

Review

A Review on Conducting Polymers and Nanopolymer Composite Coatings for Steel Corrosion Protection

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Abstract: Corrosion is the principal reason for causing degradation of steel material properties, and coating is one of the most popular and effective ways to protect steel from corrosion. There are many kinds of coatings with different constituents, mechanisms and effectiveness. This paper presents a comprehensive review on the development of coating technology including traditional coatings, hydrophobic coatings, conducting polymer coatings and nanopolymer composite coatings. In particular, conducting polymers and nanopolymer composite coatings are reviewed in detail, which are the most popular and promising coatings. The advantages and limitations of each coating method as well as the influencing factors on corrosion protection are elaborated. Finally, the future research and applications are proposed.

Keywords: coating; hydrophobic; conducting polymer; nanopolymer composite

1. Introduction

Steel structures are widely used in many infrastructures, such as civil engineering and offshore engineering due to its high strength, excellent ductility, small dead weight, easy construction and other advantages. However, corrosion is a severe problem for steel structures, which could cause degradation of material properties and decrease of a structure's bearing capacity, safety and service life. Corrosion to steel has been a sustained issue and attracted many research interests. It is estimated that corrosion and its consequences cost in maintenance in developed countries is between 3% and 5% of their gross domestic product (GDP), and over CNY 4 trillion a year in China (about 5% GDP). Thus, it is essential to find highly efficient, long-term, stable, eco-friendly and low-cost corrosion prevention method.

It is well known that water, dioxygen and corrosive ions appear on the steel surface when the corrosive action occurs, and the essence of steel corrosion is oxidation reaction. Diverse methods have been developed to prevent the steel structures from corrosion considering different protective mechanisms, such as cathodic protection, anodic protection, inhibitors and hydrophobic impregnation. At present, the most popular and convenient corrosion protection strategy is coating, which consists of one or more layers with one or more mechanisms as mentioned above.

The prevailing steel coatings include traditional coatings, superhydrophobic coatings, conducting polymer coatings and nanopolymer composite coatings. Traditional metal coatings have excellent mechanical properties, high resistance to corrosion and functional properties such as magnetostatic shielding and resistance to radiation [1–4]. However, their use is restricted due to shortcomings such as toxicity, high cost and short service life. Traditional organic coatings, such as epoxy coating,

fluorocarbon coating, silicone coating, polyurethane coating and zinc-rich coating, provide corrosion protection by their barrier effect to ionic species, oxygen and water transport, which diminishes the corrosion rate [5–7], but their shortcomings are still significant, such as low impact strength, poor weatherability, poor bond strength and poor durability [8]. Almost all prevailing superhydrophobic coatings can adopt nanotechnology. Silica nanoparticles [9–11], carbon nanotubes [12,13], titanium oxide nanotubes [14–17], nanopolymers [18–20] and nanosilane [21–23] have been widely used for fabricating superhydrophobic coatings. Procedures such as the dip coating technique, electroless plating, sol–gel process and electro deposition are adopted to fabricate the superhydrophobic coatings. The water contact angles of the superhydrophobic coatings can reach 145–165 °C [9–23]. There is also some literature about using soft lithography method based on a polydimethylsiloxane (PDMS) template to prepare nanostructured superhydrophobic coatings [24,25]. Although significant progress has been achieved regarding the synthesis of superhydrophobic coatings and their anticorrosion properties for steel, the majority superhydrophobic coatings have been studied only in laboratory till now, and there are still many obstacles before they could be widely used in industry. The prevailing fabrications are complicated, costly and not suitable for on-site use. Many efforts should be made to develop an optimum superhydrophobic coating with excellent water repellency, long service life, good adhesion performance, low cost, easy fabrication and convenience in site spraying and curing.

In recent years, conducting polymer coatings and nanopolymer composite coatings have been widely used in many projects. Many studies on nanopolymer composite coatings, conducting polymers and their combinations were conducted with a good deal of progress. Some new nontoxic corrosion protection materials with the properties of high efficiency and smart corrosion protection, long effective period and easy construction have been developed.

Different coatings have different deposition mechanisms. At present, the prevailing deposition methods include physical vapor deposition (PVD), chemical vapor deposition (CVD), micro-arc oxidation (MAO), sol–gel, thermal spray, electrodeposition and electrochemical deposition coatings [26,27]. Every method has its suitable applications. In the case of polymer coatings, the main deposition methods include electrodeposition and electrochemical deposition.

This review paper focuses on conducting polymer coatings and nanopolymer composite coatings. In Section 2, by summarizing the current state of conducting polymer coatings, the mechanism, development and applications of three main kinds of conducting polymer coatings, i.e., polyaniline (PANI)-based coatings, polypyrrole (PPy)-based coatings and polythiophene (Pth)-based coatings are explored. In Section 3, a review of the studies of many kinds of nanopolymer composite coatings is provided. The review provides a systematic expatiation in research and development of steel corrosion coating over the past 30 years, and further research is also proposed.

2. Conducting Polymer Coating

The application of conducting polymer coatings to metal anticorrosion was first reported by DeBerry in 1985, and according to DeBerry, the stainless steel covered by polyaniline could remain passivated for a long time in sulfuric acid solution [28]. Since then, the research of conducting polymer coatings for metal corrosion protection has attracted lots of interest for their special properties, such as easy synthesis, high conductivity, eco-friendly nature, economical cost, nontoxicity and unique redox chemises [29,30]. It was generally believed that conducting polymer coatings can protect metal by forming a physical barrier, inhibition and passive oxide layers, although there are still some controversies about its protective mechanism [31]. The barrier effect prevents the penetration of aggressive matters such as water, dioxygen and ions to the steel surface. Conventional polymers such as epoxy and polyurethane are often used as topcoats because the conducting polymer coatings are porous, which results in the barrier function with low efficiency. The strong adsorption of the conducting polymers on the metal substrate suppresses the active dissolution process of metal. The strong oxidative capability of the conducting polymer helps the potential shift and long maintenance of the passive state of the metal, leading to the formation of a protective layer on the metal interface. When the coating and

passive oxide are locally damaged, some ions doped in the conducting polymer will be hydrolyzed and react with metal ions on the flawed site producing a new passive oxide on the damaged site [29,32–39]. Some studies indicated that the protective ability of the conducting polymers would decrease with the decrease of the charge stored in the polymer, and thus the polymer coating should be changed continuously for effective protection [38,39]. At present, the polyaniline (PAni), polypyrrole (PPy), polythiophene (Pth) and their derivatives are the most popular polymers studied.

2.1. Polyaniline(PAni)-Based Coatings

The polyaniline and its derivatives have been the most popular studied polymer coatings for corrosion protection, because they are cheaper, easier to synthesize and have better environmental stability compared with other conducting polymers [40,41]. The properties of some kinds of PAni-based coatings are listed in Table 1.

Table 1. Properties of PAni-based coatings.

Type	Properties	Comments	Refs.
Polyaniline emeraldine salt form (PAni-ES)	Conducting; Passivation of steel surface; Anodic protection; Excellent pitting and corrosion resistance.	The effect of PAni deposited on stainless steel in sulphuric acid has contradictory conclusion in chloride-containing medium.	[42–49]
Bilayered	Superior anticorrosion performances; Improved barrier, stability and bond strength compared with monomer; PPy/PAni offers superior corrosion protection than PAni/PPy; PAni-Zn is the best among PAni-metal coatings.	The efficiency is mainly affected by medium pH, the deposition order, the layer thickness, the doped anions and properties of the steel substrate.	[50–58]
Epoxy-PAni	Improved barrier effect, adhesion, mechanical and chemical resistance; Self-healing in NaCl solution.	Epoxy with PAni modified pigments (such as metal oxides, graphite, Zn) has more excellent corrosive protection.	[59–72]

2.1.1. The Polyaniline Emeraldine Salt Form Coatings

The polyaniline emeraldine base form (PAni-EB) and polyaniline emeraldine salt form (PAni-ES) are two kinds of polyaniline forms, and both of them are studied for anticorrosion coatings. PAni-EB is nonconducting, and the present researches confirmed its barrier effect [73–77]. However, some researchers showed that PAni-EB had anodic protection effect [75–80], while other researchers got contradictory results [81–85], so it is essential to continue to explore the mechanisms of PAni-EB based coating on steel.

Compared with PAni-EB, the conducting PAni-ES as coating on steel has been more widely studied and used in practical projects. The conducting polyaniline is usually polymerized using aniline in organic or inorganic acid solutions, and the main acids used include phosphoric acid (H_3PO_4), sulphuric acid (H_2SO_4), hydrochloric acid (HCl), oxalic acid ($H_2C_2O_4$), sodium salicylate ($C_7H_5NaO_3$), p-toluenesulphonic acid (PTSA) and 5-sulphosalicylic acid (CAS). Table 2 shows the information of some PAni-ES coatings polymerized in different solutions on different substrates.

Table 2. Summary of test data of the polyaniline emeraldine salt form coatings.

Substrate	Deposition Solutions	Deposition Method	Test Medium	Observations	Refs.
AISI 420 stainless steel	0.5 M aniline solution in 1.5 M H ₂ SO ₄ ; 0.5 M aniline in 3 M H ₃ PO ₄	Electrochemically synthesised	H ₂ SO ₄ solution; H ₃ PO ₄ solution, 0.5 M HCl	PANIPO ₄ had better protective than PANISO ₄ ; Oxide film formed on the substrate, the layers offered better protection in H ₂ SO ₄ medium and H ₃ PO ₄ medium than in HCl medium.	[42]
Stainless steel	0.07 M aniline solution in 0.07 M H ₂ SO ₄	cyclic voltammetry	1 M H ₂ SO ₄ , 1 M HCl, and 1 M NaCl solutions	PANIPO ₄ had better protective than PANISO ₄ ; The coatings offered good protection in acid medium, but it was not protective in NaCl media.	[43]
304 stainless steel	2 M sulphuric phosphoric acid containing 1 M aniline	cyclic voltammetry	3 M H ₂ SO ₄ solution; In a mixture of H ₂ SO ₄ and HCl	PANISO ₄ layer was thicker and enriched with Fe, Cr and Ni components than PANIPO ₄ , and it was superior in protection against pitting in aggressive chloride solutions	[44]
Carbon steel	0.1 M aniline solutions in oxalic acid (0.3 and 0.1 M) and sodium salicylate solution (0.3 and 0.5 M).	cyclic voltammetry	–	0.3 M or higher oxalic acid was required to complete passivation of carbon steel. The films obtained in salicylate were transparent, uniform, compact and adherent.	[45]
Mild steel	An aqueous solution of 0.5 M Na benzoate and 0.25 M aniline	electrochemical synthesis	3% NaCl, atmosphere, and the Sahara sand	The coating doped benzoate anions offered cathodic protection to mild steel.	[46]
316L stainless steel	0.15 M o-anisidine in 0.50 M sulphamic acid solution	cyclic voltammetry	3.5% NaCl solution	Poly (o-anisidine) synthesized at low scan rate and PANi coatings provided a remarkable anodic protection to stainless steel substrate for longer exposure time than the one observed for that produced at high scan rate.	[47]
304 austenitic stainless steel	0.1 M H ₂ SO ₄ solution containing 0.05 M o-phenylenediamine	cyclic voltammetry	3% NaCl solution	The passive film underneath the poly (o-phenylenediamine) on stainless steel was enriched with chromium and nickel which led to excellent protection of stainless steel against pitting in aggressive chloride environments	[48]
Mild steel	Evaporation of the solvent N-methyl-2-pyrrolidone at temperature 85–90 °C	chemical evaporation method	0.1 M HCl, 5% NaCl solution, artificial seawater, distilled water and open atmosphere	The terpolymer coated steel had significantly lower corrosion rate than the individual copolymers coated steel in all corrosive mediums	[49]

As shown in Table 2, PANi-ES coatings could offer good corrosion protection for steel in aggressive medium, but the properties of the coatings are affected by many factors such as the composition of substrate, the composition and concentration of the deposition solution, the concentration of the monomer, pH value, the electrochemical methods and its applied potentials. Reference [80,81] reported that PANi could not offer good corrosion protection in a chloride-containing medium, but Ganash and his coworkers [82] reported that the film deposited on stainless steel in sulphuric solution had an excellent pitting and corrosion resistance in aggressive chloride solution. The contradictive results may be caused by the difference substrate, the difference of the composition and concentration of the deposition solutions.

It can be concluded that some coatings from the derivative of PANi have better corrosion protection properties than that of PANi coatings [47–49]. Ozyilmaz et al. [47] found that PANi and its derivative,

poly (o-anisidine) synthesized on stainless steel in monomer containing 0.5 M sulphamic acid solution at low scan rate exhibited effective anticorrosive behavior by a remarkable anodic protection even for long exposure time in 3.5% NaCl solution. Hermas [48] found that the passive film underneath the poly (o-phenylenediamine) (PoPD) on 304 stainless steel deposited in sulphuric acid solution was enriched with chromium and nickel, which led to excellent protection of stainless steel against pitting in aggressive chloride environment. Tanveer and Mobin [49] synthesized a soluble terpolymer poly (2PA-co-AN-co-XY) and two copolymers, poly (AN-co-XY) and poly (2PA-co-AN). The experimental results showed the terpolymer coated mild steel had significantly lower corrosion rate in corrosive environments such as in 0.1 M HCl solution, 5% NaCl solution, artificial seawater, distilled water and open atmosphere.

2.1.2. Bilayered Conducting Polymer Coating

To enhance the anticorrosive properties of conducting polymer coatings for steel, some researchers deposited double layers conducting polymer on steel. Table 3 shows the information of some bilayered coatings in different conditions [50–58].

Table 3. Summary of test data of bilayered conducting polymer coatings.

Substrate	Deposition Solutions	Layers (Under/Top)	Test Medium	Observations	Refs.
Carbon steel 304L stainless steel	PAni film: 0.1 M aniline in either 0.05 M H ₂ SO ₄ for stainless steel or 0.3 M oxalic acid for carbon steel. PPy film: 0.1 M pyrrole in acetonitrile and 0.5 M LiClO ₄	PAni/PPy PPy/PAni	0.028 M NaCl solution	Bilayered coatings revealed better protection especially against pitting corrosion compared with single polyaniline coatings for stainless steel. However, in case of carbon steel, bilayers had no obvious improvement. PPy/PAni revealed better performance than PAni/PPy.	[50]
Steel	PPy film: 0.1 M pyrrole in 0.3 Moxalic acid; PAni film: 0.1 M aniline in 0.3 Moxalic acid	PAni/PPy PPy/PAni	1 M H ₂ SO ₄	The inhibition efficiency: PPy/PAni > PAni/PPy > monolayer (PAni and PPy)	[53]
Steel	PPy film: 0.1 M pyrrole in 0.3 Moxalic acid; PAni film: 0.1 M aniline in 0.3 Moxalic acid	PAni/PPy PPy/PAni	0.5 M NaCl 0.1 M HCl 0.5 M H ₂ SO ₄	PPy and PPy/PAni coatings served as a stable host matrix on mild steel against corrosion. Bilayers of PAni and PPy did not exhibit good combined properties of each polymer, PPy exhibited the best corrosion resistance.	[51]
Mild steel	PPy film: 0.1 M pyrrole in 0.3 Moxalic acid; PAni film: 0.1 M aniline in 0.3 Moxalic acid 2 g·L ⁻¹ phosphotungstate (PW ₁₂) in the polymerization solutions	PPy/PAniPPy/PAni-PW ₁₂ PPy-PW ₁₂ /PAni	0.1 M HCl	PAni/PPy-PW ₁₂ coating exhibited better corrosion resistance for mild steel, the presence of PW ₁₂ in the inner layer of PPy/PAni may hinder the maintenance of passive layer and reduce the corrosion resistance.	[56]
304L stainless steel	An aqueous solution containing the monomer, sodium dodecylsulfate (SDS) and oxalic acid	PBTh PAni/PBTh	0.5 M NaCl 0.5 M HCl	Polybithiophene (PBTh) and PAni/PBTh exhibited the effective anticorrosive properties in highly corrosive media containing neutral and acidic chloride anions.	[54]
Mild steel	0.3 M oxalic acid and 0.3 M aniline or PNMA or their combinations	PAni/PNMA PNMA/PAni	3.5% NaCl	Poly(N-methylaniline) (PNMA)/PAni layers showed higher stability and better protection than the PAni/PNMA layers.	[55]

Table 3. Cont.

Substrate	Deposition Solutions	Layers (Under/Top)	Test Medium	Observations	Refs.
Mild steel and iron	Aqueous oxalic acid medium	PAni/Zn Zn/PAni PAni/Ni Ni/PAni	3.5% NaCl	PAni/Zn coatings offered the maximum protection, followed by PAni/Ni coatings. Metal/PAni coatings offered the least resistance to corrosion. Zn offered sacrificial protection, and both PAni and Ni acted by the barrier mechanism.	[52]
Carbon steel	0.20 M aniline containing 0.20 M sodium tartrate solution	Zn-Co/PAni	3.5% NaCl	PAni coating led to decrease of the permeability of metallic plating and provided an effective barrier property on zinc-cobalt coating and a remarkable anodic protection to substrate for longer exposure time. Zinc-cobalt improved the reduction of PAni coatings.	[57]
Carbon steel	PAni film: 0.1 M aniline in 0.3 M oxalic acid Co-polyamide film: electrostatic spraying	PAni/Co-polyamide	Neutral salt spray 4% NaCl	Single co-polyamide and PAni on carbon steel both were not sufficient to prevent corrosion in a chloride medium by itself, but the combined coating (a primer of PAni and a top layer of co-polyamide coating) could result in a minimize corrosion.	[58]

As shown in Table 3, most of the bilayered coatings exhibited superior anticorrosive performances than monomer conducting polymer coatings, and the deposition order significantly affects the efficiency of the bilayers [50–57], and doping some anions such as DS and PW₁₂ ions in the inner or outer layer of coatings could improve the anticorrosion properties [54,56]. Some bilayered coatings such as PAni/Zn coating could exhibit the synergistic effect of the barrier mechanism of the PAni and the sacrificial protection of the zinc, however, the combination of PAni and Ni only acted by the barrier mechanism [52]. Sometimes the combined coating could result in minimized corrosion when monomer coating is not sufficient to prevent corrosion in aggressive medium by itself [58].

There are lots of factors influencing the properties of the bilayered coatings, and more elements such as the composition of substrate, the deposition order, the layer thickness, corrosive medium, medium pH and the exposing time should be comprehensively considered in later studies.

2.1.3. Epoxy-PAni Coatings

Considering that polyaniline is not a good coating binder which tends to produce a brittle film with poor adhesion properties and its barrier effect is not good for porous, some researchers blended PAni with other traditional organic coatings in the hope of combining their synergies. As the most popular organic coating, epoxy coating has the excellent properties such as good adhesion, high mechanical and notable chemical resistance under harsh aggressive environments. So epoxy coatings combining with PAni have been widely studied, and researches indicated that it exhibited more outstanding corrosive protection on steel than single epoxy and PAni coatings.

Epoxy blended with a low concentration PAni-EB or PAni-ES (doped or undoped anions) both revealed excellent anticorrosive behaviors on steel, and can be used to replace the conventional toxic inorganic pigments [59–72]. Table 4 shows the information of some Epoxy-PAni coatings in different conditions.

Table 4. Summary of test data of Epoxy-PAni coatings.

Substrate	Coatings	Test Medium	Observations	Refs.
F111 steel	Epoxy + PAni-ES Epoxy + PAni-EB Epoxy + Zn ₃ (PO ₄) ₂	3.5% NaCl	The epoxy + PAni-EB provided more protection than the epoxy + PAni-ES and the epoxy + Zn ₃ (PO ₄) ₂ , the inorganic corrosion inhibitors, which may have detrimental effects on both the environment and the human health, could be replaced by a small concentration of environmentally friendly organic polymers.	[59]
Carbon steel	Epoxy + PAni-ES	3.5% NaCl	Undoped PAni epoxy blend coating (PAni pigmented paint) on carbon steel revealed passivation characteristics in 3.5% sodium chloride solution up 300 days and acceptable protection against the corrosion.	[60]
Steel	Epoxy + PAni (low doping: 0%–7%)	3.5% NaCl	Epoxy + PAni coatings showed no deterioration after 1400 h of hot (65 °C) saline treatment. The outstanding corrosion resistant properties arise from the two fold action of PAni, i.e., it led to higher crosslink density after curing giving improved barrier and it imparted self healing behavior to the coatings even after scratch was formed.	[61]
Steel	Epoxy + PAni (10%)	3% NaCl	Epoxy + PAni (10%) revealed better corrosion protection performance compared to that of PAni free epoxy coating after 30 days of exposure in 3% NaCl. The passivation of steel achieved by PAni due to its redox activity. Scanning vibrating electrode technique confirmed the self-healing capability of the epoxy-PAni composite coating system.	[62]
Mild steel	Epoxy + PAni	0.1 M H ₂ SO ₄	Thin PAni film used as modification of mild steel prior to epoxy coating deposition had provided better corrosion protection.	[63]
Mild steel	Epoxy + PAni (doped with Dioctyl phosphate)	3.5% NaCl	PAni-dioleil phosphate (DOPH) containing epoxy coating offered protective performance for longer period compared to other resins.	[64]
SAE 1020	Epoxy + PAni (doped with dodecylbenzene sulfonic acid)	Salt spray (5% NaCl)	Steel coated with epoxy containing 0.1% PAni-dodecyl benzene sulfonic acid (DBSA) had improved performance when PAni-DBSA was used as pigment, and the active electronic barrier model seemed to be a more reasonable explanation for the mechanism of protection.	[65]
Mild steel	Epoxy + PAni (doped with hydrofluoric acid) Epoxy + PAni (doped with camphorsulfonic acid)	3.5% NaCl	The different PAni coatings could offer the corrosion resistance of mild steel, but the camphorsulfonic acid-doped PAni coating had the best corrosion resistance.	[66]
Steel	Epoxy + PAni (graphite-based pigments)	High humidity and with SO ₂ and NaCl	The PAni coating of the synthetic graphite and especially of the natural form of graphite had the excellent results of anticorrosion efficiency	[67–69]
Steel	Epoxy + PAni (Zn dust pigments)	SO ₂ and NaCl	PAni + Zn-dust created a synergic effect, and the efficiency of their combination is higher than that of the PAni particles alone or of the Zn-dust particles.	[70]
Steel	Epoxy + PAni	3.5% NaCl	Zinc dust of the epoxy coatings could be partially replaced by 0.3 wt.% PAni-ES and their corrosion protection did not reduce, and the adherence properties of the coating were enhanced.	[71]
Steel	Epoxy + PAni-graft-basalt plates	12% NaCl	The coating containing 10% PAni-g-BPs (1:4) exhibited the best protective performance and it was more excellent than the counterparts containing inorganic fillers.	[72]

As shown in Table 4, epoxy blended PANi could offer improved corrosion protection and the anticorrosion performance will be further improved when PANi doped with some dopants or counter-ions such as dioctyl phosphate and camphorsulfonic acid. This is because PANi can release anions when damage occurs to the coating, forming a second physical barrier that counteracts penetration of aggressive ions. When suitable inorganic particles used as pigments in PANi coatings, such as metal oxides and graphite, the corrosion protection ability of the coating will be enhanced, because the particles with good conductivity could not only act as carriers of PANi to assure the efficient transport of electrons involved in redox processes but also promote the formation of a barrier by particles sedimenting during the drying [68].

2.1.4. Other PANi Blending Coatings

Except blending with epoxy resin, PANi is also blended as pigment doping or undoping different anions in other organic coatings such as acrylic, vinyl acrylic, chlorinated rubber, vinyl, polyester acrylate, polyvinyl chloride and alkyd coatings, and the blends exhibited excellent corrosive protection in most cases. Table 5 shows the information of some other PANi blending coatings in different conditions.

Table 5. Summary of test data of other PANi blending coatings.

Substrate	Coatings	Test Medium	Observations	Refs.
Iron	Acrylic PANibends (doped with camphorsulphonate or phenylphosphonateanions)	1 M H ₂ SO ₄ with or without 0.1 M NaCl	A redox reaction between Fe and PANi took place leading to PANi reduction and concomitant anion release. Then, iron cations formed a passivating complex with the PANi doping anion. The coating could release anions in a smart way when damage is produced on the surface of the coating.	[86]
Steel	Vinyl acrylic + PANi	0.1 M HCl, 3% NaCl Cement extract (pH 13.0)	The coating could passivate steel in neutral and alkaline media, and it may be only offer protection by barrier effect in acid media.	[87]
Mild steel	Chlorinated rubber + PANi (doped with benzene-sulfonate or lingsulfonate)	3.5% NaCl solution	The anticorrosive properties were very sensitive to the concentration of PANi pigment, the PANi concentration should be preferably below 1 wt.% with benzene-sulfonic acid while higher (1.5 wt.% and 3 wt.%) with lingo-sulfonate for better corrosive protection on steel in neutral salt media.	[88]
Steel	Vinyl + PANi (doped with benzoate)	3% NaCl 0.1 M HCl	The coating could provide better corrosion protection to steel in 3% NaCl solution than in 0.1 M HCl solution, because the benzoate ions would passivate the steel and form a passive iron oxide film along with Fe-PANi complex in the former media.	[89]
Galvanized steel	Polyester acrylate + PANi (doped with methane sulfonic acid)	3% NaCl	The coating exhibited excellent anticorrosion performance, and a zinc oxide film formed at the metal-coating interface as a second barrier layer by the redox action of PANi.	[90]
1010steel	Polyvinyl + PANi	3% NaCl 0.1 M HCl	The best 1:1 proportion of polyaniline and polyvinyl coating on 1010 steel in 3% NaCl and 0.1 M HCl showed superior corrosion protection as compared to pure PANi and pure polyvinyl coatings.	[91]
Mild steel	Palm oil-based polyester + PANi	3.5% NaCl solution	The coating was a stable and homogeneous coating and its adhesion and corrosion resistance properties were both significantly improved.	[92]
Mild steel	Alkyd + PANi	3% NaCl	The composite coatings reduced the possibility of blister formations and delamination, and the corrosion products on the coatings surfaces closely followed the initial oxidation state of the polyaniline.	[93]

As shown in Table 5, in most conditions, like epoxy coatings, other organic blended PANi coatings could promote the synergy of organic coating and PANi too, the anticorrosion properties and other performances are improved.

2.2. Polypyrrole (PPy)-Based Coatings

As an important member of conducting polymers, polypyrrole has been widely studied for the corrosion protection of metals in view of its high conductivity, stability, easy synthesis and eco-friendly proprieties. Tüken [94] reported that polypyrrole films on stainless steel had low permeability and high stability, which exhibited important anodic protection behavior and enhanced the self-passivation of steel with protective oxide film.

Single PPy coatings for corrosion protection have some limitations. For example, protective behavior may be lost with the charges stored in the polymer layer consumed during the redox reactions, porosity and ion exchanges of PPy coatings might be disadvantageous in case of localized corrosion caused by small and aggressive anions [95]. Therefore, most researches focused on using PPy as constituent of composites and bilayer coatings. Table 6 shows the information of some PPy composite coatings.

Table 6. Summary of test data of PPy composites coatings.

Substrate	Coatings	Test Medium	Observations	Refs.
Mild steel	PPy/DGEBA	3.5% NaCl 5% HCl,	Acamphorsulphonic acid complex passivating layer was formed which enhanced the corrosion inhibition remarkably. The composite coatings showed far superior anticorrosive performance than PANi/epoxy coatings.	[95]
Carbon steel	PPy/saccharin	0.1 M NaCl	Adding 0.5 g/L saccharin in polypyrrole coating could form a more compact and smoother surface morphology that led to more noble corrosion potential and higher corrosion resistance.	[96]
Carbon steel	PPy/PW ₁₂ O ₄₀ ⁻³	0.05 M NaOH 0.10 M NaCl	The coating provided improved protection against corrosion.	[97,98]
Carbon steel	PPy/tungstate	3.5% NaCl	Tungstate ions increased the stored charge of the polymer coating, the participation of tungstate ions in the passivation process achieved a primary passive layer with higher quality.	[99]
316L stainless steel	PPy/molybdate and nitrate	0.15 M NaCl	The coating had strong adherent performance and could provide against pitting corrosion in chloride solutions.	[100]
304 stainless steel	PPy/nitrate ions	3% NaCl	The coating with nitrate ions enhanced the pitting corrosion resistance and also increased the ageing time of polypyrrole coating.	[101]
Carbon steel	PPy/molybdate	0.1 M HCl	The enhanced corrosion resistance was associated with the complex passive film on the metal surface and the barrier effect of the coating, and the films' thermostability, wettability, adhesion and hardness were improved too.	[102]
Stainless steel	PPy/p-toluene-sulfonate (pTS) PPy/benzene-sulfonate (BS) PPy/dodecyl-sulfate (DS)	0.1 M NaCl	The PPy-BS and PPy-pTS films presented better protection due to the smaller molecular size of the dopant.	[103]
Carbon steel	PPy/p-toluene-sulfonate (pTS) PPy/sulfuric acid (SA) PPy/camphor sulfonic (CSA) PPy/sodium dodecyl sulfate (SDS) PPy/sodium dodecylbenzene sulfonate (SDBS)	3.5% NaCl	p-TSA and SDBS were the best dopants for polypyrrole coating on carbon steel	[104]

Table 6 shows that the composite coatings of polypyrrole-doped different counter anions exhibited better anticorrosion performance such as superior inhibition, stronger adherence, longer ageing time, enhanced thermostability, wettability, and hardness [95–104].

PPy-based bilayer coatings have been widely studied and exhibit excellent protection behavior, such as a higher barrier effect, better pitting protection and longer durability [37,38,50,105–112]. Table 7 shows the information of some PPy-based bilayer coatings.

Table 7. Summary of test data of PPy-based bilayer coatings.

Substrate	Layers(Under/Top)	Test Medium	Observations	Refs.
Carbon steel stainless steel	PAni/PPy PPy/PAni	0.028 M NaCl solution	Bilayered coatings revealed better protection especially against pitting corrosion compared with single polyaniline coatings for stainless steel. However, in case of carbon steel, bilayers had no obvious improvement. PPy/PAni revealed better performance than PAni/PPy.	[50]
Mild steel	PPy/polyphenol	0.05 M H ₂ SO ₄	The polyphenol layer improved the barrier effect of the coating remarkably. The polypyrrole/polyphenol could provide better and longer corrosion protection for mild steel than single PPy layer.	[105,106]
stainless steel	PPy/PPy	0.15 M NaCl 0.15 M HCl	The under layer polypyrrole was electropolymerized in the presence of molybdate and nitrate, and the top layer polypyrrole was electropolymerized in aqueous solution of salicylate, which led to the formation of hollow rectangular-sectioned microtubes. The coating could prevent the steel from uniform as well as pitting corrosion during long exposure times in acid and neutral chloride solutions.	[110]
Carbon steel	PPy-PMO ₁₂ O ₄₀ ³⁻ /PPy-NDS	3.5% NaCl	The coating PPy-PMO ₁₂ O ₄₀ ³⁻ /PPy-naphthalenedisulfonate (NDS) kept the steel in passive state and prevented corrosion of the steels for the longer time period than single coatings, and the bilayer PPy films on steel in 3.5 wt.% NaCl solution exhibited corrosion resistance performance as the following order: PPy-PMO ₁₂ /PPy-DHNDS < PPy-PMO ₁₂ /PPy-NDS < PPy-PMO ₁₂ /AnqDS < PPy-PMO ₁₂ /PPy-DoS	[37,38]

Except the papers listed in Table 7, other researchers also found that synthesizing polyindole [107], polypyrrole/Poly(N-methyl pyrrole) [108] or poly (5-amino-1-naphthol) [109] coatings on top of polypyrrole layer for mild steel could significantly increase the barrier effect of bilayer films and improve the anticorrosion performance. Deposited PPy on the top of the zinc layer [111] and SiO₂ layer [112] could both improve the corrosion protection performance.

As another efficient method, modification of polymer coatings can improve the anticorrosion property and other physical performances. Tüken [113] reported that zinc particles modified polypyrrole coating could provide both effective cathodic protection to mild steel for the existence of zinc particles and better barrier performance because the corrosion products of zinc centers plugging pores of the polymer film filled up pores of the PPy film. Lehr and Saidman [114] drew the same conclusion as Tüken when zinc-modified polypyrrole coatings were applied onto SAE 4140 steel. Tüken et al. [115,116] found that intercalating a thin graphite layer between two PPy layers on mild steel or stainless steel both exhibited excellent anticorrosion performance due to the graphite layer hindered the water mobility and permeability against corrosive environment.

2.3. Polythiophene (Pth)-Based Coatings

Although polythiophene is an important conducting polymer with remarkable electrical properties and stability [117], previous reports mainly focused on the synthesis methods. Research about the protection for metal as coating are rare because it is difficult to synthesis polythiophene coating on steel surface directly. The study of the Pth-based coatings was conducted only recently.

Kousik et al. [118] used electropolymerized polythiophene on mild steel in acetonitrile solution, which could prevent mild steel from corroding by forming a passivate film for the redox chemistry property. Tüken et al. [119] reported that polythiophene could not be synthesized on mild steel in CAN-LiClO₄, but it could be achieved on top of a thin PPy coating. The PPy/Pth coating had low porosity and excellent barrier properties in 3.5% NaCl solution. Tüken et al. [120] found that depositing Pth film on nickel-coated mild steel could improve the barrier efficiency remarkably for long time in 3.5% NaCl solution. Ocampo et al. [121] found that adding 0.2 wt.% poly (3-decylthiophene-2,5-diyl)-regioregular into epoxy-based resin could greatly improve the anticorrosion property for steel in marine environment. Palraj et al. [122] prepared interpenetrating polymer networks (IPN) with epoxy, silicone and thiophene using a cross-linking agent and a catalyst, and found that the adhesion was improved with the increase in temperature, and impedance measurements showed that IPN exhibited perfect corrosion resistances. Ai et al. [123] reported that mixing polythiophene nanoparticles (0.6 wt.%) in waterborne epoxy coatings on mild steel could offer high protection and the impedance values remained at $1 \times 10^6 \Omega\text{-cm}^2$ higher after being immersed in 3.5 wt.% NaCl solution for 360 h. Gutiérrez-Díaz et al. [124] reported that coatings of polythiophene with ash or MCM-41 particles containing iron (III) nitrate as inhibitor on mild steel exhibited excellent anticorrosive performance in chloride media.

2.4. Other Conducting Polymer Coatings

Except for the popular conducting polymers, i.e., PANi, PPy and Pth, other conducting polymers, such as polycarbazole [125,126] and polyvinyl alcohol [127], were also studied as corrosion protection coatings for steel, but they are all not widely studied and used for various reasons.

3. Nanopolymer Composite Coatings

Coating with the properties of long-term corrosion resistance, high adhesion, good durability and high surface mechanical abrasion are in high demand. It has been proved that using nanoparticles in conducting polymer coatings could not only fill the pores to enhance the barrier effect but also improve the electrochemical anticorrosion and other performances such as adhesion, thermal stability, mechanical strength, hydrophobic property and magnetostatic shielding [128–161]. Many kinds of nanoparticles such as TiO₂, Zn, ZnO, Si, SiO₂, Al₂O₃, CeO₂, nanoclays and nanotubs have been added in polymer coatings and showed better protective behavior than normal polymer coatings. The properties of some nanopolymer composite coatings are listed in Table 8.

Table 8. The properties of nanopolymer composite coatings.

Nano-Particles	Mechanisms	Advantages	Refs.
Nano-PANi	Fill pores; The redox behaviour of PANi; Form oxide layer.	High barrier property; High adhesion; High anticorrosion efficiency.	[130–132]
nanoPANi-DBSA	DBSA reacts with the iron cations when the corrosion process is initiated.	High barrier property; Smart protection. High anticorrosion efficiency.	[133]
Nano-metal oxides-PANi	Fill pores and improve film structure; The redox behaviour of PANi;	High barrier property; High electrochemical anticorrosion; High durability.	[134–137]

Table 8. Cont.

Nano-Particles	Mechanisms	Advantages	Refs.
nanoZn-PAni	Fill pores; Sacrificial protection; The redox behaviour of PAni;	High barrier property; High mechanical property; High electrochemical anticorrosion.	[138]
Nanoclay-PAni	Unique combination at molecular level; The electrochemical behavior of the nanocomposites is reversible.	High adhesion; High gas barrier; High thermal stability, High mechanical strength, Excellent anticorrosion.	[139–145]
Nanotubes-PAni	The high surface area of the nanotubes decreases the porosity of the PAni and forms a higher resistant passive film.	High thermal stability; High mechanical properties; Excellent hydrophobic; High anticorrosion.	[146–149]

3.1. Nanocomposite PAni Coatings

Bagherzadeh et al. [130–132] found that water-based epoxy coatings containing 0.01 wt.% nanopolyaniline (polyaniline particles 50–60 nm), 0.07 wt.% of ScCO₂-synthesized self-doping nanoPAni (2–3 nm particle size) or 0.02 wt.% nanopolyaniline (50–57 nm particle size) on carbon steel all improved the anticorrosion efficiency. It is believed that nanopolyaniline particles could increase the barrier properties and lead to formation of a thin and uniform oxide layer between metal and coating interface, and the adhesion of composite coating was also improved [134]. Arefinia et al. [133] reported epoxy coatings containing 1.0 wt.% nanoPAni-DBSA (less than 30 nm) on the carbon steel substrate would release dopant anions when the corrosion process was initiated on the metal substrate, and the released dopant anions would react with the iron cations, forming a secondary barrier layer, that would passivate the substrate.

Zinc metal is usually used as additive for sacrificial protection in coatings. Some researchers studied the anticorrosive performance of nanoZn metal and PAni composites, and the results showed nano-ZnO or nano-Zn mixed with PAni could exert their synergy [134–138]. Patil et al. [134] reported that poly (vinyl acetate) mixed with nanoZnO-PAni hybrid composite showed remarkable improvement in corrosion protection of steel in saline water, which was attributed to combination of the enhancement in barrier properties due to nanoparticulate additives, and the redox behaviour of PAni leading the protective oxide layer formation near the substrate. Mostafaei and Nasirpouri [135] found that epoxy coatings containing PAni-nanoZnO could significantly improve the barrier and corrosion protection performance. Olad and Nosrati [136] reported the improved anticorrosion behavior of the polyvinyl chloride mixed with nano-ZnO-PAni. Olad et al. [137] found that PAni/nano-Zn composite films had higher electrical conductivities and improved anticorrosive properties compared to PAni/Zn composite films. The polyaniline coating containing both 4 wt.% nanoZn and 3 wt.%–7 wt.% epoxy resin as additives had the best anticorrosion performance due to the enhancement of barrier properties and electrochemical anticorrosion behavior [138].

Nanoclay particles blending with polymer can enhance the gas barrier, thermal stability, mechanical strength, fire-retardant and anticorrosive properties of metal coatings [139,140]. A few reports on the behavior of polymer/nanoclay composites coatings were published. Olad and Rashidzadeh [141] reported that the anticorrosive property of both hydrophilic and organophilic PAni/nano-montmorillonite composite coatings on iron samples were better than that of the pure polyaniline coating, and the conductivities of PAni/hydrophilic nano-montmorillonite composite films were lower compared with pure polyaniline film and higher in the case of PAni/organophilic nano-montmorillonite composite films. Olad and Naseri [142] found that PAni/natural clinoptilolite nanocomposite with 3 wt.% clinoptilolite content has the best protective properties for steel in acidic environments. Akbarinezhad et al. [143] found that polyaniline-Cloisite 30B nanoclay could modify

zinc rich epoxy coatings, inhibit zinc powder consumption and extend its cathodic protection period via improving its initial barrier effects. Mousavinejad et al. [144] found that water-based epoxy resin mixed with a polyaniline-Cloisite 30B nanoclay showed superior long-term stability, high adhesion and enhanced corrosion resistance. Navarchian et al. [145] found that the corrosion protection efficiency of a steel panel coated with epoxy/PAni/OMMT (alkyl ammonium ions in organo-modified montmorillonite) was much higher than that of epoxy/PAni/MMT (Na^+ in natural clay).

Nanotubes (CNTs) have outstanding mechanical characteristics, good electronic conductivity, nanometer size and highly accessible surface area. Some researchers prepared CNT/PAni composites which exhibited improved anticorrosion behavior than pure PAni coatings on steel [146–149]. It can be explained that the coating containing nanotubes have higher anticorrosion behavior because the higher surface area of the nanotubes decreases the porosity of the PAni and forms a more resistant passive film on the steel under the composite layer. Mahmoudian et al. [146] found that the resistance of the coating containing PAni nanotubes was three times higher than that of the coating containing PAni nanofibers on mild steel in a 3.5% NaCl aqueous solution based on electrochemical impedance spectroscopy (EIS). Hermas et al. [147] reported that PAni-multiwalled carbon nanotube (PAni-mCNTs) composites had improved morphological structure, electrical properties, thermal stability and anticorrosion behaviour on steel in H_2SO_4 solution. Kumar and Gasem [148] prepared a kind of functional PAni/f-mCNT composite, which showed uniform dispersion of CNTs in PAni matrix, enhanced mechanical properties, excellent hydrophobic nature and electrochemical corrosion behavior on mild steel in a corrosive environment. Kalendová et al. [149] found that CNTs can partially replace Zn dust in steel coating whilst increasing the coating's anticorrosion efficiency.

CeO_2 and TiO_2 nanoparticles were also studied as additives in conducting polymer coatings. Ramezanzadeh et al. [150] mixed the polyaniline (PAni) nanofibers- CeO_2 -grafted graphene oxide nanosheets into the epoxy matrix for mild steel protection, and the test results revealed that both the barrier and active corrosion inhibition properties of GO nanosheets were enhanced by the deposition of PAni and CeO_2 compounds. Hosseini and Aboutalebi [151] measured the anticorrosion performance of epoxy coating containing imidazole modified CeO_2 and unmodified CeO_2 nanoparticles (0.5 wt.%, 1 wt.% and 2 wt.%) on mild steel in NaCl 3.5 wt.% solution, and the results showed that the modified coating had higher resistance and lower water-absorption comparing with unmodified coating, and the best percentage of embedded CeO_2 nanoparticles in the epoxy coating was 0.5 wt.%. Sababi et al. [152] reported that polyaniline doped with phosphoric acid (PAni-PA) could passivate the steel, and ceria nanoparticles could significantly slow down electrolyte transport and improve the barrier protection. Adding both the PAni-PA and the ceria nanoparticles in epoxy coatings could offer a synergistic effect on improving the corrosion protection properties in the NaCl solution. Ecco et al. [153] found that adding 1.0 wt.% of ceria nanoparticles and PAni into the alkyd coating could remarkably reduce the delamination rate and the presence of blisters in comparison to the alkyd blank coating. Radoman et al. [154] modified the TiO_2 nanoparticles surface with vitamin B6 (TiO_2 -B6) first, and then synthesized PAni in the presence of TiO_2 -B6 (PAni- TiO_2 -B6). The test results revealed that epoxy-based coating containing PAni- TiO_2 -B6 nanocomposites had lower dielectric loss, higher hardness and better anticorrosion properties than the pure epoxy resin and epoxy/PAni nanocomposite.

3.2. Nanocomposite PPy Coatings

Adding nanoparticles in polypyrrole have been used widely for the corrosion protection of metal substrate, which increased the solubility, stability, and adhesion of the polymers to the substrate, and also enhanced their barrier and passivation property. Ioniță et al. [155] found that PPy doped with carbon nanotubes exhibited an enhancement of conducting features and an improvement of anticorrosion protecting ability for carbon steel in 3.5% NaCl solution. Mahmoudian et al. [156] reported that the size of PPy/Ni-doped- TiO_2 nanocomposites was smaller than PPy/ TiO_2 nanocomposites, so the area of synthesized PPy in the presence of Ni-doped TiO_2 nanocomposites was increased, which improved its anticorrosion ability in NaCl solution. Saremi and Yeganeh [157,158] added mesoporous

silica nanocontainer powders in the polypyrrole matrix and found that a protective compound on the interface was formed and provided better protection for mild steel in a salt corrosion environment. Ruhi et al. [159] reported that the epoxy resin with 3.0 wt.% loading of polypyrrole/SiO₂ composite could passivate the defect up to 99.99% of the corrosion protection efficiency, and steel panel coated such coating suppressed the spread of corrosion and very few blisters were produced; it was a well-adherent, high quality, and superior anticorrosive coating for mild steel substrates. Alam et al. [160] synthesized a kind of organic–inorganic nanocomposite (PPy/GNS/RE³⁺/DBSA) involving pyrrole, graphene nanosheets (GNS), rare earth elements (RE³⁺ = La³⁺, Sm³⁺, Nd³⁺) and dodecyl benzene sulfonic acid (DBSA), and the nanocomposite coatings exhibited excellent corrosion protection for carbon steel due to their barrier and passivation behavior. Contri et al. [161] found epoxy containing 5 wt.% nanostructured composites based on montmorillonite-polypyrrole exhibited high aspect ratio, easy dispersion, high electrical conductivity, high impedance and enhanced barrier property. It was concluded that epoxy/Mt-PPy was an excellent corrosion protective coating for carbon steel.

4. Summary and Perspectives

At present, coating is the most popular and effective way to protect the steel structures from corrosion, although many barriers still need to be studied. Based on the existing research, some conclusions can be drawn as follows.

- For most coatings, the protection mechanism includes a physical barrier, electrochemical protection or a combination of both.
- The monomer-conducting polymer coatings protect steel from corrosion by physical barriers and excellent electrochemical behavior, but the physical barrier, adhesion, mechanical strength and durability behavior are not very effective.
- Most bilayered coatings exhibit superior anticorrosive performances than monomer-conducting polymer coatings due to their synergistic effect. Doping some anions such as DS and PW₁₂ ions in the polymer coatings could improve the anticorrosion properties.
- Adding nanoparticles in conducting polymers usually could not only fill the pores to enhance the barrier effect, but can also improve the electrochemical anticorrosion and other performances such as adhesion, thermal stability, mechanical strength and hydrophobic properties. Contrasted with other coatings, the nanopolymer composite coatings reveal excellent anticorrosion behavior and longer durability.
- For more efficiency and wider use, some issues should be considered carefully in future research.
- Nanoclay and nanotube-composite coatings have revealed a full range of prominent anticorrosion behavior, and the reaction mechanism and microstructure should be further studied to develop more efficient coatings.
- Considering that the coating protection period is mainly affected by weathering, surface treatment, environmental pH value, crack resistance and construction craftwork, further research should take all these factors into account and draw a definitive conclusion.
- Further research should have a stronger focus on low-cost, eco-friendly, convenient construction, especially in-site construction and long-service life coatings, and these aspects will directly decide whether the coating is suitable to use and how long it can provide effective protection to steel.
- There is a high demand for specifications and codes for construction technology and quality inspection, which are crucial and necessary for applications.

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