

A State-of-the-Art Review of Graphene-Based Corrosion Resistant Coatings for Metal Protection

Ganesh S. Zade¹ and Kiran D. Patil^{2,†}

School of Chemical Engineering, Dr. Vishwanath Karad MIT World Peace University, Pune-411038, India

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Any design engineer or coating formulator's primary objective is to protect metals. Large investments in terms of money, time, labour, and other resources are necessary for constructing large-scale machinery and structures. In terms of economy, the structure's lifespan should be as long as feasible to create revenue. It is becoming essential to protect metal substrates from corrosion to prolong the lifespan of such huge structures. One of the most exciting, durable, useful, and effective methods to protect metals from corrosion is the application of corrosion-resistant coating. Graphene is a novel material with a wide range of applications because of its extraordinary features. The use of graphene in coating creates an obstacle and complicates the path for corrosive medium to reach the metal. As the path to the metal elongates, the corrosion medium takes longer to reach the metal. Thus, metal corrosion can be avoided. In this paper, the importance of graphene in coating formulation is discussed, including chemical modifications of graphene, the effect of graphene concentration on corrosion inhibition, and the contact angle of coating. This review also highlights the significance of water-based corrosion-resistant coating for preventing environmental damage.

Keywords: Graphene, Corrosion resistance, Water base coating, Metal protection, Corrosive media

1. Introduction

The most common cause for metal structure failure has been discovered to be 'corrosion'. It has been discovered that, rate of corrosion is much faster in acidic than alkaline medium. Once the corrosion of metal is started it starts deteriorating the properties of metal like ultimate tensile strength, toughness, hardness, ductility etc. [1]. Corrosion is a most challenging and expensive problem in many sectors. Corrosion professionals, asset owners and coating formulators are still focused on understanding and lowering the cost of corrosion and mitigating its effect on the life of structure [2]. Based on atmospheric exposure conditions corrosion is classified as wet corrosion and dry corrosion [3] and based on mechanism of corrosion, it can be classified in different types; some of them are, uniform corrosion, stress corrosion, galvanic corrosion, crevice corrosion, pitting corrosion, inter-granular corrosion, erosion corrosion and water line corrosion [4,5].

Uniform corrosion is known for its uniform corrosion rate all over the surface. This happens due to anode area

and cathode area occupying the equal surface area. Because of uniform corrosion rate all over the surface it forms rust of uniform thickness on entire metal surface [6]. Crevice corrosion is known for its localized attack on metal substrate. Crevice corrosion takes place as crevice gets formed at specific locations on a metal surface. Crevice corrosion is more prominent when metal establishes contact with either metal or non-metal [7,8]. Pitting is one of the most catastrophic types of metal damage. This is because of its poor traceability even after large deterioration of metal [9]. Difference between the chemical compositions of metal makes grain boundaries more acidic which forms inter-granular corrosion [10]. Stress corrosion is a combined action of mechanical stress present on metal and corrosive environment around the metal despite the fact that neither factor has a corrosive effect on the metal alone [6]. When two metals of different electronegativity come in contact each other, it establishes the electrochemical cell. In formed electro-chemical cell one of the metal acts as anode while other becomes cathode depending upon the electronegativity. The metal which is more reactive gets corroded fast while other metals get protected [5]. This is also called bimetallic corrosion. Erosion type of

[†]Corresponding author: kiran.patil@mitwpu.edu.in

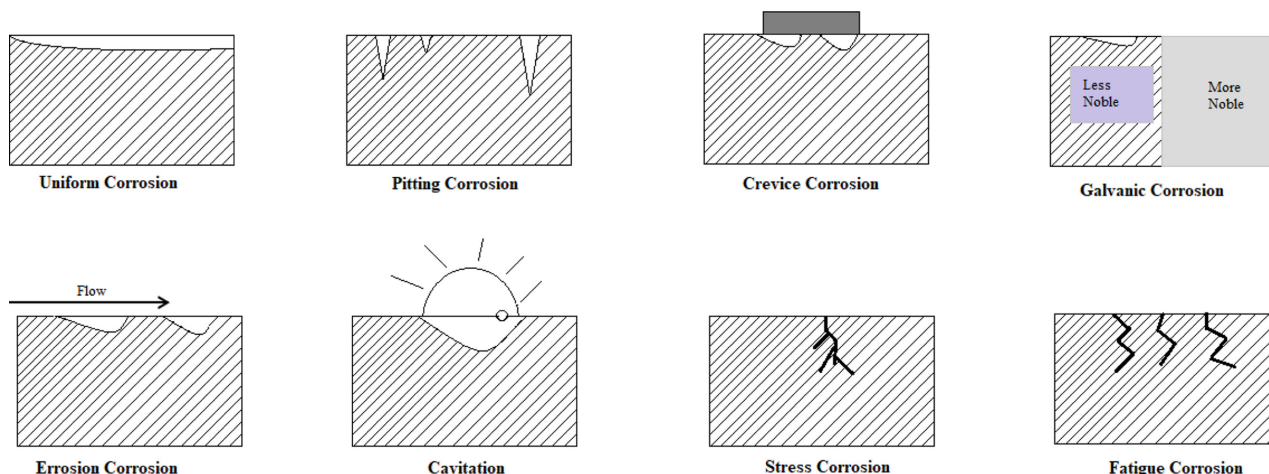


Fig. 1. Types of corrosion [12]

corrosion occurs due to mechanical movement of corrosive fluid through the metal. This happens when mechanical friction between metal and particles of the corrosive fluids takes place [11]. Waterline corrosion occurred in metallic water storage tanks when filled partially. Area below the water surface acts as anode because it has exposure to very little oxygen while area above the water level has ample of oxygen and thus acts as cathode and thus corrosion occurs just below the water surface called as water line corrosion [5]. Antifouling coating is the best choice of coating formulators and scientist to avoid water line corrosion to some extent. Fig. 1 indicates the pictorial representation of various types of corrosion.

2. Formation of rust

Top layer of any metal is always getting exposed to atmosphere and thus it will be the first part of any metal where corrosion starts. In some cases if such corrosion product is insoluble then this corrosion layer act as barrier for further corrosion to occur but if this corrosion product is unstable in that case corrosion will remain continue until entire metal get corroded. The mechanism of corrosion reaction is best explained by Zaki Ahmed [13] as follows;

At anode

Oxidation of metal takes place as follows;

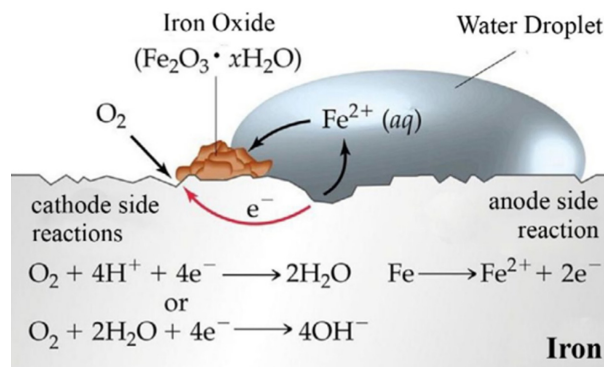
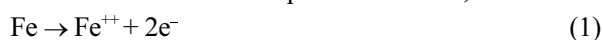


Fig. 2. Schematic representation for corrosion mechanism [15]

At Cathode

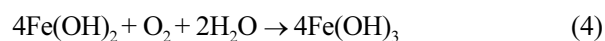
Reduction of oxygen takes place as follows;



The OH^- ions react with Fe^{++} ions which are generated at anode as follows;



Formed $\text{Fe}(\text{OH})_2$ reacts with excess oxygen and moisture present in the environment and further it forms rust i.e hydrated ferric oxide by losing water molecules as follows;



The above cathodic and anodic reaction can either take place all over the surface or at location specific depending upon the metal composition [14]. Fig. 2 indicates mechanism of rust formation on metal surface.

3. Need of corrosion protection

Designing and constructing large infrastructures like bridges, wind turbines, ships, oil refineries (onshore/offshore), storage tanks, reactors, distillation columns etc. involves investment of large amounts of resources viz. man, money, time, energy etc. The life of such huge infrastructure is a crucial aspect under consideration during its designing and construction phase. As a part of the returns on investment, life of these structures must be as long as possible. On the other hand; these infrastructures always encountered challenges by means of environmental shocks during the entire service life. During the service, these structures come in contact with various corrosive environments like rain water, sea water, sunlight, air pollutants, moisture, etc. When metal of these structures comes in contact with such corrosive mediums, it initiates the metal corrosion. And once the corrosion of metal starts it becomes a big challenge for engineers to protect the structure from corrosive damages.

Corrosion is a principle challenge to industries as it causes structural weakness, reduced bond strength, ductility, and shear capacity of metal [16]. According to international studies, the reports indicates that overall cost of corrosion that happens interms of loss of metal as a result of corrosion is at least four to five percent of the gross national product (GNP), and out of this 20 to 25 % loss can be saved using efficient and correct corrosion prevention technology [17]. Mitigation of corrosion is more practical than its complete elimination [18,19]. Metal can be protected against corrosion to occur by various ways like use of non-corrosive metals, provide corrosion free environment, using principles of galvanic protection, electroplating and barrier corrosion resistant coating.

It is always a challenge to designer and coating formulator to select most suitable, correct and efficient methods for metal protection. Selection of correct method for metal protection involves various factors viz. environmental conditions, structure dimensions, working

Sectorwise consumption of protective Coating

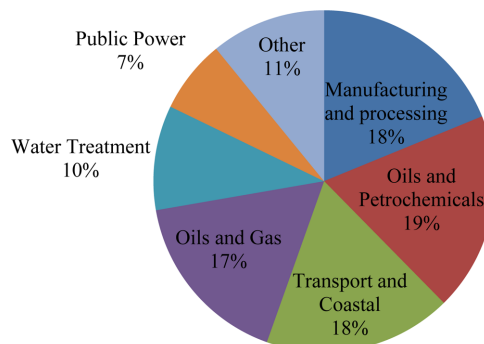


Fig. 3. Sector wise shares of protective coatings [29]

parameters, financial considerations etc. Use of non-corrosive metals such as stainless steel, aluminium or other noble metals sometime finds limitations due to process parameters and other working conditions of the equipment. Similarly it is not practically possible to provide a corrosion free environment to entire infrastructure during entire service span. Galvanic protection also suffers from some limitations [13] as it requires different galvanic series for different environments. Polarizations of metal and metal composition are also important factors to be considered while selecting these methods for metal protection. And thus; the most promising and effective solution to protect the metal against corrosion left with engineers is an application of corrosion resistant coatings/ protective coatings on metal surfaces. The applied corrosion resistance coating provides the barrier to external corrosive medium/agencies to reach up to metal surface and thus avoid the corrosion to occur. Applied coating also resists the spread of corrosion on the metal surface [19-28].

Various industrial sectors are using protective coatings for their jobs to protect them from the corrosion. Industrial sectors which involves use of heavy amount of protective coating includes oil and gas sector, marine sector, power sector, transport sector. Fig. 3 represents the consumption of protective coatings in various sectors across the globe [29].

4. Corrosion resistance coatings

Coating comprises resin/polymer/binder, pigment/filler,

solvents/thinners and additives as main ingredients. All these ingredients are characterised for their own typical characteristics. Solvent gets evaporate out from the coating during drying process and hence never be an integrated part of dried coating. Selection of correct ingredients in correct proportion for formulating the coating is always a challenging job for the coating formulator. Formulator has to consider all the factors like application of coating, availability of raw material, curing mechanism, financial aspects of coating etc. Requirements of coating differ as per the end application therefore selection of coating ingredients also differs accordingly. Resins are polymeric materials and responsible for almost all functional properties of the coating like adhesion, gloss, film formation, hardness, flexibility, chemical resistances etc. Pigments are used to give colour and hiding to the coating materials. Some of the pigments also impart functional properties to the coating. Functional properties imparted by the pigments include heat resistance, light fastness, corrosion resistance etc. Solvent in coating formulation is used as thinner to facilitate the ease of applicability. Once the coating is applied, solvents evaporate from the film and dried film is obtained on the surface. Additives are used as a performance accelerator for the coating. Addition of small quantities of the additives will have dramatic change in the performance of the coating.

Substantial research work is carried out for development of variety of coatings to protect metal when exposed to severe corrosive medium such as seawater, industrial salt water, biofluids, thermic fluids, high-temperature gases etc. Examples of such advancements include use of nanoparticles and nanotubes in coating formulation, new conversion coatings, novel plasma coatings etc. This is evidenced by recent advanced research work include use of innovative electrochemical and metallic conversion coating approaches. Investigation of new coating materials such as hybrid polymers, composites, nano scale materials and ceramics results in the discovery of multifunctional corrosion resistant coatings also evidenced a new era of protective coating segment.

Electrically conductive coating is a one of the promising way to avoid metal corrosion. On the other hand, thick coatings are undesirable for metal protection of thermal systems as it decreases heat transfer due to induced of thermal resistance by coating material. Hence, Saivash

Khodakarami et al. developed silicone dioxide based coating which is suitable to produce a thin film with superior performance properties [30]. Addition of small amounts of nano-particles in coating formulation, improves the coating properties to great extent, such properties include mechanical, chemical, functional, optical properties etc. Nanoparticles are characterised by its particle size of less than 100 nm. Coatings based on nanoparticles coatings are mainly applied to mitigate the effects of a corrosive environment. Nano pigment based coatings are also suitable to apply with minimum dry film thickness which is provides more flexibility to for designing the equipment [31].

Epoxy resins possesses excellent adhesion to wide range substrates, excellent solvent resistances to solvents like esters, ketone, petroleum solvents, Excellent acid and alkali resistance, low contraction during drying process, excellent mechanical properties like hardness, flexibility etc. and most important it shows excellent corrosion resistance in wide range of corrosive environments. Such extraordinary properties of epoxy resins make it the best choice for formulator to formulate corrosion resistant coating [32,33]. Epoxy resins are used in wide range of sectors includes space coating [34], automobile [35], construction [36], electronic [37], adhesive [38,39]. M.R. Bagherzadeh and his coworker develop another water-based epoxy resin. This epoxy resin system comes in two parts. The inclusion of 3-glycidoxypopyl trimethoxy silane together with the curing agent increased the corrosion resistance of manufactured water base epoxy resin [40].

Strong water repellent abilities of super-hydrophobic materials made its enormous uses in anti-corrosion coatings. The super-hydrophobic coatings are characterized by strong water- repellency which isolates the corrosive medium from the metal surface results in achieving remarkable anti-corrosion performance [41].

Angle of contact is the best method to differentiate

Table 1. Angle of contact of different surfaces

Sr. No.	Contact Angle	Types of coating
1	< 90°	Hydrophilic coating
2	>90°	Hydrophobic coating
3	>150°	Super-hydrophobic coating

substrate as hydrophilic, hydrophobic and super-hydrophobic [42]. Table 1 illustrates the different contact angles for respective type of coating

Surface with minimum contact angle allows the water droplet to wet the surface to maximum extent and does not resist water spreading on metal surface. On the other hand, a super-hydrophobic surface possesses high surface tension and resists water droplet to spread on surface.

Super-hydrophobic surfaces do not allow water droplet to retain on the surface therefore, such surfaces perform well against corrosion. Behaviour of water droplet on surfaces with different contact angles is shown in Fig. 4.

The super-hydrophobic graphene coating has been developed and effectively applied via electrodeposition. This coating has a very high surface tension and a contact angle of roughly 160 degrees. In a 3.5 percent NaCl

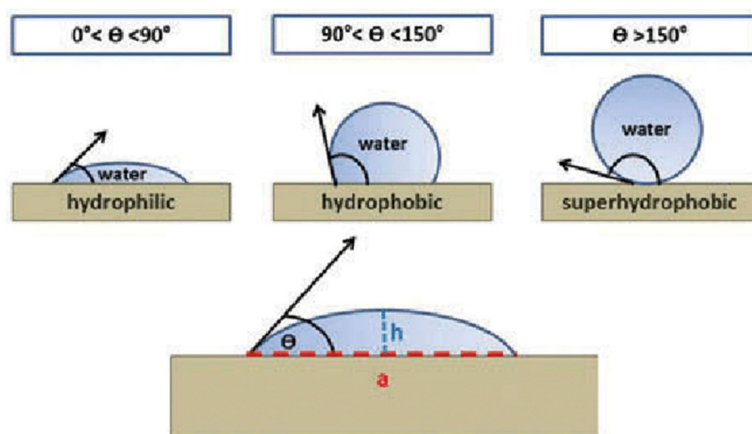


Fig. 4. Schematic representation of angle of contact and hydrophobicity of surface [43]

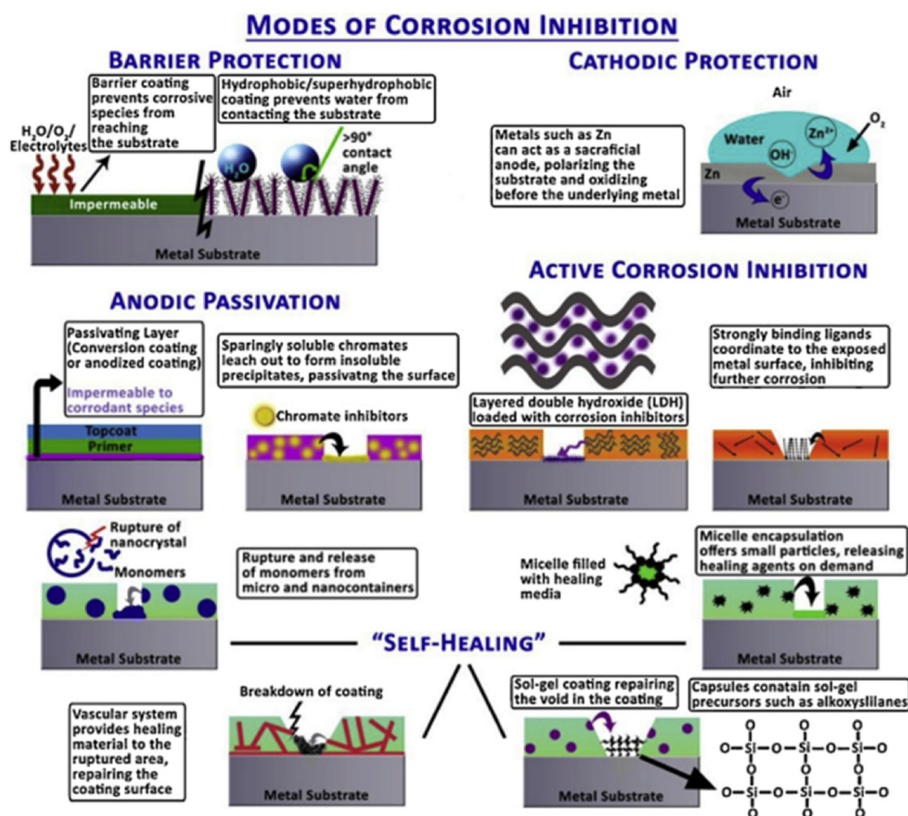


Fig. 5. Pictographic representation of corrosion prevention mechanisms [45]

solution, this coating also provides outstanding corrosion resistance [44].

Mechanism involved in corrosion protection is the best way to classify corrosion resistant coatings. Corrosion protective mechanism includes cathodic protection/galvanic protection, barrier protection, anodic passivation, electrolytic inhibition, and active corrosion inhibition. Nurul *et al.* represented these corrosion protection mechanisms in pictographic form as shown in Fig. 5.

4. Water based coatings for corrosion protection

Coatings are frequently named by the resin from which it is made. Resins that give a coating its name include epoxies, alkyds, urethanes etc. However, there are some other raw materials also which are used to make the coating. Such coating raw material includes pigments, fillers, solvents and additives. Pigments are responsible to provide hiding and colour to the coating. Solvents are volatile component of coating and it is mainly used to improve the ease of applicability by reducing the viscosity of coating while additives are used to improve coating performance.

Organic hydrocarbon solvents are used in solvent-based epoxy resins. The presence of organic volatile solvents in the coating formulation creates a risk to the environment. It is now vital to produce water-based coatings in order to minimise environmental damage. As a result, Shunli Zheng *et al.* designed a water-based epoxy resin coating that is further enhanced with nano pigments to increase the coatings' functional properties. Bio-based epoxy resin, silane-based coupling agent, and hydrophobic curing agent were used to create hydrophobic coatings. The results reveals that corrosion prevention efficacy of coating was increased to 93.75 percent [46].

Water or any hydrocarbon solvent is commonly used as a thinning agent. Based on which types of thinning agent are used to reduce the viscosity of coating material, coatings are named either solvent-based or water-based coatings. The surface coatings industry has undergone a profound shift in recent decades, largely due to environmental concerns [47]. Due to rising environmental and health regulations, efforts are made to decrease the VOC (Volatile Organic Compound) of coatings. Reducing the VOC of organic coating is one of the most challenging

jobs nowadays in the paints industries. A 'VOC' i.e. volatile organic compound can be defined as a compound that evaporates from the coating system and takes part in photochemical reactions in the atmosphere to produce health hazards [48]. Therefore, it is foremost important to develop the coating with no or minimum VOC. Thus, use of water in coating formulation is vital requirement in today's industrial scenario. However, water-based coatings may not always contain zero solvents. Many water based coatings comprise what we called 'co-solvents'. These Co-solvents belongs to glycol or similar families and present at very low quantities. These co-solvents are added to facilitate the drying of water based coating by expelling water out from coating film. Thus, for reducing the VOC of the coating use of water is the best choice for coating formulator.

Use of water base coating not only reduces the VOC of coating it also helps to reduce the chances of fire hazards during storage, transportation and handling. Organic solvents used in solvent based coating are highly flammable and need very special care during the handling and storage. Such risk of fire hazards is minimized by using water based coatings.

5. Graphene as novel material for corrosion protection

Graphene is characterised by its two dimensional (2D) material where carbon atoms are arranged hexagonally and possess sp^2 hybridization [49]. Graphene nanomaterial is available in several allotropic forms, including graphene nano-ribbons, nano-sheets, nano-plates, and 3D graphene. Each of them established with incredible applications as all these form possess different properties. Graphene's electrical and quantum characteristics are still under investigation [50]. The bond length of C-C atoms in graphene molecule is around 0.142 nanometre [51]. The graphene molecule thickness is 0.335 nanometre while a diameter of graphene molecule is varying from few microns to several 100 μm [52]. Fig. 6 indicates intermolecular properties of graphene nano particles (lattice).

The discovery of graphene paved the way for fresh study into carbon materials. As a result, the Nobel Prize was awarded to British scientist Andre Geim and Russian scientist Konstantin Novoselov in 2010. Graphene

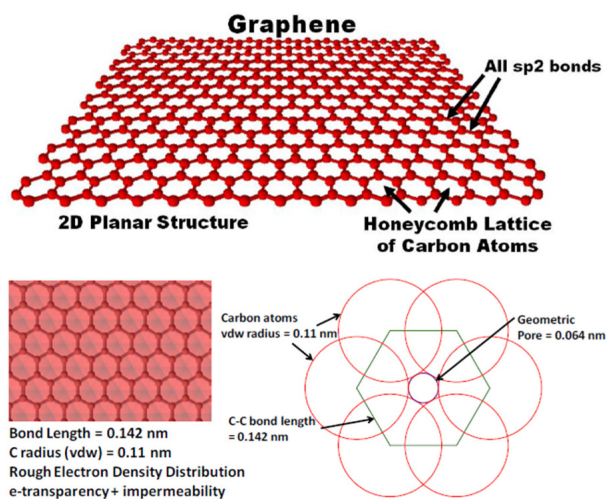


Fig. 6. Schematic representation of graphene lattice [53]

possesses outstanding characteristics that set it apart from other materials. Graphene is the strongest substance that has ever been found. It has a Young's modulus of 1 Terapascal (TPa) and tensile strength of 130 Gigapascal (GPa) [54,55]. Graphene also possess has electric conductivity as high as 6×10^5 S/m [56], thermal conductivity of approximately 3000 to 5000 W/m·K [57], high electron mobility 20,000 cm²/V·s [58]. Due to two dimensional structure of graphene it also characterised by high surface area of approximately 2,600 to 2,630 m²/grams [55,59]. Graphene, a single layered hexagonal carbon atoms proven to be chemically stable at temperatures ranging from 400 to 500 °C [60]. Graphene is also characterized by exceptionally high mechanical properties, gas permeability, remarkable thermodynamic performance, excellent barrier properties, corrosion resistance etc. [61-65]. This has been established that graphene's ultra-dense lattice of carbon atoms provides a hermetically sealed barrier that protects the material against corrosion while being so thin that properties of coated surface remains unaffected [66]. Though graphene shows such excellent characteristics, due to its inherent re-stacking tendency, this novel material suffers from poor dispersion and formation of aggregation during coating preparation [33,67]. Formation of aggregates and agglomerates because of strong Van der Waals' forces in graphene molecule [68]. Enormous research is being conducted to improve its dispensability in coating medium. Graphene and its allotropes with necessary modifications are extensively employed in synthesis of polymeric

coating due to its outstanding anti-corrosion properties. The anticorrosive properties are exhibited by graphene due to their lamellar structure. This plate like structure of 2D graphene creates highly convoluted pathways and prevent penetration of corrosive medium like oxygen or moisture from atmosphere to reach to underneath metal surface thus, protecting the metal from corrosion [45].

Application of graphene to enhance performance of coating against corrosion can significantly reduce the dry film thickness of the coating and also improves their protective efficacy [69]. The capacity of graphene to operate as a physical barrier against corrosive species was originally demonstrated by its impermeability to gases [70].

Coating of graphene on metal surface can be carried out by various ways like chemical vapour deposition (CVD), electrodeposition, solution processes etc. Excellent adhesion can be obtained by using CVD process but it possesses limitation as this CVD can be carried to limited types of surfaces [71]. By modifying the ionic liquid, graphene oxide may be utilised to alleviate the friction and wear of epoxy [72]. Graphene oxide is made by oxidising graphite with the Hummers technique [73].

6. Advances in graphene based corrosion resistant coating

Dispersibility of graphene in polymeric medium is the biggest challenge for coating formulator. A diverse research work is undertaken by many researchers to modify the graphene and its allotropes to alter the surface nature, so that it will boost the dispersibility of graphene particles in resin medium. Chang Peng et al. found diazonium compounds suitable for modification of graphene. Modification made by reacting with diazonium compounds considerably improved its dispersibility by successfully preventing reunion of graphene nanoparticles. For the first time, Author has employed phenyl carboxylic functionalized graphene and reacted it with phthalocyanine. The Author also revealed that dispersibility of graphene molecules is also improved as a result of functionalization of graphene particle [74]. The graphene can be chemically modified by self-reducing at high temperature. Author has made a coating by varying the concentration graphene from 1 to 10% in resin medium. The prepared coating is

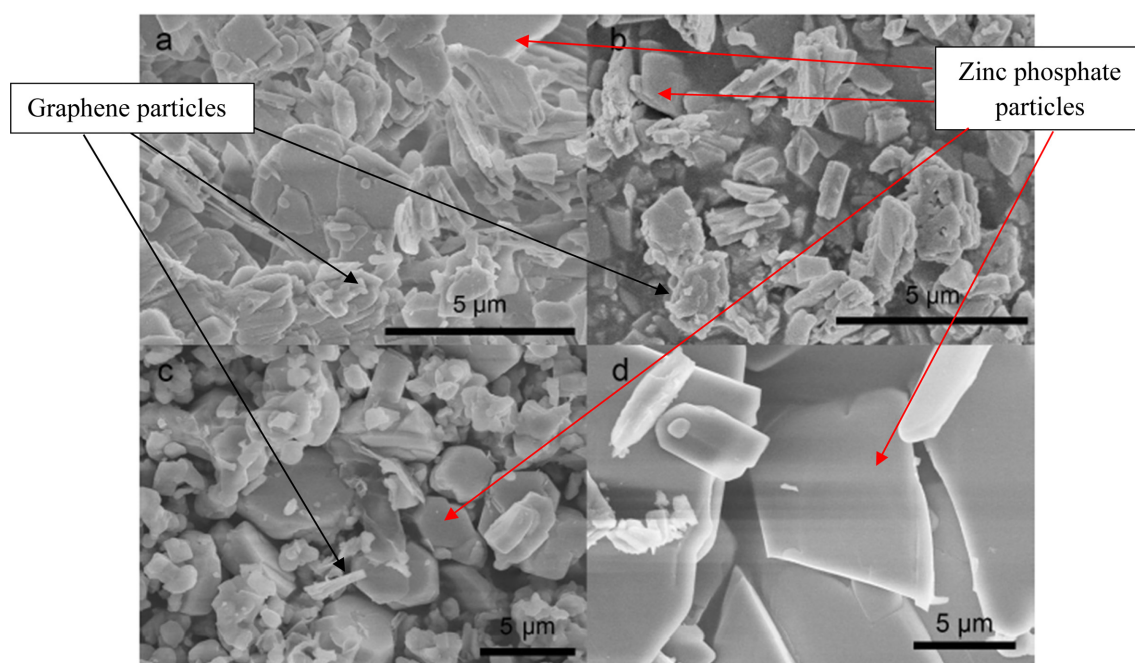


Fig. 7. SEM image representing deposition of graphene on zinc phosphate surface. (GO:ZP) a) 1:1, b) 3:1, c) 5:1, d) pure zinc phosphate [78]

further modified by adding a corrosion inhibitor as ferric nitrate. Well prepared coating is applied on carbon steel and evaluated for various performance properties using electron scanning microscopy (SEM), 3% NaCl solution. Author established the relation of noise and modules of impedance as the functions of chemically modified graphene and its concentration in coating [75]. Seungwoo Son et al. developed a unique process to deposit monolayer of zinc oxide on graphene particles. The graphene like structure of the zinc oxide monolayer is deposited by the spontaneous redox reaction. The ultra-thin layer of zinc metal is directly deposited on graphene oxide particles. This deposition involved spontaneous redox reaction. The deposited thin layer is a two dimensional hetero-structure of graphene oxide and zinc oxide. Oxygen required to carry out necessary oxidation of zinc metal and its deposition is supplied from graphene oxide [76]. M. Rajabi et al. prepared several coating compositions by varying the concentration of graphene in epoxy resin medium. The prepared coatings were evaluated with the help of electrochemical analysis. These analysis reveals that best corrosion resistance can be obtained by graphene concentration of 0.25% [77]. Youtong Wu et al. prepared zinc phosphate-graphene oxide hybrid compound to

increase the zinc phosphate system's corrosion resistance. This research mainly conducted to study effect of graphene oxide, its concentration in coating composition against the corrosion protection of metal. This hybrid material is prepared using a one-step ultrasonic precipitation method. The prepared material were evaluated for its performance using several instruments such as transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray diffraction (XRD), etc. [78]. The deposition of graphene oxide-zinc phosphate is ensured with SEM images as shown in Fig. 7.

Qingsong Zhu et al. developed a coating formulation using zinc phosphate and functionalized graphene (ZGP). Graphene used here was modified with polypyrrole (PPy). This research mainly conducted to modify the surface nature graphene thereby improving its dispersibility in resin medium. This modification is carried out in situ on the surface of graphene. On revealing the data of electron impedance spectroscopy, the author confirms the functionalized graphene performed very well against the corrosion and this happened due to much complex lattice formed in the path of corrosive media [79]. For modifying the properties of graphene against erosion and abrasion,

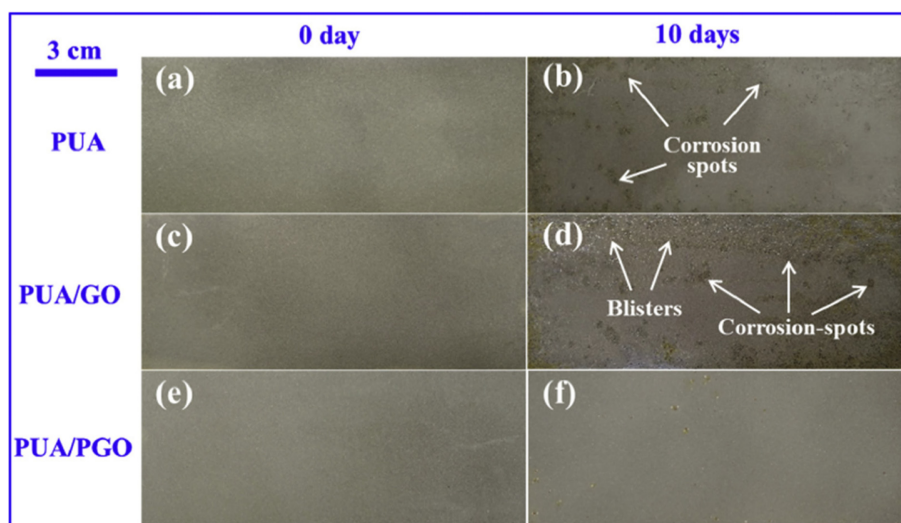


Fig. 8. Performance of coating against corrosion after 240 hrs. exposure to 3.5% NaCl solution spray test: a) and b) pure polyurethane acrylate, c) and d) polyurethane acrylate-graphene oxide coating, e) and f) polyurethane acrylate-functionalized graphene oxide [82]

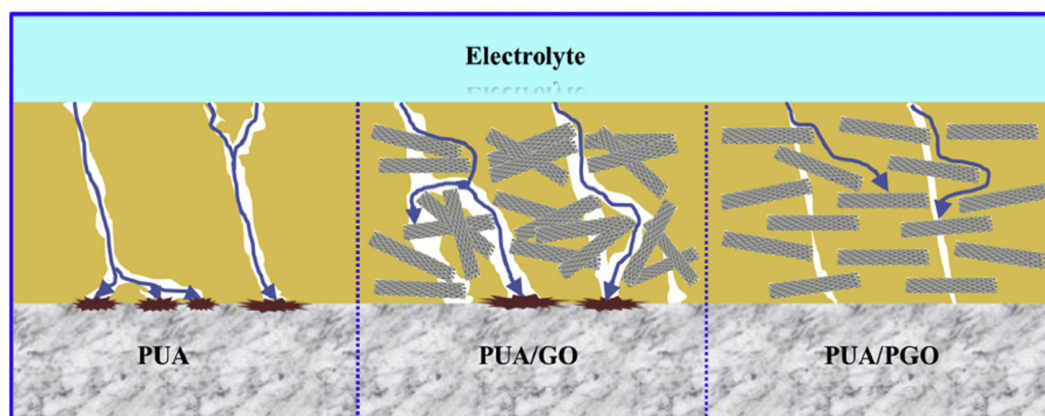


Fig. 9. Representation of Graphene based barrier mechanism of coating [82]

the author have developed a coating comprises reduced graphene oxide and di-atomaceous earth modified with poly-dimethyl-siloxane. Super-hydrophobicity of the coating is further improved by addition of nano TiO_2 particles in coating composition [80]. A water based coating is prepared by M. Ajay Krishnan, et al. for copper surface. This research carried out by exfoliation of micro-graphite and graphene nanoparticles. Graphene synthesis herewith further modified with 3-amino propyl-triethoxy-silane to insure the formation of covalent bonding with copper surface. Corrosion resistance of coating is tested using 3.5% solution of NaCl salt. Author also reveals that use of 4% graphene (wt. basis) reduces the corrosion current by almost 20% which results in dramatic

protection of copper metal from the corrosion [81].

Yanjun Ma and his co researchers were inspired by the outstanding performance of the graphene coating and developed the coating based on functionalized graphene and PU acrylate. Prepared coating film is cured by using UV rays. This modification of graphene improved dispersibility of graphene in resin medium. Graphene nano-particles present in coating forms more dense structure of coating on curing, thus, porosity of the coating is reduced to great level. Formed dense structure of coating, improves the barrier properties of coating and enhance anti-corrosive properties of coating. Fig. 8 represents performance coating against the corrosion. Fig. 9 indicates barrier mechanism established by two dimensional graphene

based coatings [82]. The diffusion path for corrosive media get increased. This results in creating resistance to reach the corrosive media to reach up to the metal surface and thus, protect the metal from corrosion.

Long-Cheng Tang and his co-researcher prepared a dispersion using graphene nano-particles. This research is carried out to study the effect of dispersion of graphene on the mechanical properties of coating. Dispersion of graphene nano-particles in epoxy resin medium is carried out in a ball mill. Applied shear stress is controlled by using balls of different diameters like 3, 6, 11 mm. After

conducting several experiments and analysis of the prepared sample, the author observed that coating with high strength and high toughness is obtained with highly dispersed graphene-epoxy composite [83]. Graphene were functionalized using 3-aminopropyl triethoxysilane (APTS). This hybrid of graphene with APTS greatly improved the dispersibility of graphene in the resin medium. Silane modification also facilitates better interfacial interactions in resin medium and graphene nano-particles. The reaction mechanism of graphene modification with APTS is best explained in Fig. 10.

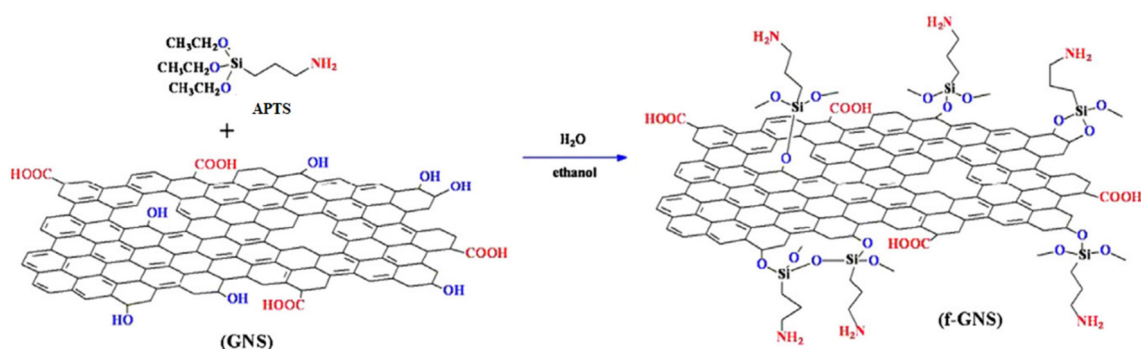


Fig. 10. Modification of Graphene with APTS [84]

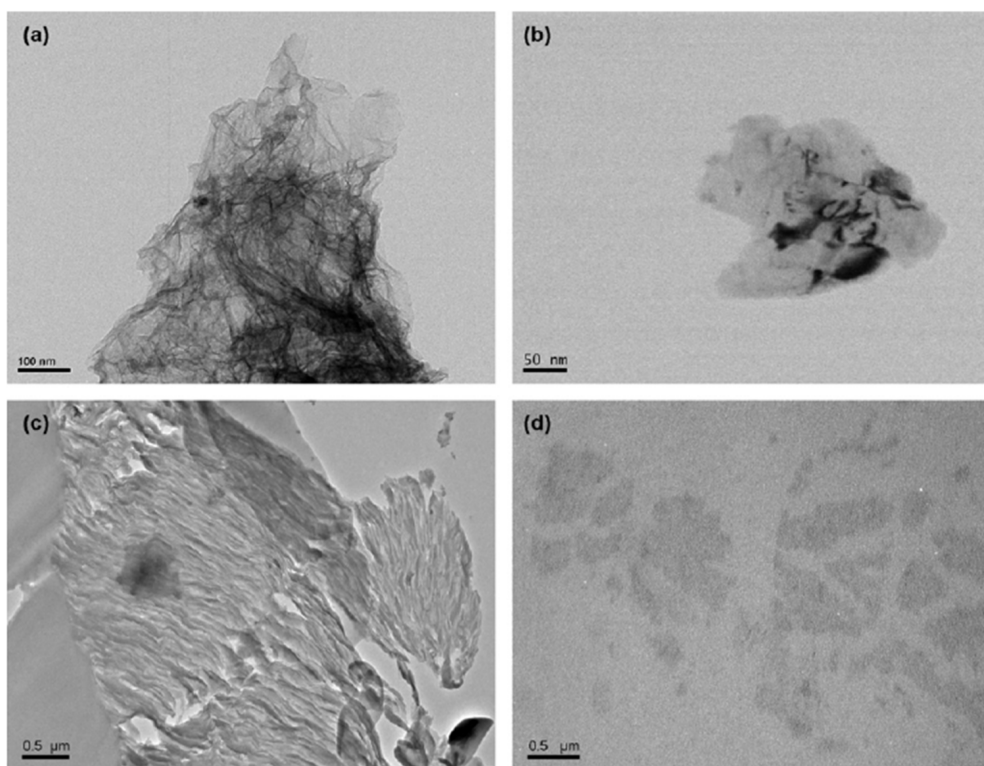


Fig. 11. TEM images for a) Pure graphene nano sheets b) Functionalized graphene particles, c) Pure graphene with epoxy resin d) Functionalized graphene with epoxy resin [84]

The improvement of graphene dispersibility with modification can be observed through the images of Transmission electron spectroscopy as shown in Fig. 11. Images of transmission electron microscopy indicate that functionalized graphene is more dispersible. Fig. 11a indicates that dispersion of graphene particles is obstacles due to thin layer structure. Fig. 11b represents nano-platelet shape of graphene. Fig. 11c shows dispersed nano sheet of untreated graphene in epoxy resin media in aggregate form. Fig. 11d clearly indicates better dispersion of treated graphene in epoxy resin media. As a result of breaking aggregate and agglomerate it gives a more homogenous matrix with polymer solution.

L. Cao et al. reacted epoxy resin with renewable material like gallic acid. This bio-based modified resin medium is capable to get absorbed on graphene surface. Result also reveals that this modification also improved the properties like excellent thermal conductivity, electrical conductivity, mechanical properties etc. [85]. To get the best performance of graphene based coating, it is mandatory to get graphene nanoparticles dispersed properly in resin solution. Sepideh Pourhashem et al. [86] developed a solvent based coating using epoxy resin. Results of experiments reveals that barrier properties of graphene particles are improved to great extent and coating performance against the corrosion also amended to great level. Dispersibility of graphene particles were improved by modifying it with poly-etheramine. Author reveals that modification of graphene with poly-etheramine improves the wettability of graphene nano particles in resin medium. This happened due to increase in interfacial interaction between epoxy resin solution and graphene nano particles [87]. The Modification of graphene with 3-amino-propyl tri-ethoxy-silane and 3-glycidyloxy-propyl tri-methoxy-silane also attempted to improve its dispersibility. Author also found the surface modification of graphene with silane compounds, improved the adhesion of epoxy base coating. This modification also improved the contact angle of coating which significantly helped to accelerate corrosion resistance of prepared coating [88]. Saurav Ramesh Nayak et al. modified graphene surface by reacting it with 4-nitroaniline. The coating was prepared using these functionalized nano graphene particles and epoxy resin as binder for coating. Corrosion resistance of the coating composition is checked on MS panels.

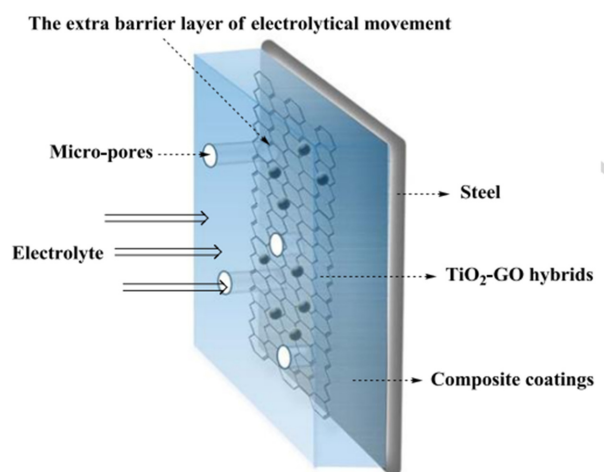


Fig. 12. Mechanism of metal protection of GO-TiO₂ hybrid coating [90]

Electrochemical impedance spectroscopy (EIS) and potentiodynamic studies are used to determine the corrosion resistance of coating. Experiment outcomes reveals that modification of result successfully upgraded the corrosion resistant properties of prepared coating matrix [89].

Zongxue Yu et al. identified the problem of film porosity as result of solvent evaporation from the coated film during its drying stage. Generated porosity in the film will result in degradation of barrier properties to great extent. To overcome the problem of film porosity, the author developed a coating based on functionalized graphene and epoxy resin. Graphene was functionalized using (3-aminopropyl)trimethoxysilane. The author designed a schematic representation of barrier mechanism for corrosion protection as shown in Fig. 12.

A new approach in scope of metal protection by coating was established by Kamalon Rajitha et al. Author and his co-worker developed graphene particles by modifying it by 8-bromo-triazolo pyridin-2-amine. The protective coating is made by mixing functionalized graphene and polycaprolactone as polymer. The prepared coating shows superior properties of anti-corrosion as result of better dispersibility and better exfoliation of graphene particles in polycaprolactone polymer matrix [91]. To improve the dispersibility of graphene nanoparticles Xingnan Zhou *et al.* has modified graphene particles with natural amino acid with double amines (Lysine) in water. Reaction scheme of graphene modification is represented in Fig. 13;

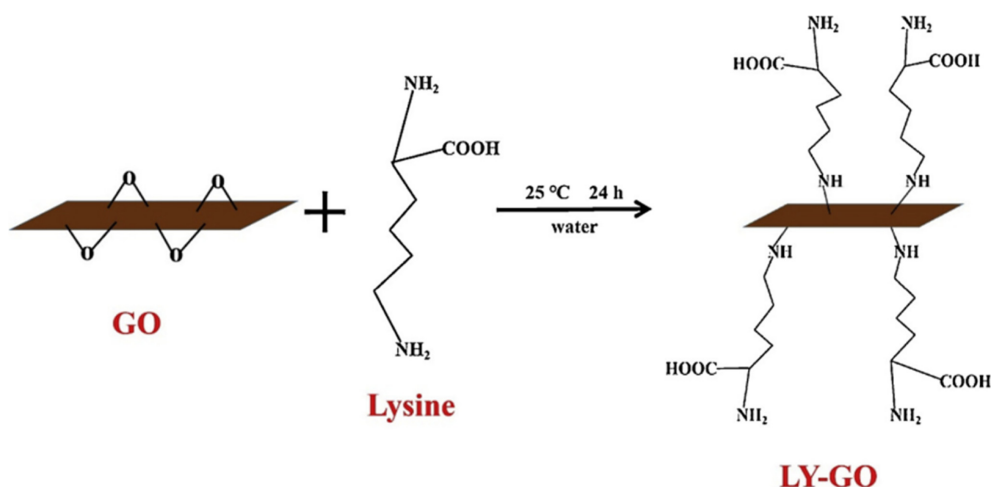


Fig. 13. Reaction of graphene oxide and lysine [68]

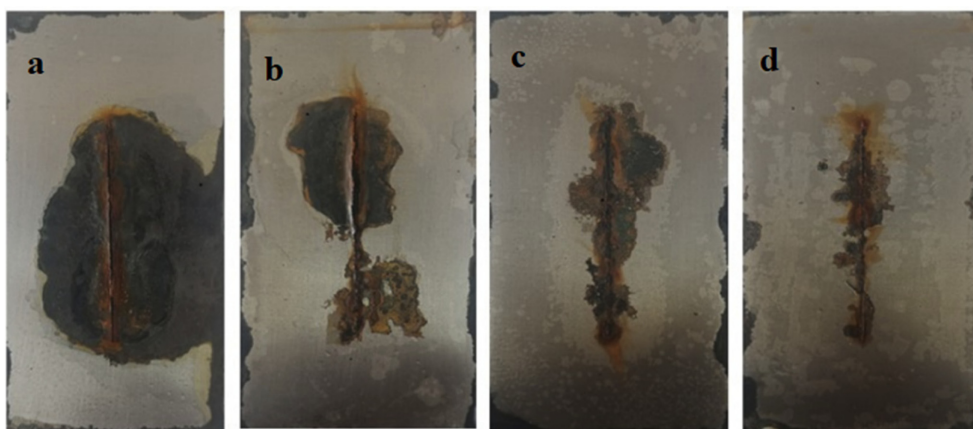


Fig. 14. Salt spray panels [68]; a) 0.0% lysine, b) 0.1% lysine, c) 0.2% lysine, d) 0.3% lysine [68]

The experimental samples were prepared by adding lysine modified graphene (LY-GO) in to water based epoxy resin. The concentration of LY-GO in final coating composition varying from 0.0% to 0.35 by weight. The corrosion performance of lysine modified graphene particles is also evaluated using a 3.5% NaCl salt spray test. After exposure to 500 hrs to salt spray solution the performance of the coating against corrosion are revealed from the Fig. 14.

The effect of graphene and its concentration is examined by Patricia Azuka Okafor et al. Several coating compositions were prepared by varying concentration of graphene nano-particles. Homogenous coating is made using hybrid polymer as epoxy-ester-siloxane-urea. Author established a correlation between polarization resistance and mechanical behaviour of coatings [92].

Unique study was made by G. Christopher et al. For the first time, the author and his co-worker compared the performance of the carbon black and graphene oxide for its performance against the corrosion. The prepared coating comprises water borne polyvinyl alcohol modified polyurethane resin, carbon black/ZnO (CB/ZnO) and modified GO/zinc oxide (GO/ZnO). The surface tension of the coating is measured with the help of angle of contact. From the results of the experiments it observed that the amount of nano filler in the coating has direct effect with angle of contact as reflected in Table No.2 [93].

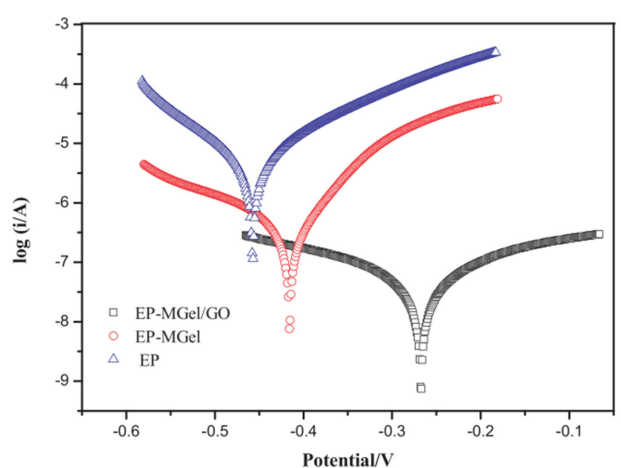
Thermal properties and mechanical properties of graphene nanoparticles and epoxy matrix were studied by S. Chatterjee and his co-workers. During the research graphene was modified by reacting with suitable amine compounds. Experimental results reveal that amine

Table 2. Behaviour angle of contact against the concentration of graphene [93]

Sample Name	Contact Angle
Water borne polyurethane on MS panel	65.78°
Water borne polyurethane + 0.1% PVA/GnO/ZnO	65.78°
Water borne polyurethane + 0.2% PVA/GnO/ZnO	66.47°
Water borne polyurethane + 0.3% PVA/GnO/ZnO	67.97°
Water borne polyurethane + 0.1% PVA/CB/ZnO	65.12°
Water borne polyurethane + 0.2% PVA/CB/ZnO	66.34°
Water borne polyurethane + 0.3% PVA/CB/ZnO	66.75°

modification considerably improve affinity of graphene nanoparticles with the epoxy resin medium [94]. A protective coating was synthesised by Saurav Ramesh Nayak *et al.* using epoxy resin and functionalized graphene. Graphene was modified with 4- fluoro phenol. The experimental data shows that addition of 0.25% graphene has improved the corrosion resistance of coating to a great extent. Author has reported that there is an increase in corrosion resistance by 30.46% by addition of 0.25 % functionalized graphene particles [95]. A bio based protective coating was developed by Kamalon Rajitha and co-researchers. This eco-friendly coating is based on gelatin-graphene oxide composite mixed with epoxy resin. Author initially modified gelatin with DETA (Diethylene triamine) to obtain modified geletin. The corrosion resistance of functionalised graphene were improved by reacting with geletin. Author reveals that modification of graphene with geletin improved he corrosion resistance of coating by 59% as compared to non-modified epoxy resin coating [66]. Tafel polarization curve for the prepared coating are shown in Fig. 16. The values of corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic and cathodic slops (b_a and b_c) are shown in Table 3. Fig. 15 represents the Tafel curve for pure epoxy resin modified gelatin-epoxy coating [66].

When coating establishes higher corrosion potential and

**Fig. 15. Tafel Curve pure epoxy resin modified gelatin-epoxy coating [66]**

lower corrosion current then it indicate the better corrosion resistance of coating [96]. Equation (6) is used to calculate the rate of corrosion of coating [66].

$$CR = \frac{87600 \times E_w \times i_{\text{corr}}}{n \cdot \rho \cdot F} (\text{mm/year}) \quad (6)$$

Where,

E_w : Molecular weight of iron/steel (55.85 gms/mol)

i_{corr} : Current density obtained from polarization curve

n : Chemical valency of iron.

F : Faraday constant.

P : Density of iron (7.85 gms/cm³),

Table 3. Polarization parameter for prepared coating composition after exposure to 24 hrs to 3.5% NaCl solution [66]

Sample	E_{corr} (V)	i_{corr} (A/cm ²)	b_c (V/dec)	b_a (V/dec)	CR (mil/year)	η (%)
Pure epoxy resin coating	-0.457	5.345×10^{-6}	11.408	7.875	2.432	40.96
Gelatin modified epoxy coating	-0.416	4.565×10^{-7}	5.015	12.495	0.208	94.90
Gelatin modified graphene oxide epoxy coating	-0.267	6.836×10^{-8}	4.446	5.094	0.031	99.2

Chunyan Wang *et al.* synthesised amino functional graphene by carrying poly-imidization of graphene oxide with p-phenylenediamine. Modification of graphene with p-phenylenediamine facilitates better interfacial interaction between graphene particles with resin medium. Reaction for this graphene modification can be best drawn as represented in Fig. 16. Amine modification of graphene

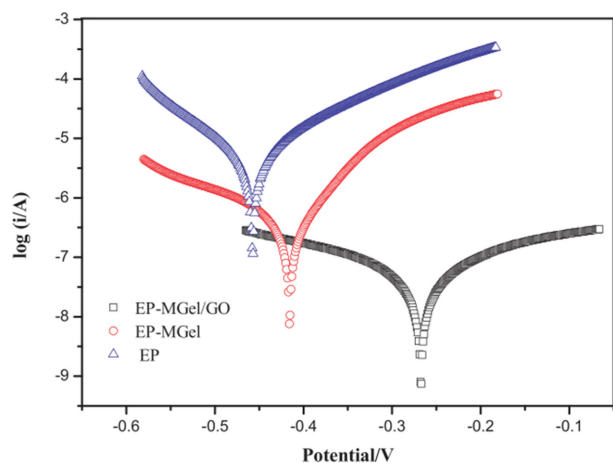


Fig. 16. Reaction of graphene oxide with p-phenylenediamine [97]

oxide particles also leads to improved contact angle and introduces hydrophobicity in the coating composition. Behaviour of contact angle over the different concentrations of graphene in coating is shown by Fig. 17. In Fig. 17a the contact angle is observed as 47° which indicates the presence of a hydrophilic amino group associated with the graphene oxide. But as the concentration of graphene in coating composition increases there is dramatic improvement in contact angle [97].

Water-based corrosion-resistant coatings based on graphene nanoparticles and water-based epoxy resin are being developed using a unique method. The curing agent for epoxy resin was changed using graphene oxide. The endcapping modification procedure is used to make a water base curing agent by reacting tri-ethylene tetra amine with alkyl glycidyl ether. To get a homogeneous coating mixture, graphene oxide was also added to the reaction mixture and evenly distributed for up to 8 hours. This innovative curing material for epoxy resin provides superior corrosion qualities than non-modified coating material [98]. Fig. 18 shows the chemical pathway between graphene oxide and tri-ethylene tetra amine.

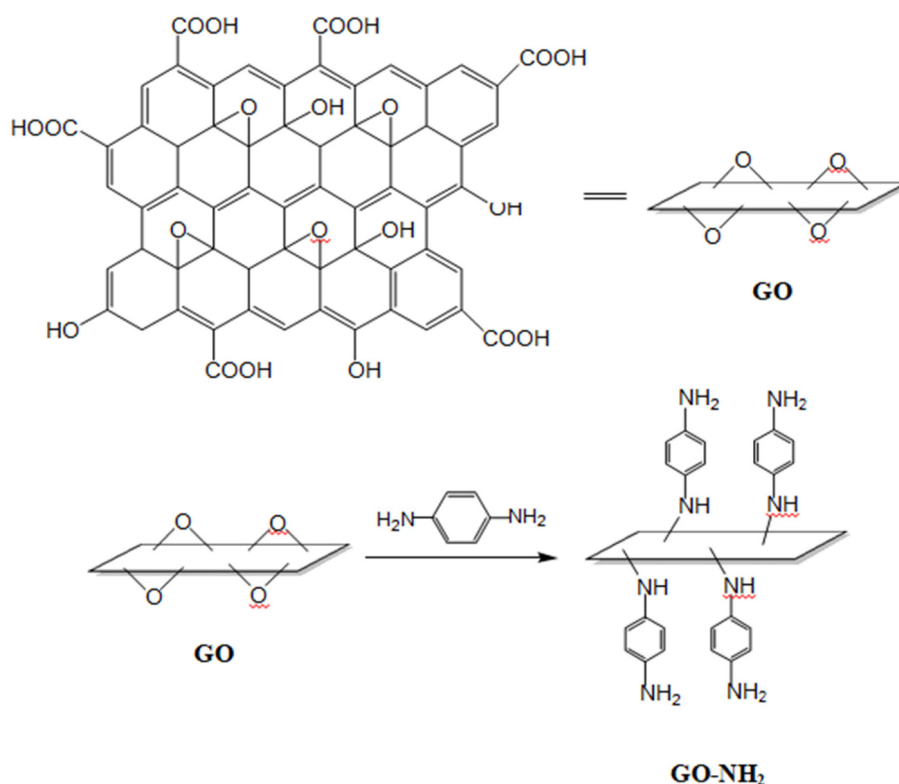


Fig. 17. Behaviour of angle of contact V/s concentration of graphene [97]

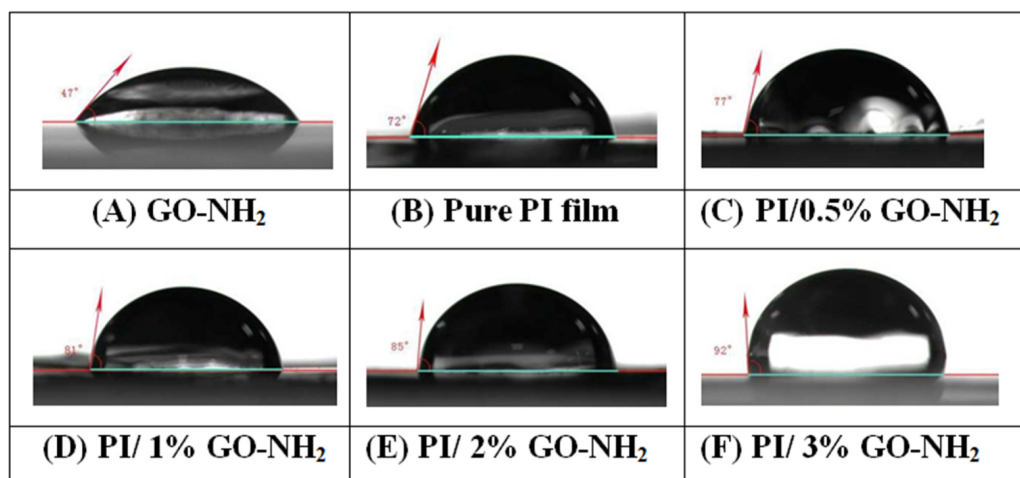


Fig. 18. Reaction of graphene oxide with waterborne curing agent [98]

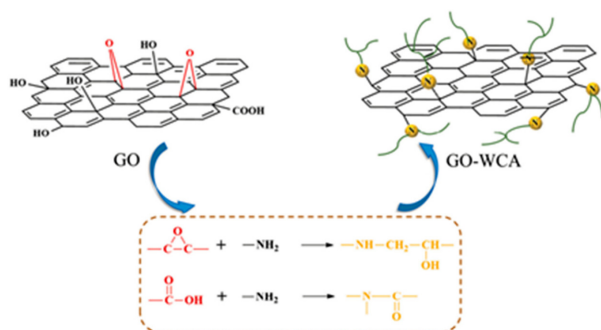


Fig. 19. X-ray diffraction (XRD) patterns of GO, PANI and GO/PANI nano-composites [99]

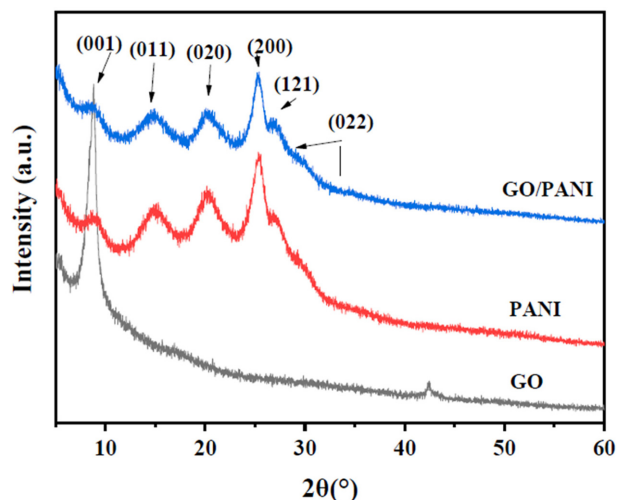


Fig. 20. Open Circuit potential for 3.5% NaCl salt solution [104]

7. Graphene-Polyaniline based coating a new approach for metal protection

One of the main areas for study is corrosion resistant coatings based on graphene and conductive polymers like poly-aniline (PANI) [99]. The XRD patterns of graphene oxide, poly-aniline, and modified graphene oxide-poly-aniline composites are shown in Fig. 19. The XRD pattern of GO indicated a strong and sharp peak at $2\theta = 8.8^\circ$, which can be seen at position (001). The presence of oxygen-containing groups and water absorption in the GO structure cause this inter-laminar distance [100]. PANI's molecular chain structure was not damaged, according to the XRD pattern. The graphene oxide nanoparticles were entirely disseminated in the mixture but totally reacted in the reaction mixture.

Modification of epoxy based corrosion resistance with poly-aniline and graphene oxide also help to improve the

hardness of coating [101]. Molecules of poly-aniline are homogeneously deposited on graphene particles, this happens due to two dimensional structure of graphene nano particles [102]. Addition of graphene nano particles also helps in increasing the conductivity of poly-aniline. This also helps in increasing the anticorrosion performance of graphene nano particle based [103].

Arian Mohammadzadeh et al. modified the graphene using montmorillonite (MMT). Sodium dodecyl benzene sulfonic acid was employed to modify graphene with montmorillonite. These nanoparticles are further modified by reacting with polyaniline as a conductive polymer. Open circuit test results reveal that nanocomposite prepared

Table 4. Electrochemical impedance parameters obtained by simulation of the EIS data [104]

Sample	$R_c (\Omega \text{ cm}^{-2})$	$R_t (\Omega \text{ cm}^{-2})$	$CPE_c (S^n \Omega^{-1} \text{ cm}^{-2})$	n	$CPE_{dl} (S^n \Omega^{-1} \text{ cm}^{-2})$	n	x^2
Comp 0.8	7.624×10^5	5.117×10^5	1.483×10^{-9}	0.9349	7.560×10^{-12}	0.6632	0.008
Comp 0.4	2.435×10^5	3.980×10^5	8.615×10^{-9}	0.9125	9.322×10^{-11}	0.5485	0.010
Comp 0.2	9.115×10^4	1.836×10^5	9.509×10^{-9}	0.8563	1.370×10^{-11}	0.7896	0.027
Pani-mmt-epoxy	8.038×10^3	7.368×10^4	5.8663×10^{-8}	0.7785	7.752×10^{-9}	0.4583	0.050
Rgo-pani-epoxy	5.141×10^3	6.001×10^4	3.481×10^{-8}	0.9652	7.012×10^{-8}	0.7125	0.019
Rgo-mmt-epoxy	2.914×10^3	1.850×10^4	6.052×10^{-6}	0.8531	9.171×10^{-8}	0.6542	0.009
Rgo-epoxy	1.139×10^3	9.302×10^5	7.931×10^{-5}	0.9421	5.012×10^{-7}	0.5198	0.028
Pani-epoxy	1.003×10^3	3.761×10^3	3.021×10^{-5}	0.5647	2.540×10^{-6}	0.6874	0.017
Mmt-epoxy	9.821×10^2	1.561×10^3	9.730×10^{-5}	0.7756	1.425×10^{-6}	0.5521	0.032
Pure epoxy	7.963×10^2	4.061×10^3	9.246×10^{-4}	0.9654	3.314×10^{-6}	0.7541	0.015
Bare steel	7.124×10^2	1.918×10^2	6.191×10^{-4}	0.8841	5.890×10^{-6}	0.6012	0.021

shows higher corrosion potential than other samples as shown in Fig. 20. In General, higher potential of coating represents the higher resistance to corrosion and vice versa. Table 4 represents EIS values of electrochemical impedance and it reveal that values of R_c and R_{ts} are significantly higher for synthesized nano-composites as compared to other samples [104]. This indicates the increase in corrosion resistance of the coating. The experimental samples were prepared by varying the composition of graphene, epoxy resins, PANI, reduced graphene, MMT etc. After making the coating samples, hardener was added to the coating composite just before the panel application.

8. Conclusion

Use of protective coatings is one of the most preferred way to protect the metal structures from corrosion. Enormous work is going on various new concepts and technology to develop novel coating raw materials, formulations, application methods etc. to obtain maximum corrosion resistance from applied coating. This new concept includes use of metal conversion coating, use of nano-particles in the coating formulation, use of conductive polymers in coating formulation etc. Graphene nano particles because of its outstanding properties mentioned here above found to be a one of the best choice for corrosion resistance coatings. Though improving the corrosion resistance of the coating is a key agenda for formulating

such coating, environmental aspect need to keep in mind while formulating coating formulation. Use of organic solvents in any coating formulation significantly contribute the VOC of the coating. As per the environmental safety aspect having high VOC of the coating is going to biggest challenge to coating formulator. Therefore, it is time to think about eco-friendly coating formulation for corrosion resistance application.

Use of graphene is opening a new field for coating formulator to take the advantage of its novel properties. To make the graphene useful in coating formulations, it is foremost important to address its dispersibility in various polymer materials. Graphene being single layer carbon sheet like morphology it improves the corrosion resistance to great extent.

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