine (PEI), anionic poly(acrylic acid) (PAA) and exfoliated MMT clays in a (PEI/PAA/PEI/MMT) arrangement. Their results revealed that films as thin as 90 nm reduced corrosion over copper coupons by a 1000× factor, when exposed to a highly corrosive H_2S

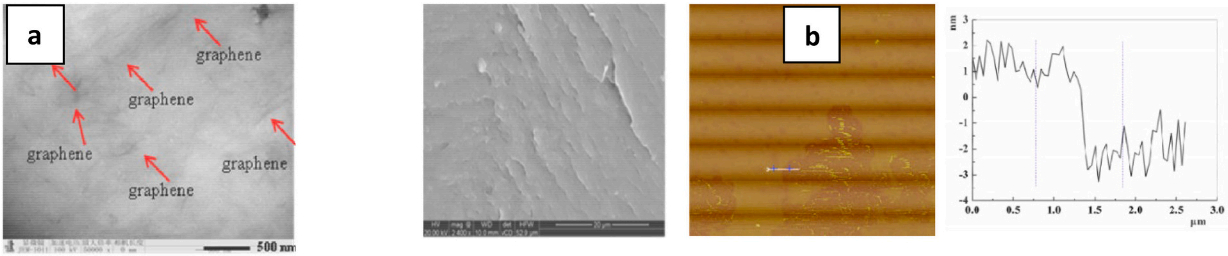

Fig. 10. a) TEM image for dispersibility analysis and b) SEM micrograph, AFM image and profilometry plot for morphology characterization. (Reprinted with permission of Li et al. [153]. Copyright 2015, Elsevier).

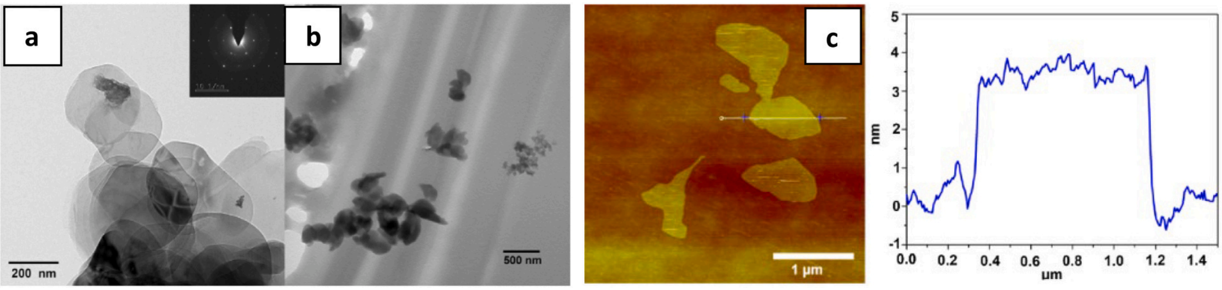

Fig. 11. TEM images of a) h-BN dispersed by CAT in aqueous solution and b) the corresponding dispersion of h-BN in EP matrix. c) AFM image of h-BN and thickness measurement. (Reprinted with permission of Cui et al. [32]. Copyright 2017, Elsevier).

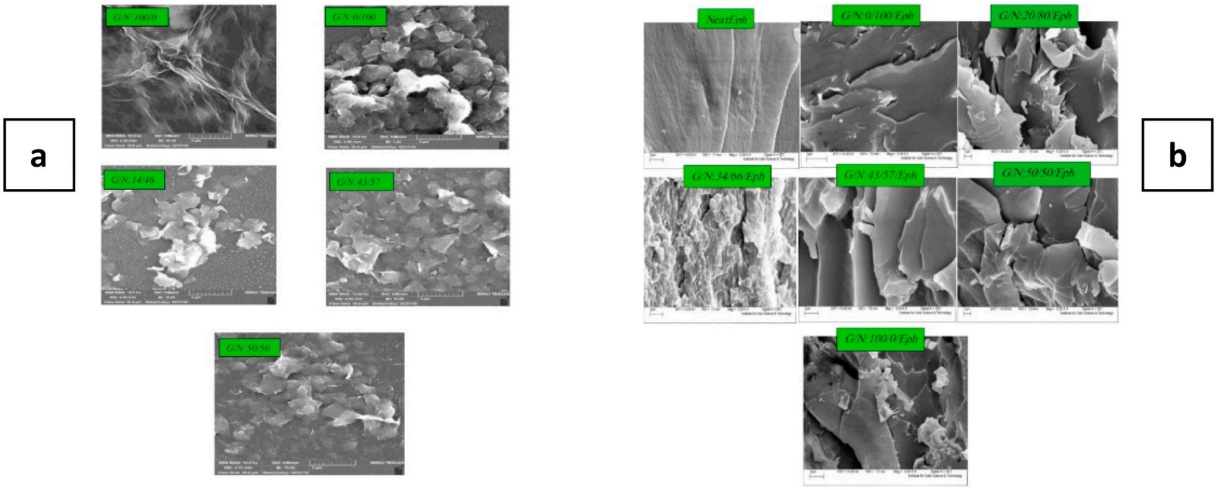

Fig. 12. FE-SEM micrographs to obtain information over the a) microstructure and dominant morphology and b) dispersion state and mechanical properties. (Reprinted with permission of Jiang et al. [155]. Copyright 2017, Elsevier).

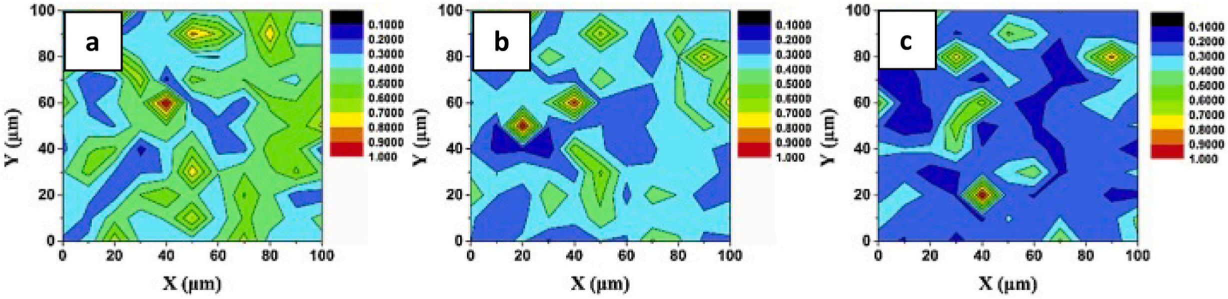

Fig. 13. Raman mapping of normalized intensity ratio of GO D-band (1350 cm^{-1}) to the epoxy band (1110 cm^{-1}) in (a) 0.1 wt% GO-a/EP, (b) 0.1 wt% GO-b/EP and (c) 0.1 wt% GO-c/EP. (Reprinted with permission of Jiang et al. [156]. Copyright 2017, Elsevier).

atmosphere (Fig. 15), mainly attributed to the combination of the improved gas antipermeation property of multiple deposited quadlayers (2QL, 6QL, 10QL) together with protective chemical interaction with Cu(II) cations, immobilized in the structure by interactions with the -COOH groups in PAA.

On the other hand, there are sepiolite-type clays, with a fibrous structure composed by blocks and tunnels in the fibers directions [165]. The high density of silanol groups on their high surface area, open up numerous possibilities for different organic modifications that could enhance their corrosion resistance and barrier protection in composite coatings. Examples of this found in the literature include the work by Henriques et al. [165] in which the anticorrosion properties of modified sepiolites (SepIL) with three different phosphonium-based ionic liquids, through a cation exchange process, are evaluated as anticorrosive pigments for epoxy coatings. After the successful modification, assessed *via* FTIR and X-ray diffraction (XRD) analysis, the samples were submitted to EIS (Fig. 16) that allowed the estimation of corrosion potential, corrosion resistance, double layer capacitance, coating resistance and coating capacitance for each epoxy/SepIL coating. According to the results, the epoxy/SepIL coatings shown a decay in their coating resistance (main parameter employed to evaluate the anticorrosion capability) ten times lower than the epoxy/Sep coatings after 3600 h of immersion in the electrolyte, assessing the viability of ionic liquids as anticorrosion additives.

An even more recent example of the use of organic modified sepiolites (OMSep) in epoxy coatings is reported by Xiong et al. [167] where the anticorrosion effect provided by these nanofillers modified with acid and silane KH-570 coupling agent is studied (Fig. 17). After checking the

Table 1
State of art summary on graphene-based anticorrosion systems.

Chemical system	Composition	Thickness	Deposition technique	Main properties	Ref.
Poly vinyl alcohol/Reduced graphene oxide (PVA/rGO)	PVA (1 wt% in deionized water), graphene oxide (2 mg/mL in DW). PVA:GO = 40:60	Airbrushing	≈8 μm	Brick and mortar structure, minimal corrosion products, good adhesion, improved anticorrosion capability (conducting hybrid, alternative pathway for electrons)	[108]
Polyvinyl alcohol/Reduced graphene oxide (PVA/rGO)	rGO (4 mg/mL in deionized water) PVA (50, 70, 90 wt%)	Spin assisted layer-by-layer	752 nm (50% PVA), 660 nm (70% PVA) and 647 nm (90% PVA)	Superior antiwear properties (50% PVA), enhanced anticorrosion performance,	[109]
Polystyrene/Graphene oxide - 4,4′-methylenebis(phenyl isocyanate) (PS/MDI-GO)	MDI-GO (0.05 g) in PS (4 g)	55 ± 5 μm	Not specified	Improved GO dispersibility (covalent modification), improved thermal stability, better electrochemical impedance	[133]
Polyurethane/Graphene oxide - (3-glycidyloxypropyl) trimethoxysilane (PU/GO-GPTS)	Acrylic resin (66 g), Polyisocyanate hardener (2:1 *w*/w with resin), GO-GPTS (100 mg)	70 ± 5 μm	Film applicator	Improved GO dispersibility (covalent modification), higher storage modulus, higher T_g, increase strain (54%), energy (104%) and stress (25%) at break, higher adhesion strength, improved electrochemical impedance	[137]
Polyurethane/Titanate treated reduced graphene oxide (PU/TrGO)	TGO (0.4 wt%) in waterborne PU (20 wt%) matrix	15 μm	Bar coater	Improved dispersibility (covalent modification), Self-alignment of TGO hybrid nanoplates, fully utilized surface area improved electrochemical impedance	[111,138]
Epoxy resin/Graphene-poly (2-butylaniline) (G-P2BA)	Graphene (0.5 wt%), P2BA (0.5 wt%), amine hardener (25 wt% of epoxy resin)	20 ± 2 μm	Wire bar coater	Improved graphene dispersibility (non-covalent modification), improved anticorrosion capability, improved reduction of friction coefficient and wear resistance	[142]
Graphene oxide/benzimidazole-cerium (GOBiCe)	Graphene oxide (385 mg in deionized water), benzimidazole (500 ppm) cerium (500 ppm)			Smart pH-sensitive system for targeted delivery of adsorbed organic-inorganic corrosion inhibitors, inhibition efficiency > 72%,	[158]
Alginate/Graphene oxide (Al-GO)	Alginate (1% *w*/*v* in deionized water), graphene oxide (6 wt%)	70 ± 10 μm	Direct casting over petri dishes	Improved interfacial filler-matrix adhesion, improved tensile strength and Young's modulus, improved thermal stability	[144]
Epoxy resin/Graphene-Tannic acid - 2,3-epoxypropoxy)propytrimethoxysilan (epoxy/GR-TA-KH560)	Waterborne epoxy resin (16 g), Gr (0.1 g) (−TA (0.05 g)-KH560 (0.05 g) (0.7 wt%)	Not specified	High pressure spraying	Improved graphene dispersibility (covalent and non-covalent modifications), improved anticorrosion capability (reduced corrosion products), improved hidrophobicity (greater water contact angle)	[148]
Polyvinyl alcohol/Graphene (GR/PVA)	PVA (5% *w*/*v*), graphene (0.1 g, 10 wt%)	Dip coating	Not specified	Lower corrosion current and corrosion rate, higher polarization resistance, great corrosion inhibition over Al-2219 (99.99%)	[159]
Polyvinyl alcohol/Reduced G graphene oxide (PVA/rGO)	GO (5 mg/mL), PVA (1 mg/mL)	Dip coating	Not specified	Enhanced corrosion resistance, PVA used as *in-situ* thermal reducing agent for GO	[160]

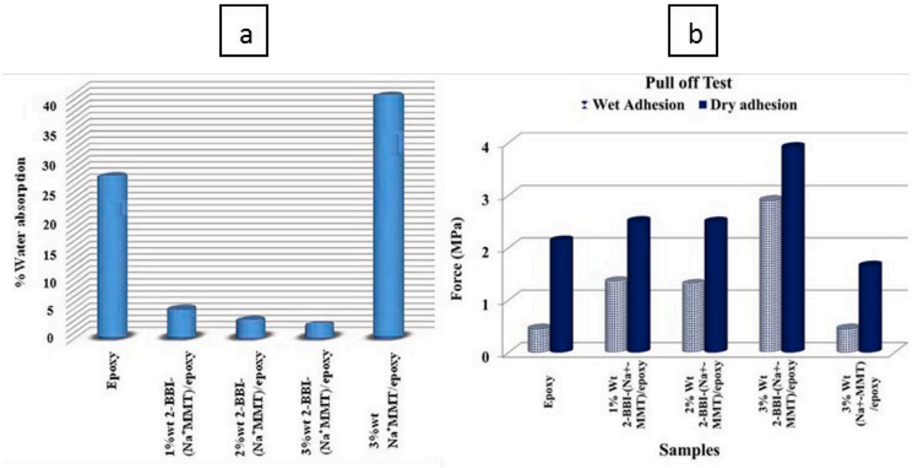

Fig. 14. Results of the a) swelling degree analysis and b) pull off tests in Mehrabian et al. (Reprinted with permission of Mehrabian et al. [164]. Copyright 2017, Wiley).

correct modification of OMSep by means of XRD and FTIR analysis, different concentrations (0, 1, 3, 5 wt%) were added to the epoxy coatings. An initial measurement of the water contact angle of OMSep (101°), greatly increased when compared with unmodified Sep (16°), assesses a better interaction OMSep-epoxy, thus improving its dispersibility. Their anticorrosion capability was evaluated by EIS measurements determining a concentration of 3 wt% of OMSep to be the optimal value for maximizing this property, resulting in an electrochemical impedance for OMSep/epoxy coatings 3 orders of magnitude higher than that of pristine epoxy coatings.

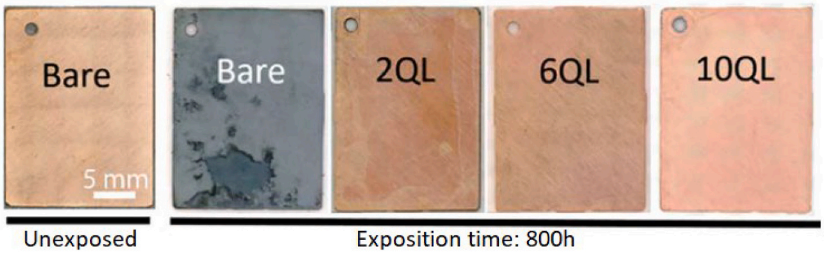

Fig. 15. Anticorrosion efficiency on copper substrates with different amount of deposited (PEI/PAA/PEI/MMT) quad-layers. (Reprinted with permission of Schindelholz et al. [166] Copyright 2018, ACS).

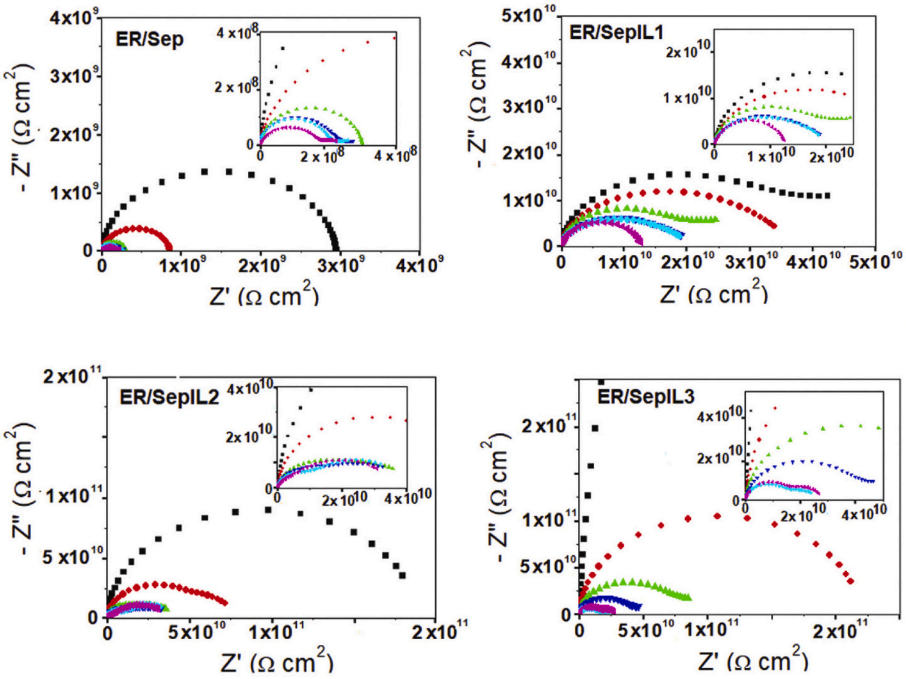

Fig. 16. EIS results (Nyquist and Bode plots) for the prepared hybrid systems with different ionic liquid in their compositions. (Reprinted with permission of Henriques et al. [165]. Copyright 2020, Elsevier).

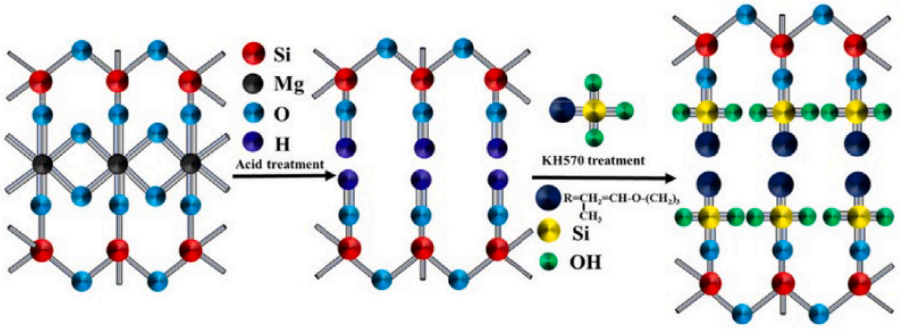

Fig. 17. Schematics of the synthetic route for the obtention of organically modified sepiolite. (Reprinted with permission of Xiong et al. [167] Copyright 2020, Elsevier).

It is also worth mentioning the recent use of conductive polymers, such as polythiophene, polyaniline and polypyrrole, which are being explored due to their interesting physical and chemical properties and the ability to provide alternative electron pathways preventing them to reach cathodic sites, thus slowing the whole corrosion process. Apart from its conductivity, polypyrrole, having the characteristics of an easy preparation, biocompatibility and antioxidant properties, makes it an excellent candidate to be part of clay-polymer composite anticorrosion systems. However, polypyrrole displays some drawbacks such as a low chemical stability and the lack of good mechanical properties, both of which can be compensated through its incorporation in composite systems with other polymers or bio-based materials such as cellulose or clays. An example of its use is described by Jlassi et al. [168] who organically modified bentonite, a natural clay, through aminosilanization to subsequently give form to a clay/polypyrrole-Zinc oxide hybrid material *via in-situ* photopolymerization of pyrrole in the presence of ZnO (5 wt%) and $AgNO_3$ employed as photoinitiator (Fig. 18). This hybrid material was finally incorporated, in different concentrations (1, 3, 4 and 5 wt%), in a commercial epoxy resin to evaluate its anticorrosion and antibacterial performance once deposited over carbon steel coupons employing a doctor blade instrument. The results gathered by EIS evidenced a maximum charge transfer resistance for epoxy coatings with a 4 wt% content of the hybrid filler, evidenced by a high charge transfer resistance of 9.85 $M\Omega \cdot cm^{-2}$ compared with 0.213 $M\Omega \cdot cm^{-2}$ of pristine epoxy coatings. Furthermore, the hybrid filler displayed a reduction of *E. coli* growth by 86%, thus opening new routes for the preparation of high added value anticorrosion and antibacterial coatings.

5.2. Layered double hydroxides

Layered double hydroxides (LDHs) are a type of inorganic 2D-layered anionic compounds formed by the non-covalent interaction between a positively charged laminate and interlayer anions. Their structure is based on MO_6 sharing edges octahedra and resembles that of brucite $Mg(OH)_2$, with the general formula $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}[(A^{n-})_{x/n} \cdot mH_2O]^{x-}$. The main property that makes LDHs excellent materials for corrosion protection is the exchangeability of the interlayered anions [169]. Some examples of the use of LDHs taking advantage of this property have been reported, as in the study by Du et al. [170], where a hybrid material is obtained by producing the *in-situ* polymerization of sulfonated polyaniline (PANI) in the galleries of Mg-Al layered double hydroxide as host matrix (Fig. 19). The prepared LDH-polymer nanohybrid showed an irregular lamellar shape with monolayer thickness (2.67 nm) allowing it to adopt a nanosheet structure. The PANI/LDH hybrid was applied to waterborne epoxy coatings for steel substrates showing a significantly increased corrosion protection capacity, evaluated by means of EIS analysis during 35 days of immersion in 3.5% *w/v* NaCl solution, when compared with neat epoxy and epoxy/SPANI coating composites.

Peng et al. [171], employing Mg-Al LDHs, reported its use as pore sealant of a poly(ethylene oxide) coating, enhancing its corrosion resistance and cytocompatibility and providing with a drug delivery ability to the composite system. Initially a PEO coating (≈5 μm) is deposited over the substrate (AZ31 Mg-alloy coupons) and subsequently a Mg-Al LDH nanosheet (≈2 μm) is formed *in-situ* over its surface by a hydrothermal treatment (Fig. 20). Once the correct formation of the bilayered composite was assessed by XRD analysis, a lower free current density and corrosion potential was determined, using EIS, for the LDH/PEI hybrid coatings when compared with those of pristine LDH and PEI separately. The results also shown lower hydrogen evolution and corrosion rate for the combined coating system. This study also evaluated the biological performance of this novel coating by measuring its cell growth viability and measuring its drug loading ability, gathering results that assessed a promising applicability in orthopedic surgeries. Table 2 summarizes the overviewed chemical anticorrosion systems, as well as their most interesting characteristics.

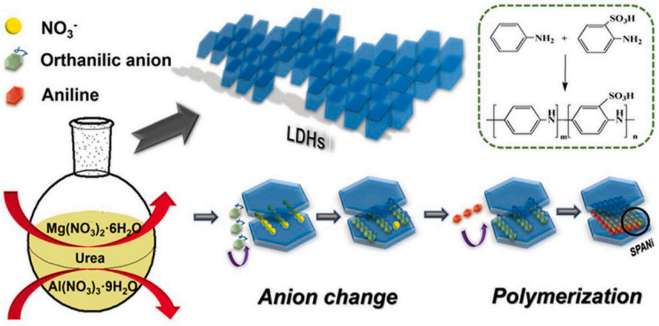

Fig. 19. Preparation of SPANi/LDHs hybrid material *via* an *in-situ* intercalative polymerization procedure. (Reprinted with permission of Du et al. [170]. Copyright 2018, RSC).

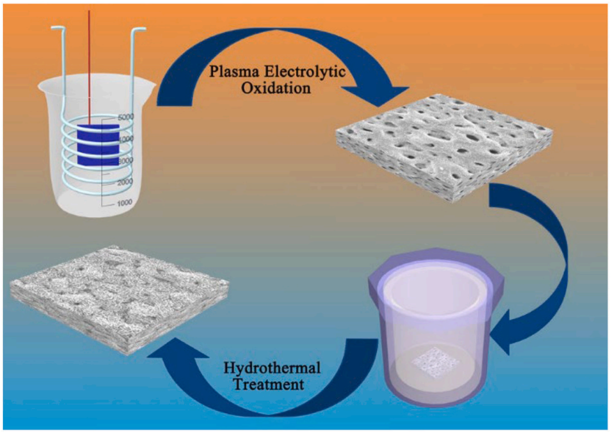

Fig. 20. Pore sealing process during the fabrication of PEO/LAH bilayered coating. (Reprinted with permission of Peng et al. [171]. Copyright 2017, Springer).

6. Multi-functionalization possibilities in graphene-family inorganic-organic anticorrosive composite coatings

Graphene-based materials have been recently utilized for a variety of applications thanks to their especial shape, electronic and chemical structure.

6.1. Loading/controlled release of capabilities

An interesting feature in anticorrosion systems is to employ different inorganic materials with the ability to load and controllably release corrosion inhibitors or other functional molecules. Several inorganic hosts with this capability have already been studied as layered double hydroxides (LDHs) [172,173], zeolites [174], bentonites [175], montmorillonites [176], and carbon-based materials [177], among others.

Graphene oxide, owning to the partially conjugated system and the multiple functionalities on its surface and sheet boundaries, could be an

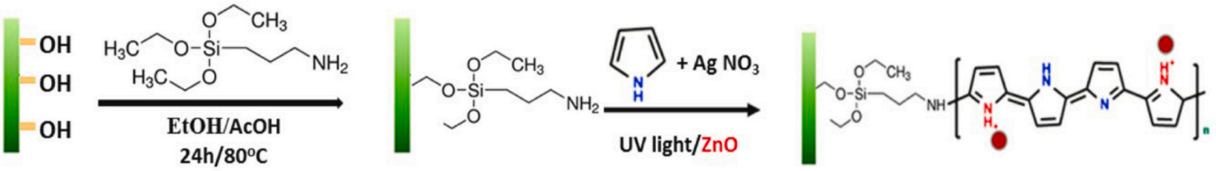

Fig. 18. Modification mechanism of aminosilanized clay through photopolymerization of pyrrole. (Reproduced with permission of Jlassi et al. [168]. Copyright 2020, Elsevier)

Table 2
Nano-clays and layered double hydroxides-based hybrid inorganic-organic composite anticorrosion coatings.

Chemical system	Composition	Thickness	Deposition technique	Main properties	Ref.
Epoxy resin/Tungstate loaded Al-Mg LDH (Epoxy/LDH-WO_4^{2-})	Coprecipitation Mg^{2+}/Al^{3+} (molar ratio 2) WO_4^{2-}/Al^{3+} (molar ratio 1) LDH-WO_4^{2-} (10 wt% in epoxy resin)	≈100 ± 5 μm	Brush coating of prepared hybrid paints with 1:2 ZY curing agent added	Ability to release loaded WO_4^{2-} anions with corrosion inhibition activity. Low corrosion current density values.	[39]
2-benzylbenzimidazole/Na^+-montmorillonite/epoxy (2-BBI-(Na^+-MMT)/epoxy)	MMT (6 g), 2-BBI (3:1 to CEC) 2-BBI-(Na^+-MMT) = 0, 1, 2, 3 wt%	120 ± 5 μm (wet)/90 ± 5 μm (dry)	Manual application	Improved dispersion of Na^+-MMT modified with 2-BBI, improved barrier anticorrosion protection mechanism, slightly decreased T_g, decreased water absorption	[164]
Sepiolite-phosphonium-based ionic liquid/epoxy (SepIL/epoxy)	Sep (4 g), IL1, IL2, IL3 (4 g) SepIL (1 wt% to epoxy) IL1: trihexyl-(tetradecyl) phosphonium bistriflimide IL2: ethyl-tri(butyl)- phosphonium diethylphosphate IL3: 11-carboxyundecyl-(tri-phenyl)-phos- phonium bromide	220-250 μm	Painting brush + curing (168 h, room temperature)	Sep < SepIL1 < SepIL2 < SepIL3, enhanced anticorrosion barrier type mechanism, better interfacial adhesion increased storage modulus.	[165]
Branched polyethyleneimine/poly(acrylic acid)/exfoliated montmorillonite (PEI/PAA/PEI/MMT)	Consecutive quad-layers (QL) (PEI/PAA/PEI/MMT) = 2QL, 6QL, 10QL	90 nm	Layer by layer deposition by dip-coating	Low-cost conformal anticorrosion barriers. Corrosion in copper coupons (x10^{-4}). Metal protection in acidic oxidizing atmospheres (H_2S)	[166]
Sepiolite-KH570/epoxy (OMSep/epoxy)	OMSep (0, 1, 3, 5 wt%)	80 μm	Not specified + curing (80 °C, 1 h)	Improved electrochemical impedance (x10^3) over carbon steel substrates	[167]
Bentonite-polypyrrole/ZnO-Ag NPs (B-PPy/ZnO)	Amino-modified clay (0.1 g), Pyrrole (0.1 M in 100 mL ethanol), ZnO (5 wt%), Epoxy resin (1.7 g) B-PPy/ZnO (1, 3, 4, 5 wt%)	500 μm	Doctor blade + curing (48 h, room temperature)	Eco-friendly Improved charge resistanmce transfer (x40) and antibacterial activity (*E. coli* ≈86%)	[168]
Sulfonated polyaniline/Mg Al layered double hydroxide (SPANI/LDHs)	Mg-Al LDH (0.2 g), orthoanilic acid (2 mmol), aniline (2 mmol), ammonium peroxydisulfate (2 mmol) SPANI/LDH (0.5, 1 wt%)	SPANI/LDH monolayer (2.67 nm), 50 ± 2 μm	Bar coater + curing (96 h, room temperature)	Improved anticorrosion performance through synergistic barrier and passivating (formation of Fe_2O_3 + Fe_3O_4) anticorrosion protection mechanisms	[170]
Poly ethylene oxide/Mg-Al layered double hydroxide (PEO/LDHs)	Hydrothermal process with $AlNO_3$ (0.02 M) over PEO deposited by plasma electrolytic oxidation on AZ31 Mg alloy	PEO (5 μm) + Mg-Al LDH (2 μm)	Mg^{2+} ions released during plasma electrolytic oxidation process, hydrothermal process (120 °C, 2 h) with $AlNO_3$	Remarkably enhanced corrosion resistance, enhanced cytocompatibility, hemolysis rate compatible with clinical applications, excellent drug delivery ability	[171]

adequate container to capture various types of corrosion inhibitor species. Thus, it can be considered as a candidate for encapsulating corrosion inhibitor species and delivering them at affected coating regions. Recent promising examples taking advantage of graphene loading/releasing properties, include the work by Javidparvar et al. [158]. In this work, the different pH conditions near anodic and cathodic areas, together with the anticorrosion protective effect of rare earth elements, such as cerium [178] (Fig. 21) are considered. Cerium displays the capability for electrostatical adsorption on graphene oxide nanosheets surfaces [179] in a process highly reliant on the acid-base behavior of the oxygen containing groups. Furthermore, it may form stable cerium-organic complexes [180,181] with molecules that are able to act as corrosion inhibitors on their own, as benzimidazole [182]. With all these considerations, a synergistic anticorrosion coating system has been developed capable of the controlled release of cerium and benzimidazole near cathodic areas.

The adsorptions of Ce^{3+} and benzimidazole were characterized kinetically, where it followed a pseudo second-order-model, and thermodynamically, following a Freundlich isotherm model. Their anticorrosion efficiency, 72% for GO-Ce-Benzimidazole systems with cerium: benzimidazole≈1 compared to the blank solution, was assessed by electrochemical impedance spectroscopy. These systems opened a new

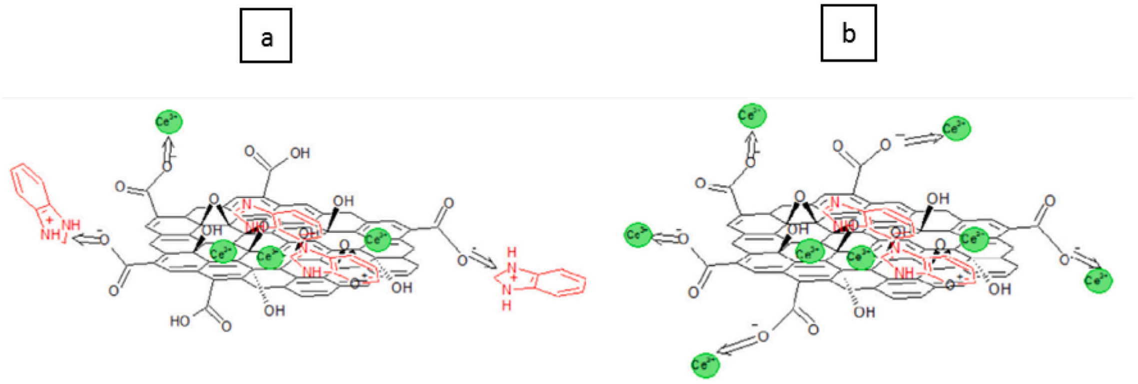

Fig. 21. Schematics of cerium and benzimidazole adsorption on the GO surface at (a) pH < 4 and (b) pH > 4. (Reprinted with permission of Javidparvar et al. [158]. Copyright 2019, Elsevier).

way to overcome some of the major drawbacks when using rare earth elements as anticorrosion protection species as it is their uncontrollable consumption when added directly on aggressive environments.

The capabilities of loading/releasing on GR-family products is fully taken in advantage in anticorrosion systems with the so desired self-healing property, as is presented subsequently.

6.2. *Self-healing*

The introduction of the self-healing capability into anticorrosive coatings is a really interesting opportunity. Coatings with self-mending ability would possess longer operational lifetimes, while further inhibiting the reaching of corrosive species to the substrate [183], when the material surfaces are automatically repaired after being damaged.

The main mechanisms responsible for self-healing capabilities in coatings are the controllable release of anticorrosion additives or self-healing agents and the supramolecular approach. Anticorrosion substances incorporated during the fabrication can be released upon suffering mechanical damage. These corrosion inhibitors either early block damaged regions or form protective films in intact zones delaying corrosion processes in damaged areas (Fig. 22.a). Meanwhile, self-healing agents consist on appropriate monomers and catalysts stored in containers embedded within the coating matrix [184]. Once released, these molecules produce an extrinsic healing effect through *in-situ* polymerization reactions. The supramolecular approach, relies on physical and dynamic interactions (*i.e.* electrostatic, host-guest, hydrogen bonds…) to facilitate an intrinsic healing mechanism to mend mechanical damage by recovering lost interactions.

An optimal strategy is to combine chemical and physical interactions in double network systems to compensate with the poor mechanical properties associated to systems based on dynamic interactions with a much more rigid covalent structure. All the mentioned strategies could be combined in unique anticorrosion systems (Fig. 22.b).

As a corrosion inhibitor example, benzotriazole (BTAH) is a commonly used substance that performs well when protecting copper surfaces, as reported by Chen et al. [187] when BTAH quickly interacts both with metallic copper (Cu) to form a thin protective film in non-corroded areas and with copper cations (Cu^{1+}) to form a thick polymeric $[Cu^{+}BTA^{-}]_n$ complex on the Cu_2O substrate where corrosion appears. In a recent research work by Ye et al. [188], GO porous lattice was modified with a polyhedral oligomeric silsesquioxane framework (POSS) with paraformaldehyde (8-PG), as appropriate container for BTAH (Fig. 23), and introduced in an epoxy resin matrix to form a self-healing coating with improved anticorrosion performance. The results obtained indicated that the prepared 8-PG, with a surface area of 215.841 m^2/g, pore volume of 0.920 cm^3/g with sizes between 10 and 80 nm, presented a 18.6% loading rate of BTAH and a higher release rate, between 60 and 80% in 20 h. The applied coating anticorrosion performance was highly efficient due to the improvement of the system compactness assessed *via* water absorption tests after 90 days immersion. Water absorption of 8-PG-BTA/EP coating was only 2.87%, significantly lower than that of pristine EP (3.89%) and 8-PG/EP (6.51%).

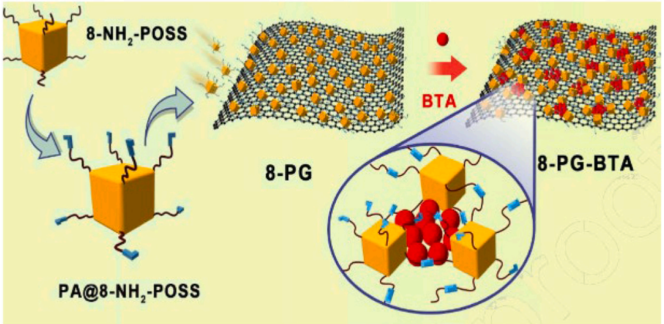

Fig. 23. Preparation process of graphene-based nanocontainers and the loading with BTAH. (Reprinted with permission of Zhang et al. [188] Copyright 2018, Elsevier).

GR self-healing capability has been already reported from experimental works and molecular dynamics simulations. GR sheets may heal their vacancy and other topologycal defects by employing different metal doping [189] and without any external aid. This unaid mending mechanism has severe limitations. It has only been observed in single layer graphene sheets with critical crack opening displacement in the range of 0.3–0.5 nm and when all external forces were eliminated and the GR sheets were completely relaxated [190]. Thus, GR-polymer composite anticorrosion coatings with self-healing capability have not been widely elucidated yet.

More promising results have been obtained when employing GO instead of GR as self-healing promotor. The many oxygen containing groups on GO sheets surfaces allow this material to form numerous hydrogen-bonding interactions with compatible matrixes, promoting through them the self-healing behavior. An example can be found in the work by Pan et al. [191] in which a composite GO-copolymer was obtained through *in-situ* radical copolymerization of acrylamide and 2-(dimethylamino)ethylacrylatemethochloride (p(AM-co-DAC)) in the presence of GO. The resulting composite systems possess high stiffness

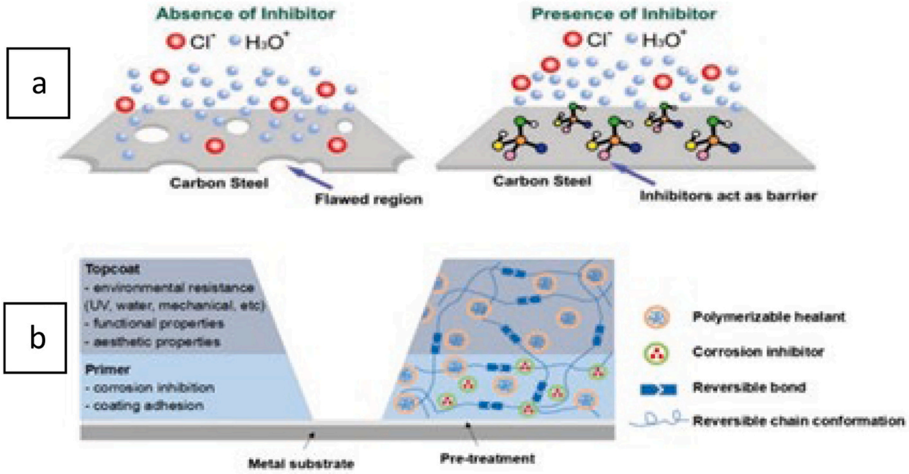

Fig. 22. Schematics of a) active corrosion inhibition. (Reprinted with permission of Mariana et al. [185], *J. Braz.* Copyright 2018, SciELO), and b) combination of multiple self-healing strategies in a singular anticorrosion coating system. (Reprinted with permission of Zhang et al. [186] Copyright 2018, Elsevier).

(Young's modulus: ≈1.1 MPa), high toughness (≈9.3 $M\cdot J\cdot m^{-3}$), and high fatigue resistance, as well as high self-healing efficiency (>92% of tensile strength, >99% of tensile strain and > 93% of toughness) through the multiple interactions between GO and p(AM-co-DAC) in a double network system. These self-healing systems are achieved by water assistance (spraying) without any other stimuli, demonstrating that its efficiency is connected to the density of hydrogen bonding and ionic bonding sites, an optimal proportion of both interactions types and a facilitated molecular motion.

6.3. *Antifouling*

Coatings for marine applications are highly susceptible to fouling problems, thus, providing these systems with antifouling properties should always be addressed to ensure their maximum lifespan and protective capacities. The fouling results in the deposition of organic and inorganic materials on marine ships, vessels and all kind of marine structures, such as, oil rigs, wind turbines, desalination systems, heat exchangers or oceanographic sensors, among others. In 2008 the use of tributyltin (TBT) was permanently banned due to its toxicity for aquatic life. The overall estimated cost for annual US navy fleet hulls maintenance is between $180 - $260 millions, which has demanded new materials in this sector to cut the costs [192]. Most common strategies followed during the early research steps have been biomimetic nanostructures and self-cleaning, biocidal or amphiphilic surfaces [193].

With many possibilities for GR-family materials surface modification, allowing desirable properties for antifouling surfaces as tuneable polarity [194] and wettability [195], the examples of superhydrophobic and super-hydrophilic GR based coatings have been already proposed to prevent particulate fouling [196]. Furthermore, graphene impermeable structure exerting an increased salt rejection [197], its superb antibacterial properties [198], controlled protein adhesion [199] and the ability to covalently bind with polymers when functionalized [200], make them good candidates for anticorrosion antifouling multifunctional coatings.

Several recent research works point to the use of GR-family fillers in GR-polymer composite coatings as among the easiest way to take advantage of their antifouling properties [201–205]. With the aim of obtaining both anticorrosion and antifouling systems, GO nanosheets functionalized with polyaniline (PANI-GO) through an *in-situ* polymerization were introduced in epoxy resin coatings [205]. The as obtained PANI-GO/EP coatable mixtures were deposited over steel carbon substrates through dip-coating with an average thickness of 200 ± 15 μm. EIS analysis allowed to assess the anticorrosion efficiency, characterized by coating resistance (R_c) parameter, being 7.9 times higher for coatings with a 12 wt% of PANI-GO load than those with 3 wt%. Meanwhile, after 3 months immersion time in simulated sea water containing microorganisms the Epoxy/PANI-GO (12 wt%) also shown the highest antifouling behavior, probably mainly due to the filling of micropores in the epoxy matrix, although more detailed studies are needed to fully understand this antifouling behavior mechanism. Continuing in this line of research, same authors reported in a paper published in 2021 [201] that the modification of GO with a PANI derivative as *p*-phenylendiamine (GOP) in a 1:1 ratio, prior to its modification with PANI, could further improve the anticorrosion and antifouling properties of the previously studied EP/PANI-GO coatings. After 192 h immersion time in brine, EP/PANI-GOP coatings with 2 wt% of PANI-GOP load presented a R_c value (8.87×10^6 $\Omega\cdot cm^2$) slightly superior than that of EP/PANI-GO (2.7×10^6 $\Omega\cdot cm^2$) in which up to 12 wt% filler loads had to be used, leaving room for improvement with an increased amount of filler over 2 wt%. Furthermore, when the PPDA-GO 1:1 ratio was adjusted to 0.2 g/each in 25 mL deionized water during synthesis stage, coatings with an improved antifouling stability, comparable with coatings without PPDA modification, could be obtained.

The compatibility of GO with biopolymeric, eco-friendlier, matrixes for marine anticorrosion applications is demonstrated by works such as the one by Jena et al. [202]. In this study, the synergistic effect between GO excellent barrier properties and the enhanced antibacterial property of chitosan/silver (CS/Ag) composite films are investigated and exploited in the construction of efficient anticorrosion/antifouling coatings over CuNi 90/10 alloy, ideal for marine applications. Electrophoretic deposition (EPD), a rather inexpensive and industrially scalable technique, was employed for the coating deposition. The CS (0.5 g/L) / GO (0.025 mg) / Ag^+ (1 mM) composition coatings (CAG1) showed a remarkable anticorrosion property with an $R_c = 2 \times 10^5$ $\Omega\cdot cm^2$ and a coating capacitance $Q_{coat} = 0.1 \mu Mho\cdot cm^{-2}$, indicating the lowest uptake tendency of corrosion electrolytes among studied specimens. This may be because chitosan-based coatings with cathodic nature may affect the oxygen reduction rate and shift polarization curves to lower current densities. Meanwhile, the antibacterial property was investigated with epifluorescence microscopy analysis and viable count methodology. The bacterial density was observed to be reduced in one order of magnitude, from 1.4×10^4 $CFU\cdot cm^{-2}$ to 1×10^3 $CFU\cdot cm^{-2}$, confirming maximum antibacterial efficiency for the CAG1 coating as well.

6.4. *Fire retardant*

Some of the most employed fire-retardants additives are based on halogens (Br_2 and Cl_2), inorganic phosphorous and melamine compounds that present some degree of toxicity for humans and the environment [206]. The use of GR-family new materials as fillers, with the ability to withstand high temperatures without losing mechanical stability, could increase the operating temperature, reduce moisture uptake, induce antistatic behavior and give lightning strike protection, that could be very useful for some applications (*i.e.* coatings on wind turbines towers or blades) by improving the systems compressive strength limit [207]. These materials with high thermal conductivity (2000 to 5000 $W\cdot m^{-1}\cdot K^{-1}$), heat dissipating capability [208] and impermeability to gases along with a high mechanical strength, make them ideal for high temperature applications. When GR-family products are introduced into polymer nanocomposites, they could be granted with interesting fire-retardant properties as increased thermal stability [209], smoke suppression [210], melt viscosity, antidripping properties [211] and char yield or residual mass [212], while limiting oxygen index value [213] and decreasing in the heat release rate [214]. Despite many advantages, it is also important to consider the total amount of filler, as a high loading of GR/GO/rGO into polymers can sometimes reduce their mechanical strength [215].

6.5. *Early-sensors*

Although there are several instrumental techniques that allow the early-detection of corrosion beneath polymeric coatings, such as, ultrasonic analysis, thermal imaging and electrochemical spectrums, their use in already coated materials, furthermore in marine applications, imposes several technological difficulties. A more facile approach would be to introduce the early-sensing technology through the coating formulation, in which different substances are able to produce visual signals (color change, fluorescence, phosphorescence, …) in response to different stimuli (pH change, redox reactions, presence of heavy metals, electrical current changes, …) allowing early-detection by simple visual monitoring [216].

In the work by Li et al. [217], instead of employing more traditional encapsulation techniques that require the formation of microcracks for the sensing molecule to be released, the corrosion indicators are directly grafted onto GO nanosheets. Researchers hypothesis was to achieve an improvement in the sensing molecules dispersion that would allow an earlier signaling of incipient corrosion. The GO was chemically modified with 1, 10-phenanthroline-5-amine (pGO), which can form a red complex with Fe^{2+} ions, so as to give a signal of corrosion reaction at very early stage. Modified GO (0–0.2-0.4 wt%) was dispersed in a PU matrix with the assistance of laponite clay nanoparticles (60 mg) and applied over cold-rolled steel surfaces with a bar coater. Laponite had to be employed due to the lack of carboxylic groups on GO sheets that have been employed when reacted with amino groups on phenanthroline, thus reducing the hydrophilicity of pGO that formed more unstable dispersions. Evaluation of the corrosion protection performed *via* neutral salt spraying tests (NSST) over 24 h revealed an improved performance over neat PU coatings, accompanied by an intense red color for samples with 0.2 and 0.4 wt% after 20 h NSST.

7. Conclusions and outlook

Advances in alloying field have produced almost perfect metallic materials, regarding their mechanical properties, availability and costs, which perform excellently in many structural applications. However, their lack of chemical stability in corrosive environments needs to be addressed, increasing the required maintenance and overall costs during their lifespan.

The ever-increasing demand of metallic materials for marine applications, where they must withstand a highly corrosive media, makes mandatory the use of anticorrosion protection mechanisms to ensure their optimal performance. The use of coatings or paints is usually the preferred approach to delay the effect of corrosion. These coatings make use of one or various protection mechanisms based either on impeding the permeating of corrosive species to the metallic interphase (barrier effect), actively inhibiting/repairing the corrosion effects (active inhibition or self-healing effect) or acting as sacrificial cathodes when coatings or any of their components is oxidized instead of the metallic substrate. Traditionally, these coatings have been manufactured from metallic oxides, such as CrO_3 or, more recently, some polymeric materials, such as epoxy resins or polyurethanes. All these materials present some concerns, mainly, limited efficiencies up to a factor of 2 in commercially available products, the need of periodical reapplications as they display shorter lifespans than the protected substrates and the potential release/lixiviate of pollutants or toxic substances (Cr(VI), bisphenol-A, toxic components).

In the last decades the advances in nanotechnology allowed to start designing new composite/hybrid anticorrosion coatings which combine the best properties of metallic and polymeric materials as well as more than one protection mechanism in one final coating. An emerging approach, based on a “brick and mortar” arquitecture, are hybrid polymeric-inorganic layered coatings in which a 2D inorganic component exerts as barrier preventing the diffusion of corrosive species through a polymeric matrix. Inorganic layered components (bricks) increase the impermeability acting as barriers or even contribute with additional anticorrosion mechanisms. Meanwhile, the polymeric matrix (mortar) accounts for the protection of the fillers and the achieving of adequate mechanical properties for each specific application. Several inorganic 2D-layered materials have been studied for candidates as filling components in these systems. Natural nanoclays, layered double hydroxides, some nitrides/carbides, metal organic frameworks and graphene and its derivatives are some of the most studied. Parameters such as fillers concentration, and a homogeneous and stable dispersion in selected matrixes are key for achieving highly efficient coatings. The self-agglomeration tendency of these materials must always be considered as it could hinder the overall performance. At this regard, the preparation methodology, employing hard ultra-sonicating methods or synthetic routes that facilitate the application step, as *in-situ* intercalated polymerization are of great help. Graphene and its derivatives, mainly graphene oxide and reduced graphene oxide are gaining notoriety due to their eco-friendliness, accessibility, extraordinary impermeability and the possibility of and *ad-hoc* tuning of their functionality through chemical or physical processes, addressing the self-agglomeration issue.

The analysis of state of art research attempts reveals a focus on the development of more efficient and cheaper coating systems unifying several protection mechanisms or additional functionalities *i.e.,* self-healing, anti-fouling or controlled substances release, in smart anticorrosion novel coatings. Together with impermeability, graphene-family fillers antibacterial effect, affinity for the adsorption of different substances in inter-layered spaces and compatibility with a wide range of polymeric matrixes make them ideal candidates. However, cases with higher enough efficiencies (>85%) and low economical requirements (products, techniques, times) are few. The employment of alternative biodegradable and environmental-friendly polymers that could substitute epoxy resins, still present in 75% of the new, already published, proposed systems, remains as a clear challenge for the upcoming years.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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