Progress in Organic Coatings 119 (2018) 138–144

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

The influence of the polyaniline initial oxidation states on the corrosion of steel with composite coatings

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ARTICLE INFO

Keywords:
Conducting polymers
Reprotonation
Dopant anions
Alkyd binder
Mechanism

ABSTRACT

The chemically synthesized polyaniline in the powdered form by the procedure recommended by IUPAC is reprotonated using sulfamic, citric, succinic and acetic acid. The UV–vis spectroscopy is applied to estimate doping degree of the reprotonated samples. The estimated doping degrees are as follows: the polyaniline doped with sulfamic acid 0.28, with succinic acid 0.18, with citric acid 0.15 and with acetic acid 0.13. The composite coatings are prepared by mixing the alkyd based commercial paint with 5 wt.% of the reprotonated samples and painted on mild steel. Using linear polarization method, the polarization resistances of the composite and base coatings are determined in 3% NaCl. It is shown that initial oxidation state of the polyaniline determined the values of polarization resistance which decrease in the following order: R_p(sulfamic) > R_p(succinic) > R_p(citric) > R_p(acetic) ~R_p(base coating). For all composite coatings, increases in the corrosion potentials are observed during the time, while for base coating decrease. The steel samples with base and composite coatings are also immersed in 3% NaCl, after 150 h visually inspected, and by the optical microscope. It is shown that composite coatings reduce the possibility of blister formations and delamination. The appearance of the corrosion products closely follow the initial oxidation state of the polyaniline. It is suggested that such behavior could be connected with the oxygen reduction mechanism that proceed mainly via two electron path on the polyaniline particles, releasing a much smaller amount of hydroxyl ions, responsible for the delamination and blister formations.

1. Introduction

Composite organic coatings in which the polyaniline powder is added are intensively investigated in the active protection of steel against corrosion [1–4]. Polyaniline in the emeraldine form, can exist as a base or salt, but there is still a debate which form offers better corrosion protection [5]. Due possibilities of doping with different organic and inorganic anions which produces different doping degree and corresponding conductivity of the initial polyaniline powder, there are a huge dissipations of reported results concerning corrosion protection of mild steel [6–10]. The synthesis of polyaniline in powdered form by the oxidative polymerization using ammonium persulfate [11] is widely used, but the synthesis procedures vary. In many papers, authors added different organic and inorganic acid in the reaction mixture claiming that only used acid anion is doped in the polyaniline chain [12–15]. However, in our opinion, under this synthetic condition, there are no reasons that sulfate anions will be doped as well, because a significant amount of the sulfuric acid is released during polymerization reaction. Therefore, to avoid this confusion, for the reproducibility, the well-established procedure of polyaniline synthesis as recommended by IUPAC [11] should be used, and the reprotonation of the polyaniline base route with corresponding acid will be the best method to obtain well-defined polyaniline salt, as proposed by Stejskal et al. [16]. In addition, the mechanism of the corrosion protection of the steel by polyaniline is still not completely clear [1].

Hence, the aim of this work will be to investigate corrosion protection of mild steel with composite base coating-polyaniline in the form of powder as an anticorrosion additive. The polyaniline will be prepared according to recommended IUPAC procedure [11] and reprotonated with different common organic dopant anions that possess a wide range of initial conductivity [16]. The main goal will be to determine does the initial oxidation states of polyaniline influenced the corrosion behavior.

2. Experimental

The chemical synthesis of polyaniline is conducted according to the standard IUPAC procedures, recommended by Stejskal et al. [11].

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https://doi.org/10.1016/j.porgcoat.2018.02.032
Received 26 June 2017; Received in revised form 21 November 2017; Accepted 27 February 2018
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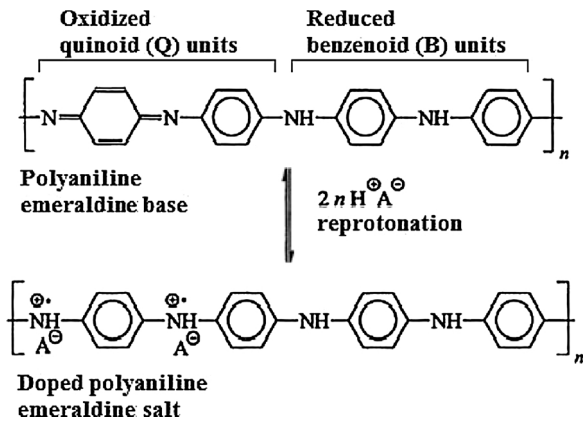

Scheme 1. Representation of polyaniline base reprotonation with corresponding acids (HA).

Aniline hydrochloride is prepared by mixing of 0.22 mol HCl (8 g or 26 cm^3 of 37 wt.% HCl, p.a. Merck) with 0.22 mol aniline monomer (20.46 g or 20.8 cm^3, p.a. Sigma Aldrich, previously distilled under reduced pressure) at room temperature in 500 of distilled water. After stirring, 500 ml of 0.22 mol HCl contained 0.275 mol (62.81 g) of $(NH_4)_2S_2O_7$ is slowly added dropwise. After 24 h of stirring, the green powder is filtered, washed several times with 0.1 M HCl, distilled water and acetone, and dried overnight. Part of the obtained as synthesized polyaniline powder (ES-IUPAC) is treated with 1 M NH_4OH for 24 h to obtain the emeraldine base. After washing with distilled water, acetone and drying, the obtained emeraldine base (EB-IUPAC) powder is separately treated 24 h with 0.8 M of sulfamic, succinic, citric and acetic acid solutions, to produce the polyaniline in the form of emeraldine salt. In a typical procedure, 2 g of the polyaniline base is added to 100 cm^3 solutions of corresponding acids. The process of the reprotonotation of the polyaniline emeraldine base in salt form is shown in Scheme 1.

Composite coatings are prepared using the commercial finishing paint for iron, "*Professional emajl lak*", Nevena Color Xemmax, Serbia, based on an alkyd binder and white pigments in organic solvents, containing 67% of solids (determine by a measure of wet and dry paint). The base paint and base paint modified with 5 wt.% polyaniline emeraldine salt (based on dry paint), after proper mechanical mixing, is applied using a scalpel-blade based method on the properly cleaned AISI 1212 mild steel, in the shape of cylinders inserted in plastic holder to avoid edge effects on the free circle side ($A = 2\ cm^2$) of the sample. Sample holders, shown in Fig. S1, is constructed to simultaneously measure five samples. After drying in the air for 24 h, the average coating thickness is 40 ± 2 μm, measured using Byko-test 4500 FE/NFe (Germany) coating thickness tester.

The UV–vis spectra of the polyaniline samples in powdered form dispersed in the water (~15 mg/20 cm^3) is recorded using a LLG uniSPEC 2 spectrophotometer. The water dispersion of polyaniline is prepared by vigorous sonication during 30 min, and precipitation of a larger particle during one hour. The rate of the corrosion of the samples is investigated in 3% NaCl by the linear polarization method using a Gamry PC3 potentiostat controlled by a computer. The rectangular glass cell with volume 1 dm^3 is used. The stainless steel series 304 counter electrode (4 cm × 16 cm) and saturated calomel electrode as reference are used.

Qualitative investigations of the coatings are also performed. In that manner the base and composite coatings are painted on well-cleaned mild steel samples, 5 cm × 4.5 cm, using roller brushes, which back side and the edges are protected with thick ~200 μm epoxy based paint. The average coating thickness of d ~25 ± 5 μm is measured. The samples are separately dipped in a 200 cm^3 of 3% NaCl solution. The quality of the coatings is visually compared after 150 h of immersion, and the images are taken with a digital camera. Optical micrographs are obtained with an optical microscope Olympus CX41 connected to the personal computer.

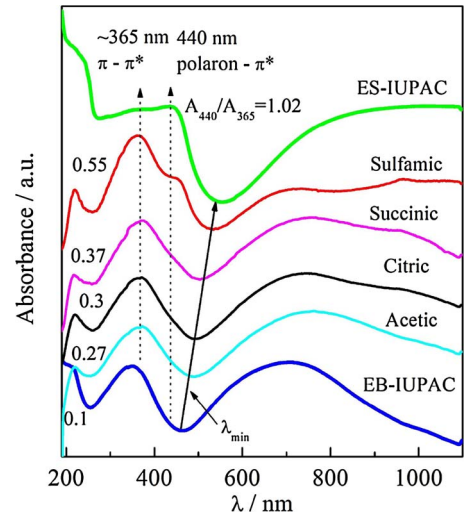

Fig. 1. UV–vis absorption spectra of the polyaniline samples dispersed in distilled water.

3. Results and discussion

3.1. Characterization of the polyaniline powder

The UV–vis spectra of the different polyaniline samples dispersed in distilled water from 190 to 1100 nm are shown in Fig. 1. For as synthesized polyaniline in the emeraldine salt form (ES-IUPAC) the absorption peak at 365 nm is assigned to the π–π* transition within the benzenoid ring (B). The peak at 440 nm could be assigned to polaron − π* transition within the quinoid structure (Q), followed by a broad tail associated with polaronic structures [17,18]. The spectra of the deprotonated polyaniline in the emeraldine base form (EB-IUPAC) among red shifted B peak to ~340 nm, had a strong broad peak centered at ~700 nm, which is attributed to the molecular excitation associated with the quinoid-imine structure [17]. The ratio of absorbance of benzenoid, 365 nm (π–π* transition) to quinoid, 440 nm (polaron– π* transition) bands can be taken as a measure of the oxidation state in the polyaniline type conducting polymer [19–23].

For the chemically doped (reprotonated) samples, Fig. 1, the peaks at ~200–240 nm can be assigned to the absorption of corresponding acids (Fig. S2). Broad tail above ~500 nm is associated with polaronic structures in the polyaniline [17,18]. All the reprotonated samples have a peak at 365 nm from π–π* transition, and more or less pronounced absorption at 440 nm from polaron-π* transition. From Fig. 1 can be seen that sulfamic acid doped polyaniline have a peak at 440 nm, polyaniline doped with succinic acid have a shoulder, while samples doped with citric and acetic acids has increased absorption in comparison with emeraldine base form. So, the ration of A_{365}/A_{440} absorptions could be used as an indicator of the reprotonated polyaniline oxidation level. The absorption A_{365}/A_{440} ratio of as synthesized polyaniline emeraldine salt form (ES-IUPAC) sample is 1.02, for sulfamic acid 0.55, for succinic acid 0.37, for citric acid 0.30 and for acetic acid 0.27, as shown in Fig. 2. Hereafter, if we assume that as synthesized sample of the polyaniline (ES-IUPAC) is fully oxidized emeraldine salt with doping degree, y equal to 0.5, the doping degree of the reprotonated polyaniline could be estimated as $0.5 \times A_{365}/A_{440}$. Accordingly, the doping degree, of the polyaniline doped with sulfamic acid is 0.28, with succinic acid 0.18, with citric acid 0.15 and with acetic acid 0.13. It should be also mentioned that minimum absorption, λ_{min}, in the range of 450–500 nm, is shifted to the higher wavelengths by increasing the A_{365}/A_{440} ratios, as showed by an arrow in Fig. 1, indicating increased of the polyaniline oxidation level. The value of

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