



Review

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



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ABSTRACT

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

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

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1. Introduction

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

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

2. Role of conducting polymers in corrosion protection

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

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

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

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

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