



Review

Recent advances in corrosion protective composite coatings based on conducting polymers and natural resource derived polymers



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ABSTRACT

Conducting polymer (CP) coatings have been extensively investigated for corrosion protection of iron, steel and other metals owing to their superior performance in highly aggressive environments and eco-friendly characteristics. Corrosion protective coatings based on CP nanocomposites have opened a new area of research for obtaining low cost coatings with enhanced performance and tailored properties. This mini review highlights the latest developments in the corrosion protective performance of CP composite coatings with natural resource derived polymers. The presence of nanoscale dispersion of CP as filler significantly improves the barrier properties and lifetime of the organic polymeric coatings. These low-cost nanocomposite coatings are expected to play an important role in combating corrosion which can lead to drastic improvement in corrosion protection.

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Abbreviations: Cb, carbon black; COPU, castor oil polyurethane; CP, conducting polymer; CPEAU, coconut oil based poly(esteramide urethane); CSA, camphor sulfonic acid; DAB-AM-4, N,N,N',N'-tetrakis(3-aminopropyl)-1,4-butanediamine; DGEBA, diglycidyl ether of bisphenol A; EB, emeraldine base; EIS, electrochemical impedance spectroscopy; ES, Emeraldine salt; EP, Epoxy; EPA, Environmental protection agency; HELA, N,N'-bis-(2-hydroxyethyl) linseed oil amide; HMDI, hexamethylenediisocyanate; IPN, interpenetrating polymer network; LO, linseed oil; LOPU, linseed oil polyurethane; LPUA, linseed polyurethane amide; MO, methyl orange; MS, mild steel; PANI, polyaniline; PEAs, polyesteramides; PEDOT, poly(3,4-ethylenedioxythiophene); PNA, poly(1-naphthylamine); POA, poly-*o*-anisidine; PPE, poly(2,6-dimethyl phenyl ether); PPy, polypyrrole; PPO, polyphenylene oxide; PSS, poly(styrene sulfonate); PTh, polythiophene; PPV, poly(phenylenevinylene); TMDA, trimethylhexanediamine.

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1. Introduction

Metals and alloys form the backbone of industrial and engineering structures because of their high strength and ductility. However, metals in most of the aggressive environments are thermodynamically unstable and undergo corrosion. Economic losses resulting from metallic corrosion amount to billions of dollars per year worldwide [1]. The use of organic coatings is one of the most important approaches for minimizing these enormous corrosion losses. The use of renewable resources in the preparation of various corrosion protective coatings has been revitalized because of environmental concerns. Natural oils are considered to be one of the most important classes of renewable resource. They can be obtained from naturally occurring plants, such as sunflower, cotton, linseed. They predominantly consist of triglycerides [2]. Vegetable oil-based polymers are gaining popularity due to some attractive properties related to the specific chemical structure of oils, as well as concerns about the environment and sustainability. Although they have been used since the 19th century for formulating paints, preparation of polymers from renewable sources has lately become a subject of intense research and investigation to overcome the problem of petroleum shortage [3–6]. The utilization of triglyceride oil-based polymers is now primarily focused towards their application as corrosion protective based pigments and coatings.

Organic-inorganic composite coatings provide protection and reliable long-term performance. To protect the underlying substrate, the barrier effect and self-healing properties are provided by the organic part of the coating while the corrosion protection is offered by the inorganic pigments that are commonly used as inhibitors. However, nearly all powerful corrosion inhibitors are detrimental to both environment and health due to their toxic and carcinogenic nature. Current coating systems used for corrosion protection consist largely of zinc/chromate primers and chromium conversion coatings [7,8]. While these coatings have been proven to prevent corrosion, they continue to come under scrutiny by the Environmental Protection Agency (EPA). Regulations concerning lead and hexavalent chromium are one of the most widespread and restrictive [9,10]. These regulations have led to considerable research activity for developing environmentally acceptable alternatives to both corrosion inhibitors and components of organic coatings. Several inorganic replacements for chromate pigments have been proposed and applied in practice [11–16]. Although, the potential of conducting polymers (CP) for corrosion protection is a topic of current interest, the efficacy of these materials depends on their doping level and the conditions of the corrosive environment.

2. Role of conducting polymers in corrosion protection

Corrosion protection using conducting polymers (CPs) was first suggested by DeBerry [17]. The common CPs used in corrosion protection are – polyaniline (PANI), polypyrrole (Ppy), poly(phenylenevinylene)(PPV), polythiophene (PTh) [18–21]. CPs can be synthesized both chemically and electrochemically. It is observed that CPs stabilize the potential of the metals in the passive regime via the formation of a protective layer. PANI and its derivatives are among the most frequently studied CPs used for corrosion protection [19–22]. CPs have been evaluated for corrosion protection of mild steel [23–25], stainless steel [26–30], iron [31–34], copper [35], zinc [36,37], aluminum [38], and other metals [39]. Effective corrosion protection has been achieved by CPs when they are in the doped state. Electrochemical and chemical methods are generally adopted to deposit an electroactive polymer on a metal surface [39]. When CPs are used as a primer alone, they are deposited on metal surface via electrochemical deposition and this is regarded as one of the easiest techniques for the direct deposition

of CPs on metallic surfaces. Investigations on the corrosion protection imparted by CP coatings to metals, particularly iron and steel (mild or stainless) have been extensively reported [20–22]. Drastic improvements have been achieved by adding a relatively small concentration (2–10 wt%) of inorganic pigments as fillers [40–44]. It has been observed that most CPs can be electrochemically synthesized by anodic oxidation, forming a conducting film directly on the surface [45–47]. CPs can be converted from insulating to conducting state through several doping techniques such as chemical doping by charge transfer, electrochemical doping, photo doping and also through charge injection at a metal–conducting polymer interface [22]. The characteristic feature of their ability to anodically protect metals against rapid rates of corrosion is because these polymers can store and transport charges [48]. Their mechanisms of corrosion protection are not only complex but also influenced by many factors [49–63]. Some theories have predicted that CP based coatings provide protection by barrier mechanism while others have proposed the formation of a passive oxide film on metal surface through oxidation–reduction process [47–51].

Brusic et al. [19] studied the corrosion protection properties of spin coated thin PANI films on copper as a function of the applied potential and temperature. They found that the chemical nature of the polymer backbone, oxidation state and the extent and nature of polymer doping significantly affected the corrosion protective properties. They also discussed the efficiency of polymers in the insulating/conducting state. On the other hand, Fenelon et al. [64] eletropolymerized polypyrrole (PPy) onto copper and showed that the films exhibited good adhesion and significant protection against corrosion in acidified and neutral solutions. Aeiayach et al. [65] successfully electrodeposited PPy on zinc and these films showed considerably higher corrosion resistance. Kinlen et al. [61,66] provided direct information on the redox processes occurring in the polymeric layer by using the scanning reference electrode technique (SRET). De Souza et al. [67] used micro-Raman spectroscopy to demonstrate redox interaction between PANI and iron. In addition, they also showed that the reduction of PANI was provoked by the galvanic coupling with iron, which led to the formation of a second protective layer at the metal–film interface. This inner layer was made of a salt formed by the metal cation (Fe^{3+}) and the dopant-anion of the polymer. The studies pointed towards the possible importance of “galvanic coupling” between the metal and the CP as a way to provide active corrosion protection to the metal. The mechanism of the active protection offered by CPs has been investigated using different electrochemical and analytical techniques such as electrochemical impedance spectroscopy and Raman spectroscopy, as well as local probing techniques such as scanning Kelvin probe, scanning reference electrode and scanning vibrating electrode techniques [57,58,66,71]. Corrosion protection of steel by coatings containing PANI can be offered by a number of operating mechanisms such as barrier protection, corrosion inhibitors, anodic protection, shift of electrochemical interface, etc. The anodic protection (ennoblement) has been evidenced by the widely observed shift in corrosion potential into the passive region, although there is a large variation in the magnitude of the shift observed in different investigations [68–70].

Blending is a promising approach for taking advantage of the good mechanical properties and processability of conventional polymers and of the electroactive properties of such CPs [72–74]. Corrosion protective applications of CPs have been reported as multilayered coatings [75], composite films [76,77], ultrathin films [78], and in the form of primers [79–83]. The quality and conductivity of these blends depends significantly on the solvent, dopant and preparations conditions. Conducting polyblends can be made by co-dissolving PANI and a suitable matrix polymer. Conducting blends and composites have been prepared by solution blending [30–36], melt processing [37–39] and polymerization

of aniline in the presence of an inert polymer. A variety of CPs have been added to different organic coatings i.e. epoxy resins, polyurethanes, polyalkyds, etc. to provide corrosion protection in aggressive environments. Coatings formed by mixing PANI (8–50 wt%) and polyurethane or alkyd resins have showed better corrosion protection of iron than the coatings without PANI [84,85]. The formulations modified by the addition of very low concentrations of CP (less than 1 wt%) result in better corrosion resistance than the unmodified formulations [86–91]. The use of ICPs in epoxy or acrylic blends is a facile strategy for corrosion protection aiming to profit from the enhanced mechanical properties of such materials and overcome the difficulty of electroplating CP films onto large areas [73,74].

3. Commercial epoxy based conducting polymer composite coatings

Epoxy resin is well known for its chemical resistance and as a maintenance coating [92,93]. Silicone resins are mainly used for protecting the metal surface from high temperature corrosion [94]. Dhoke et al. [95,96] reported the performance of epoxy–silicone, silicone–polypyrrole and silicone–polythiophene interpenetrating polymer network (IPN) for high temperature applications. Anandakumar and Sankaranarayanan [97] have reported the thermal properties of silicone based IPN.

3.1. Polythiophene–epoxy coatings

Palraj et al. [98] reported the corrosion-resistance of IPNs prepared from immiscible resins (epoxy, silicone and thiophene) using a cross-linking agent and a catalyst. GPC, FT-IR, NMR, TG, DTA and SEM studies were done to investigate the best performing IPN. SEM confirmed the incorporation of silicone and polythiophene into the epoxy polymer to form homogeneously micro structured IPN, Fig. 1. It can be seen from Fig. 1(a) that the silicone domains (white globes), confirm the existence of the thiophene polymer in the IPN. The major portion covered by black region is indicative of epoxy resin dominating the IPN. This confirms that the thiophene monomers are incorporated within the epoxy to form IPN. The non-uniformity vanished when the hardener was added and dried. Fig. 1(b) shows a uniform morphology of the cured polymer with the existence of excess silicone domains. The increase in the black region indicated the formation of cross links between the IPN and the polyamide hardener. The corrosion resistance of the IPN was evaluated by AC impedance measurements. Fig. 2 shows a Bode plot of the IPN resins with the hardener coated on mild steel in a 3% NaCl solution at the end of the 168th hour of immersion. The IPN was mixed with a hardener (polyamide) and applied over the pickled mild steel panels and dried at room temperature for 7 days. Four sets of panels of uniform thickness of S1 (56.5 μm), S2 (66 μm), S3 (72.5 μm), and S4 (76.5 μm) compositions were selected for corrosion studies. The charge transfer resistance of S1, S3 and S4 combinations in 3% NaCl decreased by 2–3 folds at the end of 168th hour of immersion while the double layer capacitance increased by an order of 1. However in case of S2-IPN incorporated coatings, the changes in charge transfer resistance and double layer capacitance were observed to be less with little deviation from their initial values. The values of the parameters related to the high frequency are C_{dl} and R_{ct} , which are considered to be coating properties changed with immersion time. Usually C_{dl} increases with the immersion time in the initial period and then remains approximately constant since the absorption of the water becomes saturated even if the immersion time is increased. Due to the porous nature of the coatings, formation of micro-cells occurred at the metal surface/coating interface and with the increase of immersion time and

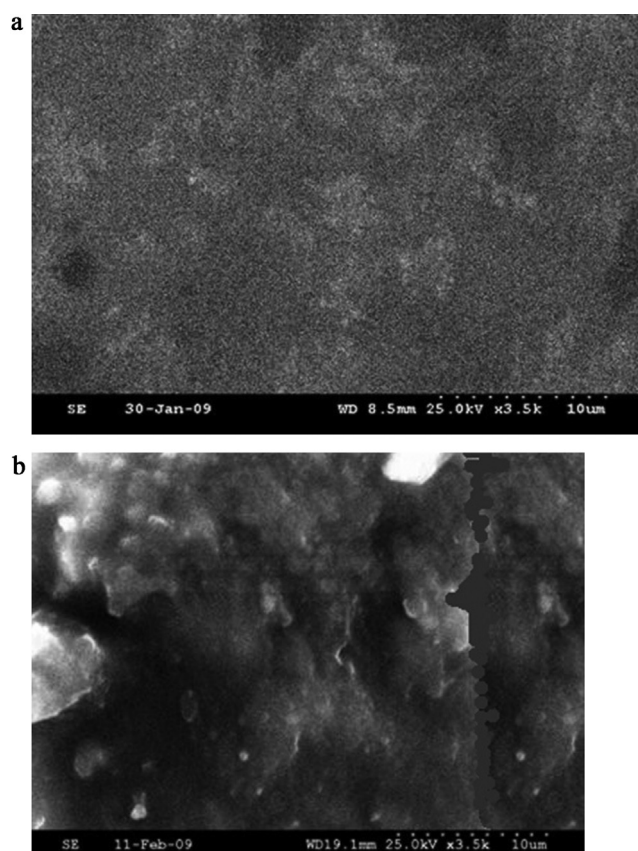


Fig. 1. (a) SEM micrograph of the IPN resins and (b) SEM micrograph of the IPN resin with hardener. Palraj et al. [98].

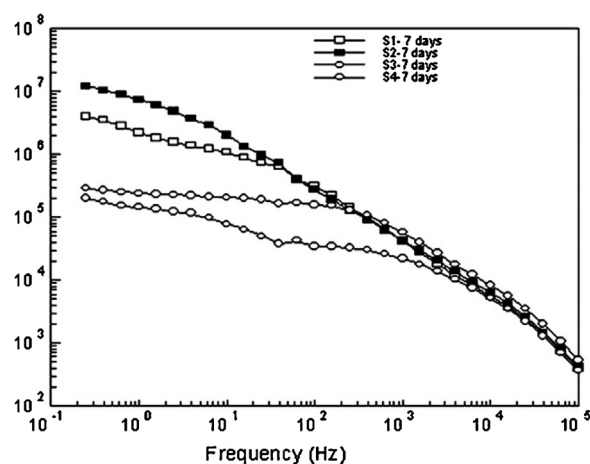


Fig. 2. Impedance behavior of IPN resin with hardener coated on mild steel in 3% NaCl. Palraj et al. [98].

accumulation of corrosion products at the metal/coating interface, diffusion process was established. But S2-IPN with polyamide, the structure of the cross-linked IPN-Polyamide contributed to the compactness of the coating which made water and chloride ions hard to transport and reduced the trend so that the corrosion resistance was improved. The EIS results also supported the fact that the IPNs with optimal silicone concentrations were comparatively less pore free with improved compactness.

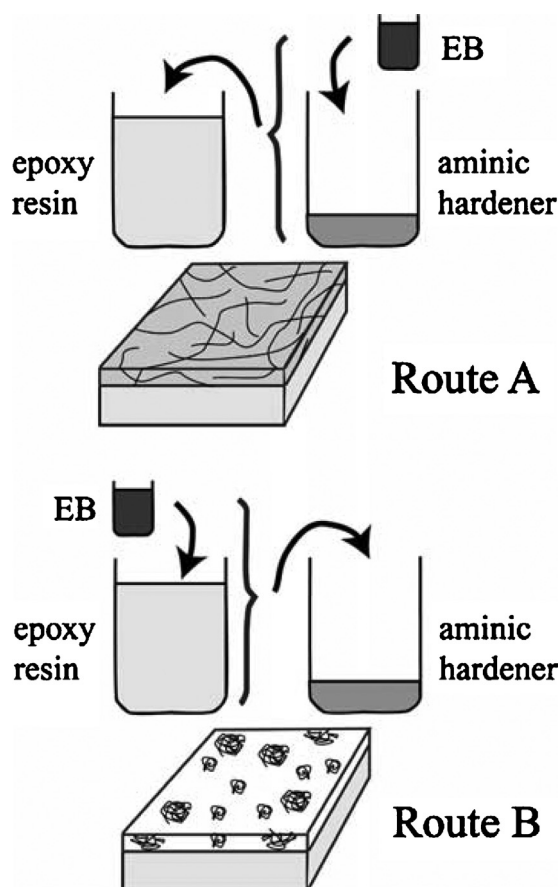


Fig. 3. Schematic illustration of the used concepts. (a) Route A: Amine hardeners are identified which dissolve EB at low concentrations and which, therefore, efficiently disperse EB at higher concentrations. The EB/hardener mixture is subsequently cross-linked by adding the epoxy resin. (b) Route B: Mixing EB first in epoxy resin leads to macroscopic phase separation unless an additional solvent is used. The macroscopically phase separated morphology remains after adding the basic hardener to EB/epoxy mixture and cross-linking. Reprinted with permission from Elsevier, Tiitu et al. [104].

3.2. PANI/epoxy coatings

Meijer et al. [99–103] introduced techniques to process semi-rigid nonconjugated CPs such as poly(2,6-dimethyl phenyl ether) (PPE), using reactive solvents. They first mixed PPE in oligomeric epoxy resins, such as diglycidyl ether of bisphenol-A (DGEBA) which was observed to be a solvent for PPE, and subsequently cured the mixture by adding amine hardeners. Also additional polymer components and fiber reinforcements were added in the composite. Ikkala et al. [104] used amine oligomers N,N,N',N'-tetrakis(3-aminopropyl)-1,4-butanediamine (DAB-AM-4) and trimethylhexanediamine (TMDA) to dissolve EB at low concentrations, and also to provide hardeners to the epoxy resin. They allowed reactive solvent approach to prepare cross-linked EB/epoxy composites upon adding the DGEBA component, see Fig. 3(a). For comparison, exactly similar net compositions were studied where EB was first added to DGEBA, and subsequently cured by adding TMDA, Fig. 3(b). The feasibility in corrosion prevention applications was assessed by investigating corrosion front propagation and electrochemical impedance spectroscopy in aqueous saline solutions. To preliminarily investigate the effect of curing on the morphology, DGEBA was added in the above 0.5 wt% solutions of EB/DAB-AM-4 and EB/TMDA and cured at 60°C for 24 h. The hardener and DGEBA resin ratio was fixed as 190/40 w/w. The cured composites were viewed under the

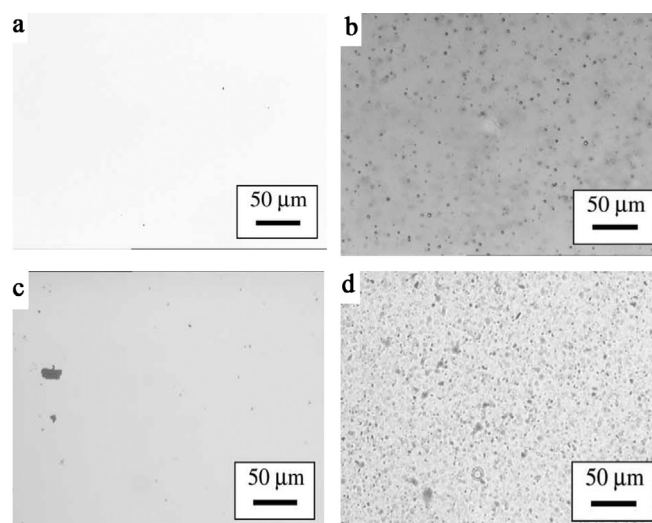


Fig. 4. Optical micrographs (a) 0.5 wt% EB in DAB-AM-4 stirred for 7 days. (b) The corresponding cured epoxy composite which contains 0.1 wt% of EB upon adding DGEBA. Note that closer inspection shows that most of the dark spots are in fact air bubbles and not phase separated EB. (c) 0.5 wt% EB in TMDA stirred for 7 days. (d) The corresponding cured epoxy composite which contains 0.1 wt% of EB upon adding DGEBA. Reprinted with permission from Elsevier, Tiitu et al. [104].

optical microscope to observe phase separation, Fig. 4(b) and (d). It was noticed that phase separation of PANI did not take place during the curing process because of the increase of molecular weight of the solvent towards infinity. On the other hand, the extent of phase separation was topologically limited due to formation of the cross-linked sites. The actual morphology depended on the details of the processing conditions. Even for the cured compositions, Fig. 4(b) and (d), were not claimed to be completely homogeneous. The cured EB/DGEBA/DAB-AM-4 resins rendered hard and brittle coatings that were susceptible to delamination in the immersion tests. It was observed that the amine solvents of the emeraldine base (EB) form of PANI acted as hardeners for DGEBA epoxy resin. Suitable compounds were N, N, N', N'-tetrakis(3-aminopropyl)-1,4-butanediamine and trimethylhexanediamine. By reverting the conventional order of preparation, the EB/TMDA-mixture was cured by adding DGEBA. As little as 1% EB in such compositions suppressed the propagation of corrosion front considerably in mild aqueous conditions as compared to similar samples where EB was in poorly dissolved aggregated state. The 0.5 wt% EB/TMDA mixtures were essentially particle-free while 2.9 wt% mixtures showed clear undissolved but soft-walled particles and 5.8 wt% mixtures were in microscopy rather unhomogeneous (see Fig. 5(a)). Some phase separation was seen in the cured composition (Fig. 5(b)). In electrochemical impedance studies, the increase of both the potential and impedance values showed the corrosion protective effect of EB.

3.3. Polyaniline, polypyrrole and poly(3,4-ethylenedioxythiophene based epoxy paints

Alemán et al. [105] compared the protection against corrosion imparted by different CPs when used as anticorrosive additives in the formulation of conventional epoxy paints. The polymers employed as anticorrosive additives were polyaniline emeraldine salt composite (EP/PAni-ES), polyaniline emeraldine base composite (EP/PAni-EB), with carbon black (EP/PAni-ES/cb), polypyrrole composite with carbon black (EP/PPy/cb) and poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrene sulfonate) (EP/PEDOT/PSS). Initially, the structural, thermal and

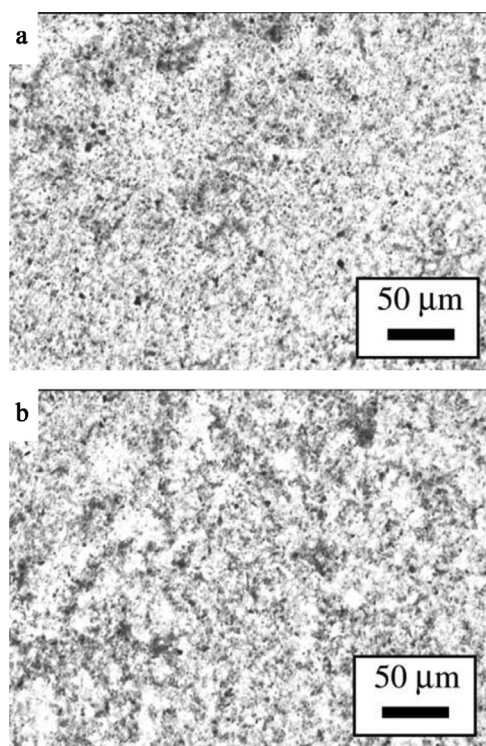


Fig. 5. Optical micrographs for (a) 5.8 wt% EB in mixed TMDA and stirred for 7 days and (b) the corresponding cured EB/DGEBA/TMDA composite which contains 1.0 wt% of EB.

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mechanical properties of the unmodified epoxy paint as well as the modified coatings, obtained by the addition of 0.3 wt% of conducting polymers, were characterized. After this, controlled accelerated corrosion assays in an aggressive solution medium were developed using coated steel panels. The steel pieces coated with the EP-standard, EP/PAni-ES, EP/PAni-EB, EP/PAni-ES/cb, EP/PEDOT/PSS and EP/PPy/cb formulations after 120, 240, 480 and 720 cycles of accelerated corrosion tests are shown in Fig. 6. Visual inspection of the steel panels submitted to corrosion cycles indicated that the resistance against corrosion of the epoxy primer depended on the CP composition. The incorporation of PAni-ES, PAni-EB and PEDOT/PSS improved the protection. Conductive carbon black particles showed a positive influence on the electrical contact between the CP contained in the polymer matrix and the underlying metal substrate to form a protective oxide layer. However, the protection imparted by the formulations containing PAni-ES/cb and PPy/cb was clearly disadvantageous with respect to the EP-standard evidencing the negative role played by carbon black particles. This behavior was attributed to the formation of a non-protective oxide layer in the metal coating interface, which was promoted by the presence of carbon black particles. This layer contributed to the reduction of the adherence of the coating to the metal accelerating the substrate corrosion. The black carbon particles promoted the corrosion process by inducing the transport of electrons over the coating and increasing the film porosity providing poor adherence and corrosion resistance. The evolution of the corroded area under the films vs. time according to the ASTM D-1654 shows that the best protection was obtained with EP/PAni-EB, being fully consistent with the excellent results recently reached for other paints modified with the non-conductive form of PAni. Thus, the corrosion resistance of the epoxy paint modified with PAni-EB remained practically constant during 720 h of immersion test in NaCl solutions. The percentage of corroded area under the film and around the scribe was about 40% of the total sample area.



Fig. 6. Scrapped test panels of EP-standard, EP/PAni-ES, EP/PAni-EB, EP/PAni-ES/cb, EP/PEDOT/PSS and EP/PPy/cb after 120, 240, 480 and 720 corrosion cycles. Corrosion resistance was evaluated according to the ASTM D-1654.

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Furthermore, excellent results were also provided by EP/PAni-ES, the epoxy paint modified with the conductive form of PAni. PAni-ES (in xylene) showed better dispersion properties than PAni-EB (a solid compound). The EP/PAni-EB remained strongly adhered to the substrate during the first 120 cycles, the corroded area being exactly the same as that for EP/PAni-ES/cb in the same period (27%). This initial corrosion resistance was attributed to the partially doped state of the PAni-ES composition. The CP converted into PAni-EB when in contact with a basic medium like that of the polyamide resin used as curing agent of the two-component epoxy system. This dedoping process was reported to take place gradually, which was evidenced in white or light-gray paints by the time dependent colour change on the surface of the film. Fig. 7 confirmed that the CP in the EP/PAni-ES formulation probably changed to the completely undoped form after 10 days of immersion in the corrosive medium as its corrosion area progression was found to be almost the same as the EP/PAni-EB curve. Accelerated corrosion assays using an aggressive saline solution revealed that the panels coated with EP/PEDOT/PSS, EP/PAni-ES and PAni-EB were significantly more resistant against corrosion than those protected with the EP-standard paint. Results revealed that the protection against corrosion imparted by the formulations modified by the addition of poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate), polyaniline emeraldine salt and, especially, polyaniline emeraldine base were significantly higher than that of the unmodified paint. In contrast, the use of conducting polymer composite with carbon black reduced the efficacy of the coating. Results also

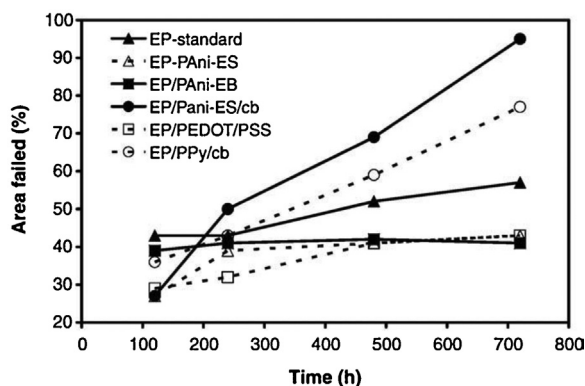


Fig. 7. Results derived from assays based on controlled immersion cycles: progression of corrosion area vs. time in the panels coated with the epoxy primer studied in this work, according ASTM D-1654.

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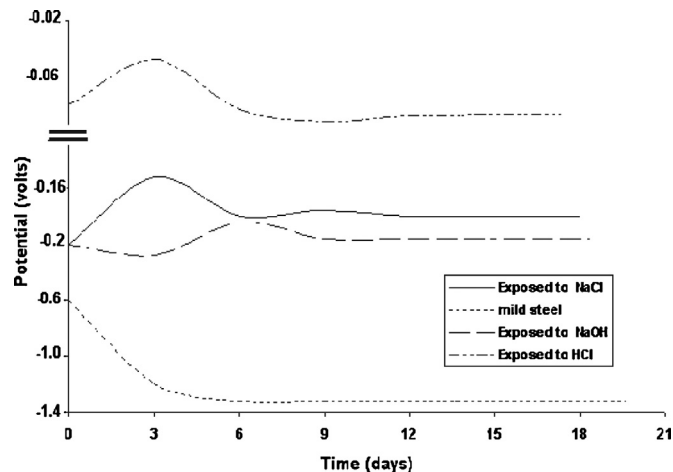


Fig. 9. Corrosion potential of 8-PANI-CPEAU in acid, alkaline and saline media. Reprinted with permission from Wiley, Ahmad et al. [109].

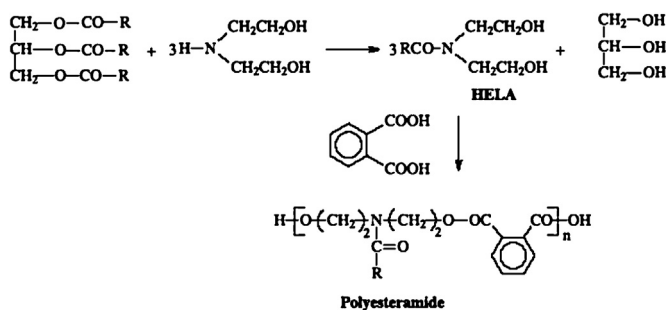


Fig. 8. Synthesis of polyesteramides from triglyceride oils.

highlighted that some conducting polymer compositions could be considered as a suitable alternative to replace inorganic anticorrosive pigments currently used in paint formulations

4. Sustainable resource based conducting polymer composite coatings

The designing of a corrosion protective nanocomposite coating to combat corrosion requires tailoring of novel and innovative materials that exhibit synergism. These materials hold immense potential to meet the goals in terms of increased payload fraction, reduced life cycle costs and high performance. Hence, recent advances in the development and application of renewable resource based CP nanocomposite coatings are discussed in the proceeding section.

4.1. Polyaniline/coconut oil polyesteramide composite coatings

Polyesters are unstable to UV radiation and undergo crack and disintegration while polyamides reveal high moisture absorption. Polyesteramides (PEAs) form a synergetic combination of the best properties of polyesters and polyamides [106–109]. PEAs exhibit thermoplastic behavior if the alkyl chain (R1) is long while if it is short, they are used as an engineering plastic. Oil-modified polyesteramide resins are amide modified alkyds that have improved properties over normal alkyds. A number of oil-based PEAs have been synthesized for their application as surface coating materials [108,109]. They are generally synthesized into two steps: preparation of N,N'-bis-(2-hydroxyethyl) linseed oil (HELA) from oil and diethanolamine, and preparation of polyesteramide from HELA and phthalic acid as shown in Fig. 8. Coconut oil based conducting blend coatings of PANI and coconut

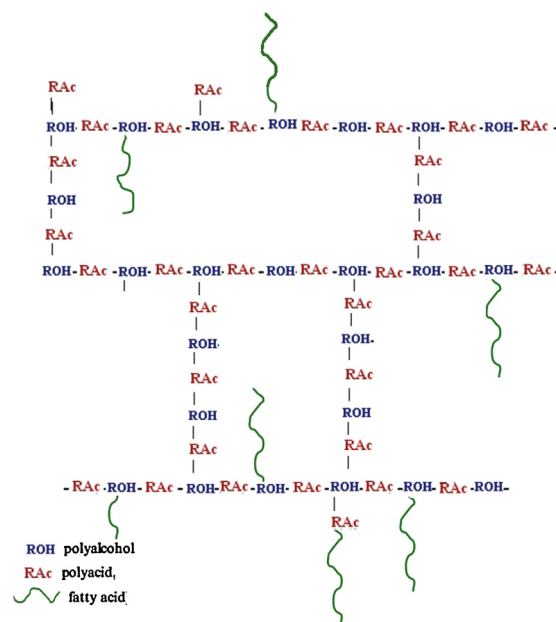


Fig. 10. Structure of oil based alkyd resin.

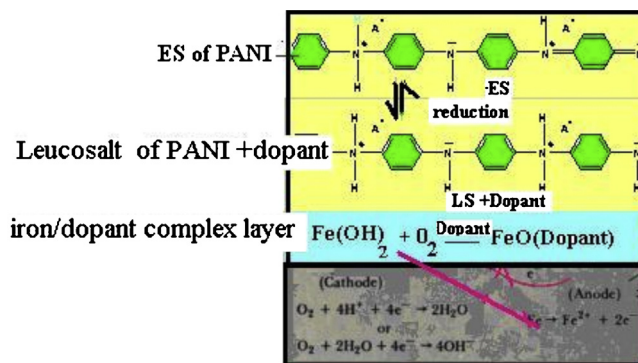


Fig. 11. Mechanism of corrosion protection of PANI/alkyd nanocomposite coating. Reprinted with permission from Elsevier, Ahmad and co-workers [112].

Table 1

Corrosion studies of PANI-CPEAU coatings. Reprinted with permission from Wiley, Ahmad et al. [109].

Sample	H ₂ O (15 days)		5% NaOH (15 days)		5% HCl (15 days)		5% NaCl (15 days)	
	Before aging	After aging	Before aging	After aging	Before aging	After aging	Before aging	After aging
CPEAU	a	–	f	–	e	–	f	–
2-PANI/CPEAU	a	b	c	e	b	c	d	e
4-PANI/CPEAU	a	a	c	e	a	c	c	d
8-PANI/CPEAU	a	a	b	e	a	b	b	c

a = the film remains intact and unaffected; (slight loss in gloss observed after 10 days).

b = the film remains unaffected till 8 days (shows loss in gloss after 8 days).

c = the film remains intact till 5 days (shows slight dissolution and discoloration after 5 days).

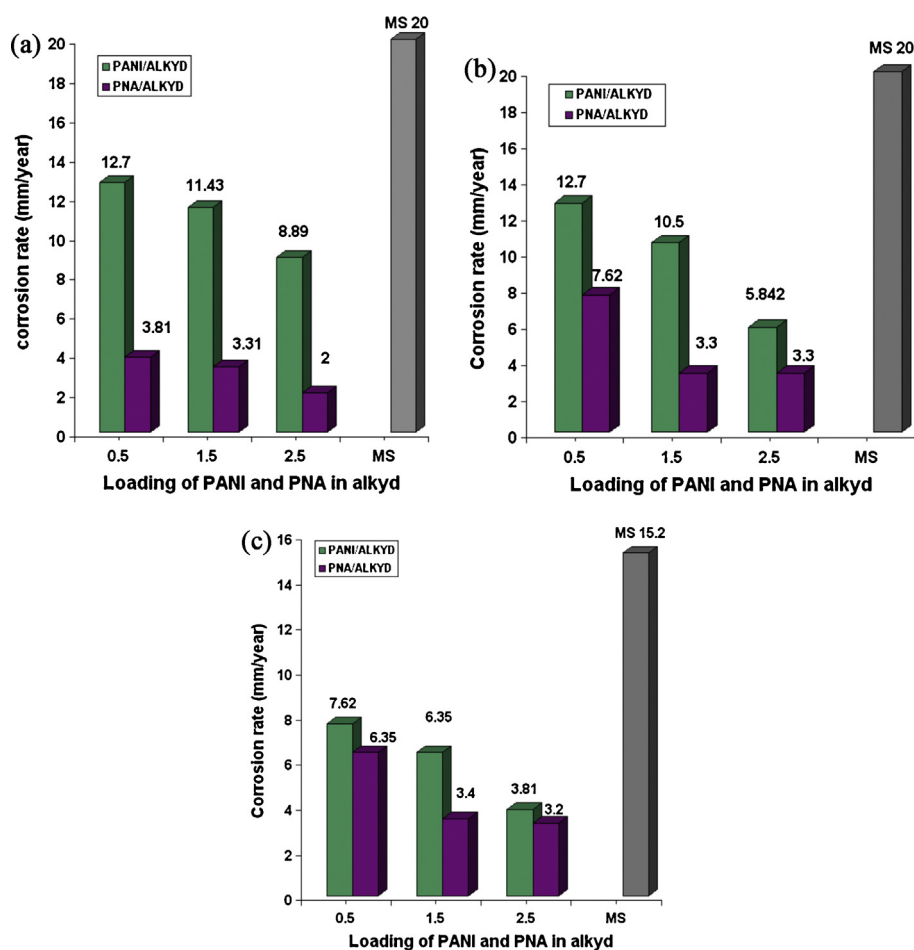
d = the film remains unaffected till 3 days (shows discoloration after 3 days and dissolution after 8 days).

e = the film remains intact and unaffected till 2 days (shows dissolution and loss in gloss after 2 days) and

f = film completely removed within 2 h.

oil based poly(esteramide urethane)(CPEAU) were prepared by Ashraf et al. [109] by loading different ratios (2, 4 and 8 wt%) of PANI in poly(esteramide urethane). The physico-chemical, thermal, morphological, conductivity and anti-corrosive coating characteristics were investigated. Results showed that the corrosion protective performance of the blend coatings was far superior to that of pristine CPEAU. The PANI-CPEAU coatings exhibited enhanced corrosion protection in acid as well as alkaline environments for 360 and 192 hrs respectively. Conductivity of the blends was found to be in the range 2.5×10^{-5} to 5.7×10^{-4} S/cm⁻¹. The corrosion potential of 8-PANI-CPEAU was found to -0.2 V in 5% HCl and 3.5% NaCl while in 5% NaOH, the corrosion potential was found to be -0.06 V.

The shift of the corrosion potential was attributed to the redox changes taking place in the conducting polymer upon exposure to different corrosive media. The effect of a 2-year environmental aging process on the coated samples was analyzed by thermal methods as well as by corrosion studies. An increase in the thermal stability of the blend coatings and a decrease in their conductivity were noticed in the aged samples which were correlated to the crosslinking effect, Table 1. The corrosion protective performance of the coatings remained almost unaffected even after 2 years of aging. The intactness of 8-PANI/CPEAU blend coatings (containing 8 wt% PANI) in 5% HCl, 5% NaOH and 3.5% NaCl exceeded 240 h without any noticeable change, Fig. 9 [109].

**Fig. 12.** Corrosion rate of PANI/alkyd and PNA/alkyd in (a) HCl, (b) NaOH and (c) NaCl. Reprinted with permission from Wiley, Riaz et al., Mater. Corros. 59 (2008) 1–12.

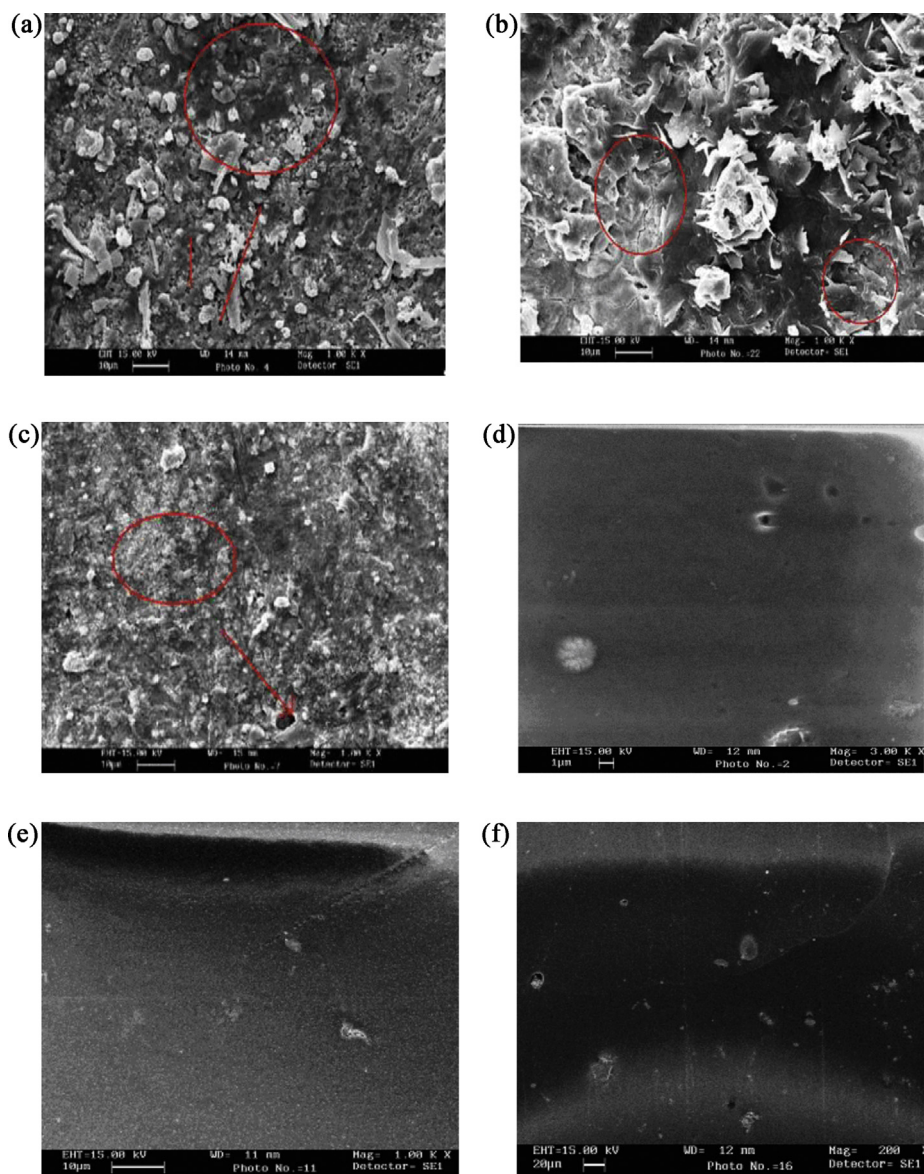


Fig. 13. SEM micrograph of (a) 2.5-PANI/alkyd corroded in 5% HCl (960 h), (b) 2.5-PANI/alkyd corroded in 5% NaOH (960 h), (c) 2.5-PANI/alkyd corroded in 3.5% NaCl (960 h) (d), 2.5-PNA/alkyd corroded in 5% HCl (960 h), (e) 2.5-PNA/alkyd corroded in 5% NaOH(960 h) and (f) 2.5-PNA/alkyd corroded in 3.5% NaCl (960 h). Reprinted with permission from Wiley, Riaz et al., Mater. Corros. 59 (2008) 1–12.

4.2. Polyaniline/alkyd coatings

Alkyd resins are widely used as coating materials due to their economy and ease of application. One of the oldest polymers prepared from triglyceride oils is alkyd resin produced by the esterification of polyhydroxy alcohols with polybasic acids and fatty acids, Fig. 10. Monoglyceride and fatty acids are commonly used to prepare alkyd resins [110]. Additionally, they are to a greater extent biologically degradable polymers because of the oil and glycerol parts. In the former case, the first stage is alcoholysis of the oil by a part of the polyol. Then, the free hydroxyls of the alcoholysis product are esterified by a polyacid. Alkyd resins have high viscosity, good drying and hardness properties. Alkyd resins are categorized based upon their oil length which refers to the oil percentage of an alkyd. Oil length is the important factor, which affects the properties of the final product [110]. A short oil alkyd contains below 40% of oil. When the amount of oil is in the range of 60–40%, it is called medium oil length alkyd and above 60%, the resin is known as long oil length alkyd.

Rout et al. [111] synthesized PANI/alkyd coating by dispersing PANI powder in a medium oil alkyd resin (binder) of molar mass 6.7×10^4 Da. The coating was formulated by incorporating PANI powder as pigment. The conductivity of the coating increased with increase in the solid concentration upto 10–15 wt% of PANI. The corrosion resistance of PANI coated steel was reported to be 10–15 times higher than the uncoated steel. Electrochemical impedance spectroscopy (EIS) study revealed that a continuous charge transfer reaction across the metal–coating interface was responsible for the increase in coating capacitance and decrease in polarization resistance. The potentiodynamic studies showed that the current density significantly decreased in PANI coated steel as compared to bare steel. Nanostructured PANI dispersed soy oil based alkyd resin was synthesized by Sharif et al. [112] by dispersing in 0.5–1.5 wt% PANI into soy oil alkyd. The dispersion of PANI at lower loadings and its intermolecular hydrogen bonding with alkyd was found to remarkably enhance the thermal, mechanical and morphological properties of the nanocomposite coating. It exhibited effective corrosion protective ability due to the formation of a compact

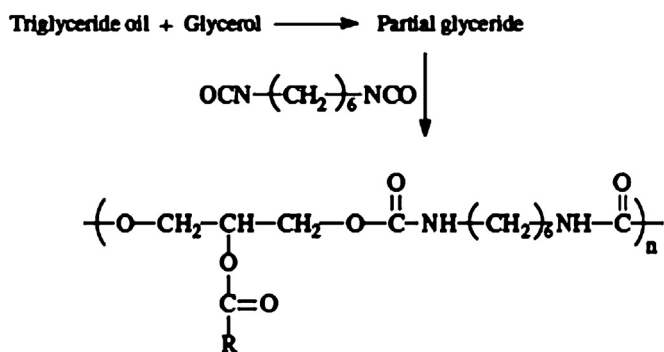


Fig. 14. Preparation of oil based polyurethane.

iron/dopant complex layer at the metal-coating interface which functioned as a passive protective layer until PANI possessed the redox capability to undergo a continuous charge transfer reaction at the metal-coating interface by reducing itself from the emeraldine salt form (ES) to the emeraldine base (EB), Fig. 11 [112]. This mechanism of corrosion protection was found to be highly dependant on the strength of the passive oxide film. As the size of the dopant increases, the adhesion strength of the iron/dopant complex film improves, thereby enhancing the protective efficiency [45,46]. The uniform dispersion of nanosized PANI as well as the higher adhesion of iron/SDS complex film remarkably enhances the corrosion-protective efficiency of PANI/alkyd coatings, Fig. 11.

Jadhve et al. [113] reported the synthesis of nanoparticles of PANI and poly-*o*-anisidine (POA) dispersed alkyd paint formulation for coatings on metal surface (mild steel). The water absorption in the prepared coatings was also studied. The corrosion rate of

polymeric film was determined by weight loss measurement and the surface morphology was examined by SEM. The nano PANI/Alkyd coatings showed considerably higher corrosion protection than the POA/alkyd coatings.

Poly(1-naphthylamine)(PNA) alkyd coatings were synthesized by Riaz et al. [114] and the physicochemical properties were compared with PANI/alkyd coatings, Table 2. The PNA/alkyd coatings were found to show enhanced protection of bare steel in acid, alkaline and saline media as compared to PANI/alkyd coatings. The corrosion rate was found to be maximum in 5% HCl (0.5 mpy), 5% NaOH (0.5 mpy) and 3.5% NaCl (0.3 mpy) for 0.5-PANI/alkyd composite coatings, Fig. 12(a)–(c). Minimum corrosion rate of 0.35 mpy in (5% HCl), 0.25 mpy (3.5% NaCl) and 0.023 mpy (5% NaOH) was observed for 2.5-PANI/alkyd. As compared to PANI/alkyd, PNA/alkyd exhibited much lower corrosion rate. Lowest corrosion rate was observed for 2.5-PNA/alkyd coatings being 0.35 mpy (5% HCl), 0.13 mpy (3.5% NaCl) and 0.13 mpy (5% NaOH). The decrease in the corrosion rate with the increase loading of conducting polymer was attributed to the effective cross-linking of the conducting polymer nano-particles with alkyd at the coating/metal interface which provided higher protective efficiency of the composite coatings as they form well adherent protective films. The ability of PNA/alkyd coatings to act as more effective corrosion inhibitors was attributed to the smaller particle size as well as enhanced crosslinking of the particles with the alkyd matrix. Even after 960 h exposure in 5% HCl Fig. 13(a), the coatings exhibited slight deposition of salt but remained completely intact. The dense and continuous structure was consistent with the corrosion protective ability. The 2.5-PANI/alkyd corroded in 5% NaOH, Fig. 13(b), and 3.5% NaCl, Fig. 13(c) showed crazing and partially localized removal of coating material. Interestingly, even at lower loading of PANI, uniform dispersion and compact structure of PANI/alkyd, enables effective passivation of MS in different corrosive media. The

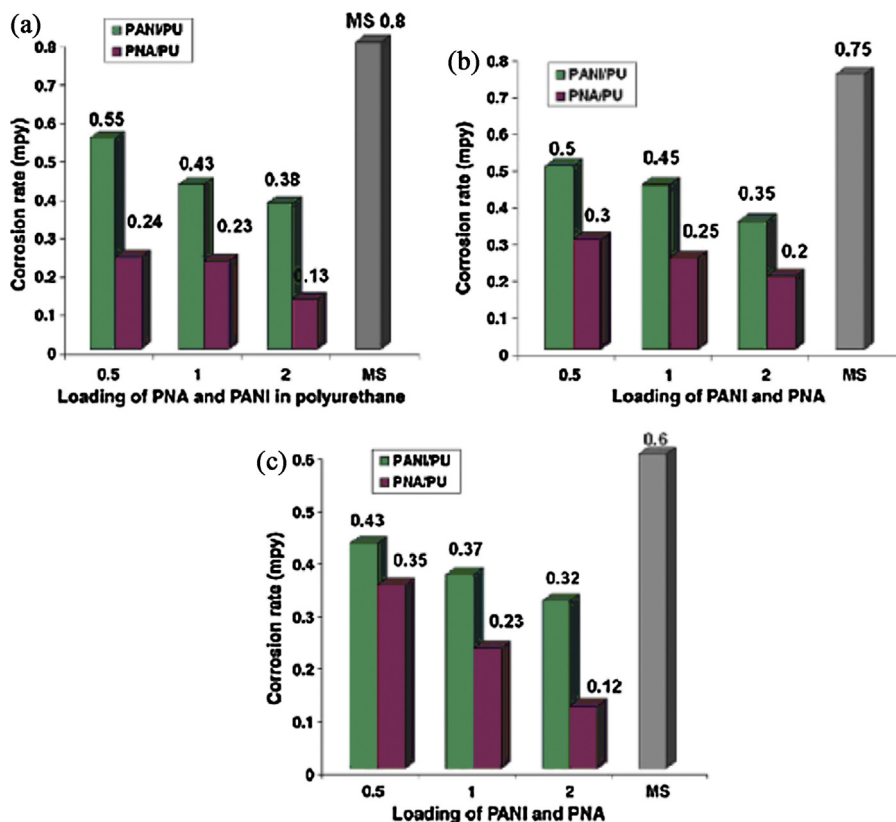


Fig. 15. Corrosion rate of MO-PANI/COPU and CSA-PNA/LOPU nanocomposite coatings in (a) 5% HCl, (b) 5% NaOH and (c) 3.5% NaCl. Reprinted with permission from Elsevier, Riaz et al. [119].

Table 2
Physico-mechanical characteristics of PANI/alkyd and PNA/alkyd coatings. Reprinted with permission from Wiley, Riaz et al., Mater. Corros. 59 (2008) 1–12.

Resin code	Drying time (h)		Scratch hardness (kg)	Impact resistance (lb\in.)	Gloss (at 45°)	Flexibility (1/8 in. conical mandrel)
	Dry to touch (DTT)	Dry to hard (DTH)				
Alkyd	0.5	96	0.2	70	85	FAIL
0.5 PANI/Alkyd	0.25	72	3	70	83	PASS
1.5-PANI/alkyd	0.15	48	3.5	84	82	PASS
2.5-PANI/alkyd	0.15	48	4.0	84	75	PASS
0.5 PNA/Alkyd	0.15	24	4	85	95	PASS
1.5-PNA/alkyd	0.15	24	4.7	90	80	PASS
2.5-PNA/alkyd	0.15	24	5	90	80	PASS

2.5-PNA/alkyd specimen 5% HCl corroded, Fig. 13(d), exhibited the formation of slight blisters pits only at a few places but the coating remained intact even after 960 h exposure. In 5% NaOH, Fig. 13(e), the onset of tunneling was revealed at one side but the rest of

the coating remained intact. As compared to the 2.5-PANI/alkyd in 3.5% NaCl, the corroded specimens of 2.5-PNA alkyd, Fig. 13(f), revealed intact coated surface with slight deposition of NaCl salt at a few places. It was therefore confirmed that PNA/alkyd coatings

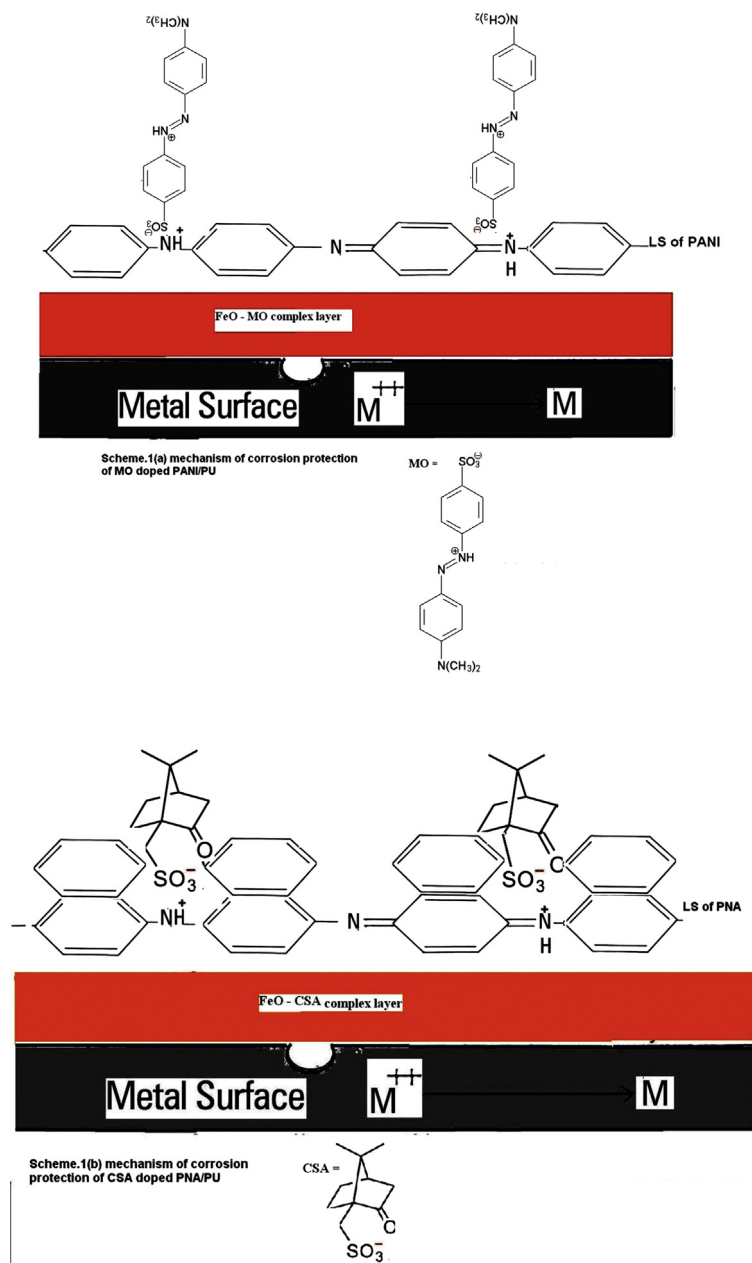


Fig. 16. Mechanism of corrosion protection by (a) MO-PANI/COPU nanocomposite coatings and (b) CSA-PNA/LOPU nanocomposite coatings. Reprinted with permission from Elsevier, Riaz et al. [119].

provided superior corrosion protection as compared to PANI/alkyd coatings

4.3. Polyaniline and poly(1-naphthylamine)-oil based polyurethane coatings

To obtain oil-modified organic solvent-soluble polyurethanes (PUs) (urethane oils), diisocyanates are reacted with hydroxyl-containing oils, such as castor oil, or with partial glycerides prepared from oil and glycerol. The reaction for the preparation of oil-modified PUs from partial glycerides using hexamethylenediisocyanate (HMDI) is generalized in Fig. 14. Polymers based on aromatic diisocyanates (TDI and PBTDI), show good water resistance. Additionally, with greater amounts of diisocyanate in the polyurethane (PU) formulation, shorter drying times can be achieved. Castor oil (CO) is widely used for the preparation of polyurethane. The presence of urethane linkage in the polymer improves adhesion, toughness, water and chemical resistance [115–118]. Castor oil and linseed oil (LO) have been utilized for the formulation of oil-based PU by Riaz et al. [119]. Methyl orange (MO) doped PANI dispersed castor oil polyurethane (COPU) and camphor sulfonic acid (CSA) doped PNA dispersed linseed oil polyurethane (LOPU) coatings were prepared to obtain the conducting nanocomposite coatings. The conducting polymers were added in the wt. ratios of 0.5–2 wt%. The effect of dopant on the anticorrosive performance of the nanocomposite coatings was explored by physico-mechanical measurements and corrosion protective efficiency in highly corrosive media of 5% HCl, 5% NaOH and 3.5% NaCl.

The maximum corrosion rate was found in case of 0.5-MO-PANI/COPU coatings and was found to decrease with the increase

in the loading of MO-PANI in COPU. Minimum corrosion rate was observed for 2-MO-PANI/COPU in 5% HCl (0.38 mpy) Fig. 15(a), 5% NaOH (0.35 mpy), Fig. 15(b) and 3.5% NaCl (0.32 mpy), Fig. 15(c). Variation in the corrosion rate was observed in case of 1-MO-PANI/COPU and 2-MO-PANI/COPU coatings which reflected the higher corrosion protective efficiency of MO-PANI nanocomposite coatings. In case of CSA-PNA/LOPU, the corrosion rate was observed to be minimum for 2-CSA-PNA/LOPU in 5% HCl (0.13 mpy), Fig. 15(a), 5% NaOH (0.2 mpy), Fig. 15(b) and 3.5% NaCl (0.12 mpy), Fig. 15(c). The corrosion rate was found to vary significantly with the increase in the loading of PNA. The enhanced protection offered by MO-PANI/COPU was due to the presence of negatively charged MO moieties (electrostatic repulsion) within PANI film that inhibited permeation of corrosive ions to the metal surface, Fig. 16. The inner part of the film, adjacent to the metal surface, was observed to be covered by a compact iron/MO complex layer whereas the outermost portions of the MO-PANI/COPU film contained PANI doped with MO anions, Fig. 16. In case of CSA-PNA/LOPU, the CSA ions participated in the formation of CSA-iron oxide dopant passivating film. The dense and compact iron/dopant complex layer formation at the metal-coating interface acted as a passive barrier layer as long as the conducting polymer showed the capability to undergo a continuous charge transfer reaction at the metal-coating interface. The presence of an additional fused aromatic ring in PNA was found to enhance the polarity as well as the electrostatic interaction between the polymer coating and the metal substrate resulting in superior corrosion resistance as compared to PANI. The strength of the passive oxide film was also observed to be influenced by the size and charge of the dopant and the dispersion of the conducting polymer in the matrix. As the charge on the

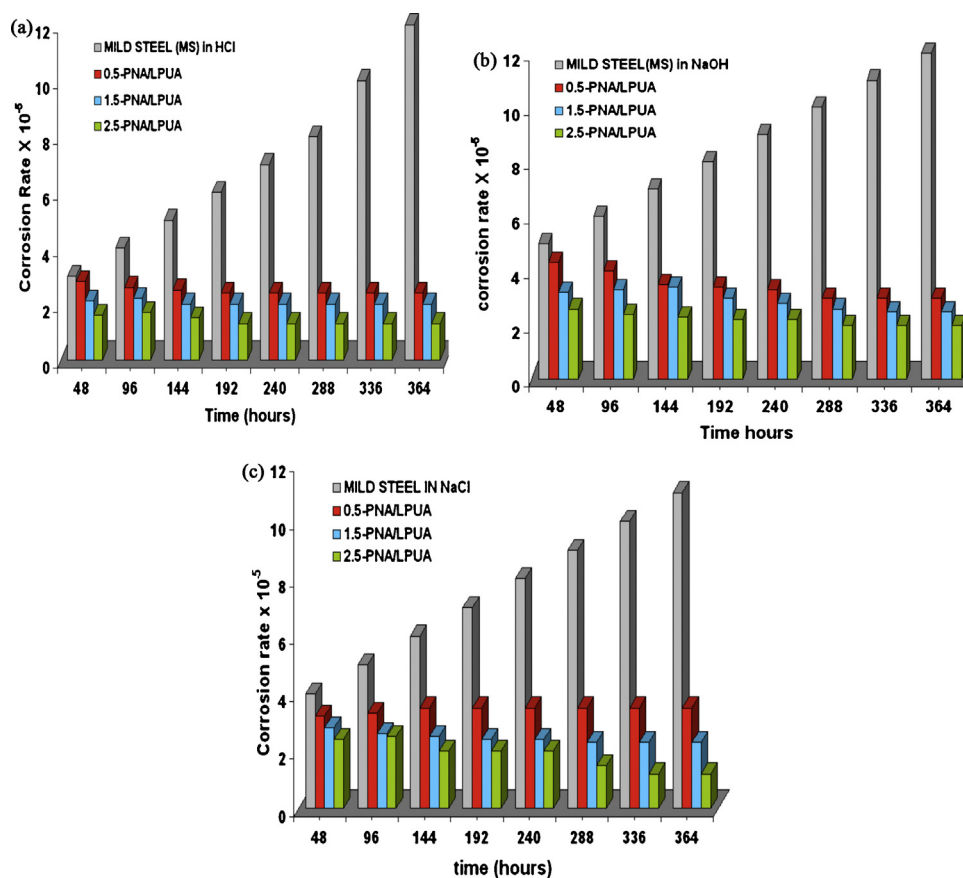


Fig. 17. Corrosion rate of PNA/LPUA coatings in (a) HCl (b) NaOH and (c) NaCl.

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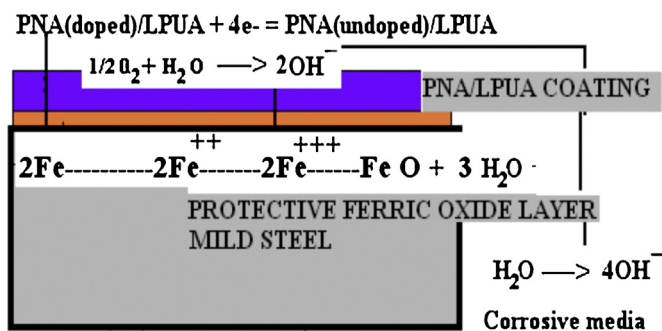


Fig. 18. Mechanism of corrosion protection by PNA/LPUA nanocomposite coatings. Reprinted with permission from American Scientific Publishers, Ahmad and co-workers [120].

dopant increased, the strength of the iron/dopant complex film increased, resulting in high corrosion protective efficiency. Sharif and co-workers [120] investigated the corrosion protective behavior of composites of nanostructured poly(1-naphthylamine) (PNA) dispersed linseed oil polyurethane amide (LPUA) coatings. The combination of the electrically conducting nanostructured PNA with the LPUA was accomplished through different weight percent loadings (0.5–3.0 wt%) of the conducting polymer. The PNA/LPUA nanocomposite coatings were found to effectively passivate mild steel (MS) in acid, alkaline as well as saline corrosive media, which was confirmed by open circuit potential measurements and corrosion rate studies. Formulation of anticorrosive coatings using oil based polymer matrix is economically feasible. The presence of a variety of oil based polymers offers the possibility to design tailored coatings systems that are ecologically safe and exhibit superior corrosion protective performance as compared to the existing commercial formulations.

The corrosion rate of 0.5-PNA/LPUA, 1.5-PNA/LPUA, and 2.5-PNA/LPUA composite coatings on MS in 5% HCl, 5% NaOH and 3.5% NaCl, Fig. 17(a)–(c), exhibited drastic decrease in corrosion rate as compared to uncoated mild steel. The corrosion rate decreased linearly with the increase in the loading of PNA 0.5–2.5 wt% and became constant after 144 h. The corrosion rate was observed to be lower in 5% HCl and slightly higher in 5% NaOH. This was attributed to the dissolution of the free urethane groups of the fatty amide chain of LPUA. This can be explained on the basis that oxygen reduction on the PNA/LPUA coating replenished the charge on the conducting polymer consumed by metal dissolution, thereby stabilizing the potential of the metal in the passive region and minimizing the rate of metal dissolution. PNA mediates the anodic current between the passivated surface and oxygen reduction on the coating. In an acidic environment, conducting form reduces reversibly to base form while in basic environment it is replaced by neutral form (non-conducting). The constant behavior observed after 144 h was correlated to the barrier protection mechanism as shown in Fig. 18 which protects the metal substrate from further attack of the corrosive species.

5. Conclusion

The use of sustainable resource based polymers for the formulation of conductive polymer based nanocomposite is a new area of research for obtaining protective coatings with synergistic properties. The presence of the nanoscale dispersion and low loading of CPs is proven to significantly improve the corrosion protective properties. The good corrosion protective properties of CP based nanocomposite coatings may be considered as energy-saving and environment-friendly materials. The future market of these specialty nanocomposite coatings lies in different industries such

as marine, building, construction, and defense. For industrial and commercial application of these coatings, they must be robust and exhibit long term stability under aggressive corrosive environments. The challenge that still remains is a better understanding of the control of the properties of these nanocomposite coating materials to enhance their shelf life. By solving this problem, eco-friendly coating materials can be developed at a large scale and also at a reasonable cost.

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