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Corrosion Protective Graphene Coating : A Mini Review

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Abstract : Graphene based paint has tremendous potential to protect metal in saline environment, owing to impermeable nature to all corrosive ions. The demand of graphene coating is increasing by leaps and bounds owing to its attractive features. In this review paper, the recent progress of graphene-based paint against corrosion is discussed in details. At the beginning, the corrosion protection mechanisms of metal surface with different types of coating materials such as graphene oxide, reduced graphene, graphene nanoplatelets, and graphene nanocomposite have been presented. In addition, market status of graphene paint and coatings have also been discussed. Subsequently, the discussion has been made on the composition and production protocol of graphene based paint with a special reference to dispersion method. Types of coating in terms of graphene metal matrix composite coatings, graphene polymer matrix composite coatings and graphene composite coatings for corrosion protection of various metal substrates have been reviewed in details with a future outlook.

Keywords *: Corrosion, graphene oxide, reduced graphene, polymers, dispersion, Graphene nanoplatelets*

I. INTRODUCTION

Corrosion is an irreversible and diffusion-controlled process in which metals deteriorate naturally which occurs due to electrochemical or chemical reactions [1]. It is one of the world's most significant challenges [2]. There are various factors that dominate the rate of metal corrosion including metal properties towards contaminated chemicals, concentration and type of pollutants in the atmosphere, temperature, humidity and type of corrosion products. The rate of corrosion in a given environment can be determined thermodynamically using the free energy equation; $\Delta G = -nFE$, where n is the number of electrons involved in the reaction, F is Faraday's constant ($F = 96500$ C) and E is the electrode potential of metal. Based on the underlying mechanism, most corrosion can be classified into the following forms; uniform corrosion, intergranular corrosion, pitting, selective leaching, crevice corrosion, erosion corrosion, stress cracking and galvanic corrosion. Uniform corrosion is the most common type of corrosion, in which the thickness of metal uniformly gets reduced. Ultimately, the metals fail. Intergranular corrosion is a form of corrosion caused by depletion of elements at and near grain boundary areas. As a result, the cohesive forces between the grains become weak. For example, when stainless steel is heated for a longer time, chromium has dwindled in the grain boundary area resulting in intergranular corrosion. Pitting corrosion is a type of localized corrosion in which pits appear in metals. It is frequently observed in the passive film where small holes or cavities exist. The rate of corrosion accelerates as the damaged area becomes the anode and the passivated area becomes the cathode. Crevice corrosion occurs mainly within crevices and other shielded areas due to concentration differences of ions or dissolved gases between two regions of the same metal section. Erosion corrosion is a natural process that occurs when there is a relative motion between the metal surface and the respective fluid media. It generally occurs in piping. In stress corrosion cracking, small cracks are formed due to the presence of tensile stress and corrosive medium, which propagates normally to the stress. On the other hand, galvanic corrosion is electrochemical corrosion due to dissimilar metals and electric currents. When different kinds of metals are electrically coupled while exposed to an electrolyte, reduction and oxidation occur. The more reactive metal gets corroded. So, the type of corrosion responsible for the deterioration of metal is dependent on the exposure environment and the physical and chemical properties of metals. It may happen that more than one number of mechanisms can also lead to corrosion-driven failure of metals. Therefore, the understanding of different forms of corrosion is very important while developing the corrosion preventive measures of metals.

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To avoid corrosion losses, industries are being paid attention to developing high-performance paints and coatings. As per the report of the World Corrosion Organization, the estimated corrosion-driven damages of steel structures is around $ 2.5 trillion every year, which is 3-4% of the global GDP. Due to corrosion, capital costs are also suffering and also decrease the lifetime of manufacturing equipment [3]. According to a study, corrosion management and corrosion management practices can result in saving 15% - 35% ($375-$875) of the cost of damage globally. In figure-1, different strategies for the protection against corrosion have been given. Corrosion has affected our daily lives directly and indirectly in some other ways. Furniture, metal tools, automobile body panels, etc. are being corroded which causes some amount of loss. In fact, when metals get corroded either it collapses or breakdown which can lead to accidents or even a threat to human life. Further, oil-pipelines break and chemical pipelines leak due to corrosion. Corrosion is also harmful to human health affecting the human digestive tracts, respiratory tracts, eyes and skin, and causes various diseases. The biological system is also adversely affected due to corrosion. When water bodies come in contact with corroded metals and mix with water bodies affects their living. Also, the air becomes polluted. Corrosion also leads to many plants shutting down. Therefore, the massive loss triggered by metal corrosion in industrial sectors is a major challenge. Therefore, corrosion protection measure of metal is useful to prevent financial losses, accidents, various diseases caused due to corrosion and environmental hazards [4]. Corrosion has an obvious effect on the metallic surface, strength, appearance, and efficiency. The economic impact due to the corrosion of metals has stimulated the development of considerable corrosion preventive strategies as metals are used in each field. Among various existing corrosion control strategies protective coatings are gaining popularity around the world due to their ease of production and superior protection. [5-7]. At present day, nanotechnology has introduced nanocoatings, which have a lot of promise in advanced engineering systems. These nanocoatings provide electrically or chemically impermeable coverings on metal surfaces and have customized functionalities such as anti-corrosion, self-repairing, wear and abrasion resistance [8-9]. Rathish et al. has suggested that nano-coatings can increase the effectiveness of protection and create a bulwark against corrosive ions [10]. Adhesion of coatings on the metal surface also plays a crucial role in corrosion shielding. Indeed, epoxy resin coatings are extensively employed due to their flexibility and superior adhesion to a wide range of surfaces. Jiang et al. evaluated the adherence and corrosion resistance of epoxy coatings amalgamated with two types of silane agents, namely, gamma-amino propyl trimethoxy silane and bis-1,2-(triethoxysilyl) ethane. The cross-linkage of epoxy coatings and the chemical bond at the coating and metal interface is effectively reinforced [11-12]. Many reports suggest that the electrochemical reaction rate of nanocoatings is strongly influenced by their grain size. Mishra et al. presented the corrosion activity of nanocrystalline nickel of grain sizes (8–28 nm) and observed that smaller grain size of nickel possessed greater breakdown potential than bigger grain [13]. In addition, the corrosion rate decreased with increasing the grain size.

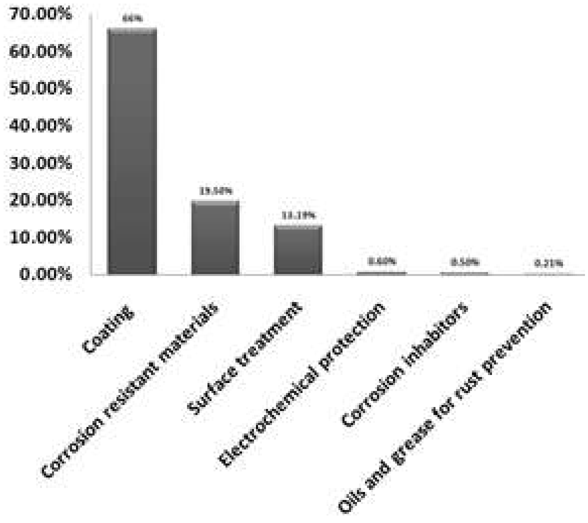

Fig. 1 Different strategies used for corrosion protection worldwide

Currently, several paint formulations have been developed to slow-down the corrosion-driven damages of structural steels. Among them, the paints containing heavy metals (Zn, Chromate or Lead) are efficient barriers for the protection of steel in a highly-corrosive environment. However, these heavy metal based paints are not eco-friendly paints due to the toxic nature of these heavy metals. In contrast, graphene (, an allotrope of carbon) based paint is an ultimate choice for durable rust-preventive coatings due to the following reasons; (a) graphene is impermeable to all the corrosive ions, (b) it improves the mechanical strength and water repelling properties of the coating and (c) it enhances the dissipation of the corrosion-induced current of the coating due to its high-conductivity that becomes harder for the acidic component to attach the steel surface. This review focuses on the usage of graphene for corrosion protection.

2. GRAPHENE : A VERSATILE MATERIAL

In 2004, graphene was discovered for the first time by Andre Geim and Konstantin Novoselov. They were rewarded with a Noble prize in physics in the year 2010 for the discovery of the wonder material. Graphene is a carbon allotrope, a single sheet of sp^2 bonded carbon atom that form a compactly packed hexagonal 2D honeycomb lattice. The sp^2 bonded carbon atoms forms a plane with a molecular bond dimension 0.142 nm. Graphene is exfoliated from graphite (stacked layers of graphene with an interplanar distance of 0.335nm) by disturbing the van der Waals force present in between the graphene layers. Graphene is the sleekest material known to the human world till date. It has unique structural, electrical and mechanical properties which are generally due to 2p orbitals which form πstate bands [14]. It is also light weight material with 1 mm^2 weighing 0.77mg and a high surface area (2630 m^2/gm). Graphene is considered to be the most robust substance known to the world (200 times sturdier than steel) due to its strength, stiffness and toughness caused by the stability of sp^2 bonds. The experimentally evaluated young's modulus is 1TPa with an intrinsic tensile strength of 130GPa and the thickness of graphene is around 0.345 nm. It has high thermal conductivity (5000 W/mK), zero effective mass, impermeable to gases, and high electron mobility (250,000 cm^2/V s at 25^oC) [15]. It has a wide range of applications due to its distinctive electronic and thermal properties. Studies have demonstrated that it can conduct current even at zero carrier concentration due to the atomic arrangement of carbon. The valence band and the conduction band merge at a point which is known as Dirac point due to which it is a zero-gap semi-conductor. Graphene used for coating gives a light weight coating and has the ability of resistance to oxidation. Water molecules and diffusion of oxygen on the surface of metals are prevented by graphene by creating a highly tortuous path. Graphene at the metal electrolyte interface also helps to prevent charge transfer [16]. Owing to the outstanding properties of graphene, several methods have been developed for the production of graphene. In table-1, the recent market status of graphene paint and coatings with the involved industries are outlined.

The problem with good quality graphene is that it is expensive. As a result, the price of graphene made of products increases several folds. Therefore, researchers have focused to develop the scalable and cost-effective processes for the production of defect free graphene. Besides, graphene would be suitable for the production of well-dispersed graphene paint. In the recent past, several potential mass production synthesis methods have been developed for the production of graphene. Some notable methods are; the plasma method has been developed for the production of high quality graphene on large scale. The authors demonstrated that the layers from graphite are separated when the high energetic ions hit the surface [17]. Further, Lee et al reported large scale (2 kg / day) continuous production method for reduced graphene oxide (rGO). The produced rGO exhibits electrical conductivity of 660 S /m and a BET surface area of 400 – 600 m^2/g [18].

3. GRAPHENE POTENTIAL AS CORROSION PROTECTIVE COATINGS

Recent past so many materials that are used for corrosion resistance coatings. Compared to these coating materials, graphene paint and coating have higher potential to show corrosion protection in saline environment. Different forms of graphene such as graphene oxide (GO), reduced graphene oxide (rGO), graphene nanoplatelets (GNP) and graphene nanocomposite are being used in the paint and coating. Among them, GO is widely used for corrosion protection in metals. The oxygen groups of GO enhance the bonding of coating with the metal substrate. It is also observed that the performance of polymer coating is improved when the GO is distributed homogeneously. So, the oxygen functional groups become handy to control the interactions through hydrogen bonding in order to agglomeration free graphene sheets. However, the high amount of polar oxygen functional groups such as hydroxyl, epoxy and carboxylic groups can facilitate hydrolysis. Consequently, it shows an adverse impact on the coatings. Therefore, one has to optimize the type and amount of oxygen functional groups of GO while using in the paint and coating for corrosion protection. The oxygen functional groups become useful for grafting with organic and inorganic polymers. In the recent past, there are many reports that demonstrated grafting of GO. Polyacrylate functionalized GO decreased the corrosion rate of epoxy coating almost three times [19]. Again the GO grafted polyaniline filler increases the hydrophobicity that leads to an increase in the corrosion resistance of epoxy coating in saline water [20]. Further, the addition of 0.5 wt.% GO grafted polypyrole filler increases the corrosion resistance of epoxy resin [21]. They have also discussed that the amino functional groups of polypyrole increase the crosslinking density of polymer that leading to a decrease in the micro-pores density. Hence, GO-polypyrole filler enables to increase the barrier effect of coating significantly. Also, tensile toughness is enhanced by the incorporation of GO in epoxy coating. In acidic media, it has a negative charge due to which it is an excellent cation absorbent and smart nanocomposite in the acidic medium as well as anticorrosive layer. This study also suggests that the size of GO sheets determine the barrier property i.e. smaller the sheet, higher the barrier property [22]. Baker et al. studied the size dependent corrosion protection efficiency of GO sheets [23]. Based on the electrochemical impedance data, they argued that smaller graphene oxide sheets have higher activation energy for water diffusion. As a result, the penetration rate of water through the coating containing smaller graphene sheets is significantly reduced.

In addition, reduced graphene oxide (rGO) is also used in the paint for corrosion protection. The rGO sheets are prepared by using suitable reducing agents. Though the reducing agents of GO are efficient to remove the oxygen functional groups, they also produce lots of defects. However, defect free graphene sheets are desirable to achieve high performance of graphene paints and coatings. Hydrazine, hydrogen iodide and ascorbic acid are widely used reducing agents for the preparation of rGO chemically. Some researchers reported that hydrogen iodide produces low defect density rGO sheets. Su et al. reported that rGO film produced using hydrogen iodide reducing agent is an efficient barrier to all gases, liquids and aggressive chemicals including hydrogen flouride [24]. They explained that the reducing agent converts the oxygen functional groups into H_2O, therefore, no structural damage occurs during the reduction. The thermal reduction also transforms GO to rGO. A mild amount of rGO was added to polyurethane (PU) matrix which leads to good physical barrier to corrosion [25]. Researchers also used MoS_2-rGO composite modified with propytrimethoxysilane and MoS_2-rGO/epoxy composite coating for corrosion

Table-I Recent market status of different companies using graphene

Company	Country	Product
Applied Graphene Materials	U.K.	Graphene incorporated water based coatings
The Sixth Element Materials	China	Graphene-Zinc based primer
Graphenano	Spain	Graphene based paints
Talga Resources Ltd	Australia	Graphene coating
The British Electro Conductive Products	U. K.	Graphene based conductive coating
Garmor Inc.	United states	Graphene oxide based coatings
Rusgraphene	Russia	Graphene - epoxy based paints
Tata Steel	India	Graphene paints
Global Graphene Group	United states	Graaphene coating
Nanoxplore	Canada	Graphene based paint

protection applications [26]. Graphene nanoplatelets (GNP) are another form of graphene is made up of tiny heaps of graphene sheets and has 3-10 nm thickness. These graphene nanoplatelets have dimensions of about 100 nm to 100 microns. These GNP's have more than 99 % of carbon content and oxygen content is less than 1%. These GNPs help in decreased permeability and also decreases the diffusion coefficient which is helpful in various applications. X. Cao et al. used GNPs in zinc rich epoxy coating for better corrosion barrier performance. It acts as an oxygen and hydrogen barrier and helps in good electrical conductivity of the coatings on a steel substrate. The Zn-GNP-Zn network acts as better anode corrosion prevention [27]. Graphene based nanocomposites limit the rate of gas diffusion at the metal coating interface. Thus, reduces the cathodic oxygen reduction rate and also reduces the vertical oxygen diffusion. Kirkland et al. revealed the theory in accordant with the diffusion hindering effects of graphene based nanocomposites in composite layers [28]. Yu et al. described that graphene-based polyaniline can provide corrosion protection as it behaves as a gas barrier [29]. The integration of a unique 2D structure with polymer matrix also makes the coating a desirable platform for preventing corrosion, mechanical wear and abrasion, heat or radiation loss, fouling, and bacterial infection [30-31].

Graphene has been also explored for corrosion protection film in biological environments. W. Zhang et al has shown astounding results of graphene coated Cu foils implanted in living body for corrosion inhibition. The cell viability test results demonstrate the effective performance of graphene in reducing the toxicity of Cu by corrosion inhibition [32]. Graphene based thin films have been also reported to provide a protecting layer while functioning as lubricants to minimize surface wear by getting adsorbed by the frictional surface. [33]. Its stability is the reason for it working as an excellent anti-oxide and anti-corrosion layer on metal surface. Graphene used for coating gives a light weight coating and has the ability of resistance to oxidation. Water molecules and the diffusion of oxygen on the surface of metals are inhibited by graphene by creating a highly tortuous path. It acts as a blocking shield on the metal surface to the passing of gas molecules. The hexagonal 2D structure of graphene is an important aspect of the impermeability of other molecules [34]. There are various corrosion protection mechanisms like barrier protection, sacrificial protection, electrolytic inhibition, anodic passivation, etc. based on which the anticorrosive coatings are categorized. Graphene and its derivative based coatings are classified as barrier protective coating because the exfoliation of graphene sheets is a mandatory procedure in forming films over the metal surface. In the barrier protection mechanism, the coating acts as a shield at the coating - substrate interface and restrain the passage of electrolytic ions into the metal. The degree of dispersion of graphene sheets plays a vital role. When the graphene sheets are well suspended in the matrix it acts as an efficient barrier layer at the interface. But sometimes, the lipophobic nature of the graphene induces corrosion. Therefore, the functionalization of graphene proves to be an important step for the production of efficient barrier coatings. Zheng et al. has shown the difference between barrier protection mechanisms of modified and unmodified reinforced graphene epoxy coatings. When the GO/EP coating was exposed to a corrosive environment, the electrolyte molecule got accumulated at the interface, thereby forming defects that further played the role of diffusion channel. Whereas on incorporating functionalized GO in the epoxy coating, the conversion of hydrophilic GO to lipophilic GO aided in better barrier properties [35]. Ramezanzadeh et al. has explained the corrosion protection mechanism of covalently grafted GO sheets with polyimide (PI) chains. The functionalization of the binding sites on GO with PI upgraded the interfacial interactions among graphene sheets and PU matrix. The interpolated PI–GO sheets boost the tortuosity in the path of electrolyte. Along with the coating-substrate interface the PI–GO layers deterrent the diffusion of electrolytes through the parallel directions among local anodes and cathodes [36].

Various factors like adhesion, wettability, electrochemical parameters have an impact on corrosion protection properties of graphene coatings in many ways. Many papers discussed the dependence of corrosion protection of graphene coatings on bonding to the metal surface. Abakah et al. has claimed better adhesion of graphene nanoplatelets incorporated epoxy coatings than neat epoxy coating with 9.6% coating loss in pull-off test studies. Adhesion of coating to a substrate determines the strength of the coating [37]. Water absorption on the coating surface implies poor corrosion protection ability. Water uptake can be measured by two methods namely the gravimetric technique (weight variation on exposure to atmosphere) and capacitive technique (change in electrical capacitance over long-term exposure to aqueous environment) [38]. Aneja et al have recorded that the addition of graphene drops the water uptake. Decreasing the amount of water absorbed is an indicator of the ability of a graphene-modified coating to provide a tortuous path [39] or industrial application the motto is to obtain defect free coating. The pore resistance is inversely related to defect concentration. Zhou et al. found in their electrochemical studies that graphene/epoxy coatings with high pore resistance ($1.21x10^6\ \Omega cm^2$) have low defects which enhances corrosion protection potential [40]. Coating capacitance is a measure of determining defects in the coating surface. Defect-free coatings are highly protective. Aneja et al. reported high conductivity ($5\ Sm^{-1}$) of graphene coating which may also offer an alternate path for ions, discharged at the anode to travel, thereby delaying the overall corrosion process. [41]. In coatings usually, cracks are induced and move through the grain boundaries. However, graphene incorporated coatings have the least amount of cracks due to the layered structure. Graphene structure in a coating depends on its dispersion in the matrix chosen. The next section briefly describes the dispersion of graphene in various ways.

4. METHODS FOR DISPERSION OF GRAPHENE IN MATRIX

Graphene has very good chemical, physical and barrier properties, but it has a very low dispersibility. Thus, for widening its application in various fields, the problem of dispersibility is solved. Different ways are used for the dispersibility of graphene are: physical dispersion methods, covalent bonding methods and non-covalent bonding methods [42]. Some tips must be followed for dispersion methods which are: (a) the type, position, and amount of the binding materials on graphene needs to be controlled, (b) the processing effect on matrix materials and graphene must be minimized, (c) unwanted components must be removed and (d) should be cost-effective for large scale production.

4.1 Physical dispersion methods

For even distribution of graphene to obtain anti-corrosion coating, it is mixed in steps and then blended. Fig 6 briefs the exfoliation of graphite to obtain graphene sheets through various ways. The polymerization method is used in which graphene is added with the monomer of resin. The dispersion methods include unmodified simple mechanical dispersion and conventional wet transfer dispersion. Stirring or ultrasound is used in the conventional mechanical dispersion route to disperse graphene directly, without any modification, but this showed difficulty in compatibility. However, this method is acceptable for graphene oxide [43] and could be used for corrosion prohibiting coatings, as the carboxyl and epoxy groups are present on the surface. Chang et al. explained that due to the principle of impermissibility and similarity, the resins having the same functional groups owns compatibility with the oxidation groups and carboxyl. In unmodified wet transfer dispersion, firstly, the graphene is dispersed in water. After dispersing graphene in water, with the help of extraction and evaporation, it is then transferred to resin. [44] In the case of GO, with the help of the wet transfer method, it is extracted directly from aqueous dispersion into epoxy resin. The extraction process is done by the addition of triglycidyl-p-amino-phenol to bisphenol-A epoxy resin. In the formation of a graphene/epoxy dispersion system, phase transfer agents simplify the stages of agitation, temperature, and energy consumption. This method is stable in dispersion and very less time consuming [45].

4.2 Covalent bonding methods

This method of dispersion is most widely used at present as it is carried out by using 3 aspects of small organic molecules, polymers, and inorganic nano-oxides. Using small organic molecules, graphene is modified by mixing oxygen containing groups and small organic molecules. The organic molecules include silane coupling agents, titanite coupling agents, isocyanate, thionyl chloride, etc. This takes place with the help of covalent interactions on the surface of GO. The silane coupling agent (EPTES), forms Si-OH bonds on decomposition. EPTES, on the surface of graphene, is covalently bonded to an active oxidation site. EPTES modified GO along with epoxy resin shows improved compatibility as a number of epoxy groups of EPTES is directly proportional to compatibility modified graphene/epoxy resin, which leads to good dispersion results [46]. Titanate coupling agent also used to modify graphene, showed excellent stability in aqueous dispersion for several weeks. GO, GO-Ti and Nano-Ti particles could be dispersed in epoxy resin using ultrasonic dispersion [47]. Li et al. explained that the coating, with waterborne polyurethane shows good barrier properties for corrosion protection [48]. At present, the dispersion of graphene using polymers is more considerable. In polymers, its structural parameters can be altered which helps the graphene by providing useful properties. The properties include ductility, toughness, etc. by altering the function and type of the polymer [49]. In epoxy resins, the polymers which can be used for dispersion include polyaniline, polyvinylpyrrolidone by mechanical stirring, and aniline trimmer. Fully-oxidized polyaniline was used to modify GO. After that modified GO, with the help of mechanical stirring was dispersed in polyvinyl butyral resin uniformly [50]. Graphene modified with polyvinylpyrrolidone is dispersed in epoxy resin. This enhances the anti-corrosion ability of epoxy resin with good adhesion. The mechanical and thermal property of epoxy resin coating is enhanced which is useful for corrosion protection [51]. GO surface modified with sulfonated aniline trimmer (sulfonated with 3-aminobenzenesulfonic acid) was dispersed in epoxy resin. Sulfonated aniline trimmer and graphene oxide have a synergistic effect and this makes the dispersion easy. The solvent property of sulfonated aniline trimmer shows excellent compatibility with epoxy resin and enhances the anti-corrosion ability of epoxy resin coating. [52] Yu et al. explained that dispersion of graphene oxide is enhanced by the formation of a chemical bond between vinyl-grafted graphene oxide and styrene monomer in a polystyrene matrix. This material was used for corrosion protection coating and it enhanced the anti-corrosion ability. He also discussed about the graphene sheets which were water dispersible. Carboxylatedoligoanilines were used to stabilize these graphene sheets. These were used for corrosion protection coatings [53]. Yeh et al. reported that polyaniline with graphene used for coating leads to excellent corrosion protection. Better dispersion of graphite was shown by 4-aminobenzoyl group functionalized graphene sheets [54]. The use of inorganic nano-oxides for dispersion of graphene for corrosion protection coating is also considered a promising method. Chemical bonding takes place for modification GO with inorganic nano-oxides. GO-Al_2O_3 hybrid with epoxy shows excellent corrosion barrier property. 3-aminopropyltriethoxysilane is used to anchor Al_2O_3 on GO sheets and then the GO-Al_2O_3 hybrid was dispersed in epoxy matrix. It was dispersed uniformly in epoxy resin [55]. TiO_2-GO hybrids dispersed in epoxy resins show anti-corrosion properties. TiO_2, with help of (3-aminopropyl) trimethoxysilane (APTS) was synthesized on graphene oxide sheets and was dispersed in the epoxy resin [55]. SiO_2 is anchored with the help of 3-glycidoxypropyltrimethoxysialne and 3-aminopropyltriethoxysilane on GO sheets. Then, this SiO_2/GO is dispersed into epoxy resin and this showed enhanced corrosion protection ability [56]. Graphene is modified with 4-aminobenzoic acid and then a covalent bonding, as well as polymerization takes place with the aniline monomer to form graphene/polyaniline. This graphene/polyaniline is used for coating as it acts as a barrier for oxygen and water, hence acts as an excellent corrosion protective barrier [57].

4.3 Non-covalent bonding methods

Dispersion of graphene also becomes stable by modifying the surface with the help of non-covalent bonding methods such as π-π interactions, ionic bonding, and hydrogen bonding. Li et al. described Ionic bonding help the graphene oxide to dissolve in water, as there is a negative charge in the surface carbonyl of graphene oxide. Thus, a stable colloidal solution is formed due to the repulsion of negative charges. Thus, by controlling the reduction process, carboxyl ions are retained and get good dispersion of graphene in water [58]. Electrostatic adsorption was used to disperse GO in the aluminium powder and anionic surfactant without the use of any chemical catalysts. Then, with the help of sintering method, GO/Al_2O_3 composite was prepared. Then, graphene was mixed with the sodium polyacrylate (anionic surfactant) and this mixture showed an excellent dispersion in water and can be used in water-borne epoxy coatings [59]. Dispersion of graphene can also be done by π-π non-covalent interactions. π-π non-covalent interactions give excellent dispersibility of graphene with the same conjugated structure. It absorbs the organic molecules on the graphene surfaces. Molecules that have conjugated structures with the plane and aromatic rings have good dispersion of graphene. Hence, these graphene-based epoxy coatings also show good anti-corrosion properties. Poly (2-butylaniline), a dispersing agent, was immersed on the graphene surface. Then P2BA was mixed with graphene and ultrasonicated. A stable dispersion was obtained due to non-covalent π-π interactions between graphene sheets and P2BA. Then, by curing the reaction of P2BA/GO, epoxy resin, and amine hardener, graphene sheets were integrated with the coating matrix. [60] Corrosion protection property of epoxy coating, with 3, 4, 9, 10-perylene tetracarboxylic acid and graphene is enhanced. PTGA was added to graphene and ultrasonicated. Due to π-π interactions between PTGA and graphene, PTGA was absorbed on the graphene surface and showed good dispersion of modified graphene in epoxy resin [61]. Iqbal et al. explained the dispersion of graphene in polyethylene. Polyethylene, graphene, and oxidized polyethylene with the help of the solvent blending method were mixed. Polyethylene was blended with oxidized polyethylene to enhance the dispersion of graphene in polyethylene [62]. Graphene oxide forms hydrogen-bonding interactions with various substances. as a large number of –COOH and -OH groups are present. Therefore, the dispersion of graphene is improved as it does not change the molecular structure. Li et al. using the method of solution blending, dispersed, graphene oxide in thermoplastic polyurethane. Thus, due to the presence of hydrogen bonds, graphene is uniformly distributed on the polyurethane matrix. Then, in-situ thermal reduction method was used to reduce graphene oxide nanosheets in the composites [63]. The surface of graphene oxide was absorbed by the doxorubicin hydrochloride under no light and ultrasonic surroundings. This was mainly due to the existence of the hydroxyl group in graphene oxide and also in the doxorubicin hydrochloride [64]. A highly efficient dispersant, vitamin B_2, namely FMNS (flavin mononucleotide) is used in the preparation of aqueous dispersions of a few layers of graphene flakes which are defect free. FMNS is used for graphene colloidal dispersion and inks. This process is done with the ultrasonic exfoliation of graphite powder. Due to the presence of hydrogen bonding interactions between the graphene and FMNS, a stable dispersion of graphene is observed during the process of ultrasonic stripping of graphene sheets. [65] Chemical plating is one of the dispersion methods in which graphene surface is chemically plated. The surface of graphene is firstly coated by some metals and then combined with other metal matrix. In this process, metal ions are reduced to metal atoms in the solution and deposited on the surface of materials. However, chemical plating cannot be used with every material, only materials which have autocatalytic properties can be chemically plated. Graphene nanoplates do not have catalytic properties. Thus, activation and sensitization are performed. This is the process in which chemical plating is possible in graphene if some catalytical property particles are absorbed on the surface of graphene [66]. Graphene was dispersed in water by stirring and ultrasonication. Using the electroless plating method, containing no reducing agent, Fe and Fe-rGO coatings were formed on Cu substrate. The Fe-rGO coating shows better corrosion protection as it has a dense structure owing to the plating bath in which GO is added [67].

5. TYPES OF GRAPHENE COATING

5.1 Graphene Metal Matrix Composite Coatings

This section is brief about the various graphene reinforced metal matrix composite coatings. Kumar et al. explored the anticorrosive property of Ni and Ni-Gr composite coatings. They suggested that the introduction of graphene in Ni metal matrix affects the crystal growth which leads to a small average crystallite size of 20 nm as compared to 30 nm of pure Ni coating. He explained the mechanism of increasing nucleation growth and reducing crystal growth of Ni at the Ni/Gr has a more positive shift in E_{corr} with lower I_{corr} which shows the corrosion resistance of Ni/G coatings. He also suggested that the insertion of graphene may lead to high mechanical strength and hardness of the composite coating [68]. Nazir and his co-workers also investigated the corrosion behaviour of various nickel matrix-based nanocomposite coatings. Among different metal oxide reinforced nanocomposites, graphene was also used as one of the reinforcing elements in the metal matrix. Graphene platelets were used to disperse in prepared Ni solution and were electrodeposited on steel. They reported that Ni/graphene coatings formed a very fine coating resembling glass with low porosity and least surface roughness. When the prepared coated samples were exposed to an aggressive corrosion environment, they found that in the case of Ni/graphene coatings there was the lowest percentage rise in grain size leading to enhance impermeability to oxygen and electrolyte ions this was confirmed from the obtained corrosion product (0.3wt % Fe) [69]. Srivastava et al. has presented the remarkable results of the incorporation of graphene in Cr metal-based coatings by electrodeposition. They observed that the incorporation of graphene in the CF (Chromium coating containing Zinc-Oxide nanoparticles deposited using formic acid) ensued in improving the topology and surface morphology of bare Chromium coating. In their electrochemical studies, they found that CFG (Chromium coating containing Zinc-Oxide nanoparticles and graphene deposited using formic acid) has a more positive Ecorr value than other CF & C (Cr coating) coatings which explains the inertness of CFG towards corrosive media. Also, they found that the corrosion rate and corrosion current value was lowest with respect to other Cr coatings which support the stability of graphene incorporated Cr coatings. They also suggested further study of the photothermal conversion behaviour of Cr-G coatings [70]. Raghupathy et al. explained the surface modification of Cu-GO coatings on mild steel. The electroplated Cu-GO coatings showed crystal growth along <220> atomic plane. The electrochemical corrosion test verified that with the loading of GO the coating yielded higher corrosion potential. He studied the long-term corrosion resistance property of Cu-GO coatings and found considerable surface change after 5 days of exposure to corrosion media [71].

5.2 Graphene Polymer Matrix Composite Coatings

Many researchers have shown their interest in graphene and its derivative, as a filler material for polymer composites due to the uniqueness of graphene. Already some scientists have claimed the novel properties of graphene incorporated polymer composites for corrosion protection. The uniform distribution of graphene as reinforcement plays a significant role in the production of graphene-based nanocomposites. Graphene used as nanofiller acts as a physical blockade that descends the permeability of polymer-based coatings by extending the tortuosity of the wandering route for particles. Chang et al. illustrated the principle of enhanced corrosion protection of polyaniline/Graphene and polyaniline/clay composite coating on steel. They incorporated functionalized graphene into polyaniline which worked as a gas barrier that retards the penetration of gases like O_2 and H_2O molecules into the coating, thereby protecting the metal surface. K.C. Chang and his fellow workers presented the better corrosion resistance properties of hydrophobic epoxy graphene composites (HEGC) than epoxy / graphene composites. The electrochemical studies of HEGC coatings showed a higher E_{corr} value (-411mV). They demonstrated that 1 wt. % graphene inclusion in epoxy - graphene composite can inhibit up to 60% of O_2 permeability [72]. Pourhashem et al. has presented the importance of dispersion graphene derivative in the matrix for the efficiency of coating over the substrate. They claimed via his electrochemical measurements that the increasing GO content lowers the barrier properties as there is a chance of GO aggregation with higher wt.%. They also suggested that GO directly added hardener has superior dispersion and corrosion resistance properties than GO incorporated in epoxy. Hayatdavoudi et. al. presented the influence of an adequate amount of graphene in Zn-rich epoxy (ZRE) coatings for protection against corrosion. The long-term corrosion studies revealed that the role of graphene content in galvanic coupling corrosion as lower content of graphene act as a cathodic site for sacrificial ZRE coating and increase the percolation period thereby deteriorating the efficiency of the coating against corrosion. Also, in the salt spray test, they noted the formation of white rust in high graphene content ZRE coatings which indicate better protection while there was the formation of red rust in the scribed areas of lower graphene content in ZRE coatings after 1000 hrs of spray test [73]. Zheng et al. has reported the anticorrosion property of modified graphene-based epoxy coating. The graphene was modified using poly- urea formaldehyde via in-situ polycondensation reaction followed by a mixing of epoxy resin. From the characterization results, they proposed that the hydrophilicity of GO no longer existed after the modification. Also, the GO/UF composite acts as a sheet pigment in epoxy. Ramezanzadeh et al. showed in his report, the advanced barrier properties of functionalised GO sheets into Polyurethane coatings. The GO sheets were conjugated with polyisocyanate (PI) resin. They concluded from the obtained SEM images that the PI–GO/PU composite has smooth surface fracture which signifies the reduction of cracks by graphene derivative. Li et al. studied the corrosion protection of different forms of graphene reinforced into waterborne polyurethane (PU) coatings. He found that except functionalized GO (FG), GO and mildly reduced GO (RGO) were well dispersed in PU due to the hydrophilic character of GO. They concluded through his investigations that RGO with low content of 0.2 wt% showed the best anti-corrosion properties in the electrochemical test as well as salt spray test. However, increased content of Functionalized Gr of 0.4 wt% has better resistance than 0.2 wt% Functionalized Gr he expected the reason behind improved properties is due to the parallel alignment of FG to the substrate [74].Other than coating as a corrosion barrier, Graphene paints also attracted researchers to investigate the properties for practical applications. Krishnamoorthy et al. demonstrated the inhibition performance of GO nano paint in an acidic medium by weight loss method in the saline medium. They reported the inhibition efficiency of GO nanopaint to be 88.70% in an acidic atmosphere. The corrosion-resistant efficiency was calculated 76.61% in 3.5 wt% NaCl solution [75].

5.3 Graphene composite coatings for corrosion protection of various metal substrates

Chen et al. has explained the corrosion hindrance ability of graphene for Cu and Cu/Ni alloys. They have reported the chemical inertness of monolayer and bilayer graphene coatings in both air oxidation and liquid solution environment [76]. For the nickel surface coated with graphene acts as an ionic barrier. This decreases the corrosion rate leading to corrosion protection. Ni coated with graphene by chemical vapour deposition, graphene acts as a barrier for electrochemical reactions [77]. There is a mechanism of greater solubility of carbon in nickel and surface catalysis. The graphene coating has great coverage of the surface, has good adhesion and correlation. Also, the Ni surface coated with graphene has very less defects, as a result of which there is high corrosion resistance. When graphene is coated on nickel, the rate of corrosion is 10.45 x 10^{-3}mm/year, corrosion potential -233 mV and corrosion current of 0.85 $\mu A/cm^2$ in 0.5 M NaCl. Kumar et al. examined that the corrosion rates become 7 times slower as compared to nickel coating where there are no additives. The preparation route of coating also affects the efficiency of coatings to corrosion barriers. Prasai et al. had presented the difference between the corrosion resistance of graphene-coated Ni formed by mechanical transfer and CVD. They found that CVD-developed coating has 20 times corrosion resistance while few layers of mechanically deposited coating resulted in excellent property [78]. However, there are other methods used for coating prepared graphene composites on metal like rapid thermal annealing, spin coating, electrophoretic deposition, vacuum filtration, powder spray, solution spray, dip coating, brush painting, or drop-casting [79]. Graphene-coated copper has lower corrosion densities and corrosion current dropped by 20 times with respect to bare Cu [80]. The rate of corrosion for graphene-coated copper is observed to be 0.08 mm/year

Table-II. Electrochemical data of some graphene coated metal substrate in 3.5 wt.% NaCl solution

Composite coating	Coating method	Substrate material		Immersion time	Electrochemical parameters				Ref.
					E_{corr}(mV)	**I_{corr} ($\mu A/cm^2$)**	**R_{corr} (mm/y)**	**R_p ($K\Omega\ cm^2$)**	
G/PANI	Nano-casting	Steel		_	−537	0.38	0.00044	135.22	[54]
GO/isocyanate	Electro deposition	Copper		_	−211	3.49	0.04068	0.025	[91-92]
G/polyimide	Spin coating	Cold rolled steel		30 min	−432	0.15	0.00176	165.29	[93]
G/epoxy	Nano-casting	Cold rolled steel		30 min	−411	0.10	0.00009	442	[73]
GO/per nigraniline	Dip coating	Copper		168 hours	-23	5.98×10^{-5}	6.99×10^{-7}	9.86×10^{5}	[50]
GO/epoxy	Film applicator	Mild steel		240 hrs	−	0.2015	2.366×10^{-3}	1.669	[94]

rGO / diatomaceous earth / TiO_2	Cold spray	Copper		15 min	12.2	0.159	0.00158	_	[79,95]
rGO/epoxy	Spin coating	Zinc		144 hrs	−957	0.18	0.00272	_	[51]
GO/PMMA	Drop casting	Copper		100 hrs	−250	0.069	_	_	[83]
rGO/silicon-acrylate resin	Spin coating	Zinc		144 hrs	−585	0.45	0.00682	_	[96]
G/polyurethane–	Film applicator	Mild steel		_	−27.2	2.45×10^{-5}	2.88×10^{-7}	_	[97]
G/PANI	Electro polymerization	Copper		_	−234	0.1	0.00005	1.5×10^{2}	[98]
GO/chitosan	Dip coating	Carbon steel		48 hrs	−374	3.9	0.0017	1.44	[99]
G/epoxy	Film applicator	Q235 steel		48 hrs	−566	0.0551	0.0007	369.4	[100]
GO–ZrO_2epoxy		P110 steel			–432	0.37			[101]
rGO/PPy	Electrodeposition	Mild steel		1 hr	-544	0.85	0.0099	66.9	[102]

whereas for bare copper it is 0.18 mm/year [81]. Singh Raman et al. described that Cu coated with graphene by CVD was ensured to have improved corrosion resistance by magnitude of two orders. Raman spectroscopy was to determine the number of layers. There are 4-5 layers of graphene on copper films (I_G /I_{2D} ratio = 1.36) [82]. Kalita et al. described that copper coated with graphene provide oxidation resistance for an only a short period of time and inferior corrosion resistance for long period of time [83]. Electrochemical Impedance spectroscopy (EIS) and potentiodynamic polarization is used to study corrosion protection due to graphene. Kirkland et al. had shown in their study, that there was an anodic shift for Ni and cathodic shift for Cu substrate layered with CVD-grown graphene. Coating thickness and exposure to a corrosive environment have an effective impact on the protection tendency of coatings. Qi and co-workers have explained the effect of exposure time and Coating thickness on different concentrations of PMMA-g-GO. They noted that 81% PMMA-g-GO film has better performance than 62% PMMA-g-GO. Also, with the increase in film thickness from 2µm to 10µmthere were no corrosion traces with 10 µm thickness. 81% PMMA-g-GO proved to provide corrosion protection up to 100 hrs [84]. For steel, graphene acts as an ionic barrier. For corrosion protection of mild steel substrate, epoxy-GO nanocomposite coating is used which has enhanced barrier properties. Diffusion of corrosive species is restricted by GO nanosheets in epoxy coating. For enhanced corrosion protection, GO is directly added to polyamide hardener. To deposit GO onto carbon steel, nowadays EPD (electrophoretic deposition) is being used.

The sheets of GO are smooth and clear, have high functionality, and improve adhesion. Park et al. described that GO sheets were inactive as an oxidation barrier because it was less dense [85]. In the case of aluminum, graphene coating served as a barrier layer which was highly protective. Al substrate coated with graphene has corrosion protection efficiency of magnitude order 3 that was higher than bare Al substrate. Graphene coatings by dip coating on the Al surface worked as a barrier between the Al surface and the electrolyte. Lui et al. reported that by Raman spectra it was found that graphene dip-coating covered the Al surface uniformly. XPS analysis described that from graphene dip coatings, oxygen-containing functional groups were removed. [86] Al-2219 alloy was coated with graphene blended PVA. This was done by using multiple dip coating. Hikku et al. reported that there was a uniform coating of GPVA on the Al surface. As compared to bare Al, Al-2219 coated with GPVA showed lower corrosion current, lower corrosion rate, and higher polarization resistance [87]. Chen et al. had represented the corrosion protection ability of graphene-coated Cu and Cu-Ni alloys when exposed to high temperatures. They claimed that multilayer graphene act as passivation coating for a short time period. They found that the multi-layered graphene-coated Cu/Ni alloy samples remained shiny even after two days in air at the 200°C. Meanwhile, iron is considered the most active metal for corrosion. Bare iron easily turns brown when exposed to harsh conditions due to oxide layer formation over its surface. Kang and his co-workers have confirmed that the colour of five bilayer rGO coated iron foil does not change even in oxidation conditions [88] Gan et al. reported that further research is required for the protection mechanism of graphene composite coatings [89]. Bohm et al. discussed that steel coated with graphene has corrosion rates of 0.000196 mm/year as compared to bare graphene which had a corrosion rate of 0.7 mm/year. Galvanized steel had corrosion rate of $3.87*10^{-2}$ mm/year whereas 20% wt.% unfunctionalized graphene had corrosion rate of $8.46*10^{-4}$mm/year [90]. Table 3 shows graphene-based coating on different substrates.

6. FUTURE OUTLOOKS FOR CORROSION PROTECTION USING GRAPHENE

Researchers are working on graphene paints for corrosion protection and have demonstrated that in the future graphene paints can be used to protect steel and other metals in corrosive atmosphere. In the future graphene will have greater progress as much researches is going on for the improvement of defects and to make perfect graphene that gets evenly spread in the polymer resin. The key element that diminishes the competence of graphene for various applications is the number of defects. It is found crucial to achieve defect-free, ordered arrangement of graphene, and develop environment-friendly modification methods for the original structure of graphene which are not harmful to human health as well as the environment, the amount of graphene domain boundaries is to be reduced thereby producing sheets of a larger area. Graphene waterborne anti-corrosive coatings are also given attention for the future. The main global goal is to make graphene useful for commercial products in society and in the market. In the next 10 years, it is believed to achieve this goal and benefit society with the astonishing properties of graphene.

7. CONCLUSIONS

Graphene coating is regarded as an ultra-thin coating that protects the metal from oxygen and water by providing a good shielding. It is also regarded as an eco-friendly coating free from any hazardous chemicals. Compared to ceramic coating graphene is always better in terms of its durability, hydrophobicity, glossy, and it's easy to apply, still, the challenges for its application as effective material against corrosion lies in terms of its high cost. Researchers are working in this area to make this material less cost-effective by devising various new synthesis techniques.

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