Plastics in Corrosion Resistant Applications

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Key Terms

Corrosion: A natural process that converts a refined metal into a more chemically stable oxide or hydroxide by chemical or electrochemical reaction with the environment.
Corrosion resistant: The the ability to withstand deterioration of properties caused by chemical or electrochemical reactions.

Introduction

Corrosion has been the focus of researchers and industrialists due to its adverse effect in terms of economic importance, safety concerns, and environmental contamination. Corrosion is defined as an irreversible interfacial reaction between a material and its environment which results in consumption of the material or degradation in its properties (Czichos et al., 2011; Cwalina, 2014). The corrosion of metals can also be defined as the destructive chemical or electrochemical reaction of a metal with water, oxygen, sulfur, etc. found in the surrounding (Hiromoto, 2019). Metallic corrosion is inevitable as it is the thermodynamic stabilization process for a metal, reverting to its stable oxide or sulfide form. From the thermodynamic point of view, potential difference between anodes and cathodes is the driving forces in any electrochemical reaction (Czichos et al., 2011; Burt, 2015). The removal of either anode, cathode or the electron-conducting path is the basic concept of corrosion control. Corrosion of metal is commonly known as rusting.

Corrosion Mechanism

In the efforts to overcome metallic or non-metallic corrosion problems, the thorough knowledge about the interactions between the substrate and the material is crucial. In general, corrosion mechanism can be classified into electrochemical, chemical, and physical reactions. Electrochemical reaction is regarded to the metallic corrosion. Components that involved in this reaction are anode, cathode, electrolyte, and metallic path as shown in Fig. 1. This reaction corresponded to the electrolyte composition, the interfacial reactivity of the metal with respect with the service environment, the physical-chemical oxidation and reduction process occurs on the metal surface (Berradja, 2019). In general, metallic corrosion refers to oxidation process occurs at anode where metal atoms dissolve into the electrolyte as metal ions. This process involves metal with higher reactivity to release electrons. Electrons generated will be transferred to cathode and consumed for reduction reaction to occur, thus rust will be deposited at cathode site. The anodic and cathodic reactions occur simultaneously at equal rate to form an electrical circuit where electrons conduction occurs in the metal substrate and ionic conduction in electrolyte (Pehkonen and Yuan, 2018).

On the other hand, chemical corrosion of metallic material is the corrosion of metal under non-electrolytes or dry conditions (Pehkonen and Yuan, 2018). It is subject to the basic laws of chemical kinetics of heterogeneous reactions, without the generation of electric current. Physical corrosion of metallic material is based on the penetration of the liquid metal into the grain boundaries
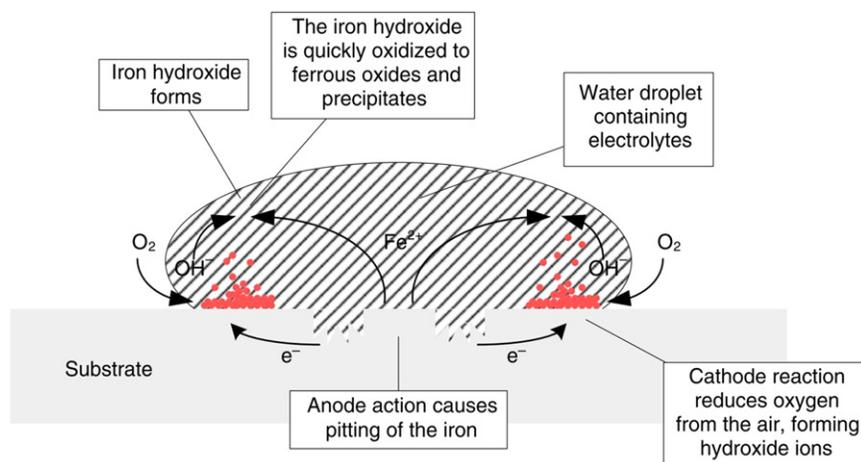
Fig. 1 Corrosion mechanism of iron-based material. Reprint with the permission from Sørensen, P.A., Kiil, S., Dam-Johansen, K., Weinell, C.E., 2009. Anticorrosive coatings: A review. Journal of Coatings Technology and Research 6, 135–176, Copyright (2020), Springer Nature.

of the solid metal (Pehkonen and Yuan, 2018). The plastic-coated metallic substrates will be experiencing corrosion when defections (pinholes, pores, scratches), delamination or blisters appeared on the coating surface (Ecco et al., 2014; Behzadnasab et al., 2017). This is attributed to delamination of the coating from the metallic surface and the diffusion of water through the coating layer, reaching the metallic interfacial. The polymer matrix structure of the organic coatings can be destroyed by the water absorbed, leading to swelling, stresses and cracks, which promote the diffusion of electrolyte.

Prevention by Anticorrosive Coating and its Mechanism

Compared to total elimination, corrosion control and prevention is often more practical and achievable. Application of anticorrosive coatings on metals is among the most effective way used to isolate metals from a corrosive environment. This is attributed to its simple operation and high efficiency. For this purpose, metallic (noble and sacrificial) and non-metallic (organic and inorganic) coatings have been developed. Noble metal that resist to corrosion is coated to protect the underlying metal, such as copper, palladium, silver, platinum, and gold. This method is adequate if provided the surface coating remains intact and have no holes or flaws. Base metal coating will provide both physical barrier and cathodic protection to the substrate. (Hammonds, 1989; Bayliss and Deacon, 2002).

Non-metallic protective coatings include enamels (glass coating), waxes, paints, and plastics. The primary function of enameling is to prevent acids or alkalies corrosion. Paint, waxes or greases and plastic coatings have barrier properties towards water, salt, and dirt. These can be classified into inorganic and organic coatings. Cement linings, glass coatings and linings, and other corrosion resistance ceramics are some of the examples of inorganic coating. Various organic coating formulations, such as epoxy and polyurethane, are available for different applications. Organic coatings isolate substrate from corrosive environment and block the ionic paths along the coating-substrate interface. Corrosion active pigments and inhibitors can be incorporated into organic coatings. Nanocoating and smart coating are much interest in the coating industry (Behera et al., 2020). Unlike bulk coating that form a protecting layer at the surface, nanocoating contribute an alteration at molecular level where nanoparticles bind themselves physically and chemically to the surface. Each material mentioned above can be applied as nanocoating. Smart coatings are coatings, which are responsive, adaptive, or active toward stimulus.

Coatings protect substrate through three fundamental mechanisms, which include barrier protection, sacrificial protection, and inhibition effect protection (Behera et al., 2020). Barrier protection is achieved by impeding the reaching out of aggressive elements (liquids, gases, and ions) to the surface of the substrate. A thicker barrier coating system acts as semipermeable membranes to provide better anticorrosion performance and better in avoiding delamination. In case of polymer coating, the permeability is dependent on the type and extent of crosslinking. The resin with higher crosslinking density has lower permeability and better adhesive bond onto the substrate surface (Sangaj and Malshe, 2004). The crosslinking restraint the segmental mobility in the resin and thus slow down the diffusion process.

Galvanic corrosion is the primary principle in the mechanism of sacrificial protection. A metal coating or a zinc-rich polymer coating with higher tendencies to be oxidized can provide sacrificial protection. The coating will behave as an anode and sacrifice itself to protect the substrate (cathode). This mechanism is effective only if there is intimate electrical contact between the substrate and coating, and it is shown as **Fig. 2** (Cubides and Castaneda, 2016).

Inhibition effect can be attained by adding inhibitor into the organic coating system. This mechanism relies on passivation of the substrate through building up of protective layer consisting of insoluble metallic complexes (Sørensen et al., 2009). Phosphates, chromates, nitrates, and borates are some commonly used cations in inorganic salts. When moisture pervades into the coating, the constituents of the pigments partly dissolve and move to the substrate surface. The dissolved ions will then react with the substrate to passivate its surface. The pigment content must be at optimum to ensure sufficient leaching from the coating and at the same time avoid blistering. The efficiency of the inhibitive pigments is very dependent on the barrier properties of the coating as the degree of permeability determine the solubility and mass transfer of pigments within the coating system.

Types of Plastics in Corrosion Resistant Applications

As compared to metals, plastics exhibit more resistance to water and most of the chemicals, which make them resist corrosion from the surrounding, thus become the potential materials in replacing the metal for corrosion resistant application (Abraham and
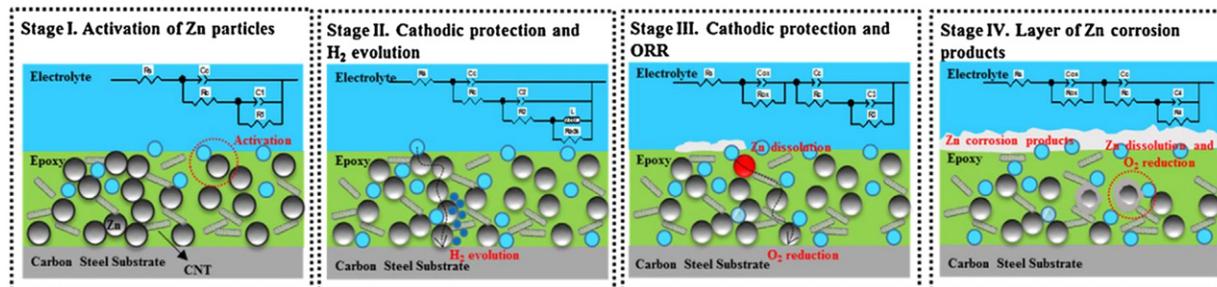
Fig. 2 Working mechanism. (from Stage I to IV) of a zinc-rich epoxy coating system. Reprint with the permission from Cubides, Y., Castaneda, H., 2016. Corrosion protection mechanisms of carbon nanotube and zinc-rich epoxy primers on carbon steel in simulated concrete pore solutions in the presence of chloride ions. Corrosion Science 109, 145–161, Copyright (2020), Elsevier.

Höfer, 2012). However, plastics never possesses mechanical strength and thermal stability similar as that of metals, thus making them more suitable to be the coating materials to protect metals from corrosion, instead of replacing the metals in an application. The barrier properties provided by the plastic coating is one of the main criteria to prevent or slow down the corrosion initiators such as water and oxygen molecules from contacting the metal surface (Deyab et al., 2018). Hence, plastics as the corrosion-resistant coatings will be focused on this section. Both thermosets and thermoplastics can be used as protective coatings for corrosion resistant applications Epoxy resin is the example of thermoset, whereas acrylic resin is the example of thermoplastic. Interestingly, alkyd resin and polyurethane (PU) can be either thermoset or thermoplastic, but their thermoset form is mainly used in the corrosion resistant application as the protective coating materials for metals.

Epoxy

Epoxy resins are the polymeric materials with the presence of more than one three-membered ring which known as epoxide and belong to thermosetting polymer. Epoxy resins included one with uncross-linked monomers containing epoxides, as well as the cured epoxy systems, where the cured or very high molecular weight epoxy resins contain less epoxides (Pham and Marks, 2005). Nowadays, there are many types of epoxy resins that commercialized, include aliphatic, cycloaliphatic, and aromatic backbones, in a broad range of molecular weights. For example, liquid epoxy resin (diglycidyl ether of bisphenol A, DGEBA), solid epoxy resin, bisphenol F epoxy, phenol epoxy novolac, etc. DGEBA as the first commercialized epoxy resin is relatively low cost and adequate-to-superior performance in many applications, thus it dominated the market and used by many researchers. The hydroxyl and epoxy groups of epoxy resins allow them to be cured with the suitable curing agents depend on the desired end properties, to achieve superior performance in adhesion, as well as resistance towards electrical, chemical and heat.

Epoxy resins used as protective coatings are dominant among all their applications because they exhibit many properties that excel in protecting the coated metals, particularly corrosion attack. Epoxy resins have excellent performance in terms of mechanical strength, toughness and dimensional stability with great resistance to most of the chemicals, especially towards alkalies, due to the presence of ether linkages (Pham and Marks, 2005; Gibson, 2017). Epoxy resins also are electrical-insulated, where their coatings on the metal surface able to prevent metal from corrosion via electrochemical reaction. Besides, epoxy resins possess satisfactory water resistance in protecting metals from rusting, as epoxy coatings on the metal surface only have water update of 0.9 wt% after immersed in water for 10 days and 65° of water contact angle (Chen et al., 2017; Monetta et al., 2017).

The force between the epoxy resins and the coated surface is greater than the intermolecular force within the polymer due to the presence of hydroxyl groups and epoxides, thus allows them to have excellent adhesiveness that suitable for coating application (Pourhashem et al., 2017a; Ammar et al., 2019). The adhesion strength of epoxy coatings on the mild carbon steel substrate is 8.5 MPa based on the pull-off adhesion test according to ASTM D4541 (Pourhashem et al., 2017b). Good thermal stability of epoxy resins also gives heat resistance property and thus able to protect the coated metal substrate even at elevated temperature. Degradation temperature of epoxy resins is 309°C based on thermogravimetric analysis (Kumar et al., 2017).

Several studies reported the performance of pure epoxy resins as corrosion-resistant coatings in the comparison with uncoated bare metals. Tafel polarization and electrochemical impedance spectroscopy (EIS) are some of the corrosion tests used, which the results are tabulated as **Tables 1** and **2**, respectively. The visual observations shown in **Fig. 3** also support epoxy resins as good protective coatings to prevent coated metals from corrosion.

Unfortunately, pure epoxy resins may have many pores produced during the curing process, which cause relatively poorer barrier properties as compared to the epoxy resins that filled with fillers or blended with other polymers for desired properties enhancement (Xu et al., 2019). The pores within epoxy coatings allows the corrosion initiators from surrounding able to penetrate to the underlying metal surface easily. This drawback will be obvious when a scratch is made on the epoxy-coated surface, where severe corrosion products, rust, and blisters will be observed as shown in **Fig. 3**. Besides, the water molecules that diffused into epoxy coatings and will be causing the deterioration of adhesion bonds between the epoxy coatings and metal surface in the presence of water films existed on the coated metal surface (Sari et al., 2017). This is because water molecules are strong hydrogen bonding agent, which they will be forming hydrogen bonds with the polar groups of epoxy coatings. Epoxy coatings also found to be low in abrasion resistance, thus give lower corrosion protection efficiency for the coated metals if constantly taking damage from surface abrasion and wear (Shi et al., 2009).

Therefore, since epoxy resins are extremely versatile, it is necessary to improve the properties and overcome the drawbacks by incorporating fillers or blending with other polymers, to achieve the desired properties for corrosion resistant application to protect the coated metals (Buchheit, 2018). Graphene, halloysite, carbon nanotubes (CNT), montmorillonite (MMT), and even green filler of cashew gum are some of the fillers that incorporated into the epoxy coatings for enhanced properties (Nematollahi et al., 2010; Kumar et al., 2017; Xu et al., 2019; Arukalam et al., 2020). The effect of fillers on the corrosion resistivity of epoxy coatings and how they improved the performance in protecting the coated metals from corrosion will be discussed at the next section.

Alkyd

Alkyd resins are oil-based polyester consist of dibasic acid, polyols, and fatty acid, which belong to thermosetting polymer. The fatty acid content and glycerol of alkyd resins can be derived from either animal or vegetable oils, which are biologically renewable (Salata et al., 2019). Thus, due to their renewable feedstock, alkyds are inexpensive and having a large market share. The commercialized

Table 1   Tafel polarization results of uncoated bare metals and epoxy-coated metals

No.	Parameters	Samples		References
		Uncoated bare metals	Epoxy-coated metals	
1	Corrosion potential, E_{corr} (mV)	-689	-536	(Kumar et al., 2017)
	Corrosion current, I_{corr} ($\mu A\ cm^{-2}$)	30.2	1.23	
	Corrosion protection efficiency (%)	–	95.9	
	Corrosion rate (mm year^{-1})	4.10×10^{-1}	1.69×10^{-2}	
2	Corrosion potential, E_{corr} (mV)	-1024	-575	(Liu et al., 2016)
	Corrosion current, I_{corr} ($\mu A\ cm^{-2}$)	21.3	8.09	
	Corrosion protection efficiency (%)	–	61.9	
	Corrosion rate (mm year^{-1})	5.66×10^{-10}	3.87×10^{-10}	
3	Corrosion current, I_{corr} ($\mu A\ cm^{-2}$)	0.994	0.501	(Rajabi et al., 2015)
	Polarization resistance, R_p (k Ohm cm^2)	0.4154	0.7565	
	Corrosion protection efficiency (%)	–	49.6	
	Corrosion rate (mm year^{-1})	1.17×10^{-2}	5.88×10^{-3}	
4	Corrosion potential, E_{corr} (mV)	-831	-655	(Nematollahi et al., 2010)
	Corrosion current, I_{corr} ($\mu A\ cm^{-2}$)	59.5	1.34	
	Polarization resistance, R_p (k Ohm cm^2)	7.45	264	
	Corrosion protection efficiency (%)	–	97.7	
	Corrosion rate (mm year^{-1})	6.83×10^{-1}	1.54×10^{-2}	

Table 2   EIS results of uncoated bare metals and epoxy-coated metals by Bode plot

No.	Parameters	Samples			References
		Uncoated bare metals	Epoxy-coated metals (Unscratched)	Epoxy-coated metals (Scratched)	
1	Corrosion resistance, $|Z|_{f=0.01\ Hz}$ (Ohm cm^2)	–	3.17×10^9	2.59×10^4	(Arukalam et al., 2020)
2	Corrosion resistance, log $|Z|_{f=log(-2)}$ (Ohm cm^2)	1.2	–	3.1	(Behzadnasab et al., 2017)
3	Corrosion resistance, log $|Z|_{f=log(-2)}$ (Ohm cm^2)	–	4.1	–	(Liu et al., 2016)
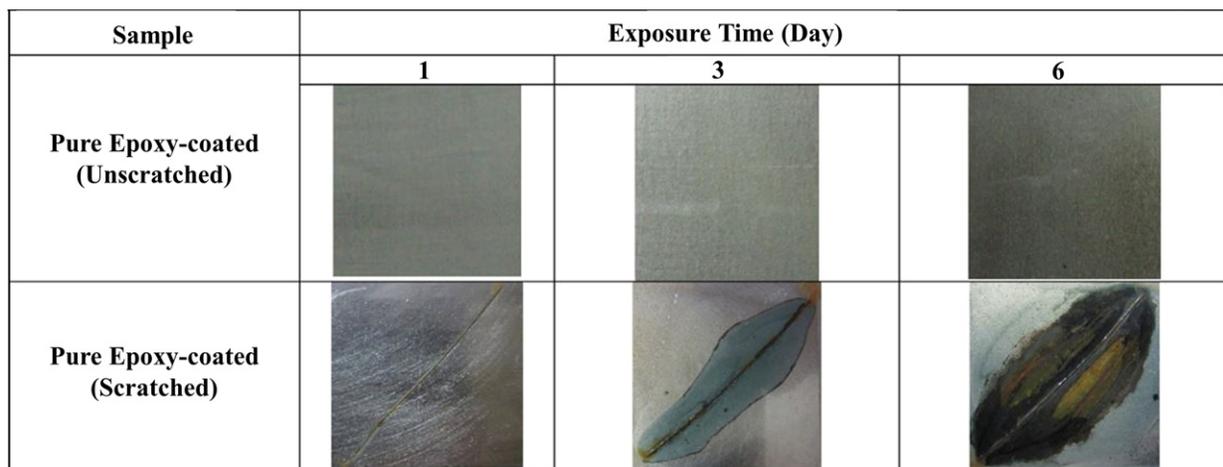
Fig. 3   Visual observation of unscratched and scratched epoxy-coated steel during 6 days exposure in salt spray chamber. Reprint with the permission from Behzadnasab, M., Mirabedini, S.M., Esfandeh, M., Farnood, R.R., 2017. Evaluation of corrosion performance of a self-healing epoxy-based coating containing linseed oil-filled microcapsules via electrochemical impedance spectroscopy. Progress in Organic Coatings 105, 212–224, Copyright (2020), Elsevier.

Table 3   Effect of degree of unsaturation on the properties of alkyds

No.	Degree of unsaturation	Hydroxyl value	Properties enhancement
1	Increase	–	Adhesiveness
2	Increase	–	Water resistance
3	Decrease	–	Resistance to yellowing
4	Decrease	–	Drying time
5	Increase	–	Tendency to skin and gel in the container
6	Increase	–	Pigment wetting
7	–	Increase	Adhesion and pigment wetting

Note: Elliott, W.T., 1993. Alkyd resins. Surface Coatings, third ed. Dordrecht: Springer. pp. 76–109. (Oil and Colour Chemists' Association).

Table 4   Tafel polarization results of alkyd-coated stainless-steel sheet in comparison with uncoated stainless-steel sheet

Samples	E_{corr} (mV)	I_{corr} ($\mu A\ cm^{-2}$)	R_p (k Ohm cm^2)	Corrosion rate (mm $year^{-1}$)
Uncoated low-carbon 316 stainless-steel sheet	– 0.470	9.20	4.00	0.840
Alkyd-coated low-carbon 316 stainless-steel sheet	-8.00×10^{-2}	2.26×10^{-2}	2.94×10^3	2.10×10^{-3}

Note: Kordzangeneh, S., Naghibi, S., Esmaeili, H., 2018. Coating of steel by alkyd resin reinforced with Al_2O_3 nanoparticles to improve corrosion resistance. Journal of Materials Engineering and Performance 27, 219–227.

alkyd resins can be classified to long, medium, and short oil resins. There are many types of alkyd resins depending on the choice and amount of components involved during the esterification process, such as high solid alkyds and alkyd emulsions that have replaced the conventional alkyd resins nowadays (Hofland, 2012). It is interesting that the properties of alkyds can be tailored based on the type of oil used, oil length, and the extent of derived side group (Buchheit, 2018). The long oil alkyds generally used as the primer coatings on metals for anticorrosion purpose, while short oil alkyds give better gloss and hardness. Besides, the properties of alkyds also can be influenced by the degree of unsaturation of fatty acids and hydroxyl value, as tabulated in **Table 3**. For example, when pentaerythritol used as the polyols, the alkyds produced will be fast drying with greater hardness, better gloss and water resistance, as compared to other alkyds that based on glycerol of same fatty acid content (Sharmin *et al.*, 2016).

Instead of the bio-renewability and versatility of alkyd resins that make them being used widely as paints and coatings to protect the metals from corrosion, they possess good adhesiveness towards the metal surfaces with adhesion strength of 3.2 MPa (Deyab, 2015). Alkyds also have good thermal stability as the degradation started at 164°C, showing that alkyd coatings able to withstand heat and high temperature from the exposure under the sun while coated on the metal surface (Li *et al.*, 2015). Moreover, alkyds exhibit satisfactory water resistance as corrosion-resistant coatings with water permeability of 1.56 g m^{-2} per day and contact angle of 92° (Deyab and Keera, 2014; Deyab *et al.*, 2018). As compared to other polymers used in corrosion resistant application, alkyds are high gloss as there is no loss in appearance when quantified using 20° and 60° gloss measurements, with the values of 101.9 and 111.3 respectively, according to ASTM D2457 (Salata *et al.*, 2019). Hence, alkyds become one of the best choice of polymeric coating materials in protecting the metals from corrosion, due to its relatively low cost, good adhesiveness and thermal stability, excellent gloss, as well as relatively low cost and ease in processing with good durability.

Kordzangeneh and colleagues carried out the Tafel polarization test to compare the corrosion resistivity of bare metal with alkyd-coated metal, and the results are tabulated in **Table 4**. Meanwhile, the condition of coated metal shown in **Fig. 4** proved that alkyd coatings greatly slow down the underlying metal surface from rusting after 72 h of exposure on salt spray test. Thus, alkyds able to protect the coated metal surface in the case that the coated surface is not damaged by any physical attack from surface abrasion or wear.

As compared to the aforementioned epoxy resins, alkyd resins have relatively lower performance in chemical resistance, especially in alkaline medium (Sharmin *et al.*, 2016). Thus, modification is crucial to improve the chemical resistance and other desired properties for alkyds to excel in corrosion resistant application. For example, chlorinated rubber-modified alkyds have improved chemical and water resistance, as well as adhesiveness towards substrate; phenol-modified alkyds have improved gloss retention, as well as resistance towards alkali and water. Furthermore, as alkyds are extremely versatile, alkyds can be blended with other polymers such as polyurethane, acrylics and epoxy as reported by Hofland (2012). Alkyds also can be incorporated with different types of additive, such as iron(III) oxide (Fe_2O_3), titanium dioxide (TiO_2) nanoparticles, and aluminum oxide (Al_2O_3) nanoparticles for properties enhancement, especially in the aspect of barrier properties to meet the requirement as corrosion-resistant coatings (Deyab *et al.*, 2017; Kordzangeneh *et al.*, 2018; Sumi *et al.*, 2020).

Polyurethane

Polyurethane (PU) is another highly versatile synthetic polymer produced from di-, tri, or polyisocyanate group and polyol group (Ammar *et al.*, 2019). The isocyanates used in producing PU can be either aromatic or aliphatic, which give different properties to
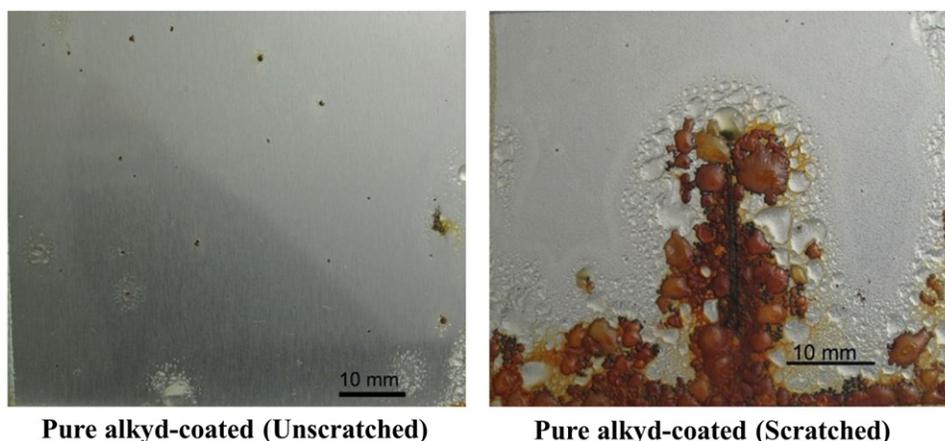
Pure alkyd-coated (Unscratched)   **Pure alkyd-coated (Scratched)**

Fig. 4 Visual observation of unscratched and scratched alkyd-coated steel after 72 h of exposure in salt spray chamber. Reprint with the permission from Ecco, L.G., Fedel, M., Ahniyaz, A., Deflorian, F., 2014. Influence of polyaniline and cerium oxide nanoparticles on the corrosion protection properties of alkyd coating. Progress in Organic Coatings 77, 2031–2038, Copyright (2020), Elsevier.

PU itself (Buchheit, 2018). When used aromatic isocyanates for PU production, higher rate of cross-linking and curing can be achieved, but with lower resistance to yellowing and chalking if exposed to sunlight; whereas when aliphatic isocyanates are used, the properties of PU produced are in contrast with one produced with aromatic isocyanates. The polyols in PU production also have great influence to determine the properties for desired application.

PU exhibits good resistance towards chemical and hydrolysis, as well as weathering effect, which makes it often to become a choice for corrosion-resistant coatings. Besides, PU coatings also possess excellent mechanical strength. Interestingly, PU has better abrasion resistance as compared to aforementioned epoxy and alkyd, as the impact energy of the erosion particles are absorbed with minimal damage due to its flexibility and resilience range on deformation (Ammar et al., 2019). Furthermore, it is important for coatings to adhering on the metal surfaces, PU also exhibits great adhesiveness towards the substrate with adhesion strength at rating of 3B (moderate) by cross-cut tape test according to ASTM D3359 (Tsai et al., 2018). In another study, the adhesion strength of PU coatings on carbon steel and galvanized steel is about 6.49 MPa and 2.75 MPa based on pull-off adhesion testing (González-García et al., 2007). The adhesiveness of PU may be attributed to the isocyanate and polar functional groups that able to form strong physicochemical interactions with the polar metal surfaces.

Although PU coatings are slightly hydrophilic with contact angle of 65.8°, the equilibrium water uptake of the coatings are low, which is only 1.12 wt% (Heidarian et al., 2011; Christopher et al., 2015). This shows that PU coatings possess good water resistance and able to slow down the corrosion of coated metal surfaces. Moreover, PU has great thermal stability with the initial degradation temperature at 280.5°C, and reaching the maximum at 373.3°C (Chen-Yang et al., 2005), which shows good heat resistance as well for utilizing as coating materials.

Number of studies reported the corrosion resistance performance of PU coatings, based on Tafel polarization and EIS by Bode plot, as tabulated in **Tables 5** and **6**, respectively. **Fig. 5** shows the condition of steel substrate that coated with commercial PU when exposure to different duration in salt spray chamber. It showed only a few little spots of corrosion is observed, proving that PU coatings are effective as corrosion-resistant coatings.

PU do have limitation as corrosion-resistant coatings in terms of permeability towards water and oxygen, especially for the waterborne PU coatings (Christopher et al., 2015; Cai et al., 2016). This is attributed to the existence of pores or gaps within the coatings, although it is observed smooth surfaces based on scanning electron microscopy (SEM) result. This later leads to the corrosion initiators diffuse easier into the coatings and causes corrosion on the metal surfaces. The incorporation of fillers can offset the weakness possessed by PU, and graphene is one of nanofillers that commonly used for properties enhancement of PU (Tsai et al., 2018). Instead of that, the corrosion resistance of PU can be further improved by blending with other polymers, such as epoxy, alkyds, and acrylic; or producing PU based on different types of polyols depending on the desired properties (Buchheit, 2018). For example, epoxy and acrylic urethanes give better corrosion resistance with aliphatic isocyanates, polyester urethanes give highly cross-linked resins, polyether urethanes give elastomeric properties, and vinyl urethanes give better abrasion resistance with improved toughness.

Acrylic

Acrylic resins are transparent thermoplastics that can be produced from acrylic acid, methacrylic acid, cyanoacrylic acid, acrylonitrile and acrylamide (Sastri, 2010). Acrylic resins can be either in the form of solid, solution in organic or inorganic solvents, or emulsions (Ammar et al., 2019). Among many types of acrylic resins, poly(methyl methacrylate) (PMMA) is the most widely used polymer which produced by the free radical polymerization of methyl methacrylate. Some examples of acrylic resins are poly(ethyl acrylate) and poly(butyl methacrylate). It is known that the properties of acrylic resins can be tailored by using different types or amount of

Table 5   Tafel polarization results of uncoated bare metals and PU-coated metals

No.	Parameters	Samples		References
		Uncoated bare metals	PU-coated metals	
1	E_{corr} (mV) I_{corr} ($\mu A\ cm^{-2}$) Corrosion rate (mm year^{-1})	-154 2.62 4.90×10^{-2}	-106 0.117 2.70×10^{-3}	(Dutta et al., 2018)
2	Corrosion rate (mm year^{-1})	0.921	2.37×10^{-4}	(Li et al., 2016)
3	E_{corr} (mV) I_{corr} ($\mu A\ cm^{-2}$) R_p (k Ohm cm^2) Corrosion protection efficiency (%) Corrosion rate (mm year^{-1})	-857 58.8 12.2 – 0.685	-552 2.07×10^{-3} 516 41.3 2.41×10^{-5}	(Cai et al., 2016)
4	E_{corr} (mV) I_{corr} ($\mu A\ cm^{-2}$) R_p (k Ohm cm^2) Corrosion rate (mm year^{-1})	-778 28.4 0.750 0.330	-739 10.5 2.71 0.120	(Christopher et al., 2015)
5	E_{corr} (mV) I_{corr} ($\mu A\ cm^{-2}$) Corrosion protection efficiency (%)	-1.00×10^4 21.3 –	-526 8.54 59.8	(Mo et al., 2015)
6	E_{corr} (mV) I_{corr} ($\mu A\ cm^{-2}$) R_p (k Ohm cm^2) Corrosion rate (mm year^{-1})	-757 64.0 0.700 0.744	-749 32.0 1.10 0.371	(Yeh et al., 2008)
7	E_{corr} (mV) I_{corr} ($\mu A\ cm^{-2}$) R_p (k Ohm cm^2) Corrosion rate (mm year^{-1})	-434 6.81 55.3 2.23×10^{-2}	-360 0.488 234 2.62×10^{-4}	(Chen-Yang et al., 2005)

Table 6   EIS results of uncoated bare metals and PU-coated metals by Bode plot

No.	Parameters	Samples		References
		Uncoated bare metals	PU-coated metals	
1	Corrosion resistance, $|Z|_{f=0.01\ Hz}$ (Ohm cm^2)	3×10^3 to 4×10^4	1×10^6 to 2×10^6	(Li et al., 2016)
2	Corrosion resistance, $|Z|_{f=0.01\ Hz}$ (Ohm cm^2)	1.68×10^3	3.50×10^4	(Khun and Frankel, 2016)
3	Corrosion resistance, log $|Z|_{f=log(0)}$ (Ohm cm^2)	3.13	3.82	(Liu et al., 2016)

monomers during the production for desired applications. As compared to the thermosets used as corrosion-resistant coatings, the usage of thermoplastic acrylics is lesser because it is found out the corrosion degree of thermoplastic coatings is higher than that of thermoset coatings, when immersed in NaHSO$_3$ solution for 1000 h in laboratory accelerated test (Laco et al., 2005).

Similar to the aforementioned thermosets, acrylics exhibit adhesiveness towards the metal surfaces. Acrylics generally have adhesion strength about 4.5 MPa and a rating of 3B with only 1.43% of area removed during the test, based on pull-off and cross-cut adhesion test respectively (Jafari et al., 2017; Song et al., 2017; Pajarito et al., 2018). Acrylics also have good resistance to hydrolysis, but not necessarily to acids and alkalies (Buchheit, 2018). The chemical resistance of acrylics is improved after functionalization by incorporating additional functional groups onto the hydroxyl groups of the monomers (Ammar et al., 2019). Besides of PU resins, acrylics also have good abrasion resistant, thus able to protect the substrate as corrosion-resistance coatings.

Furthermore, acrylics able to slow down the corrosion of metals with water contact angle of 74.3°, and good barrier properties (Pajarito et al., 2018). For example, the permeability towards oxygen and water vapor is about 30.3% and 23.4%, respectively for PMMA coatings (Chang et al., 2008). Acrylic coatings generally also exhibit good thermal stability, which thermally stable at 251°C
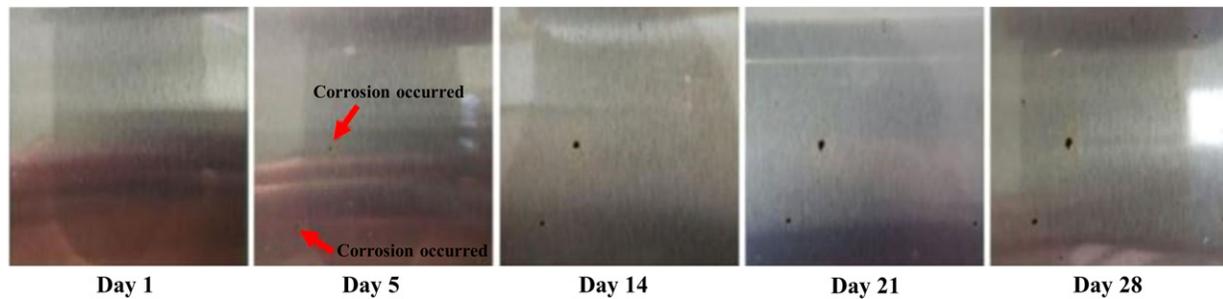
Fig. 5 Visual observation of PU-coated steel for 28 days of exposure in salt spray chamber. Reprint with the permission from Tsai, P.Y., Chen, T.E., Lee, Y.L., 2018. Development and characterization of anticorrosion and antifriction properties for high performance polyurethane/graphene composite coatings. Coatings 8, 250, Copyright (2020), MDPI Open Access.

Table 7   Tafel polarization results of uncoated bare steel and acrylic-coated steel

No.	Parameters	Samples		References
		Uncoated bare metals	Acrylic-coated metals	
1	E_{corr} (mV)	− 660	− 630	(Wang *et al.*, 2020)
	I_{corr} (μA cm^{-2})	49.4	2.42	
	Corrosion protection efficiency (%)	–	95.1	
2	E_{corr} (mV)	− 664	− 597	(Chang *et al.*, 2008)
	I_{corr} (μA cm^{-2})	3.45	1.93	
	R_p (k Ohm cm^2)	10.6	39.2	
	Corrosion rate (mm year^{-1})	8.15×10^{-2}	4.55×10^{-2}	
3	E_{corr} (mV)	− 604	− 485	(Yeh *et al.*, 2002)
	I_{corr} (μA cm^{-2})	19.0	0.120	
	R_p (k Ohm cm^2)	2.70	3.2×10^2	
	Corrosion rate (mm year^{-1})	0.932	5.84×10^{-3}	

and can be up to 302°C depending on the type of acrylics (Dhole *et al.*, 2017; Jiang *et al.*, 2020). Hence, acrylics do have the desired properties to be used as corrosion-resistant coatings to protect the metals, and the anticorrosion performance of acrylic coatings based on Tafel polarization is tabulated as **Table 7**.

Although acrylics possess many desired properties that needed for corrosion resistant application, but improvement is necessary to increase the corrosion protection efficiency to a higher value. This is because acrylics do have the common drawback as other polymer coating materials, which is the coating permeability. **Fig. 6** shows the morphology of pure acrylic coating has many cracks that allows the corrosion initiators diffuse through the coating layer, thus leading to reduction of corrosion resistivity (Fan *et al.*, 2020). Indeed, the acrylic coatings able to slow down the penetration of the corrosion initiators to the metals, but the barrier properties can be greatly enhanced by incorporating suitable additives or blending with other polymers. Wollastonite, MMT and CNT are some of the fillers incorporated into acrylics to greatly improve the barrier properties towards water and corrosive electrolyte, and adhesion to the metals (Jafari *et al.*, 2017; Song *et al.*, 2017; Pajarito *et al.*, 2018).

Effect of Additives and Fillers

The incorporation of fillers into the polymer matrix generally reinforces the polymers used for the anticorrosion purpose, as well as enhances the corrosion resistance to a higher extends. The development of nanotechnology leads to the usage of nanofillers in the polymer, as they are able to offer a significant improvement to the polymers in many aspects. As compared to the conventional fillers, only a small amount of nanofiller is required to provide better corrosion protection to the coated material by preventing the coating from delaminating or blistering (Nazari and Shi, 2016). It is found that the coating protection property improved via the increment of electrolyte diffusing length or cross-linking density in some cases and the reduction of micro-pores and cavities when the polymeric coating is incorporated with nanofillers (Sari *et al.*, 2017). MMT, graphene, graphene oxide (GO), CNT, and halloysite nanotubes (HNT) are among the most commonly used nanofillers in the application of anticorrosion polymeric coating materials.
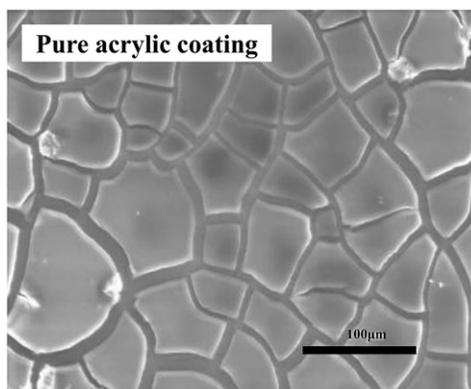
Fig. 6 Morphology of pure acrylic coating based on SEM result. Reprint with the permission from Fan, Y., Yang, H., Fan, H., *et al.*, 2020. Corrosion resistance of modified hexagonal boron nitride (h-BN) nanosheets doped acrylic acid coating on hot-dip galvanized steel. Materials 13, 2340, Copyright (2020), MDPI Open Access.

MMT is a layered clay mineral that belongs to the smectite group, which consists of two sheets of siloxane tetrahedral that fused to a sheet of edge-shared octahedral which either made up of magnesium or aluminum hydroxide (Shaikh *et al.*, 2017). The incorporation of MMT into the polymeric coating will enhance the barrier properties, by lowering the permeability and prolonging the length of diffusion pathways for oxygen and water, thus provide higher anticorrosion ability for the coated materials (Al-Shahrani *et al.*, 2018). The condition where the silicate layers of MMT completely separated and uniformly dispersed in the continuous polymer matrix to forms the exfoliated nanocomposites is the most desirable (Dlamini *et al.*, 2019). This is because of the excellent macroscopic properties that due to the high aspect ratio of MMT and the large adhesive interaction between MMT and polymer matrix. To achieve the exfoliated MMT in the polymer matrix, the combination of mechanical agitation and ultrasonication is recommended in the fabrication process (Heidarian *et al.*, 2011; Darmiani *et al.*, 2013). The corrosion rate of the MMT-filled polymeric coatings reduced to a value that is ten times lower than that of the unfilled polymeric coatings, based on the results of the electrochemical corrosion measurement (Jafari *et al.*, 2017). The enhancement of the anticorrosion ability of MMT-filled polymeric coating is greatly attributed to the tortuous diffusion pathways that created within the polymer matrix when MMT is well dispersed (Nielsen, 1967; Tan and Thomas, 2016). The tortuosity of the diffusion pathways for oxygen and water can be further increased by incorporating MMT that possesses a higher aspect ratio (Melia *et al.*, 2020).

Graphene is a two-dimensional monolayer of graphite, in which the sp^2 hybridized carbon atoms densely packed into a single layer of honeycomb-shaped crystal lattice without any functional groups present on the structure (Allen *et al.*, 2010). As graphene possesses high mechanical strength and the ability to withstand an elongation up to 23% without inducing and cracking or fracturing, it becomes a suitable nanofiller to reinforce the polymeric coatings that generally have lower mechanical properties (Pereira *et al.*, 2009; Hu *et al.*, 2014). Besides, graphene naturally is a hydrophobic material due to the non-polar double bonds (Leenaerts *et al.*, 2009). Thus, it allows graphene to exhibits excellent barrier property due to its impermeability towards the water, as well as oxygen (Dutta *et al.*, 2018). The well-dispersed graphene in the polymeric coatings will greatly enhance the barrier property against the corrosion, by increasing the tortuosity of the diffusion pathways for the oxygen and water molecules to penetrate through the coating (Tsai *et al.*, 2018). The incorporation of graphene into the polymeric coatings, such as epoxy and polyurethane greatly increased the protection efficiency against corrosion, as the corrosion rate of the coated metals drastically reduced.

As for GO, it is simply considered as the exfoliated product of graphite oxide, which has a similar hexagonal carbon structure to that of graphene but exhibits both sp^2 and sp^3 hybridized carbon atoms (Chiu *et al.*, 2013; Smith *et al.*, 2019). GO exhibits hydrophilic nature prior any treatment, which is contradicting the hydrophobic graphene due to the presence of the oxygen-based functional groups (Shah *et al.*, 2015). However, this property did not significantly affect its purpose to be utilized as a nanofiller that incorporating into the polymeric coatings to enhance the corrosion resistance. The incorporation of GO into the polymeric coatings can prevent the coated metals from rusting by reducing its corrosion rate (Catt *et al.*, 2017). This is attributed to the tortuous diffusion pathway, where the tortuosity is greatly increased by GO that possesses a large specific surface area with a high aspect ratio (Hussain *et al.*, 2019).

CNT also is used in the application of anticorrosion polymeric coatings. CNT is made from hexagonally bonded carbon atoms and it is rolled graphene layers, with sp2 hybridized carbon atom that bonded with the other three neighboring carbon atoms covalently (Tolinski, 2015; Karak, 2019). Multi-walled CNT (MWCNT) is more widely used to improve the corrosion resistance of the polymeric coatings with low filler content, by drastically reducing the corrosion rate, and increase the protection efficiency up to 99% (Shen *et al.*, 2016; Kumar *et al.*, 2017; Song *et al.*, 2017). Similar to the aforementioned nanofillers, tortuous pathways will be created with the incorporation of CNT into the polymeric coatings, which makes the penetration of corrosion initiators become difficult.

HNT is another widely used nanofiller for improving the corrosion resistivity of polymeric coatings, which has a structure similar to that of nano-clay, but geometrically analogous to CNT (Kausar, 2017). The incorporation of HNT into the polymeric coatings has the same mechanism by having the tortuous diffusion pathways to prevent the penetration of oxygen and water molecules into the coated metals (Xu *et al.*, 2019). Interestingly, HNT can be used as nanocontainers for corrosion inhibitors such as benzotriazole, to enhance more on the corrosion resistance of the polymeric coatings (Lvov and Abdullayev, 2013; Sun *et al.*, 2016). The inner HNT
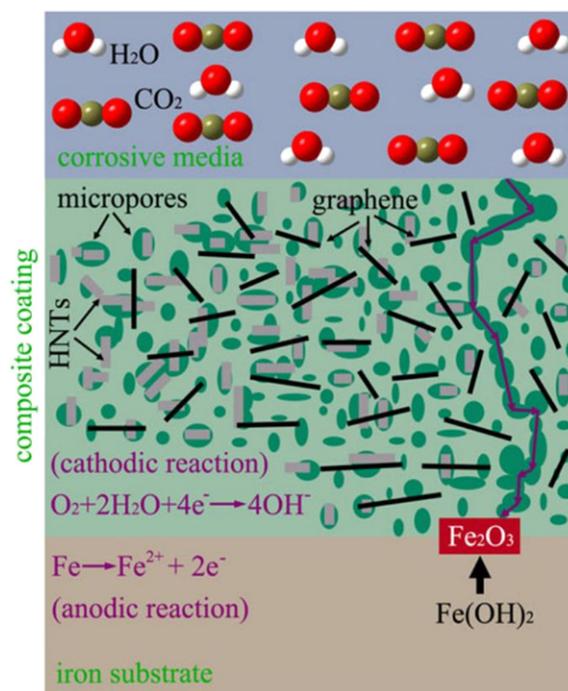
Fig. 7 Schematic diagram of the enhanced anticorrosion mechanism based on "tortuous path" model. Reprint with the permission from Xu, H.Y., Li, B., Han, X., *et al.*, 2019. Synergic enhancement of the anticorrosion properties of an epoxy coating by compositing with both graphene and halloysite nanotubes. *Journal of Applied Polymer Science* 136, 47562, Copyright (2020), Wiley.

lumen was used as a storage medium for corrosion inhibitor, where it is possible to control the release rate from HNT, to provide the best protective properties for the polymeric coating (Abdullayev *et al.*, 2009).

Nanoparticles such as silica (SiO_2), zinc (Zn), and iron(III) oxide (Fe_2O_3) were incorporated into the epoxy coatings to improve the corrosion resistance (Shi *et al.*, 2009). Based on the study, Fe_2O_3 gave the most significant enhancement on the corrosion resistance of coated steel, followed by SiO_2 and lastly Zn. These nanoparticles improved the anticorrosion property by filling up the micropores within the epoxy coating matrix, thus blocking the diffusion pathway for corrosion initiators to penetrate. Titanium dioxide (TiO_2) nanoparticles also is another nanofiller that able to improve the corrosion resistance of polymeric coatings as reported in the study of Cui *et al.* (2018). Recently, the usage of natural gum exudates as the green fillers is reported, which it is incorporated into the epoxy coatings to produce self-healing corrosion-resistant coatings (Arukalam *et al.*, 2020). Based on the study, the scribed coating surface was healed by the natural gum exudates, thus the corrosion reaction was suppressed without the aid of any other catalyst or co-reactant.

Some of the nanofillers, such as graphene and GO can be functionalized to enhance their performance in anticorrosion, by improving the dispersion of nanofillers in the polymer matrix and becoming more hydrophobic respectively (Ramezanzadeh *et al.*, 2016; Chen *et al.*, 2017). Furthermore, hybridization of one nanofiller or nanoparticle with another into the polymeric coatings gives more enhanced properties in terms of barrier effect, resistance to water, chemical and abrasion, as well as adhesiveness, stiffness, and toughness. Hybridization of GO with zinc oxide (ZnO), SiO_2, CNT, and MMT are some of the examples that reported in producing corrosion-resistant coatings with better performance based on polymeric materials (Christopher *et al.*, 2015; Hu *et al.*, 2017; Pourhashem *et al.*, 2017b; Sari *et al.*, 2017).

The main reason of polymeric coatings filled with hybridized nanofillers have greater corrosion resistivity as compared to one that is unfilled and filled with only one type of nanofiller, is the increment of tortuosity for the corrosion initiators to diffuse through the coating layer. The incorporation of more than one type of nanofiller into the pure polymeric coatings will be filling up the micropores within the matrix, as well as zigzagging the diffusion pathway for oxygen, water , and any other corrosion electrolytes to reach the metal surfaces. Thus, the hybridized nanofillers-filled polymeric coatings able to slow down and prevent the penetration of corrosion initiators at greater extent, thus showing excellent barrier effect in protecting the metals from corrosion. Fig. 7 shows the enhanced anticorrosion mechanism with increased the tortuosity of the diffusion pathway by the synergism between graphene and HNT (Xu *et al.*, 2019).

Conclusion and Future Outlook

This article describes the use of polymeric coatings as corrosion protection of metallic substrates. Corrosion is an irreversible interfacial reaction that leads to the deterioration of properties, particularly in mechanical strength, thus causing failure on

equipment and infrastructures. Corrosion can occur via electrochemical, chemical, or physical reactions when the surface of metals exposed to the surrounding without any preventions. Plastic corrosion-resistant coatings for metal surfaces are the most cost-effective solution to the problem, regardless of thermosets and thermoplastics are used. They can prevent corrosion of substrate through physical barrier, inhibition effect, electrochemical protection mechanism or their combination. Both thermoset and thermoplastic coatings generally exhibit great adhesiveness to the metal surface and mechanical strength, as well as resisting water and chemicals in preventing the coated metals from corrosion. Epoxy and alkyd resins are widely used as compared to others due to their low cost and ease in processing, whereas PU and acrylic resins are doing great in the aspect of abrasion resistance. The usage of thermoplastics in corrosion resistant application is relatively less because they may be melted and reshaped when overheated, which affects their effectiveness in corrosion protection. Furthermore, polymer coatings with additives are very common. Most of the fillers serve as the reinforcement for polymer coatings, as well as improving the corrosion resistance and barrier properties, thus slowing down, and preventing the penetration of corrosion initiators into the underlying coated metal surface. Among the additives used, graphene and GO nanofillers are the recent focus in advance polymer coatings development due to their excellent enhancement effect on barrier properties, adhesion, and mechanical strength.

Since protective performance of nanocomposite coatings greatly depends on nanofiller dispersion in polymer matrix, detailed investigation on the dispersion techniques, filler size and shape, filler content and surface properties are crucial. Furthermore, hybridization of nanofillers contributes synergic effect in enhancing corrosion resistance and other functional properties. Multi-functional polymer coating or smart coating is the future trend in advance polymer coatings developments. Various functionalities include self-healing, anti-fouling, super-hydrophobicity, ice-repellence, conductive and electromagnetic responsive have been the great interest in this research field. Yet, there are still many challenges in designing the system to integrate various functionalities of interest into coatings, getting the proposed system to meet the standard corrosion requirements in industries and predicting the lifetime of the multifunctional coatings. Hence, there is a need to understand the mechanisms and kinetics of releasing of carriers at different conditions and ages. Also, research on the low-cost, simple smart coating fabrication methods and cheap raw materials are of great importance. Smart coatings can be commercially attractive if it is low cost and easy to be fabricated. Model development to predict and validate the ability of a coating to heal at different damage events, as well as to identify the thresholds concerning geometry and dimensions of the defects to be healed is desired. Although synthetic polymer coatings are state-of-art, recent advances pursue green plastic materials in corrosion research.

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