A Review: Graphene Modified Polymer Coatings For Corrosion Protection

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Abstract

Environmental and other chemical factors lead to decimated corrosive behaviour of metallic materials that is a severe hazard and an emerging challenge for times. Different protection strategies have been proposed to suppress this problem and among them graphene based coatings are considered to be great technique against corrosive behaviour because of its hydrophobic properties and ability to provide corrosion resistance of composite material. The incorporation of functional nanoparticles can provide the corrosion resistance to mild steel. It regarded a promising nonmaterial in corrosion protection. Present written text focuses on the preventive applications of graphene based nanomaterials, nanocomposites, polymeric coating techniques and their methods to fight the corrosive act of steel.

Keywords: Graphene; Corrosion; Polymeric Coating; Metal; Technique

1. Introduction

Polymeric materials now find their most common application in coating. For the purpose of maintaining and safeguarding the key feature of a material, they may be applied to different substrates.[1] Researchers have based their attention, in addition to the defensive and decorative purposes, on the creation of basic coatings for providing add-on functions such as superhydrophobic, antifouling, anticorrosive, self-healing, antimicrobial and thermal-resistant [2], [3]. Organic coatings have emerged as a vital solution for preventing metallic substrates from corrosion by acting as a barrier against external physical factors underlying the degradation of reactive materials[4]. Some deficiencies, like local defects, pinholes, microcracks or pores, are still present, however, which may cause the tiny particles to disperse inside the polymeric coating and initiate corrosion[5]. The chemical processes that occur when the system is exposed to harsh conditions and an erosive environment are related to the adsorption between the contact surfaces and the substances used in the process. The diffusion route for the corrosive materials and also the corrosion rate is another significant factor that needs to be considered[6]. For decades, corrosion has become a significant challenge to both the economy and society because, in terms of structural applications, it affects some of the most used materials. It is an electrochemical process that mainly affects metallic materials resulting in surface oxidation and is recognised as one of the most important issue in the coating sector[7]. To prevent or suppress metal corrosion, several safety methods have been suggested, and among them, organic anticorrosion coatings are one of the most effective techniques. Anticorrosive coatings can be categorised on the basis of the safety mechanism they possess, and barrier protection, anodic passivation, cathodic protection, electrolyte inhibition and active inhibitors of corrosion are the most widely recognised[8]. For all these methods, the primary objective is to reduce or completely impede the key electrochemical phenomena that acts as a catalyst for corrosion. The
recent studies show that adding functional nanoparticles can not only fight but also eliminate the possibility of corrosion and can also increase the lifetime of the coating. Some examples of active agents that were examined for their anti-corrosion properties include nanostructures like carbon nanotubes, silicon dioxide, zirconium dioxide, zinc oxide, silver nanoparticles, gold nanoparticles, titanium dioxide, cerium dioxide, montmorillonite nanoparticles, cerium oxyhydroxides and graphene oxide[9].

Graphene, though founded recently, allotrope type of carbon that, because of its mechanical, distinguished highly specific surface area, thermal properties, and electrical, has attracted attention of the scientific world and opened new avenues in the field of application for composite materials [10]. The practical use of graphene is limited due to the expense of the processing processes, the low solubility of graphene and the propensity to agglomerate when used in composite formulations. Because of the strength of its structural similarity to graphite, graphene oxide has thus become a strong alternative. This graphene oxidised form has superior mechanical strength, chemical and thermal stability[11]. In barrier applications, graphene oxide has appeared to be a reliable nanomaterial. Thanks to the high density, the diffusion of ions is allowed by this molecule. Its amazing properties are due to its chemical structure, consisting of a two-dimensional layer of a semi aromatic network made of sp² carbon atoms properly aligned in an ideal hexagonal pattern[12]. The presence of multiple defects in its basal plane, like functional groups containing oxygen, including hydroxyl, carboxyl, and epoxide is a very important characteristic of this carbonaceous material. These oxygenated groups confer a range of benefits, including improved solubility, hydrophilicity, and the ability to shape a stable colloidal solution, as well as the ability to conduct a variety of functionalization reactions on the basal plane[13]. When used in a composite, graphene oxide forms a three-dimensional coated sheet that preserves the coating's integrity by preventing volatile compounds from leaking into the atmosphere. The size of the graphene flakes, in addition to its electrical conductivity, chemical inertness, intrinsic impermeability and electrical conductivity has a major effect on the coating's efficiency[14]. Various methods are adopted for the use of graphene oxide for coatings, which has proved to be a reliable anti-corrosion agent in high-temperature and aqueous settings[15]. Chemical vapour deposition (CVD), Electrophoretic deposition (EPD), spray coating, spin coating and solution dip coating are the most well-known. Because of its exceptional thermal and electrical properties, electrophoretic deposition[16] may be used with graphene oxide and is also used for the application of anti-corrosion.

2. Coatings for anticorrosion application

The coating of anticorrosion material acts as a safeguard(barrier) in between the metal surface and the corrosive electrolyte, preventing corrosion-causing chemical compounds from forming on the surface. Failure of coatings can occur due to differences in the characteristics of the coating layer and the structural properties of metal, compromising its corrosion-fighting ability. Anticorrosion coatings operate through one of three mechanisms to prevent corrosion: (i) inhibition effect, (ii) barrier protection inhibition effect, and (iii) sacrificial protection[17]. By forming a dense layer, barrier defence isolates the ground from the corrosive atmosphere and prevents corrosion. The presence of defects, the thickness of the film, its composition, largely affect the effectiveness of the barrier[18]. When the substrate is covered with metallic coating it is prepared for sacrificial protection and secures it by sacrificing itself in an electrochemical cell. The choice to sacrifice the metallic layer rely upon the metal's electropositivity or
electronegativity[19]. Corrosion inhibitors are non-metallic or metallic materials that are applied to a coating system to provide additional corrosion safety beyond the oxide layer's barrier protection. Organic, inorganic, metallic, and composite materials can all be used to produce anticorrosion coatings. Organic coatings, like Paints, varnishes, lacquers, and rubber coatings, are commonly used to protect metals from corroding conditions by creating a barrier between the metal surface and the surrounding atmosphere[20]. Urethane coatings, epoxy coatings, acrylic coatings and water-soluble coverings are common forms of organic and inorganic coatings. Vapor deposition, electrodeposition, hot dipping and metal cladding processes are widely applied to metallic coatings, however inorganic coatings can be developed by diffusion processes, thermal spraying or chemical conversion[21]. The base metal is corroding. While ceramic and metallic offer many benefits, a wide range of them are astronomically expensive and plenty of them are restricted from use due to its health and environmental hazards. Furthermore, ceramic coating materials are extremely brittle and will inevitably fail, resulting in a disaster[22]. Most widely used protective coatings result in a large increase in thickness and improvements to the base metal's optical, mechanical, and electrical properties. Keeping in mind all the above problems some serious research was necessary to come up with a unique coating preferably with thickness kept to minimum.[23]. The researchers were successful in developing new hybrid nanocomposite coatings which has better anticorrosion characteristics thanks to major advances in nanotechnology research over the last decade. Carbon nanomaterials like graphene, carbon nanofibers and carbon nanotubes were mixed with metals, ceramics, or polymers as the matrix material in recently established hybrid coatings[24]. By incorporating all three corrosion resistance mechanisms, the result has shown to be far better than single-material coatings, providing add-on safety from metal corrosion to the base substrate.

3 Modified graphene and graphene coating techniques

The tailoring of the Graphene structure and the resulting surface properties are known to be the most important parameters of functional coatings based on Graphene (Gr). Not only for tuneable surface properties, but also to ensure that film formation and contact deposition on the target substrate meet the requirements, the graphene surface must be structurally and chemically modified. In the last ten years, several approaches for structural and chemical modifications of graphene-based materials have been explored, most of which are inherited from carbon nanotubes (CNTs) science[26]. These techniques are divided into many groups that are discussed in the available literature, including non-covalent and covalent functionalization, nanoparticle immobilisation, and substitutional doping[27]. The simplest approach to functionalization is to regulate the oxidation of graphite flakes to produce hydrophilic graphene oxide (GrO), which on its basal plane and edges includes functional groups of carbonyl, carboxyl, hydroxyl and epoxy[28]. Furthermore, using chemical and thermal methods, stepwise and selective reduction of graphene oxide will minimise and eliminate oxygen functionalities, transforming hydrophilic GrO into hydrophobic reduced graphene oxide (rGrO)[29]. GrO's oxygen-containing functional groups (epoxy, carboxyl, and hydroxyl) on the basal plane and edges are particularly useful for forming covalent bonds with organic molecules such as polymers, chromophores and diazonium compounds. Electrochemical sensing, energy conservation, and heat spreading can all benefit from the covalent attachment of highly reactive halogen groups to graphene oxide[30]. This improved functionalization of graphene and graphene oxide plays an important role in further modification of nano-architectonics by immobilising multifunctional applications of inorganic
nanostructures (quantum dots, nanoparticles and nanocrystals,)[31]. Doping the graphene structure with boron, nitrogen, phosphorus, sulphur and oxygen improved catalytic efficiency. Non-covalent interactions involving the graphene-system with other cationic, anionic compounds, and hydrogen bonds have a major influence on the properties and structure of graphene surfaces, in addition to these alteration pathways[32]. These different Gr functionalization methods open up new possibilities for designing coatings with enhanced protective properties that can deter or defend surfaces from corrosion, poisonous chemicals, fouling, bacterial infection, and fire/irradiation[33]. The dedicated sections below would go into these topics (Figure 1) in greater detail.

Fig. 1 Graphene-based materials with protective applications

A wide variety of methods for producing graphene-based protective coatings have been investigated. High-temperature pyrolysis, Chemical vapour deposition of organic compounds, fast thermal annealing, powder spray, electrophoretic deposition, (plasma spray coating and electrostatic powder coating), dip coating, solvent spray, spin coating, brushing, drop casting, and vacuum filtration are some of the techniques used[34]. In theory, they can be split into two categories: wet processing and dry processing. Table 1 displays some of the various mechanisms for fabricating graphene-based protective coatings to prevent corrosion, fouling, flame/irradiation, scratch/wear and bacterial growth that have been documented[35]. Depending on the sensitivity of the application and environment, both wet and dry processing methods are useful to varying degrees. Early investigations find that Chemical vapour deposition-grown graphene adheres well to the metal substrate, but this approach is not ideal for long-term corrosion resistance applications[36]. On the coated surface of this CVD-grown graphene, there are numerous grain boundaries, wrinkles, folds, and point defects, rendering the underlying metal material susceptible to corrosion damage. Similarly, depending on the film forming process and curing conditions, some coating applicators have some drawbacks for specific applications[30]. The coating strength is determined by the mutual reaction among the substrate and the coating layer which is usually chemisorption or physisorption with the substrate, regardless of whether
graphene or graphene based composite coatings are used[37]. The basic interactions between the coating and the substrate are unaffected by the application technique, but the coating's ability to be in close proximity to the substrate obviously affects adhesion strength. There is no one-size-fits-all coating method that works for all applications, although some coating method may have similar film forming mechanisms. In these processes some examples shown in Figure 2.

![Figure 2](image)

**Fig. 2** Film formation mechanism of graphene and graphene oxide, (a) Physical deposition and subsequent curing, (b) Self-assembly, (c) Layer by layer deposition and (d) Sol-gel process

**Table 1**: Preparation of Graphene-based protective films using wet and dry coating techniques

| Coating Method                  | Concepts                                                                 | References |
|---------------------------------|--------------------------------------------------------------------------|------------|
| **Dry processing**              |                                                                          |            |
| Powder spray                    | A high-velocity plasma forming gas is fed onto a graphene/ceramic composite powder and collected. After being mixed with binder and pigments in powder form, graphene-based polymer composites are typically applied electrostatically and cured under heat. This powder is most certainly a thermoplastic or thermoset polymer. | [11]       |
| Chemical Vapour deposition      | Graphene coatings or acetylene gases are mixed with argon and hydrogen gases and pumped into a Chemical Vapour Deposition reactor at a high temperature to produce a corrosion-resistant methane (around 1000 °C). | [33]       |
| Rapid thermal processing        | Organic materials including naphthalene, coronene, and anthracene polyacrylonitrile are mixed with a metal substrate and pyrolyzed at 1000°C to create a multi-layer graphene-like coating. A corrosion-resistant graphene coating can be created by rapidly thermal annealing with acetone on a preannealed Cu-foil at 1000 °C. | [28]       |
| Dip coating                     | The substrate is dipped/immersed in a graphene oxide dispersion and then dried after removal. | [39]       |
| Drop casting                    | Droplets of graphene oxide solution are dropped on a cationic surfactant-treated surface and dried in the air or in a drying oven to create uniform films. | [31]       |
| EPD                             | Negatively charged graphene is drawn to an electrode of the opposite charge and deposited there by an electric field. A compact film persists until drying. | [26]       |
Wet Processing

| Solution Spray | Until being sprayed onto the substrate and cured with heat, graphene oxide or graphene oxide combined with other materials is dispersed in a suitable solvent. | [24] |
| Vacuum filtration | To deposit graphene/graphene oxide sheets, graphene or graphene oxide dispersions are vacuum filtered using a membrane support. This process is used to render antibacterial paper and antifouling membranes based on graphene oxide. | [30] |
| Brushing | Coatings prepared by brush with graphene ink and graphene oxide-based paints have been used to form corrosion-resistant thin films on metal alloys and metal. | [40] |
| Spin coating | A high-speed rotating substrate is coated with a distributed graphene oxide solution. The coating material is stretched out by centrifugal force to form a thin film. | [34] |

4. Graphene based nanocomposites coatings

Today's innovations make perfect defect-free graphene-based materials difficult to achieve. As a result, designing graphene-based nanocomposites is a viable choice for accelerating the commercialization of graphene-based materials. Researchers are especially interested in graphene-nanoparticle composites and polymeric graphene-based nanocomposites for coating applications.

4.1 G-NPs (Graphene-nanoparticles) composites as coatings:

G-based molecule is ordinarily connected on nanoparticles at after that utilized as coating materials in G-NPs. There have been a few papers published on how G-NPs can boost electrical properties. According to Wang et al. graphene oxide wrapped with sulphur can be used in rechargeable Li-S battery cathodic. This property is very useful to change the power and cyclic stability of these batteries[41]. The composites developed high and stable specific capacities of approx. 600mAhg⁻¹ for over more than 100 cycles. Other example are the development of tin oxide- silicon carbide nanocomposite for Li-ion strong high resonance. It was synthesised in situ with the help of simple ball milling process. In this tin oxide- silicon carbide was graphene coated and also tin oxide particles are uniformly deposited on the silicon carbide core. The reduction of graphene oxide produced graphene.[42]. For better electrolytic process, coating of graphene- titania nanocomposite around the conducting support medium can be done. [43]. Dip coating process is used to make a film electrode. Photo-electrocatalytic capacity in graphene- titania dioxide as compare to pure titanium dioxide film electrode and it can also be used to increase photocatalytic activity[44]. Composite coating is applied to the substrates by using spin-coating process. The titanium dioxide-dextran-graphene oxide composite showed the stronger photocatalytic activity and photovoltaic response as compare to pure titanium dioxide. Due to the layer life span of the electron-hole pairs in the composite[46]. Graphene-nanoparticles and also the effect of different carbon based materials. There are some drawbacks of graphene coating is that it is very time consuming and expensive and on top of that it is very difficult to build pore free thick layer of G-NPs coating. No doubt it have superior properties but this process is way too expensive.
4.2 Polymeric graphene based nanocomposites as coatings:

The introduction of G-based materials into polymers will boost not just a single function of a polymer, but multiple properties at once, such as mechanical and electrical properties. In-situ polymerization was used on a Teflon plate by Liao et al. to create a PUA(polyurethane Acrylate) coating reinforced by graphene[47]. It was found that the conductivity of electricity of the composite was improved as the graphene loading increased, according to their findings. Cure composites had lower percolation concentrations than uncured composites, and adding graphene to the PUA coating could improve its mechanical properties in the rubbery region. There are several articles published on graphene-based materials with reinforced composites and they can be utilised in various coating applications with the right techniques[48]. Corrosion and erosion resistance are critical for a coating's commercialization because they affect the coating system's lifetime. Only when a coating method has a long life span cycle and good characteristics it is capable of commercialization. The corrosion and erosion resistance are affected by the orientation, wrinkles, number, aspect ratios, and particle size of G-based materials in the polymer matrix. Corrosion and erosion are essentially chemical reactions that weaken the substrate and coating, diffuse through the coating layer, and damage the substrate[49]. Fillers are used to minimise or stretch the diffusion paths of the said compounds in order to create defect-free composites.

To enhance the obstacle presentation of graphene-based materials, follow these steps: (1) It is necessary to achieve superior scattering of G-based materials; (2) The graphene sheets should be line up corresponding to the overlay layer; (3) graphene sheets have high aspect ratios, and graphene particles have large particle sizes; (4) Graphene sheet aggregation and wrinkles should be avoided; and (5) Dissemination path can be spend by increasing the number of G sheets in the polymer matrix [50]. The electrical property of graphene is its most appealing function. While graphene-based materials can boost a polymer's electrical properties, the achieved electrical properties are still inadequate for electrical applications. In general, the excavate resistance among particles and the touch resistance among filler fortify polymer composite [51]. Polymers have a stubby electrical conductivity in general. While graphene can boost electrical conductivity, it is still insufficient to meet commercial standards. Since little particle size filler can serve as a overpass between two large particles, size particles to reduce tunnelling resistance among them, merge small and large particle size conductivity of polymer nanocomposites [52].

5.Conclusion

The current analysis summarises the most recent developments in the field of anticorrosive coatings based on graphene oxide nanostructures from both a formulation and operation standpoint. The hydrophilicity of an anticorrosive layer is a crucial factor to remember. The presence of oxygen-containing functionalities on the graphene oxide basal plane can facilitate water molecule diffusion and absorption, resulting in poor barrier properties. The hydrophobic properties of modified graphene oxide can reduce corrosive species migration and absorption while also improving the corrosion resistance of composite materials. A wide range of graphene oxide-based coatings methods were introduced, as well as a broad variety of basic applications involving nanocomposite coatings, which were detailed and discussed.
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