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Progress in Organic Coatings

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

Functionalized coatings based on organic polymer matrix against the process of corrosion of mild steel in neutral medium

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ARTICLE INFO

Keywords:

Corrosion
Base emeraldine
Salt emeraldine
Electrochemical impedance
Docking
Interactions

ABSTRACT

To obtain a protective system against corrosion process of carbon steel in a near neutral electrolytic solution prepared with 26.5 g NaCl and 3.5 g of $(\text{NH}_4)_2\text{SO}_4$, a series of coatings were formulated. They were based on a nitrocellulose resin in which 3% w/w of a composite material (PANIB-F or PANIS-F) prepared with either base polyaniline (PANIB) and its salt (PANIS) were formed as a matrix, in which 10% w/w of fluconazole (F) as a corrosion inhibitor was dispersed. The synthesized materials were characterized by techniques such as: FTIR, DRX, and SEM. The protective behavior of the synthesized coatings was evaluated by electrochemical impedance spectroscopy (EIS). The results of the electrochemical tests indicated that the formulated films with the PANIB-F composite, provide highest protection to the metal substrate than the one formulated with PANIS-F. For the understanding of the protection mechanism and the molecular interactions of the composite materials (PANIB-F and PANIS-F respectively), a molecular coupling simulation was performed considering the experimental conditions. Calculation of binding energies was performed and obtained using the Adaptive Poisson-Boltzmann (APBS) software. The results of the simulation suggest that PANIB has less affinity for F than PANIS, which favors the F dissolution when the electrolyte penetrates the pores of the coating.

1. Introduction

Chemical stability and its redox unique properties, generate high interest in conjugated polymers such as polyaniline, in addition to its many potential uses in a wide range of applications in various fields of science. Considering these redox properties, polyaniline can be defined as a mixture of three different oxidation states of the polymer [1]: the leucoemeraldine (completely reduced) structured type aryl amine fragments; the pernigraniline (completely oxidized) form only the fragments quinonimine; and emeraldine (partially oxidized) formed by alternate aryl amine fragments and quinonimine. When emeraldine has an oxidation state of (0.5), it is known as emeraldine base, *i.e.*, containing the same number of oxidized and reduced units. When being doped by protonation or by the action of an oxidizing agent (type-p doped polyaniline), the conductive polymer form is obtained with a

conductivity of 10^{-9} to about 10^2 Sie^{-1} [2,3]. This form of the polymer is called as emeraldine salt.

One of the most explored application areas of polyaniline during the last decades, is its protective activity of metals against corrosion process, which is a very serious problem worldwide. Although there is consensus on the observed performance; until now, it is still unclear if this is attributable to the conductive or non-conductive form of emeraldine. Because of that, it may be helpful to determine the protective action (and its mechanism) against the process of metal corrosion protection [4,5].

T. P. McAndrew [6] described several mechanisms that may be occurring at any time: the first one is a simple galvanic process in which the polymer has a lower oxidation potential than metal, and it is preferentially oxidized; the second one would be a barrier mechanism due to the insolubility of the oxidized polymers, providing protection for

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<https://doi.org/10.1016/j.porgcoat.2017.12.011>

Received 13 January 2017; Received in revised form 11 October 2017; Accepted 12 December 2017
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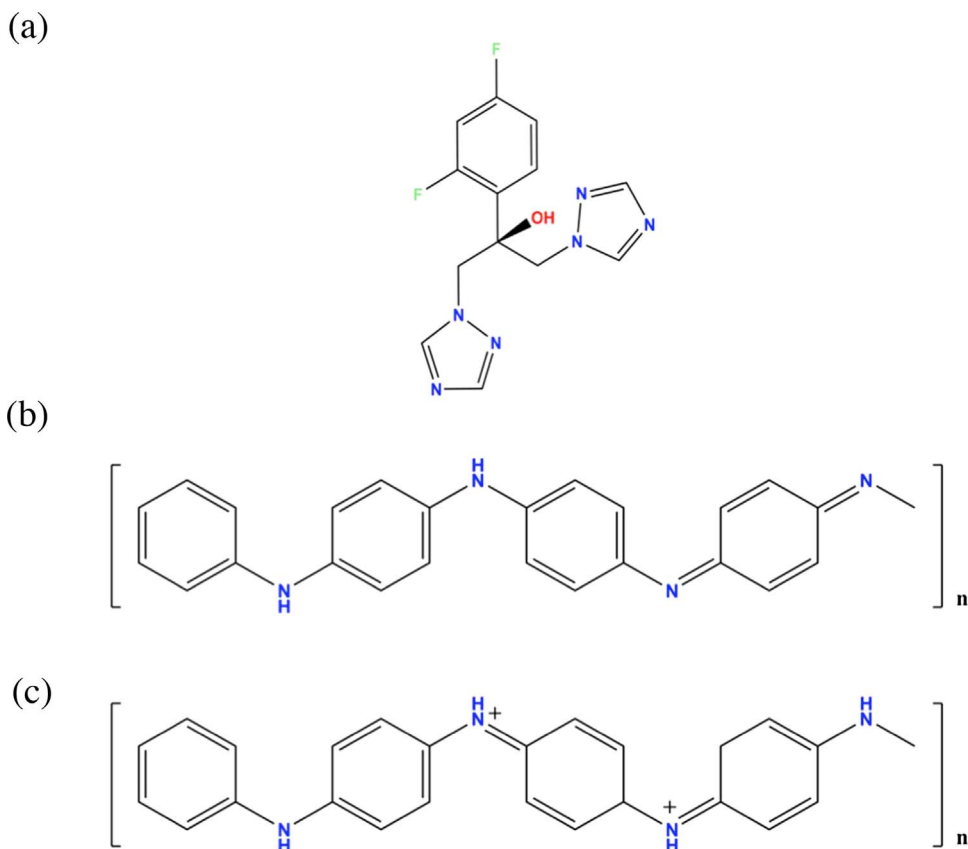


Fig. 1. Chemical structures of: a) F molecule, b) Oxidation state for base emeraldine (PANIB), and c) Oxidation state for salt emeraldine (PANIS). Structures were constructed with Maestro software [17].

longer periods of time. Another proposed mechanism is that the polymer reacts with the metal surface, which necessarily requires that the polymer has a higher potential than the metal oxidation, forming a passivation layer that inhibits further corrosion either by creating a barrier, and/or by altering the potential of the metal surface. In conclusion, the polyaniline can passivate the metal surface by forming a film of $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ between the coating of PANI and the metal surface [7,8].

Martyak et al. [9], proved that PANIB (deprotonated form of emeraldine) has better corrosion performance with respect to PANIS (doped or protonated form of emeraldine). Kalendova et al. [10] demonstrated that when the PANIB coating is exposed to an external stimulus, a coexistence of its different oxidation states can be given and thus participate in both processes: anodic and cathodic.

In this study our interest was focused in comparing the anticorrosive effect of the base and salt forms of emeraldine (PANIB and PANIS respectively) when it is used as a matrix for the dispersion of an organic inhibitor, an expired recycled medicine F (Fig. 1a); depending on interaction forces between the PANI matrix (both, its nonconductive form, Fig. 1b, and its conductive form, Fig. 1c) and the active molecule (F), whose inhibitory behavior of carbon steel corrosion in near neutral medium, has been evaluated in previous studies [11]. It was modeled PANIB or PANIS considering a single chain and four repetitive polymer chains, as some authors suggest [12–16], which are shown in Fig. 1. These docking models allowed to further determine the polar/electrostatic (ΔG_p) and nonpolar (ΔG_{np}) contribution to the free energy of binding interaction between both, PANIB, and PANIS with F. Our binding studies suggest that PANIS has more affinity because is driven by electrostatic interactions respect to PANIB (governed by hydrophobic interactions), both in its single chain form and four repetitive polymer chains. The importance of this system provides new insights at the molecular mechanism of the interaction of polyaniline with F is an essential key contributing to understand why the PANIB-F composite has better protection against corrosion process, compared with PANIS-F

composite. It also contributes to the possible use of synthesized coatings based on more eco-friendly components with recycled expired medicine drugs

2. Experimental

2.1. Reagents and materials

Carbon steel specimens were polished with abrasive paper of different grit size up to 1200. Sodium chloride (NaCl) ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$, aniline ($\text{C}_6\text{H}_5\text{NH}_2$), and ammonium persulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ were obtained from Sigma-Aldrich, with Lot. No. SLBJ2691V, NKBP2553V, SHBC4016V and SLBK1506V respectively. HCl (36.5–38%) hydrochloric acid was obtained from Meyer with Lot No. C0914593. The nitrocellulose resin was obtained from Nervión Industries (Bilbao, Spain).

2.2. Synthesis of polyaniline

The polyaniline matrix was synthesized by chemical oxidative polymerization of aniline in 2 M hydrochloric acid. To that, 5 mL of aniline were dissolved into 60 mL of 2 M hydrochloric acid. After this, 200 mL of a 0.2 M solution of ammonium persulfate (as an initiator and oxidant) were added slowly stirring gently the solution, once the aniline was dissolved. The reaction mixture remained under stirring and at 277 K for 8 h. The dark green precipitate (the conductive form of polyaniline (PANIS)), was filtered and washed with abundant distilled water. After washing again with methanol, it was dried at 353 K for 48 h.

To obtain the non-conductive polyaniline (PANIB), 1 g of PANIS was treated with 500 mL of ammonium hydroxide 0.1 M at room temperature, and stirring for 8 h. Thereafter, the suspension was filtered, washed, and dried at 353 K for about 8 h, obtaining a dark blue precipitate PANIB, according to Piromruen et al. [18].

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