



Inhibitors Incorporated Into Water-Based Epoxy Coatings on Metals for Corrosion Protection: A Review

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Abstract

Corrosion and its protection are one of the major challenges that are faced by the industries. To overcome this, new coatings with characteristic properties which are environmentally friendly are introduced. A cost-effective and most reliable way of corrosion protection is via barrier coatings, in which water-based epoxy coatings showed significant corrosion resistance. Although the epoxy coating creates a barrier between the metal and the corroding ions, there is a chance of leakage due to mechanical rupture and the formation of micropores during the curing time of the epoxy. This leads to the incorporation of inhibitors into the epoxy coatings which in turn increase the corrosion resistance. This review discusses the different types of inhibitors that are incorporated into the epoxy coating to prevent corrosion. The use of Nano/micro containers for the encapsulation of the inhibitors leads to the discovery of self-healing smart coatings. Such water-based epoxy smart coatings are also discussed.

Keywords Smart coatings · Polymer · Organic–inorganic particles · Environment friendly

1 Introduction

1.1 Metals and Corrosion

Metals have a wide range of applications in industries like refineries, electronic industries automobiles, etc. The metals are subjected to different pretreatment processes such as acid cleaning, acid descaling, and oil well acidizing which leads to corrosion [1]. Corrosion is the deterioration of metal when subjected to different corrosive environments. The disruption of the physical protective barrier of the metal leads to several chemical reactions which in turn cause a change in

the physical properties of the metal that leads to corrosion. Different types of corrosion occur in metals, which are uniform corrosion, crevice corrosion, intergranular corrosion, galvanic corrosion, stress corrosion, etc. [2]. The estimated cost of corrosion corresponds to 4.2% of the GDP of the US [3]. Since this process causes large economic losses, it is very important to prevent corrosion.

1.2 Mitigation of Corrosion

Scientists have employed different methods for corrosion protection such as cathodic protection, anodic protection, barrier protection using coatings, and use of corrosion inhibitors. Cathodic protection is the method of corrosion protection by the application of DC current on the metal thereby making it cathodic. There are two types of cathodic protection: galvanic protection and impressed current cathodic protection [3]. Although this type of protection gives optimum efficiency and safety, the cost-effectiveness and maintenance make it an unreliable method for corrosion protection.

Another potential method of corrosion prevention of metal is to make the metal anodic by the application of an anodic current. It involves the formation of a passive layer

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like oxides on the surface of the metal by increasing the metal potential. This oxide layer prevents the corrosive ions to penetrate the metal surface [4]. The major advantage is that it requires less current and can be applied to highly corrosive environments. Since the current applied for the anodic protection is equal to the corrosion rate of the metal, it gives a direct method for monitoring the corrosion rate [5]. The major disadvantage of anodic protection is that its lifespan is unknown, monitoring and designing are difficult.

When metals are subjected to aggressive environments to prevent corrosion, the use of inhibitors is considered as one of the acceptable practices. These inhibitors in small concentrations cause a significant decrease in the corrosion rate [6]. These inhibitors can be generally categorized into two (1) inhibitors that boost the oxide film which has a protective nature due to its oxidizing effect (2) inhibitors that get adsorbed on the metal surface forming a barrier layer for the aggressive ions [7]. Another most reliable and cost-effective methods for the mitigation of corrosion is barrier coatings. Barrier coatings are also modified using different inhibitors to exhibit self-healing mechanism. Such coatings are termed as smart coatings.

1.3 Barrier Coatings

Barrier coating provides a layer that prevents the passivation of corrosive ions to the metal surface [8]. Depending on the material, there are different types of coatings such as chromate conversion coatings, organic coatings, powder coatings, paints, etc. Earlier, chromate coatings were extensively used, but the government regulations regarding the environmental factors lead to the use of an alternative method of corrosion protection. Thus, came the importance of organic coatings. The organic coatings provide corrosion protection in two ways: (1) it acts as a physical barrier for the metal substrate (2) serves as a container for other compounds such as corrosion inhibitors. The organic coatings are classified based on the composition of resin in them. The common resins that are seen in the market are epoxy, acrylic, vinyl, alkyd, silicon, and urethane [9]. The properties of the coatings such as color, mechanical property, toughness, flexibility, opacity are controlled by the composition of these resins [10]. Epoxy coating shows characteristic properties such as high strength, low shrinkage, Excellent adhesion, Low toxicity, Low cost and excellent resistance to different chemicals and solvents [11]. But the disadvantage of using epoxy coating is that, during curing process of epoxy, large amount of toxic organic solvents are involved. In response to changing environmental regulations, there is a high demand for products with low

solvent concentrations or environment-friendly solvents. Thus, water-based epoxy coatings are introduced.

2 Water-Based Epoxy Coatings (WEP Coatings)

An epoxy coating consists of a curing agent as polyamide, which has a high molecular weight and is crosslinked with epoxy. To satisfy the viscosity element during the application, the demand for a high solvent level has to be satisfied. There is an increase in the viscosity observed when the solvent is evaporated and high viscosity leads to fast drying. Solvent-free or when water is used as the solvent, synthesis of resin is performed to achieve crosslinking with high viscosity [12]. The WEP coating technology consists of two types based on the physical property of the epoxy resin which is illustrated in Fig. 1.

In the first type, when the curing agent and the epoxy (either liquid or semiliquid) are mixed, emulsion particles

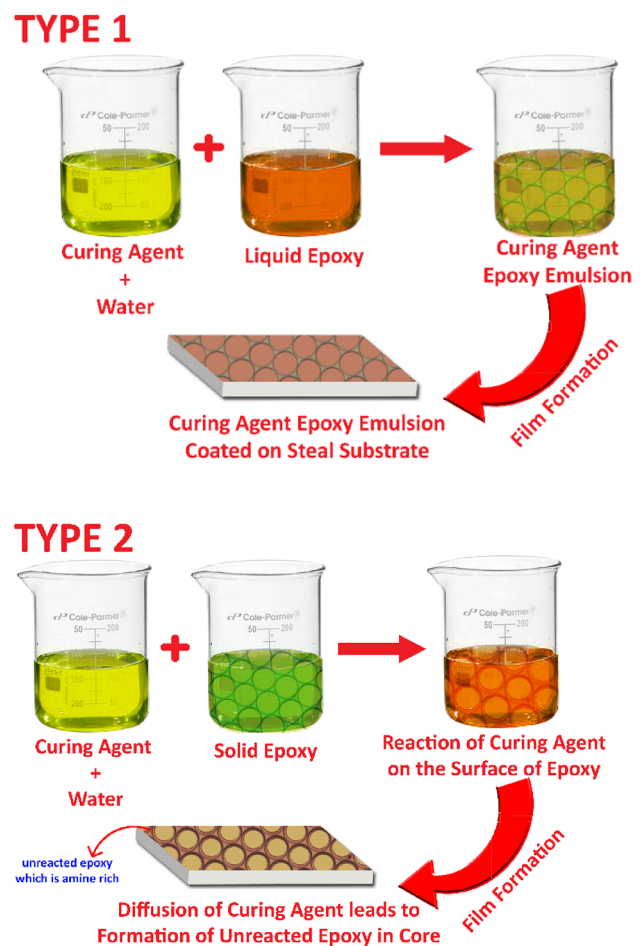


Fig. 1 Types of WEP coating based on the physical property of the epoxy resin

are formed. This typically leads to high strength, gloss, adhesion for the coating. The second type, the curing agent and epoxy does not emulsify the resin as a result the curing agent attacks the surface, which results in unreacted epoxy (amide rich) at the core. As the coating gets coalesce into the metal, the unpaired electrons on the amide group can be donated to vacant orbital of the metal which leads to good adhesion, corrosion protection, and longer life [12]. Although epoxy coating acts as a barrier between the metal and the environment, it is not a perfect barrier as water, ions can penetrate the metal surface during certain conditions such as mechanical rupture and chemical rupture. Thus, there is a need for the incorporation of other corrosion inhibiting particles into the WEP coatings [13]. Through these years scientists have modified the WEP by incorporating different particles such as polymers, nanoparticles, and graphene that are illustrated in Fig. 2.

2.1 Graphene Incorporated WEP Coatings

Graphene has a wide range of applications due to its unique characteristics such as chemical inertness, high electrical property, and good impermeability for corrosive medium [14]. This makes graphene a successful candidate for corrosion protection. It has a high surface area and strong van der Waals interaction which makes it unite with the metal matrix [15–17]. Different methods have been employed to produce graphene-based coatings such as physical vapor deposition, chemical vapor deposition, and electrodeposition, etc. [18–20]. A different liquid-phase exfoliation method is used by Cui et al. for the successful incorporation of graphene oxide modified polydopamine into the WEP coating and evaluated the corrosion resistance [21]. Phenosafranin was incorporated into graphene (PSF@G) which leads to high dispersion of graphene in water due to π - π interaction of the large aromatic system of PSF and graphene surface. The

coatings formed gave EIS results for the long term and the salt test confirmed that the durability and impedance are significantly improved which implies that the incorporation of graphene has slowed down the penetration of corrosive ions. He also studied the effect of the incorporation of graphene oxide-polydopamine into the epoxy coating. The polydopamine showed great compatibility and dispersion in the WEP coating. This coating with mechanical damage prevented corrosion in a better way than pure epoxy coating [19]. To study the effect of graphene with the different structures on the WEP coatings, two types of graphene powder Ga and Gb, graphene oxide and graphene slurry was used and from the EIS study, it was seen that Ga produces optimum corrosion protection characteristics for an immersion time of 32 days [22]. The coating exhibited higher integrity and proved that lower defects lead to higher barrier protection [23, 24]. There is evidence for the development of a small hydrophobic character and improved corrosion electrochemical behavior in aluminum when graphene is incorporated [25]. It's also proved that the presence of graphene does not alter the structural properties of the resin [26].

The effect of incorporation of lignin into graphene epoxy coating was studied by Xingnan Zhou et al. The result suggests that the corrosion resistance of lysine-GO-epoxy coatings is two-fold higher than GO epoxy coating. The remarkable improvement in the dispersion of lignin-GO-epoxy coating is demonstrated using SEM in Fig. 3 [28]. Zhou et al. have studied the effect of corrosion resistance of WEP coating by the addition of graphene oxide modified with phytic acid in mild steel substrate. Enhanced dispersion ability, anticorrosion activity, and less delamination were observed [29]. In another experiment performed by Wang et al. modified GO with zeolitic molecular sieves (ZSM-5) was introduced into WEP coating. It was found that the adhesion of the composite was significantly increased 42% when compared to the pure epoxy coating [30]. Functionalization of GO with polyetheramine and the corrosion along with weather resistance was explained by Li et al. The residual hardness of the composite at 0.5 wt% of polyetheramine/GO was three times higher than the pure epoxy. Enhanced weathering resistance was also observed [31]. Polyacrylated phosphorus monomer was used in the functionalization of graphene oxide. The vinyl group reacts with the thiol group to form the compound, which later was used for the modification of GO. High corrosion inhibition efficiency at a concentration of 0.5 wt% was achieved [32]. Lysine (LY) was modified using GO nanosheets and was filled into the epoxy coating. The LY-GO increased the cross-linking density of the WEP coatings due to the reaction between the amine group of the LY and the epoxy resin [27].

Zhong et al. modified graphene using tannic acid (TA) and self-assembled it with polyaniline enwrapped on Vanadium oxide (V_2O_5). The self-healing property observed in

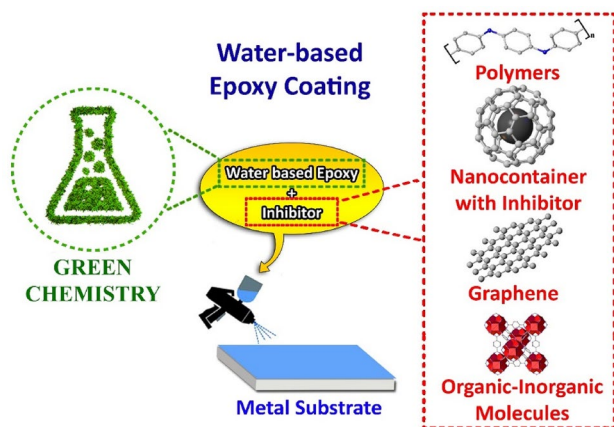
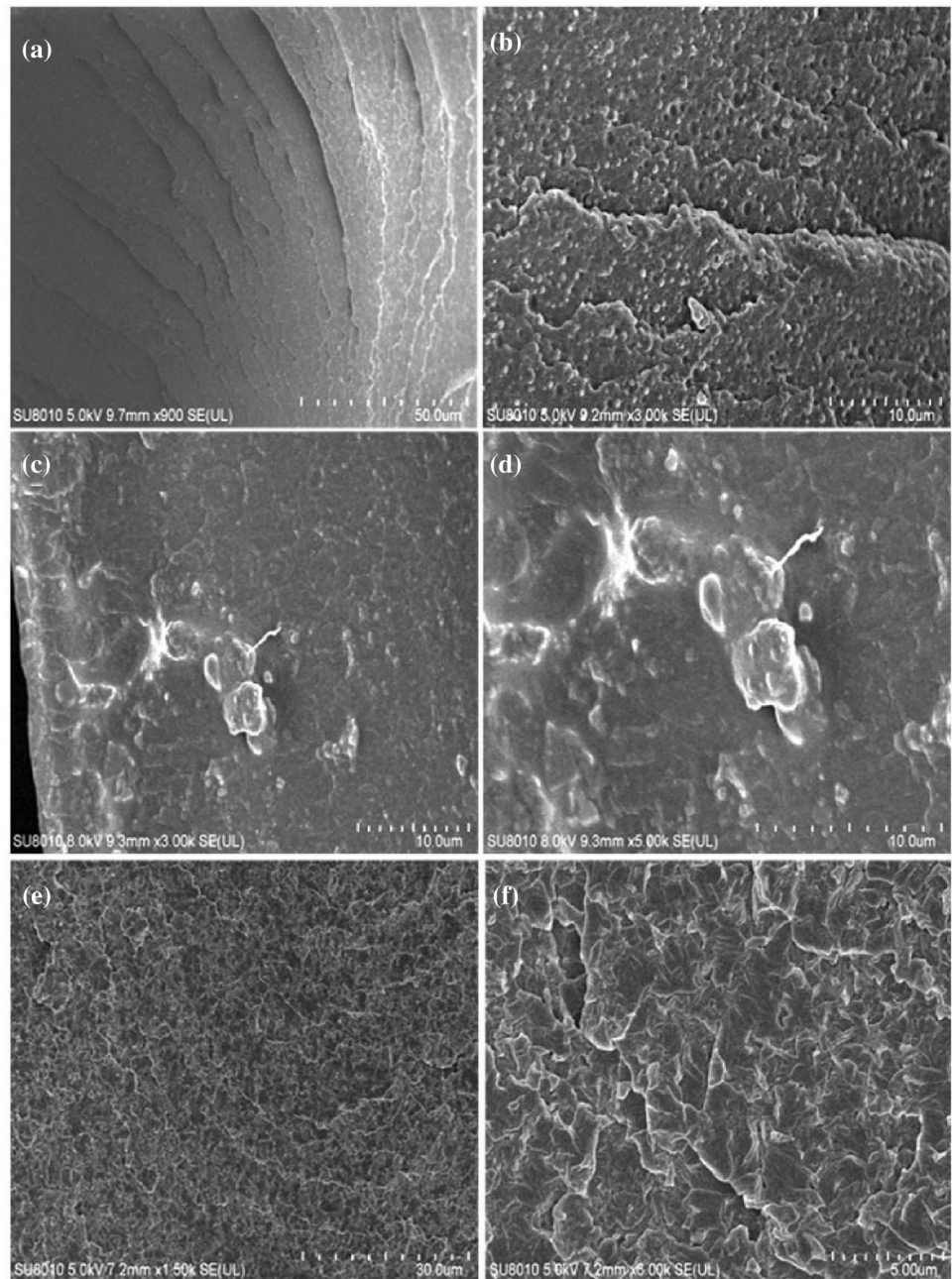


Fig. 2 Modification of WEP coating incorporating various particles

Fig. 3 The compatibility of lysine-GO with the epoxy is demonstrated through SEM images of **a** and **b** The pure epoxy shows a relatively smoother surface. **c** and **d** This shows the incorporation of 0.2 wt% Epoxy GO leads to some amount of agglomeration **e** and **f** shows 0.3 wt% lysine-epoxy-GO coatings which are well distributed. Reprinted with permission from Ref. [27]. Copyright 2019: Elsevier



the coating is due to the complex formation of TA-Fe-TA and also due to the oxide layer formed at the coating interface [33]. Amania et al. have synthesized graphene oxide decorated with nanoparticles of Fe_2O_3 and incorporated it into the WEP coatings. The synthesis was achieved using emulsion polymerization and the good dispersion without agglomeration of GO/ Fe_2O_3 was observed [34]. Enhancement in corrosion property was achieved by the addition of graphene along with halloysite nanotubes into WEP coatings was studied by Ye et al. Densification of the epoxy

occurs when the nanofillers are introduced, which prevents the micropore formation during the curing process of the epoxy that prevents the permeation of the corrosive ions [35]. Ye synthesised carbon dots was modified with graphene and used as a filler for WEP coatings. For these coating, a two-fold increase in the modulus of impedance was achieved after an immersion time of 50 days and a decrease in the water absorptivity when compared to pure epoxy [36]. The studies regarding the modification of graphene into the WEP coatings are illustrated in Table 1.

Table 1 Corrosion studies of modified graphene in water-based epoxy coatings

Modification of graphene	Amount of fillers added	Method of corrosion study	Metal	Medium	Coating characterization and tests	References
Phenosafrafinin/GO	100 mg/L	EIS Salt spray test	Q235 carbon steel	3.5 wt% NaCl	Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Scanning probe microscopy (SPM)	[21]
Polydopamine/GO	33 mg/L	EIS Scanning vibration electro-chemical technology (SVET)	Q235 carbon steel	3.5 wt% NaCl	TEM, Fourier transform infrared spectroscopy (FT-IR), UV-Vis spectroscopy (UV), x-ray photoelectron spectroscopy (XPS), SPM, Raman spectrum analysis	[19]
Graphene with and without carbon black, GO powder, Graphene slurry	0.5 wt%	EIS, SVET	Q235 carbon steel	3.5 wt% NaCl	XRD, SPM, FT-IR, FE-SEM, Raman spectrum analysis, Contact angle measurement	[22]
Lignin/GO	0.5 wt%	EIS	Q235 carbon steel	3.5 wt% NaCl	TEM, FT-IR, UV, XPS, Polarised light optical microscopy, Zeta potential analyser, Gel permeation chromatography for molecular weight determination, Raman spectrum analysis	[28]
Phytic acid/GO	0.26 wt%	EIS, Salt spray test	Mild Steel	3.5 wt% NaCl	FT-IR, XRD, SEM, Atomic force microscopy (AFM), UV, Raman spectrum	[29]
ZSM-5	0.2,0.5,0.7,1.2 wt%	EIS, Salt spray test	Q235 carbon steel	3.5 wt% NaCl	FT-IR, XRD, SEM	[30]
Polyethiramine/GO	0.1,0.2,0.5 wt%	EIS, Salt spray test	Carbon steel	3.5 wt% NaCl	FT-IR, XPS, XRD, TEM, Weathering test using UV aging chamber	[31]

Table 1 (continued)

Modification of graphene	Amount of fillers added	Method of corrosion study	Metal	Medium	Coating characterization and tests	References
Polyacrylate phosphorous/GO	0.5 wt%	EIS	Carbon steel	3.5 wt% NaCl	FT-IR, XRD, SEM-EDX, Raman spectrum	[32]
Lysine/GO	0.2 wt%	EIS, Salt spray test (SST)	Q235 carbon steel	3.5 wt% NaCl	FT-IR, XPS, XRD, SEM, Raman spectrum	[27]
Graphene/V ₂ O ₅ @polyaniline	0.7 wt%	EIS	N80 Carbon steel	3.5 wt% NaCl	FT-IR, XPS, XRD, TGA	[33]
GO/Fe ₂ O ₃ nanoparticle	0.5 wt%	EIS, PDP	carbon steel	3.5 wt% NaCl	FT-IR, SEM-EDAX, XRD, TGA	[34]
Graphene/Halloysite nanotube (GO/HNT)	HNT-0.5 wt% and GO-0.8 wt%	EIS, PDP, SST	Tin plate	3.5 wt% NaCl	FT-IR, TEM, XRD, SEM, Raman spectrum	[35]
Graphene/Carbon dots	0.5 wt%	EIS, SVET	Q235 carbon steel	3.5 wt% NaCl	FT-IR, XPS, XRD, SEM, TEM, UV Raman spectrum, Laser scanning confocal microscope (LSCM)	[36]

2.2 Polymer Incorporated Water-Based Epoxy Coatings

The anti-corrosion property of conductive polymers such as polyaniline, polyethylamine, polyethylene, polythiophene, polypyrrole has received significant interest among researchers [37–40]. Due to high electrical conductivity, simplified synthesis procedure, and low cost, the conductive polymer-polyaniline is widely studied [41–44]. The reason behind the high corrosion resistance is the redox catalytic nature of the polyaniline. Different inorganic or inorganic particles can improve the toughness, strength and stiffness of the polymer. The improvement in mechanical properties of a polymer depends on the particle size, particle loading and the interface interaction between the particle and matrix.

Bagherzadeh et al. have successfully synthesized polyaniline epoxy composite coatings and determined their corrosion property by electrochemical impedance which showed a significant decrease in the corrosion rate. A uniform oxide layer was produced which results in the lesser dissolution of metal when the polyaniline was used in the nanoscale. The micrometer-scale polyaniline showed greater water adsorption which leads to higher corrosion resistance [45]. SEM and TEM images of these nano and micro-scale polyaniline epoxy coating are illustrated in Fig. 4. His group also synthesized nanoemeraldine salt polyaniline which showed more corrosion resistance than polyaniline at a concentration as small as 0.02 wt%. But adherence to this coating was found to be the same as that of the polyaniline [46]. Polyaniline in the form of nanotubes, nanoparticles, and nanofibers has a wide range of applications in manufacturing electrical sensors, supercapacitors, and battery electrodes [47–49]. The polyaniline was synthesized in the form of nanofiber by Qiu et al., and the corrosion resistance property was determined. The

resulting nanofiber exhibits excellent aqueous solubility, good conductivity, and reversible activity which increase the corrosion property of the coating [50].

It was found that the presence of a dense film of phosphating group, implies that it can act as a corrosion inhibitor [51, 52]. By using this characteristic of phosphate groups Chetan et al. have developed phosphorylated polyvinyl alcohol doped with polyaniline nanoparticles as a potential anticorrosion coating [53]. Furthermore, polyaniline doped with ethylene units containing phosphates was studied for their anti-corrosion property [54]. Phosphoric acid doped polyaniline nanoparticles were synthesized and incorporated into water-borne epoxy coatings. The increased inhibitive action of the coating was attributed to the catalytic property of polyaniline and doping anions inhibitory effect [55].

A mussel-inspired polyaspartamide derivative (DOPA) was incorporated into WEP coating by Yang et al. The corrosion protection of DOPA is due to the formation of a polymer-Fe complex which forms a thin film. Significant improvement in the barrier properties was observed when it is subjected to aerated conditions due to the conversion of DOPA into DOPA-quinone by oxygen molecule which in turn reacts with the Fe ions released on the metal surface [56]. Fabrication of mesoporous TiO₂ modified with polyethylenamine was executed by Wang et al. Reduction in the transport path of the corrosive medium on the metal surface was observed due to interaction between polyethylenamine and epoxy [57]. Different morphologies of polythiophene microspheres were synthesized and added into WEP coatings by Ai et al. Uniform dispersion of polythiophene in the epoxy coating was achieved due to the narrow distribution of the particle size and uniform size of the particles [58].

Mesoporous silica (MCM-41) with and without template was synthesized and the pores are filled with cetyl trimethylammonium bromide (CTAB) and Pluronic F-127 and were coated into polyaniline coated epoxy metal specimen.

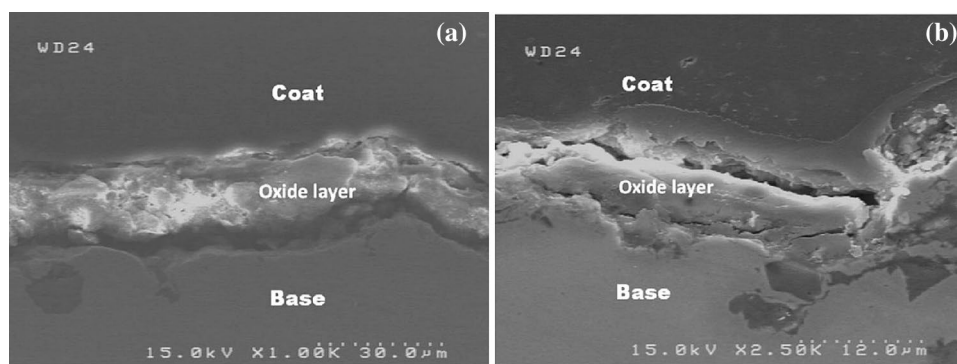


Fig. 4 SEM images of 1 **a** nanoparticle polyaniline 1 **b** microparticle polyaniline in the metal coatings. Better uniformity of the oxide layer is seen in nanoparticle polyaniline which proves that there is more uniform distribution than microparticle polyaniline. The parti-

cle is determined by TEM images 2 **a** nanoparticle polyaniline has a particle size of 50 nm and 2 **b** microparticle polyaniline has a particle size of 1–3 µm. Reprinted with permission from Ref. [45]. Copyright 2007; Elsevier

Polyaniline acts as a physical barrier for corrosion. Better curing rate and high electron density was obtained for coatings prepared through in-situ polymerization without template than with template [59]. Another modification of the polyaniline was performed using TiO₂ nanoparticles and was dispersed into the WEP coatings. The highest impedance for the prepared coating was observed after the immersion of

14 days [60]. Polyaniline/ Montmorillonite clay composite was introduced to WEP coatings. The increase in the barrier property was due to the good dispersion of silicone nanolayers of montmorillonite in polyaniline matrix [61]. V₂O₅ was modified using polyaniline and tannic acid and used as a filler for the WEP coatings. After 80 days of immersion time, the impedance modulus was found to be in the order

Table 2 Corrosion protection of Polymer incorporated water-based epoxy coating

Polymer incorporated	Amount of fillers added	Method of corrosion study	Metal	Medium	Coating characterization and tests	References
Nano/Micro polyaniline	Nano PANi-0.01 wt% Micro PANi-0.3 wt%	Salt spray test (SST)	Carbon steel	3.5 wt% NaCl	Dynamic light scattering (DLS), TEM, (SEM)	[45]
Nanoemeraldine salt-polyaniline	0.02 wt%	SST	Q235	3.5 wt% NaCl	Dynamic light scattering (DLS), TEM, SEM	[46]
Sulphonated polyaniline(PAni) nanofibre	0.5,1, 2 wt%	EIS	Q235	3.5 wt% NaCl	F-TIR, x-ray diffraction (XRD), SEM, TEM, UV, Raman spectrum analysis, x-ray photoelectron spectroscopy (XPS)	[50]
PAni/Partially phosphorylated (polyvinylalcohol) nanoparticle	1,2.5,4 wt%	EIS, SST	Mild steel	3.0 wt% NaCl	XPS, SEM	[53]
Polyaniline/Polyvinylpyrrolidone	1 wt%	EIS	Q235 carbon steel	3.5 wt% NaCl	FT-IR, XPS, XRD, SEM, Raman spectrum, UV, TEM	[55]
Polyaspartamide	5 wt%	EIS	Q235A carbon steel	3.5 wt% NaCl	FT-IR, SEM, Differential scanning calorimetry(DSC) Raman spectrum,	[56]
Polyethylenamine/ mesoporous TiO ₂	0.4 wt%	EIS, SST	Mild steel	3.5 wt% NaCl	FT-IR, TGA, SEM, N ₂ Adsorption desorption isotherm	[57]
Polythiophene microspheres	0.6 wt%	EIS	Q235 carbon steel	3.5 wt% NaCl	Dynamic light scattering (DLS), FT-IR, FE-SEM, FE-TEM, TGA	[58]
Polyaniline-mesoporous MCM-41	1.2 wt%	EIS, SST	Q235 carbon steel	3.5 wt% NaCl	FT-IR, XRD, Thermogravimetric analysis (TGA), SEM, N ₂ Adsorption desorption isotherm	[59]
Polyaniline-TiO ₂ nanoparticle	1 wt%	EIS, Scanning electrochemical microscopy (SECM)	Q235 carbon steel	0.5 M NaCl solution	FT-IR, XRD, Contact angle measurement and SEM,	[60]
Polyaniline-Montmorillonite	–	EIS,PDP	Mild steel	3.5 wt% NaCl	FT-IR, XRD	[61]
V ₂ O ₅ @Polyaniline-tannic acid	–	EIS, SST	P110 steel	3.5 wt% NaCl	FT-IR, XRD, TGA, SEM, TEM, XPS	[62]

$10^8 \Omega/\text{cm}^2$ [62]. The different polymers incorporated into water-borne epoxy coatings are illustrated in Table 2.

2.3 Organic–Inorganic Hybrid Particles that Are Incorporated Into the Water-Based Coating

In recent years, organic–inorganic hybrid molecules have been used in enhancing the anticorrosion activity of water-based epoxy coating [63]. One such molecule is the organo-functional silanes, which have a formula $(\text{ROH})_3\text{SiY}$, where ROH is the alkoxide group and Y is the organofunctional groups such as active amine groups. It has been found that epoxy-silica mixture provides enhanced adhesion and characteristic corrosion inhibition activity [64–67]. Bagherzadeh et al. have used 3-glycidoxypropyl trimethoxy silane to produce water-based epoxy coatings, which confirmed decreased level of pores, defects, and good distribution of particles in the epoxy coating [63]. Another organic–inorganic hybrid molecule is the use of metal–organic frameworks (MOF) as a potential anticorrosion water-based epoxy coating. MOF has characteristic properties such as high porosity, surface area, and is used for a wide range of applications such as gas sensing, catalysis, and drug delivery [68]–[71]. Na Wang et al. have produced a MOF-5 incorporated water-borne epoxy coating with dopamine covering. It was shown that with the incorporation of 0.5 wt% of MOF-5, corrosion resistance of $3.18 \times 10^8 \Omega/\text{cm}^2$ was obtained [72].

3 Smart Coating

Corrosion protection of metal generally involves the creation of a barrier layer between the aggressive environment and the metals, when an inhibitor is added to the coating formulation. Due to aging, leaching of these inhibitors can take place which reduces the efficiency of these inhibitors [73]–[77]. To prevent these scientists have started using nano or micro containers to load these corrosion inhibitors, which are compatible with the metal matrix. These came to be known as smart coatings [78–85]. The mechanism of action of the smart coating is illustrated in Fig. 5. The inhibitor encapsulated protective system delivers the inhibitors in a controlled manner, on exposure to different stimuli like pH change that is occurring due to UV irradiation, aggressive ions, and different redox activity [86]–[93]. This ensures the long-term performance of the coatings. Due to the change in pH, redox activity starts on the metal surface. This makes the pH-sensitive containers a promising system for encapsulation of corrosion inhibitors.

Snihirova et al. introduced a smart corrosion protective system consisting of CaCO_3 microbeads modified with several corrosion inhibitors like cerium ions, salicylal-doxime and 2,5-dimercapto-1,3,4-thiadiazolate (DMTD) impregnated into WEP coatings in AA204 coupons. CaCO_3 microbeads showed good dispersion and these loaded with cerium nitrate showed the highest resistance



Fig. 5 Mechanism of action of a smart coating

[94]. A new polyelectrolyte nanocapsule smart container was synthesized by Kope et al. by the mechanism of adsorption of polyelectrolyte on the oil phase emulsion droplet of the inhibitors 2-methylbenzothiazole (BT) and 2- mercaptobenzothiazole (MBT) [95]. Although the nanocapsules were found to have great compatibility with the WEP coatings, the need to optimize the capsule concentration is emphasized. The scheme of release of inhibitor on response to pH is given in Fig. 6.

Another polyelectrolyte nanocapsule modified TiO_2 hollow spheres were used as an inhibitor containing container synthesized by a layer-by-layer mechanism. For this nanocontainer, maximum release behavior was obtained in an alkaline medium [97]. TiO_2 nanocontainer was also used for the encapsulation of mercaptobenzimidazole and it was modified using a SiO_2 covering. From the experiments, it was found that the maximum amount of release is at pH 2 and TiO_2 is found to exhibit high dispersity inside the epoxy resin [98].

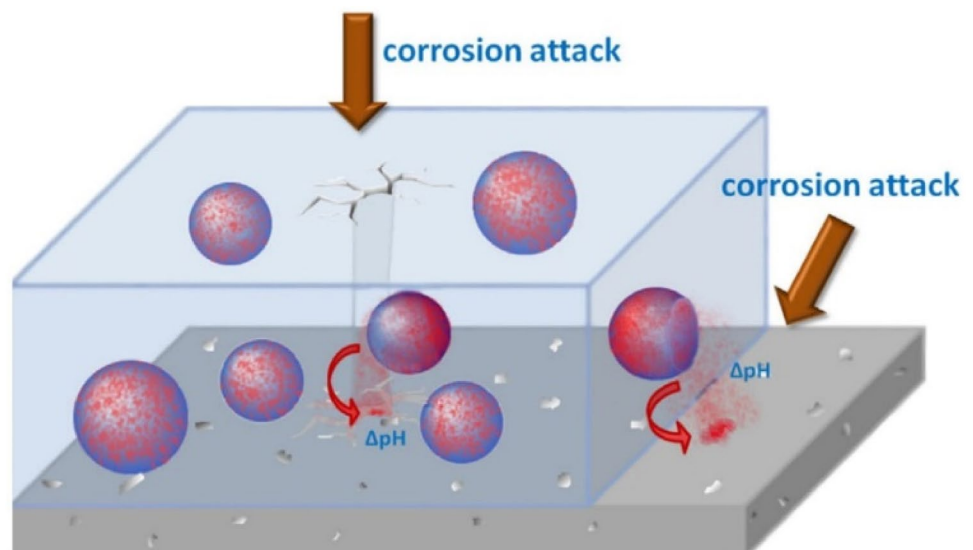
An ecofriendly smart coating was prepared using porous carbon nanosheets (PCNS) synthesized by exfoliating biomass from fallen leaves and by loading phytic acid onto the holes and amino-propyltriethoxysilane (APTES) into the surface of the PCNS. The APTES grafted to the surface is found out to be acting as a protective layer against corrosion and the phytic acid is found to be able to chelate the products of corrosion thus repairing the cracks [99]. A pH-sensitive polymer Eudragit particle was used as a reservoir to contain corrosion inhibitor 8-hydroxyquinoline as a filler for WEP coatings. During the impedance study, an evolution of a localized impedance was observed, this points out the effectiveness of the compound to prevent the local corrosion in the damaged regions [96]. The LEIS mapping of the coatings formed is give in Fig. 7.

CeO_2 hollowspheres is used as a carrier for inhibitor benzotriazole and self-healing action of it on WEP coatings were studied. In alkaline conditions, the release of inhibitor was found to be minimum. The charge transfer resistance (R_{ct}) value for the inhibitor-loaded coating was found to be $3.5 \times 10^5 \text{ Ohm cm}^2$ and epoxy coating to be $2.8 \times 10^5 \text{ Ohm cm}^2$. The increase in the R_{ct} value shows that a thin adsorptive layer of the inhibitor is formed that prevents corrosion [100]. Liu et al. synthesized mesoporous chitosan nanospheres encapsulated with sodium phytate and were added into WEP coatings. The rate of loading of sodium phytate was found to be 25.79 wt% and the fastest release was observed at a pH of 9 [101]. The slow-release of nanofiller Lecithin- SiO_2 - Etidroic acid introduced into WEP coating was analyzed by Wang et al. The synthesized nanofiller showed one order greater magnitude of impedance with the maximum inhibition efficiency of 80.7% [102]. Different corrosion inhibitors incorporated into various nanocontainers/microcontainers are illustrated in Table 3.

4 Summary and Future Prospectives

The development of modified water-based epoxy coating finds application due to the increase in the demand for environmentally friendly coatings in industries. The electrochemical impedance measurements showed that the addition of corrosion inhibiting particles such as polymers, nanoparticles, and others showed an increase in the corrosion inhibition efficiency. The development of smart coatings made way to the introduction of a better coating with double inhibition with other characteristics like self-healing. The advantages and disadvantages of the various additives in the WEP coatings are illustrated in Table 4.

Fig. 6 pH sensing response from the Eudragit particles loaded with 8- hydroxyquinoline. Reprinted with permission from Ref. [96]. Copyright 2014: Elsevier



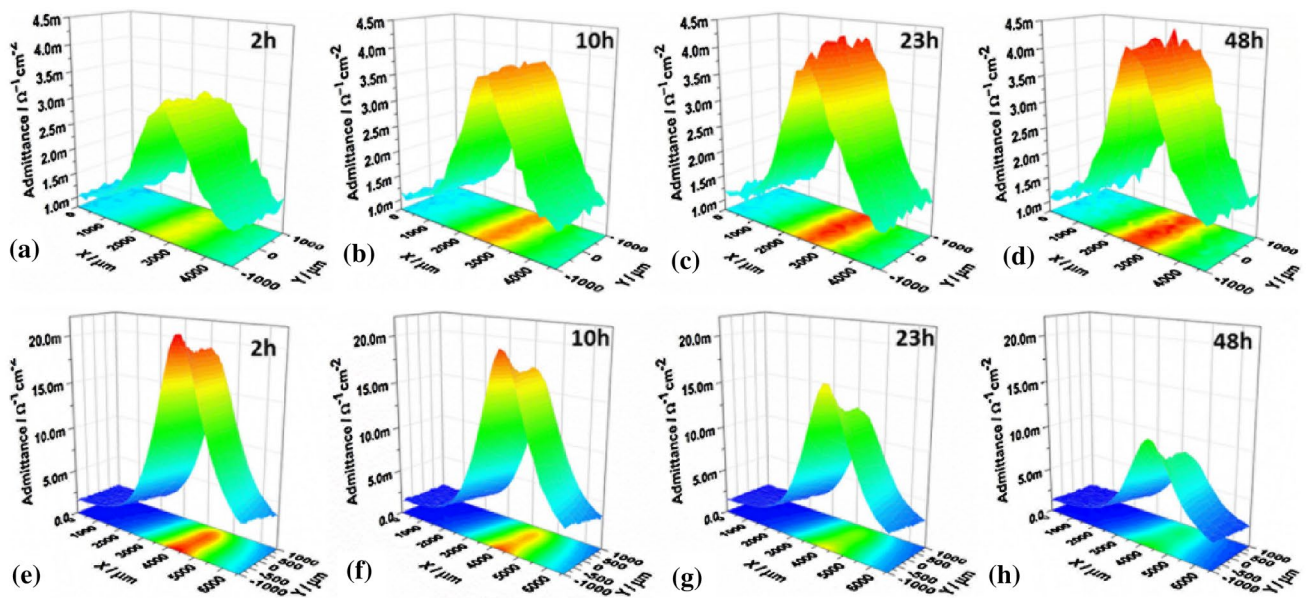


Fig. 7 LEIS mapping of **a** and **d** reference coatings and **e** and **h** coatings incorporated with Eudragit particles modified with 8 hydroxyquinoline. The increase in the admittance shows higher corrosion activity. The reference coating showed an increase in admittance

with immersion time but the particles incorporated coatings showed a decrease in admittance with immersion time which shows that the active area is getting healed by the inhibitor. Reprinted with permission from Ref. [96]. Copyright 2014; Elsevier

Table 3 Corrosion inhibition of different inhibitors incorporated in nano/micro containers

Nano/Microcontainer	Corrosion inhibitor	Amount of container with inhibitor	Method of corrosion studies	Metal	Medium	References
CaCO ₃ microbead	cerium nitrate, salicylaldehyde and 2,5-dimercapto-1,3,4thiadiazolate	5 wt%	EIS	AA204	3.5 wt% NaCl	[94]
Polyelectrolyte nanocapsule	2-methylbenzothiazole 2mercaptobenzothiazole	–	EIS,SST	AA2024T3	NaCl (0.05 mol dm ⁻³)	[95]
TiO ₂ nanocontainer	benzotriazole	1.5 wt%	EIS, scanning Kelvin probe (SKP)	Q235	0.5 M NaCl	[97]
TiO ₂ nanocontainer	2-mercaptobenzimidazole (MBI)	2 wt%	EIS and SKP	Q235	0.5 M NaCl	[98]
Carbon nanosheets	pyhtic acid and aminopropyltriethoxysilane	45 wt%	EIS	Q235	3.5 wt% NaCl	[99]
Eudragit Polymeric particles	8-hydroxyquinoline	10 wt%	EIS, Localized electrochemical impedance spectroscopy (LEIS)	AA2024	0.5 M NaCl	[96]
CeO ₂ hollow spheres	Benzotriazole	0.5 wt%	EIS and SKP	Q235	0.5 M NaCl	[100]
Chitosan microspheres	Sodium phytate	5 wt%	EIS and sea water immersion test	Copper	3.5 wt% NaCl	[101]
SiO ₂ / Lacithin	Etidroic acid (HEDP)	4 wt%	EIS, PDP, SST	Q235	3.5 wt% NaCl	[102]

The major challenge that is faced in this field is the concern regarding the solubility of certain inhibitors in water along with the attainment of superhydrophobic character. Functionalisation of graphene with suitable material is a good way to achieve superhydrophobic characteristics or the

WEP coatings. The use of computational techniques such as density functional theory (DFT) in the selection of the filler and their interaction of the metal are not much explored in the field of generation of WEP coatings. The next challenge is the cost-effectiveness of the inhibitors when used on a

Table 4 Advantages and disadvantages of various coating systems

Material system	Advantages	Disadvantages
Graphene incorporated WEP coatings	Higher integrity and lower defects High durability Enhanced weathering resistance and mechanical strength	Reduction of material flow when the resin is added to graphene, which may lead to agglomeration. This may result in the formation of non uniform coating
Polymer incorporated water-based epoxy coatings	High conductivity of the coatings Enhanced curing time and high electron density leads to greater adhesion for the coating	The processibility of the non substituted polymer material limits their practical application Less dispersion of polymers in WEP coating
Organic–inorganic hybrid particles incorporated into the water-based coating	Good dispersion of particles Less defects and Biocompatible	Large scale up faces various challenges Unfavourable reaction conditions such as high temperature and pressure during the production of the fillers
Smart coating	Double protection against corrosion The nanocontainers prevent the negative effect of corrosion inhibitor on the stability of the coating	Optimisation of the amount of nanocontainers is difficult In highly acidic conditions, the coatings are found to be lesser effective

large industrial scale. The use of statistical techniques such as design of experiment can be employed during the scale up of the coating preparation which will in turn reduce the number of steps involved in the optimization of the concentration of the fillers. The use of water soluble biopolymers is not explored to the maximum, and their effect on corrosion resistance and curing time can be studied. Cost effective green MOFs can be developed, which can act as an excellent candidate as a filler. Thus, there is a great scope in the modification of water-based coating with higher characteristics and corrosion resistance.

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Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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