

Review Article

RECENT DEVELOPMENTS IN INTRINSICALLY CONDUCTIVE POLYMER COATINGS FOR CORROSION PROTECTION

M. I. Khan¹, A. U. Chaudhry^{*2}, S. Hashim¹, M. K. Zahoor³, M. Z. Iqbal⁴¹Department of Polymer Engineering, Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Malaysia²Chemical Engineering Program, The Petroleum Institute, P.O. Box 2533, Abu Dhabi, United Arab Emirates³Department of Petroleum Engineering, Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Malaysia⁴Department of Polymer Engineering, Faculty of Chemical, Mineral & Metallurgical Engineering, University of engineering and technology Lahore, Pakistan

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Abstract: Intrinsically conductive polymers have achieved demanding interest in the field of corrosion control coatings owing to their conductive ability and also due to the strict environmental regulations on conventional heavy metals coatings. This multipurpose class of polymers has shown to be effective and proven themselves as a potential alternate for these hazardous heavy metal coatings in order to control the corrosion properties of metals or alloys. The basic purpose of this paper is only to highlight the past decade work relating to the efforts made on protection of metals from corrosion using conductive polymers. The categorization of the coatings is based on the techniques used to apply them. This paper will also discuss the synthesis and prospective applications of these coatings depending on their different formation techniques.

Keywords: conductive polymer, corrosion, coatings

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1. Introduction

The 2000 Nobel Prize in chemistry shared by Heeger, Macdiarmid, and Shirakawa for the discovery and progress of intrinsically conductive polymers (ICPs hereafter) is a hint regarding to their prospective applications. The paper published in 1977 by Shirakawa and co-workers, illustrates that the polyacetylene on doping with iodine can show higher order of conductivity up to billion times [1]. Before this discovery, carbon based polymers were famous for insulating and frequently used in the electric industries. But as a consequence of development in this new class of 'synthetic metals', having properties of metals, polymers and semiconductors, they are now being used in numerous applications [2–10] as shown in Figure 1.

ICPs belong to those classes of polymers which have π -conjugation along the polymer backbone. The partial oxidation or reduction possibility of ICPs through doping has made them the most distinctiveness materials. During the process of doping if the electrons are added to the main structure then it will be called n-doped otherwise usually p-doped states are found in which electrons are removed. Also non-conducting forms of ICPs exist. In case of Pani, out of five, four states Leucoemeraldine, Emeraldine and Penigraniline are nonconducting, while Protonated Emeraldine is the only conducting state, Figure 2 shows the chemical structure of these different forms of polyaniline [11, 12].

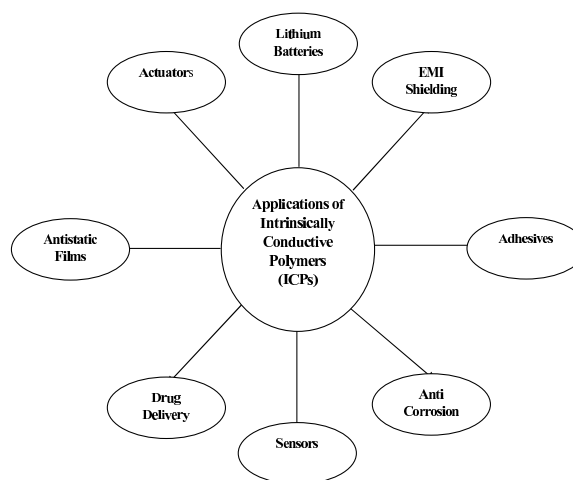


Figure 1: Applications of conductive polymers

In following paper main three common industrially applicable families of ICPs used for corrosion protection are discussed i.e. Polyaniline, Polypyrrole, Polythiophene and their derivatives. Many comprehensive and descriptive review articles have been published concerning the synthesis, blends, composites of ICPs used for different applications [11, 13–15]. The basic purpose of this paper is to overlook the progress related to conductive polymers used as anticorrosion coatings on metals in last decade.

*Corresponding author, Email: chusman@pi.ac.ae,
Phone: +971-56-742-3183

Nomenclature

AP	Anodic Protection	MS	Mild Steel
AR	Acrylic Resin	Ni	Nickel
Cr	Chromium	OA	Oxalic Acid
CS	Carbon Steel	OCP	Open Circuit Potential
CV	Cyclic Voltammetry	P	Phosphate
DBSA	p-dodecylbenzenesulfonic acid	P3HT	Poly(3-hexylthiophene)
EB	Emeraldine Base	Pani	Polyaniline
EIS	Electrochemical impedance spectroscopy	PGF	Polyaniline glass flake
EP	Electropolymerization	Ppy	Polypyrrole
ES	Emeraldine Salt	PS	Potentiostatic
Fe	Ferrous	PTh	Polythiophene
GF	Glass Flake	PU	Polyurethane
GS	Galvanostatic	Zn	Zinc
ICps	Intrinsically Conductive polymers		

2. Protection Mechanism

Corrosion phenomenon refers to the electrochemical or chemical reaction between metals or metals alloy with surroundings which leads towards their deterioration such as embrittlement, alteration in the color, de-alloying etc.

Generally, during corrosion the oxidation of metals and reduction of other groups e.g. oxygen, hydrogen ion or water occurs. The most favourable surroundings may be atmospheric humidity, offshore salt spray, acid rains, synthetic solutions and natural waters. Many categories of corrosion have been reported in the literature e.g. localized or pitting corrosion appeared as voids, corrosion due to presence of hydrogen, galvanic corrosion owing to the presence of comparable more potential metal or nonmetallic conductor in a corrosive electrolyte, corrosion-erosion due to abrasive nature of fluid, intercrystalline corrosion, de-alloying, and interdendritic corrosion [11].

Consequently, various protection mechanisms using ICps have been proposed. Spinks et al. [13] presented a review paper in which the classifications of ICps' coatings were based on their protection mechanisms. The reported mechanisms were barrier protection, corrosion inhibitors, anodic and cathodic protection. Barrier mechanism deals with the disconnection of metal surface from the corrosive environment such as coatings of surfaces with paints and films etc. In case of corrosion inhibitors, the purpose of the applied coating is to slow down the rate of corrosion due to formation of monomolecular layer on the surface. It was reported that this phenomena refers to the adsorption of ICps on the surface which endorses the adhesion and hence improved corrosion protection. Anodic protection is a technique used for passivating of the materials owing to the formation of oxide layers which change the electrode potential in passive region. During electropolymerization of the ICps this method is used for easy deposition of ICps, depending upon the material and electrolyte solution used. It was also reported that the process of anodic and cathodic protection through ICps occur simultaneously on the surface of metals i.e. at the same time, ICps reduce and oxidize on the metal surface [13].

3. Conductive Polymers used as Anticorrosion Coatings

Conductive polymers are one of their own kinds among the class of polymer owing to their electrical conductivity, low cost, fusibility, stability, good optical properties, non-toxic, low density, ease in synthesis and doping primacy [14–21]. Along with copious applications of ICps [11, 14, 15, 22] these are particularly used for corrosion protection since their discovery for this purpose [23, 24]. ICps found in different forms i.e. composite or blend, depend upon the matrix system, i.e. if incorporated component is a polymer then it will be a blend otherwise preferably composite [7, 15]. Besides developing the blends, the derivatives [25–27] and different forms i.e. EB or ES in case of Pani [28, 29] are already developed. Polyaniline, Polypyrrole Polythiophene and their derivatives have gained much consideration. The interest in Pani grew starting from 1960s (Mohilner), owing to its remarkable electrical properties and mostly used among all the ICps in terms of applications [15]. Polypyrrole and Polythiophene come under the class of poly (heterocyclic) [11] and contrary to Polyaniline are being less used because of cost, insolubility and synthesis restrictions, see Figure 3 for general heterocyclic structure.

The ICps coatings on metals can be performed by using various techniques (Figure 4) to improve the performance and according to desired properties, such as films can be electropolymerized from suitable solution in electrochemical cells, pigments of ICps mixed with conventional paints, spreading via solution casting methods etc.

3.1. Electropolymerized coatings

Electrodeposition of conductive polymers on active metals through acid medium is a tricky process due to dissolution of metals. This fact refers to the more passivation potential of active metals. Also ICps are insoluble in common solvents used for anticorrosion protection purposes. These problems can be overcome by Electropolymerization of ICps from a solution of electrolyte and monomer. But, at the same time it is compulsory to use such experimental conditions

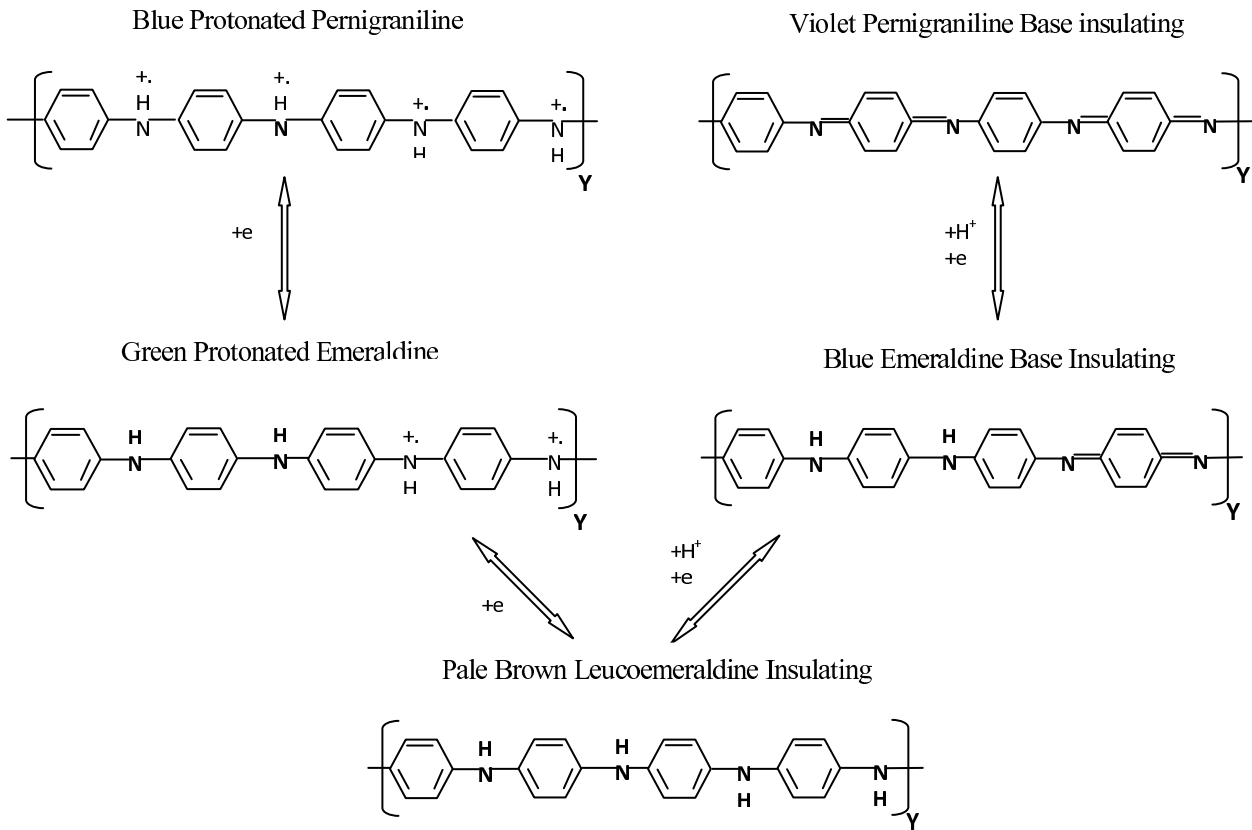


Figure 2: Chemical structure of various forms of Polyaniline

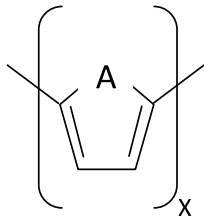


Figure 3: General Chemical Structure of Heterocyclic Conductive Polymers

which oxidize the monomers and polymerize them, without the dissolution of metals. During electropolymerization, monomer and solvent are added to an electrochemical cell, commonly having three electrodes i.e. working, reference and counter electrode. The solutions for electropolymerization are mostly used with different aqueous acids.

The conditions to improve the corrosion resistance, solubility, adhesion, brittleness, wear resistance, hardness and processibility promoted alternatives of intrinsically conductive polymers i.e. the occurrence of substituent in the skeleton of ICps, use of a various electrolytes and incorporated dopants, various synthesis conditions and different electropolymerization techniques. Following are the techniques used to carry electropolymerization of ICps.

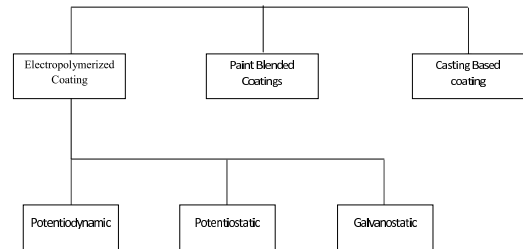


Figure 4: Coating Techniques for Intrinsically Conductive polymers

3.1.1. Polymerization using Cyclic Voltammetry Technique

The electropolymerization of ICps is mostly carried through cyclic voltammetry technique. In this method, the electrode potential is driven between the limits of monomer oxidation and reduction of polymerized ICps [15].

Adhesion of films on metals has major consequence on the protection behavior of coatings and generally depends upon the interfacial parameters such as passive interface and nature of passivator. Hossein, performed the electropolymerization of compact hybrid Ppy-Phosphate on mild steel from oxalic acid medium and demonstrated that electrosynthesis process frequently affected by the redox potential of anion on the electrode surface, ionic charge and size. The dispersed phosphate anion on the interface improved the protection be-

havior [30]. A well adherent and uniformed undoped Pani coating was electrodeposited on mild and stainless steel from phosphoric buffer solution of pH higher than 1.1. It was observed that the E_{corr} was transferred towards noble values due to development of passive film consequence of deposition of phosphorous layer on stainless and mild steel, performed as corrosion inhibitor [31]. Kralji, used phosphate and sulphate solution for electropolymerization of Pani on steel samples having different composition of Chromium. It was suggested better protective properties of Pani layers on stainless steel can be obtained through phosphate solution [32].

The Potentiodynamic EP of ring substituted aniline such as o-toluidine, m-toluidine, o-anisidine and o-chloroaniline was done on passivated iron. The general efficiency of all the derivatives in terms anodic-protection was less than non-substituted Pani. Although three methods were used i.e. cyclic voltammetry, potentiostatic or galvanostatic but the oxidation-reduction response of the polymer to cyclic voltammetry was very good for electropolymerization [33]. A comparison was made between Polyaniline and Poly(o-methoxyaniline) electrodeposited on different grades of stainless steels from 0.1 M H_2SO_4 . It was demonstrated some similarity between above mention coatings in terms of corrosion protection [34]. Shah used OA and electropolymerized poly (N-ethyl aniline) coating onto Al alloy Al-2024 through cyclic voltammetry. The passivation of alloy was proposed by using dc polarization studies [35]. Further, poly (N-methylaniline) was electropolymerized using potentiodynamic, galvanostatic and potentiostatic techniques on mild steel using aqueous oxalic acid solution. The film which was deposited using potentiodynamic with potential region between -0.5 and 1.0 V, at a scan rate of 10 mV/s, demonstrated good adherent properties. The anticorrosion behavior was fine in solution containing neutral chloride anions [36]. According to Shinde, the coating of poly (2, 5-dimethylaniline) electropolymerized from oxalic acid by means of galvanostatic technique, was not efficient enough to protect the low carbon steel [37]. In another attempt, poly (2, 5-dimethylaniline) was electrodeposited on low carbon steel from the aqueous salicylate solution using cyclic voltammetry technique. The sodium salicylate solution was recommended because it forms non-conducting passive layer without impeding the oxidation process of monomer. The overall performance of the coating was excellent [38]. Again a successful effort was made for the protection of copper against corrosion and dissolution by electrodeposition of Poly (o-anisidine) a derivative of Pani, through cyclic voltammetry in aqueous solution of sodium oxalate results. The resulted film was efficient enough in decreasing the rate of corrosion by 100 times compared to uncovered copper in 3% NaCl. The X-ray diffraction analysis described passivation of copper as a formation of polycrystalline $Cu_2O \cdot H_2O$ interface and proved that sodium oxalate as a appropriate means by making early stages copper oxalate interface, which was helpful for well adherent and homogeneous Poly(o-anisidine) layer on Copper [39]. Bereket and co-workers, make a comparative study between the electrodeposited films of Pani and its

derivative such as poly (2-anisidine) and composite of both i.e. poly (aniline-co-2-anisidine), poly (2-iodoaniline), poly (aniline-co-2-iodoaniline) and then poly(2-chloroaniline), poly(aniline-co-2-chloroaniline) on 304-stainless steel from solution of tetrabutylammonium perchlorate/acetonitrile solution containing perchloric acid and tested in 0.5 M HCl solution. There was a resemblance between Pani and poly (2-anisidine) in terms of corrosion protection but the film of poly (aniline-co-2-anisidine) was proved to be least stable corrosive solution. In case of poly (2-iodoaniline) and poly (aniline-co-2-iodoaniline), the overall efficiency of the coatings was greater than 75% after 48h in HCl solution. But the coatings were inferior as compared to Pani in terms of protection. The role played by derivatives coatings was only prevention of cathodic reaction at metal/substrate interface contrary to Pani which acted also acted as a passivator. In cases of using poly (2-chloroaniline), poly(aniline-co-2-chloroaniline), it was found that poly(2-chloroaniline) only provide barrier properties as compared poly(aniline-co-2-chloroaniline), which offered anodic protection and barrier properties comparable to Pani [40–42].

Tuken, showed the possibility of direct electrodeposition of Pani through acetonitrile- $LiClO_4$ on mild steel because it could not be done due to lack of passivation of electrode so first he coated very thin coating Pani and Ppy from oxalic acid using cyclic voltammetry as a primer coating and then further developed Pani coating from acetonitrile- $LiClO_4$. The maximum efficiency was accounted as 97% by PPy/Pani coatings combination at the end of total time comprises i.e. two hundred and forty hours in 3.5% NaCl solution [43]. Similarly, the major problem of electrodeposition of PTh on oxidizable metals is its high oxidation potential value. So, PTh film was electropolymerized through solution of 0.15M $LiClO_4$ containing acetonitrile medium on Ppy modified mild steel electrode. The film exhibit good anticorrosion properties during immersion in 3.5% NaCl solution [43].

Aluminum has very vast applications particularly in aerospace industries. electropolymerization of ICPs Aluminium is hindered by the formation of oxide-hydroxide protective layer. Pani was deposited on anodic pretreated AA1050 aluminium from 0.5 M H_2SO_4 solution using cyclic voltammetry. Aluminum was first subjected to anodic galvanostatic activation in aniline containing HNO_3 solution to create pores and pits so that more dense and quick formation of film can be achieved [44]. Similar method was used for EP of Ppy on Aluminium alloy from H_2SO_4 solution by using different techniques i.e. CV and PS techniques. It was postulated that film produced by CV was thicker than PS method. But no change in the protection behavior was seen as compared to bare metal [45].

The modifications can be done during electropolymerization of Cps so that obtained films have good physico-chemical properties and anticorrosion properties. These changes could be achieved by varying the synthesis conditions or surface modifications. Ozyilmaz and coworkers studied the anticorrosion effect of Pani as a top coat electrodeposited using 0.15M of aniline monomer from sodium

oxalate, 0.1 M aniline from OA, 0.1 M aniline from 0.2 M p-toluenesulfonic acid solutions on 1 μm Ni plated copper and 0.1 M aniline from oxalic acid on 1 μm Ni plated mild steel using cyclic voltammetry method. Nickel coating also showed protection against corrosion but increment in porosity was continuous. Pani showed catalytic effect on the formation of oxide layers preventing the increase in porosity on nickel surface in 3.5% NaCl solution acted as barrier and this oxide layer offers extended period of protection for copper and mild steel [46–49]. The author also characterized the coating structure and corrosion performance of Pani on stainless steel through electrochemical impedance spectroscopy by electrodeposition under two different potential regions using cyclic voltammetry in oxalic acid solution. It was observed that protection of Pani coating can be improved by using suitable synthesis conditions and suggested appropriate potential range was 0.25–1.00V [50]. Further, they observed the phenomena of corrosion by electropolymerization of Pani on copper from 0.2M sodium oxalate solution. The performance of the coating in terms of corrosion protection was tested in NaCl solution. The coating acted as a barrier and supported the protective films of copper oxides [51]. Also, he studied the effect of different scan rates used for the electropolymerization of Pani on stainless steel from oxalic acid solution. It was suggested that the morphology of the Pani can be changed prior to variation of first cycle and film growth scan rate and films obtained at low scan rate was efficient. Using same approach, PTh film was electrodeposited on 1 μm Ni plated mild steel from (ACN-LiClO₄) having 0.1 M thiophene showed good protection properties as compared to single coated Nickel MS [52]. Using same approach Tuken and coworkers, electropolymerized Ppy film on graphite modified MS electrode from solution of OA. The hydrophobic nature of the graphite was supportive and helpful in enhancing the corrosion resistance as compared to single use of Ppy on MS during immersion test in NaCl solution [53, 54].

The improvements in the conductivity and thermal stability in Pani films were made by using multi-walled carbon nanotube/polyaniline composites. Different loadings of multi-walled carbon nanotube were used in aniline monomer and electrodeposition took place on platinum disk through cyclic voltammetry method from 0.5 M H₂SO₄ having 0.325 M aniline dissolved MWNTs [55].

3.1.2. Polymerization using Potentiostatic Technique

Potentiostatic electropolymerization of ICps occur under constant voltage. Bernard described protection of iron through the passive layers form between the interface of Pani and iron through electropolymerization of Pani in phosphoric acid solution. This method was free from any type of casting or blending of polymer [56]. Herrasti, showed by means of a comparative study on hardness of Pani, Poly-o-toluidine and their composite electrodeposited on stainless steel. Microhardness measurements revealed the trend of hardness increased from Pani to poly-o-toluidine to composite [57].

Using different concentration of aniline in 1.0 M phosphoric solution, potentiostatically and chemically deposition of

phosphate doped Pani occurred on 304 stainless steel. The decrease in corrosion current was suggested due to the excellent film adherence and breaking potential up to 1V indicated good pitting corrosion in 3% neutral NaCl solution [58]. Herrasti, electrodeposited the Pani and Ppy bilayer system on mild steel from 0.3 OA using different techniques and in addition to it Zn microparticles were also electrodeposited in 0.01M ZnSO₄ solution using constant potential -0.7V, which played role as anodic inhibitor and improved the corrosion protection of layers. The best combination proposed was Pani/Ppy deposits in solution of NaCl and Na₂SO₄ [59]. Similarly, zinc particles were electrodeposited from solution of 0.2M ZnSO₄ using static potential of -1.20V on mild steel containing previously deposited Pani film. Improvement in the protection behavior was seen because of the deposited zinc particles which increased the conductivity and lowered the permeability of Pani film. The barrier properties of the Pani-zinc particles film was improved because of sacrificial activities of zinc due to corrosion, as a result stable products produced at the interface [60].

The synergism outcome of Pani coatings can be acquired via mixing with other organic coatings because thin films of coatings have limited protection behavior. A comparison was made between electrically deposited Non-pigmented epoxy, Pani and Pani/epoxy coatings on mild steel. In Pani/epoxy system, the supplementary role of the Pani was as a barrier to improve the corrosion behavior and the coating system was superior among others [16].

3.1.3. Polymerization using Galvanostatic Technique

Galvanostatic technique used constant current for synthesis of ICps. Ding, prepared Pani composite with Thiokol rubber and then compared it with Pani as a coating in HCl and NaCl Solution on mild steel. The GS method was used for co-electropolymerization from non-aqueous solution of aniline, acetonitrile, trifluoroacetic acid (TFA), trichloroacetic acid (TCA), thiokol rubber. The experimental work confirmed that composite coating has additional adhesion and corrosion inhabitation rather than Pani alone [61, 62]. Pawar and Koinka in two separate papers described the phenomena of Poly (o-anisidine) galvanostatic deposition on low carbon steel from aqueous solution of oxalic acid and analyzed the effect of different temperature range i.e. between 0 and 40°C on electrosynthesis. The deposition process consist of three stages i.e. induction time for synthesis, passivation through polycrystalline FeC₂O₄ · 2 H₂O, dissolution of interface followed by development of film but at 40°C no layer occurred using current density 0.66 mA/cm². So, change in temperature showed no considerable effect if the current densities were large but at low densities of current temperature was inversely proportional to induced time. At 40°C, the main obstacle in the development of coating on low carbon steel was owing to the non-dissolution of the passivated interface which should occur at third stage [63, 64].

Similarly, pretreated electrodes have shown effects on electrodeposition of ICps. This phenomenon was studied by Reut, and compared different pretreated techniques i.e. mechanical and chemical. Chemical treatment was done in

10% HNO_3 solution whereas wet abrasive paper was used for mechanical treatment. Ppy was electrodeposited on mild steel from solution of Ppy and sodium p-toluenesulphonate. It was also reported by using Potentiodynamic polarization technique that in case of chemically treated Ppy coated electrodes, maximum shift of the corrosion potential towards positive values were seen. It was also suggested that the passivation of iron is due to the formation of iron nitrides during treatment [65].

Shinde and Patil had attempted to find the alternatives for Pani by means of substituted anilines and reported in two separate papers regarding the electropolymerization of (2,5-dimethylaniline) and (2,5-dimethoxyaniline) monomers from solution of 0.1 M oxalic acid on low carbon steel respectively. The experimental work showed that the surface morphology of coating depend on applied current density, while using Poly (2, 5-dimethoxyaniline), ES form was found whereas PB form was found in Poly (2, 5-dimethylaniline) in case of at low current density. The mixed form of ES and EB in Poly (2, 5-dimethoxyaniline) contrary to Poly (2, 5-dimethylaniline) where mixed forms were present i.e. (PB) and (ES) at higher current density. Both of them found that oxalic acid is proper means of electropolymerization and suggested three stages of growth behavior regarding to the development of films on low carbon steel i.e. dissolution of metal surface while formation of iron oxalate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) interface, secondly passivation and finally polymerization of monomer on surface owing to the dissolution of interface. This trend is similar to the previous work done by the same author and coworkers [37, 39, 66].

Multilayer coatings of conductive polymer provide synergism. Pani and Ppy galvanostatically deposited on carbon and 304L stainless steel using different combinations i.e. Pani/Ppy, Ppy/Pani and composite coatings. The polymerization processes were taken from solutions of 0.1 M aniline in 0.05 M H_2SO_4 for stainless steel, 0.3 M oxalic acid for carbon steel and 0.1 M pyrrole in acetonitrile and 0.5M LiClO_4 . The resulting combinations on carbon steel were shown no improved performance in NaCl solution as compared to single use of Pani but enhancements were seen in case of stainless steels. It was suggested that corrosion factor can be reduced by 2000, if the combination is Ppy underlayer and a Pani top layer which provided closely packed morphology and acted as electronic and chemical barrier rather than physical barrier [67].

The incorporation of pigments in Cps matrix during electrosynthesis on metals showed improved protective behavior as compared to single use. The protection mechanism may be attributed to the ion exchange, barrier layers, or electrochemical performance of these pigments. Using zinc phosphate as a pigment, film of Ppy was electropolymerized on AISI 1010 steel while stirring the electrolyte solution of sodium salicylate at rate of 15 mL s^{-1} to achieve significant incorporated quantity of zinc phosphate pigment in matrix. The signals from X-ray photoelectron spectroscopy indicated that zinc phosphate dispersed in matrix in two distinctive forms i.e. as counter ion and pigment. The composite coating demonstrated enhanced anticorrosion properties

as compared to alone phosphates layers [68].

3.2. Paint Blended Coatings

The additional approach to achieve the synergism effect of mechanical and physical properties of conventional polymer and electrical properties of conductive polymers is blending of ICps with resins such as epoxy or acrylic. Although electropolymerization is a superior technique but limited in terms of coating on large structures and mechanical properties so to improve and increase the application of ICps at industrial level blending of electroactive and conventional polymer coatings is done .

A comparison was made between ES and EB with different dopants used in topcoats of epoxy and polyurethane. The immersion test was carried out in 3.5 % brine solution. EB form of Pani was proved to be superior to ES which was strongly dependent on the type of dopants [69]. Blends of protonated Pani and Poly (o-ethoxyaniline) with different acids in dissimilar paint based coatings were prepared and applied on iron substrates. Among all the combinations, the best results were shown by the HNO_3 and HBF_4 doped Poly(o-ethoxyaniline) mixed in water soluble epoxy protective coatings [70]. Pani containing coatings can be modified and develop according to necessity. Different choice of protonating acids and forms of emeraldine base with epoxy coatings on mild steel showed better protection than coating based on conductive Pani in NaCl solution [71].

Intrinsically conductive polymers have found application in marine coatings as an anti fouling agent. The cost is the main problem for the selection of solvents for different form of Pani related to processing because large area is required for coatings purposes. A new technique was employed for the processing of EB by dissolving in optimum ratio of tetraethylene pentaamine. This solvent is useful for curing of epoxy resin. It was reported that only 1% weight of EB is effective for anti corrosion [72]. Ocampo, made a comparative study by using different types of coatings for marine purposes including derivative of PTh applied on naval steel St F111 for marine purposes. Poly (3-decylthiophene-2, 5-diyl) regioregular was the polymer mixed with different 4 commercial paints. The coatings have good, adherence, smoothness and barrier properties and at 0.2% w/w percentage of incorporated polymer was proven to be effective[73].

Samui and coworkers, used epoxy coatings having HCl doped Pani on mild steel with no use of topcoat. It was recommended by using tests such as Humidity exposure, seawater exposure salt spray, Potentiodynamic measurement, water vapor permeability, that lower Pani-HCl loading gives good results as compared to higher loading. The adherence properties of the paints were found to be good but the stability of HCl as dopant was suspicious to avoid partial cathodic and anodic reaction. In the same way, instead of using HCl, Dioctyl phosphate doped Pani Pigment was mixed with different types of resins and applied on mild steel panels. Although the adhesion strength was not appreciable and it decreased with a increased in Pani-DOPH loading due to increase in Pani-DOPH/Ep interaction which effect the polar interactions but the best result was shown by Pani-DOPH (5

phr)/epoxy coating, examined after 24 months Field exposure near sea [74, 75].

Similarly, the barrier properties of Pani film can be enhanced by introducing nano-particles of fillers such as zinc. Patil, used the nano zinc oxide particulates and Pani doped with dodecyl benzene sulfonic acid as additives used in system of poly (vinyl acetate) as a major matrix applied on steel substrates. Cyclic voltammogram showed that the flow of current through system was insignificant owing to the addition of nanoparticles referred to barrier properties of the film was increased. The main thing was that the glossy and shiny surface indicated the improvements due to the nanoparticles [76].

The authors have successfully made a comparison between the epoxy coating based on strontium chromate and Pani, applied on magnesium alloy. Similarly they used phosphate doped Pani mixed with acrylic resin based paint, applied on magnesium alloy ZM 21. The coating was proved to be having excellent protection behavior. The coating has 100 M V cm^2 resistance value and impedance values increase with contact time in NaCl solution [77]. Further, Azim and coworkers, showed the protection behavior of epoxy coatings containing chemically synthesized Pani-Amino trimethylene phosphonic acid as a pigment applied on mild steel. It was noticed that protection performance of coatings was growing with time period due to the phenomena of passivation [78]. The protection behavior of undoped and doped forms of Pani with p-toluene-sulfonic, camphor-sulfonic, dodecylbenzenesulfonic acid was observed using epoxy resin as a topcoat on 3003 Al Alloy in 3.5% NaCl and 0.1N HCl. The coatings were transmitted through solution casting method and better behavior was shown by undoped Pani in neutral NaCl. The cause of superior performance of, Pani doped with p-toluene-sulfonic acid among other mentioned doped forms was due to the presence of undoped Pani near PANI- p-toluene-sulfonic acid /Aluminium interface [27].

Li using the method of emulsion polymerization produced stable nano-polyaniline waterborne latexes. The coatings were obtained by drop wise casting on iron and after drying covered with acrylic resin as top coat. The advantage of this coating was that it can be applied directly and shown good anticorrosive properties [79]. The insoluble, infusible and adhesion limited behavior of ES form of Pani (para-toluenesulphonic acid doped Pani) can be solved by using dispersion method in nonconductive polymer. Williams studied the cathodic disbandment by using Pani-PTS pigment blended with polyvinylbutyral (PVB) binder using solution of ethanol on zinc substrates. Scanning Kelvin probe method was used to determine the kinetics of delamination of coating whereas secondary ion mass spectrometry and atomic force microscopy for oxide film growth on interface. These coatings were effective in cathodic disbandment [80]. Tiitua and coworkers, used novel method of preparation of cross linked composites coatings of Non-conducting Pani i.e. EB with epoxy resin. A comparative study was made on anticorrosive properties showed by coatings prepared using different methods. In the first method EB form dissolved in

aminic hardners e.g. N,N,N',N'-tetrakis(3-aminopropyl)-1,4-butanediamine and trimethylhexanediamine and then upon adding diglycidyl ether of bisphenol-A as a epoxy resin, the mixture become crosslinked. In second method EB form was first mixed in epoxy resin and then cured upon adding trimethylhexanediamine. The main advantage of this process was the selection of solvent, which played the role of solvent for EB and hardener for epoxy coating. The coatings were applied on steel panels and subjected to immersion test in 3.5% NaCl solution and electrochemical impedance studies. It was observed that coatings produced using first method were more effective than from other method [81]. The anticorrosion properties of Pani Pigment containing coatings with vinyl resin as a binder applied on carbon steel substrates were studied by using electrochemical impedance spectroscopy in NaCl and HCl solutions. The decrease in corrosion rate after 5 days was observed due the formation of protective passive layer on iron surface. The protection behavior of coatings in acidic media was more than that in neutral media. Further, similar procedure was done and observed in cement extract of pH 13.0. The results showed that Pani pigmented with paints passivate the steel and have capability to protect metal in basic media [77, 82, 83].

Laco and coworkers, made a comparative studies between coatings of alkyd resin modified with 0.2, 0.4 and 0.6% (w/w) of polyaniline (emeraldine form which is insulating and blue in color) and thermoplastic polymers such as poly(vinyl chloride-co-vinyl acetate) 90/10 copolymer, phenoxy resin and blend of poly(methyl methacrylate) with poly(butyl methacrylate) applied on carbon steel substrates. The validity of accelerated test in laboratory was also evaluated by comparing with field tests in urban and marine environment in terms of equivalent time. Different mechanisms were proposed for the protection behavior of coatings, and alkyd coatings containing Pani were proved to be better. Also, it was suggested that laboratory test can be taken as a replacement of field tests [84]. The primer containing nanostructure fine dispersed Pani at low concentration i.e. 1% manifested good anticorrosion properties in different application [85]. Similarly, by using different loadings of Ppy powder containing acrylic paint was applied on magnesium alloy. The effect on anticorrosion properties of different fraction of Ppy loading in paint were observed through salt spray test, OCP, Potentiodynamic scans and EIS. It was suggested that 10 parts by weight of Ppy content in paint is favorable [86].

Titanium dioxide is an important pigment used in paints for different application such as paint whitening etc. Sathiyarayanan, used TiO_2 during the oxidative polymerization of aniline monomer and mixed with acrylic resin applied as primer on steel and magnesium alloys. The coated samples shown higher anticorrosion properties as compared to Pani and conventional TiO_2 pigment containing coating. The formation of oxide layer is responsible for the protection behavior of Pani. In same way, they used polyaniline- Fe_2O_3 composites prepared in different ratio as a pigment in AR applied on steel. Experimental work showed that composites prepared in 1:1 were better [87-90].

Besides, miscellaneous application of nanotechnology, it has also gained importance in anticorrosion coatings [91]. The ability to improve the mechanical and physical properties of Pani coatings loadings with nanoparticles has been proved to be effective [92]. The superior corrosion protection in EB form of poly(o-ethoxyaniline) on cold roll steel was reported, by using it as a composite with layered montmorillonite clay nanoparticles. The preparation was done via in situ oxidative polymerization. The better results were shown that up to 3% of clay loading [93]. Abu showed the anticorrosion ability of mono-dispersed Pani coated Polystyrene particles when used for protection of iron. The reduced form of film showed inferior corrosion protection properties than oxidized form in HCl and NaCl solution. Aniline was polymerized on the surface of PS particles in suspension. The advantage of this work was the possibility of growth of bulky anticorrosive nature film by painting iron with the PANI-PS aqueous suspension [94].

Composites based on glass flake and epoxy coatings are highly anticorrosive in nature and vastly used in marine coatings. The effectiveness of these types of coatings were reduced due to the presence of defects such as pinholes. Also Pani is known for its protection ability in pinholes. Hence, oxidative polymerization of aniline was performed in the presence of glass flakes and used as a pigment with epoxy based primer on mild steel. A comparison was made between PGF and GF based epoxy coatings. EIS studies shown that there is significant decline in the protection behavior of Pani Glass flake coating immersed in 3% NaCl solution for 50 days. XRD analysis showed that crystallinity of Pani was unaffected and coating was found superior to conventional GF coatings [95].

Since Pani has been proved as a successful replacement of toxic heavy metals used in protective coatings but still petroleum based polymers coatings are in action. An investigation of complete environmental friendly coating comprised of nano structure Pani and Soya oil alkyd was done. Different loading of Pani nanoparticles were mixed with alkyd xylene solution and applied on steel panels. Morphological analysis revealed that a homogeneous, dense and uniform coating was obtained. Higher values of Physico-mechanical testing and decrease in corrosion rate were seen with increases in Pani loadings [96].

3.3. Casting based Coatings

A casting of ICPs includes the process of dissolving a polymer in a suitable solvent and then spreading it over a substrate. The film of polymer can be obtained through evaporation of solvent. The main problem of this process is suitable solvent requirement to dissolve ICPs.

Polyaniline was transmitted from 1-methyl-2-pyrrolidone (NMP) and stabilized the emeraldine base solution, over iron substrate. It was revealed from electrochemical measurements that EB form of polyaniline has better protective properties as compare to PVC coating in NaCl 3.5% w/w solution. In addition, the EB form improved to some extent of protection in corrosive atmosphere [28].

Various attempts are being made to solve the unprocessable and soluble behavior of Pani. Koul, suggested a novel method instead of using conventional method for preparation of a well defined crystalline structured, water soluble named compensated sulphonated Pani, which can be used as corrosion inhibitor in HCl medium on iron. The crystallinity of the Pani was recommended due the sodium sulphonated moieties, which pack the unoccupied space in the lattice [97]. A comparison was made between two techniques of film casting on mild steel by using pure undoped Pani casted from N-methylpyrrolidinone then doped with acid and doped form Pani directly casted from xylene or chloroform. It was suggested that there was significant decrease in corrosion current when undoped Pani casted film was doped with acid as compared to doped film of Pani casted directly from xylene or chloroform [98].

Anodic protection of metals using low current is a useful technique in acidic media. Pani can be used to retain the potential of metals in passive state because of its large charge capability, proton exchange and redox properties. But, lots of problems are associated e.g. cost, maintenance, installation, optimized control etc. So, Zhong showed a new method for anodic protection of stainless steel in high concentration of H₂SO₄. In his experiment he developed a standalone Pani electrode by using Ti mesh pack in the chemically synthesized Pani film. The function of electrode was to work as current-collecting carrier and reduced where as satin less steel was oxidized to create an oxide film. It was seen that anodic protection of Pani I is a competent way to protect the metals in acidic media for a long time [99].

The enhanced coatings of Pani can be obtained by using nanoparticle forms at low loadings. So, Yeh and coworkers, by means of the casting method, develop a coating based on Polyaniline/Clay Nanocomposites and EB form of Pani through NMP solution drop wise transmitted on cold roll steel. The coating obtained were excellent in anticorrosion but when used as free standing films, the mechanical properties and degradation temperature were reduced [92]. Poly (3-alkyl thiophenes) as derivatives of PTh are reported efficient against corrosion protection of metals. The high oxidation potential of these polymers is an obstacle and make them complicated for utilization. However, casting technique provide ease for the formation of film on metals. Poly (3-octyl thiophene) and Poly (3-hexylthiophene) were casted from toluene as a solvent. A comparison was made between sheets of carbon steel surface prepared with 600-emery paper and 1 μ m alumina (Al₂O₃) particles separately. It was observed that surface treatment has some effect on coatings and the superior properties were seen in case of alumina particles' treated carbon steel, while P3HT was efficient as compared to P3OT in 0.5M H₂SO₄ [100].

The limitations of electroconductivity can be removed by increasing the number of p-bond containing monomers. It can be achieved through formations of copolymer, multilayers or composites. Wang published two parallel articles in the same issue about the nature of emeraldine base, as an anion exchanger and its part in corrosion inhibition. It was found that EB state of Pani contain OH⁻ as a counter ion.

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Appendix

Table 1: A review of cyclic voltammetric techniques

Ref.	Type of Coated ICps	Electrolyte Solution	Type of Substrate
30	Polypyrrole-Phosphate	Oxalic Acid	Mild Steel
31	Undoped Polyaniline	Phosphoric Buffer	Mild and Stainless Steel
32	Polyaniline	Phosphate and Sulphate	Stainless Steel with different composition of Chromium
33	Poly (o-toluidine), Poly (m-toluidine), Poly (o-anisidine), Poly (o-chloroaniline)	Oxalic Acid	Passivated Iron
34	Polyaniline, Poly (o-methoxyaniline)	H2SO4	Different grades of stainless steel
35	Poly (N-ethyl aniline)	Oxalic Acid	Aluminium alloy Al-2024
36	Poly (N-methylaniline)	Oxalic Acid	Mild Steel
37	Poly (2, 5-dimethylaniline)	Oxalic Acid	Low Carbon Steel
38	Poly (2, 5-dimethylaniline)	Sodium Salicylate	Low Carbon Steel
39	Poly(o-anisidine)	Sodium Oxalate	Copper
40-42	Polyaniline, Poly (2-anisidine), Poly (aniline-co-2-anisidine), Poly (2-iodoaniline), Poly (aniline-co-2-iodoaniline), Poly (2-chloroaniline), Poly (aniline-co-2-chloroaniline)	Tetrabutylammonium Perchlorate acetonitrile Perchloric Acid	304-Stainless steel
43	Polyaniline	Acetonitrile/LiClO4	Pani and Ppy Composite coated Mild Steel
44	Polythiophene	Acetonitrile/LiClO4	Ppy Coated Mild Steel
45	Polyaniline	H2SO4	Galvanostatic Anodic Pretreated AA1050 Aluminium
46	Polypyrrole	H2SO4	Galvanostatic Anodic Pretreated Aluminium Alloy Aniline
47-49	Polyaniline	Sodium Oxalate, Oxalic Acid, p-Toluenesulfonic	1 μm Ni Plated Copper
50,51,53	Polyaniline	Oxalic Acid	1 μm Ni Plated Mild Steel and using different scan rate at stainless steel.
52	Polyaniline	Sodium Oxalate	Copper
54	Polythiophene	Acetonitrile/LiClO4	1 μm Ni Plated Mild Steel
55	Polypyrrole	Oxalic Acid	Graphite Modified Mild Steel
56	Multi-Walled Carbon Nanotube/Polyaniline Composites	H2SO4	Platinum

Table 2: A review of potentiostatic techniques

Ref	Type of Coated ICps	Electrolyte Solution	Type of Substrate
57	Polyaniline	Phosphoric Acid	Iron
58	Polyaniline, Poly-o-toluidine, Composite of both	Phosphoric Buffer	Stainless Steel
59	Polyaniline	Phosphoric solution	Stainless Steel
60	Polyaniline, Polypyrrole, Bilayar and Blends Top Coat Zinc Microparticles	Phosphate and Sulphate	Mild Steel
61	Polynailine/Zn particles composite film	Zinc Sulphate	Mild Steel
16	Non-Pigmented Epoxy/ Polyaniline	Sodium Benzoate	Mild Steel

Table 3: A review of galvanostatic techniques

Ref	Type of Coated ICps	Electrolyte Solution	Type of Substrate
62,63	Polyaniline, Polyaniline/ Thiokol Rubber Composite	Acetonitrile, Trifluoroacetic acid, Trichloroacetic acid	Mild Steel
64,65	Poly (o-anisidine)	Oxalic Acid	Carbon Steel
66	Polypyrrole	Sodium p-Toluenesulphonate	Pretreated Mild Steel with 10% HNO3 and wet abrasive paper
67	Poly (2, 5-dimethylaniline), Poly (2, 5-dimethoxyaniline)	Oxalic acid	Low Carbon Steel
68	Different layers combinations of Polyaniline and Polypyrrole	LiClO4, H2SO4 Oxalic Acid	Stain less and Carbon Steel
69	Polypyrrole/ Zinc	Sodium Salicylate Phosphate	AISI 1010 Steel

Table 4: A review of paint blended coatings

Ref	Type of blended ICps	Type of Resin	Type of Substrate
27	Undoped and doped forms of Pani with p-toluene-sulfonic, camphorsulfonic, dodecylbenzenesulfonic acid.	Epoxy resin	3003 Al Alloy
70	Emeraldine Base/ Emeraldine Salt with Different Dopant	Topcoats of Epoxy and Polyurethane	Steel
71	Polyaniline and Poly (o-ethoxyaniline) Protonated with different acids	PMMA, Epoxy, water Soluble Epoxy	Pure Iron
72	Emeraldine Base	Epoxy	Mild Steel
73	Emeraldine Base with curing solvent Tetraethylene Pentaamine	Epoxy	Mild Steel
74	Poly (3-decylthiophene-2, 5-diyl)	Four Different commercial paints	Naval Steel St F111
75-76	HCl and Dioctyl Phosphate Doped Polyaniline	Epoxy, Polyurethane	Mild Steel
77	Dodecyl Benzene Sulfonic Acid Doped Polyaniline / zinc oxide composite	Poly (vinyl acetate)	Steel
78	Strontium Chromate Polyaniline	Epoxy, Acrylic	Magnesium Alloy
79	Polyaniline-Amino Trimethylene Phosphoric Acid	Epoxy	Mild Steel
80	Nano-Polyaniline Waterborne	Acrylic Top Coat	Iron
81	p-ara-Toluenesulphonic Acid-Polyaniline	Polyvinylbutyral	Zinc
82	Emeraldine Base crosslinked form with epoxy	Epoxy	Steel
83,84	Polyaniline	Vinyl Resin	Carbon steel
85	Emeraldine Base	Alkyd Resin	Carbon Steel
87	Polypyrrole	Acrylic	Magnesium Alloy
88-91	Polyaniline/TiO ₂ , Polyaniline/Fe ₂ O ₃	Acrylic	Steel and Magnesium Alloys
95	Polyaniline Coated	Aqueous Suspension Polystyrene Particles	Iron
96	Polyaniline / Glass Flake Composite	Epoxy	Mild Steel
97	Polyaniline	Soya oil alkyd	Steel

Table 5: A review of Casting Based Coatings

Ref	Type of ICps	Type of Solvent	Type of Substrate
28	Emeraldine Base	NMP	Iron
29	Emeraldine Base and Sulphonated Polyaniline	NMP, Water	2024-T3 Al Alloy
93	Emeraldine Base Polyaniline-Clay Nanocomposites	NMP	Cold Roll Steel
98	Sulphonated Polyaniline	Water	Iron
101	Poly (3-octyl thiophene), Poly (3-hexylthiophene)	Toluene	Carbon Steel
105	Blend of Polyaniline and Polyimide	Epoxy, Polyurethane	Mild Steel
106	Blends of Poly (dimethoxy aniline), Poly (vinylidene fluoride), Poly (tetrafluoroethylene-co-vinylidene fluoride-co-propylene)	N,N-dimethyl formamide	AISI 304 Stainless Steel