Progress in Organic Coatings 106 (2017) 50–59

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Polyaniline/polyvinyl chloride blended coatings for the corrosion protection of carbon steel

Rafael Marinho Bandeira[a,b], Julia van Drunen[a,*,1], Germano Tremiliosi-Filho[a], José Ribeiro dos Santos Júnior[b], José Milton Elias de Matos[b,**]

[a] Department of Physical Chemistry, São Carlos Institute of Chemistry, São Paulo University, Avenue Trabalhador São-Carlense 400, CEP 13566-590, São Carlos, SP, Brazil
[b] Department of Chemistry, Natural Sciences Center, Campus Minister Petrônio Portella, Federal University of Piauí, CEP 64049-550, Teresina, PI, Brazil

ARTICLE INFO

Article history:
Received 29 December 2015
Received in revised form 17 January 2017
Accepted 7 February 2017

Keywords:
Corrosion protection
Blended polymer coatings
Polyaniline
Polyvinyl chloride
1010 steel

ABSTRACT

This article presents the corrosion protection ability of blended polyaniline (PANI) and polyvinyl chloride (PVC) polymers applied on 1010 steel. The PANI/PVC blends, as well as pure PANI coatings, were fabricated via a casting method and characterized using infrared spectroscopy. Carbon steel substrates protected with the coatings were subjected to 40 day exposure tests in saline (3% NaCl) and acidic (0.1 M HCl) environments and subsequently analyzed using electrochemical methods Electron microscopy (SEM) and spectroscopic methods (EDS and XPS) were used to study the corroded surface of the 1010 steel underlying the protective coating, as well as the polymer coating itself. The PANI/PVC blends demonstrated superior corrosion protection in both environments as compared to pure PANI and pure PVC coatings. The PANI/PVC blend with a 1/1 proportion offered the most effective corrosion protection in acidic and saline environments based on high charge transfer resistance values and corrosion potential values that approach zero volts. The corrosion protection abilities of the blended coatings are attributed to a combination of barrier protection from the PVC and the formation of a protective oxide layer at the steel-to-polymer interface that is facilitated by the conductivity of PANI.

1. Introduction

Polyaniline (PANI) is a semiconductive polymer comprised of benzoid and quinoid rings [1]. The proton-doped form of this polymer possesses high electron conductivity that favors its use as a protective coating for metals that form a passive oxide upon corrosion [2]. Studies have suggest that PANI may be reduced to maintain surface passivation and then be successively reoxidized by air [3]. Although the mechanisms for corrosion protection with conductive polymers are not completely understood, two effects are often considered to explain the effectiveness of these coatings. The first is a simple barrier mechanism in which the polymer isolates the metal from the corrosive environment through the formation of an impermeable layer [4]. Corrosion protection based on a physical barrier is negatively impacted by cracks and defects, thus it is dependent on good adhesion of the coatings. The second effect is electrochemical in origin. In the case of certain metals and alloys, the application of a conductive polymer such as PANI facilitates the formation of a passive surface oxide [5–7]. Several studies have shown that PANI exhibits strong protection of metals and alloys, such as steels and aluminum, through this mechanism [8–12]. PANI coatings deposited via electropolymerization are often vulnerable to cracking that arises from the deposition process [13]. This problem can be mitigated through the use of a chemical synthesis process that produces a high molecular weight polymer which can effectively coat a variety of metals with different surface morphologies [14].

Polyvinyl chloride (PVC) also possesses attractive proprieties for use as corrosion protection coatings that include good mechanical characteristics (i.e. elastic modulus and shock adsorption), as well as chemical resistance to acidic, alkali, and oxidative environments. The low cost and wide availability of PVC promotes the

* Corresponding author at: Instituto de Química de São Carlos, Universidade de São Paulo, 13560-970, São Carlos, SP, Brazil.
** Corresponding author.
E-mail addresses: julivandrunen85@gmail.com (J. van Drunen), jmematos@ufpi.edu.br, jmematos@gmail.com (J.M.E. de Matos).
[1] Present affiliation: Metrohm Autolab B.V., Kanaalweg 29-G, 3526 KM, Utrecht, The Netherlands.

http://dx.doi.org/10.1016/j.porgcoat.2017.02.009
0300-9440/

immediate and facile application of this polymer in industrial processes [15,16]. In addition, PVC can be used as a capacitive coating material for corrosion protection [17]. In 2000, Oladegaragoze and Mirmohseni compared the anti-corrosive properties of PANI and PVC coatings on iron; the study demonstrated that PANI offers the superior corrosion protection as evidenced by more noble corrosion potential values [18].

The use of PANI-based blends as corrosion protection coatings has shown to be successful for iron and its alloys. Studies on this topic have demonstrated that certain PANI-containing blends are more protective than pure PANI coatings [19,20]. Chen and Liu studied PANI blended with partially phosphorylated poly(vinyl alcohol) as a coating for mild steel [20]. They attributed the observed improvement in corrosion protection to the presence of a thin and uniform oxide layer (Fe_2O_3), as expected for steel protected with a conductive polymer coating. However, the presence of additional iron-phosphate complexes was also linked to improvements in corrosion protection. Elsewhere, it was shown that more nobel corrosion potential values are measured for carbon steel protected with a polyaniline-jackfruit latex blend than for steel protected by pure PANI [19]. The same study noted that the blended coating also displayed improved adhesion to the substrate. Another promising polymeric blend for corrosion protection of steel is polyaniline combined with poly(methylmethacrylate) (PMMA) [21–23]. Besides the straightforward blending polymers with desirable properties to form superior coatings, another strategy is the addition of dopants. Silva et al. studied the effect of adding passivating dopants to PANI/PMMA blends for the corrosion protection of different metals [22]. They found that PANI/PMMA blends containing phenylphosphonic acid were effective coatings for the protection of various metallic substrates. These studies demonstrate that PANI-based blends can be fine-tuned in several ways to further optimize their properties.

1010 carbon steel is an important model alloy for corrosion protection studies because the results can be extended to many iron-based materials [3,7,18,24–26]. This variety of steel contains up to 0.3% by weight of carbon and is more susceptible to oxidation than many iron alloys [27]. In general, steel (not specifically 1010 steel) is used for structural and transport applications such as bridges, pipelines, nautical ships, and others [27–29].

Herein we have investigated the applicability of PANI/PVC blended polymers as corrosion protection coatings for carbon steel materials. PANI/PVC blended coatings were characterized by infrared spectroscopy and evaluated in comparison to pure PANI and PVC using electrochemical impedance spectroscopy and linear polarization measurements. Corrosion tests (40 days of exposure) and delamination tests (7 days of exposure) were carried out in saline ($NaCl_{(aq)}$) and acidic ($HCl_{(aq)}$) media. Scanning electron microscopy (SEM), and elemental analysis in the form of energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) were applied to investigate the steel surface after the exposure tests.

2. Experimental section

2.1. Pre-treatment of 1010 steel substrates

Uniform surfaces of 1010 steel substrates (*Ferro Norte LTDA*) were prepared by grinding using abrasive emery papers of different grades (400, 600, 800, 1000, and 1200) in order to remove scratches and irregularities. The substrates were subsequently cleaned and degreased by washing with acetone and distilled water [7]. The chemical composition of the alloy, in percent by weight, is 0.45% Mn, 0.103% C, 0.065% Si, 0.03% S, 0.02% P; the balance is Fe.

2.2. Synthesis of PANI

The polyaniline used in the coatings was prepared using a chemical synthesis method. Briefly, the oxidation of aniline (*Vetec* 99.5%) was performed in a 0.5 M solution of sulfuric acid (*Vetec* 95–99%) with 2.5 M ammonium persulfate (*Sigma Aldrich* 98%) as the oxidizing agent to obtain PANI in the emeraldine salt state. Subsequently, the PANI was treated with ammonium hydroxide (0.5 M, Vetec 30–32%) for 24 h at room temperature while stirring to obtain the emeraldine base form. The PVC used in this study is commercially available as a film (WYDA® Brazil) and was solubilized from its as-received state. More information about the PVC starting material is included in the Supplementary Information section.

2.3. Application of synthesized coatings

Films of PANI, PVC, and PANI/PVC blends were coated onto the polished 1010 steel substrates using the following method. First, the PANI and PVC were solubilized in *N*-methyl-2-pyrrolidinone (NMP) (*Sigma Aldrich*) by adding 1 g of either PANI, PVC, or PANI/PVC to 30 mL of NMP. These solutions were stirred for 1 h. In order to prepare the blends, the polymers were mixed in different proportions by mass-to-mass ratios in order to obtain 4/1 and 1/1 PANI/PVC proportions. After stirring, the solutions were filtered using a cellulose membrane (Unifil, 0.45 μm) to remove any non-solubilized polymeric agglomerates. The steel substrates were coated with 800 μL of the filtered PANI, PVC, or PANI/PVC solution. The films were then dried in air at 60 °C for 12 h. The thicknesses of the resulting films were estimated from SEM images (presented in the Supplementary information Section). Different film thicknesses were obtained for the different types of coatings: pure PVC 66 ± 4 μm; pure PANI 25 ± 2 μm; and PANI/PVC blends 19 ± 1 μm. We believe that the higher thickness values obtained for the pure PVC films is due to trapping of solvent molecules between the polymer chains brought about by the strong interaction between PVC and NMP.

2.4. Delamination tests

Delamination tests were carried out on 1010 steel covered with the PANI/PVC 1/1 coating. Artificial defects (scratches) were produced on the coating in order to induce delamination. The electrodes were then exposed to 3% NaCl or 0.1 M HCl solutions for 168 h; images of the coating and the steel surface after removal of the coating were obtained with a digital camera.

2.5. Spectroscopic and microscopic analysis

Fourier transfer infrared (FTIR) spectroscopic analysis of the polymer films was carried out using a Bruker spectrometer, model Vertex 70, with a spectral resolution of 4 cm^{-1}. The films for FTIR analysis were first formed on glass slides and then detached for analysis.

Ultraviolet and visible light spectroscopy (UV/Vis) of the polymer films was carried out using a Shimadzu UV–Vis-NIR spectrometer, model UV-3600. In the case of the UV/Vis analysis, the polymer films were deposited on 1010 steel substrates then detached for analysis, which was performed on both the top and bottom surfaces of the films.

Scanning electron microscopy (SEM) was carried out using an SS – 550 model microscope (Bara Scientific) equipped with an SEDX – 500 model energy dispersive X-ray spectrometer (EDS). An electron accelerating voltage of 15.0 kV was applied. The SEM and EDS analyses were carried out after the 40 days exposure tests for steel samples protected by PANI/PVC 1/1 coatings. The polymer coatings were removed prior to SEM analysis so that the degree of corrosion