Long-term corrosion protection of mild steel by epoxy coating containing self-doped polyaniline nanofiber

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ABSTRACT

Sulfonated polyaniline (SPANI) with good processability and well-dispersion in common organic solvent was synthesized via the copolymerization of 2-aminobenzenesulfonic acid and aniline and was identified by UV-vis, Raman, X-ray photoelectron spectroscopy, X-ray diffraction and scanning electron microscopy. SPANI/epoxy composite coatings on the steel substrate were prepared for the anti-corrosive investigations in 3.5 wt% NaCl solution via electrochemical impedance spectroscopy and polarization curves. It turned out that composite coatings with SPANI exhibited excellent protective performance with high impedance modulus during the 120 days immersion while blank epoxy coating has been invalid after 80 days immersion. Finally, the passivation of steel substrate by SPANI containing composite coating was proved by the composition and morphology of the rust products beneath the coatings. It's concluded that self-doped SPANI enhanced the anti-corrosive property of composite coatings via forming a metal oxide film composed of Fe_2O_3 and Fe_3O_4.

1. Introduction

Metal corrosion is an urgent issue in many industries and brought about one of the biggest economic lost worldwide. Despite its inevitability, corrosion is controllable by applying an organic coating on the metal to form a physical barrier between metal and corrosive environment [1] or forming polyelectrolyte coating with pH-buffering activity to stabilize the local pH [2,3]. Such organic coatings provide the protection not only through the barrier action but also via an active anti-corrosive effect obtained by the inhibiting additives incorporated in the coatings [4]. For years, the most effective corrosive inhibitors are hexavalent chromium (Cr^{6+}) or lead-based compounds and zinc-rich coatings, which are highly toxic to environment and human health [5]. The aspects of heavy metal toxicity have prompted the search for nontoxic and ecologically acceptable corrosion inhibitors for metal protection.

Conducting polymers, especially the most frequently investigated polyaniline (PANI) and its derivatives, deserve to be mentioned in the field of anti-corrosion. Its excellent environmental stability, facile synthesis and reversible acid/base doping/dedoping performance endue PANI with the potential applications for organic light weight batteries, field-effect transistors and chemical sensors [6,7]. Particularly, PANI and its derivatives are regarded as ideal corrosion inhibitors

due to the π-electrons in the benzene rings and abundant nitrogen on the conjugated backbone [8]. Researchers found that polyaniline was capable of inhibiting the corrosion of the metal such as stainless steel [9], mild steel [10], copper [11], aluminum [12] and aluminum alloys [13,14]. Kraljic and co-workers [15] electrodeposited the polyaniline film using H_2SO_4 and H_3PO_4 on low alloy steel and discovered its superior anticorrosive capability [15]. However, the necessary acid medium for the electrodeposition affects the adhesion negatively and leads to inevitable corrosion of metal substrate [16]. Besides, the insolubility of PANI makes trouble for the application of electrochemical method [17]. Another alternative strategy is adding PANI into the polymeric matrix to form composite coatings [18]. In this case, it's essential to promote its solubility and processability. Recently, we synthesized soluble butyl-substituted PANI (P2BA) and explored it to exfoliate graphene in epoxy coatings for achieving synergistic corrosion protection from electroactive P2BA and graphene barriers [19]. Rathod et al. [20] studied the corrosion resistance of polyanilines doped by sodium dodecyl benzene sulfonate (SDBS), camphor sulfonic acid (CSA) and HCl and found that PANI-SDBS salts coated on 316LN had superior resistance to corrosion. Syed et al. synthesized the water-soluble PANI-PAA composites as a corrosion inhibitor, and found that the PANI-PAA network-like structure not only avoided the sudden breakdown but also formed an insulating layer by the adsorption process on 316SS surface

[21]. Moreover, the copolymerization from aniline and its derivatives endues the polymer with improved solubility, thermal/chemical stability and processability [21–24].

The aim of this study was to prepare soluble sulfonated polyaniline (SPANI) by the copolymerization of aniline and 2-aminobenzensulfonic acid and apply it as a corrosive inhibitor in the epoxy coating. The corrosion protective performance of as-prepared composite coatings was investigated by the electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization in 3.5 wt% NaCl solution. Besides, the protective mechanism of self-doped SPANI was explained and proved by the characterization (morphology and structure) of rust layer beneath the coating.

2. Experimental procedure

2.1. Experiment materials

Aniline, 2-aminobenzenesulfonic acid, ethanol (99.5%), aniline dimer and ammonium peroxydisulfate [$(NH_4)_2S_2O_8$] were purchased from Aladdin Industrial Corporation and used by no purification. Epoxy resin (E44) and curing agents were purchased from Yunda Chemical Co., Ltd. China.

2.2. Synthesis of self-doping sulfonated polyaniline

Sulfonated polyaniline (SPANI) was obtained through the following procedure (Fig. 1). First, 50 mmol aniline and 25 mmol 2-aminobenzenesulfonic acid was completely dissolved in the 1 M HCl aqueous solution of 100 mL, respectively. And the 10 mL ethanol with 1.875 mmol aniline dimer was prepared in reserve. Then the monomer solution and aniline dimer solution were mixed homogeneously and stirred for 30 min. The 200 mL 1 M HCl solution with 75 mmol $(NH_4)_2S_2O_8$ was added into the above-prepared mixed solution with vigorously stirring for few seconds. Subsequently, the reaction was in progress without disturbed for 24 h at ambient temperature. The green-black products were collected by the filtration and washed by deionized water repeatedly. Finally, the resultant SPANI nanofibers were dried in a vacuum oven at 40 °C for 12 h.

2.3. Preparation of SPANI/epoxy coatings

The as-made SPANI nanofibers were weighed (0.125 g, 0.25 g and 0.5 g for 0.5 wt%, 1 wt% and 2 wt% per sample, respectively) and dissolved in 50 mL ethanol. After 20 g Epoxy-44 resin was added into the SPANI dispersion, the mixture was uniformly mixed by ultrasonication (1500 W) for 1 h and removed ethanol via rotary evaporation at 60 °C for 20 min. Subsequently, the curing agents (5 g) were mixed into the above SPANI/epoxy resin mixture via mechanical stirring (2000 rpm) for 10 min. The well-mixed composites were painted onto the Q235 electrodes (1 cm^2) by a bar coater (20 μm) for electrochemical measurements. It's notable that the Q235 electrodes were ultrasonicated (1500 W) repeatedly in acetone and anhydrous ethanol for degreasing and then polished by 180-grit, 400-grit, 800-grit and 1500-grit sand papers. The coatings with 0.5 wt%, 1 wt% and 2 wt% SPANI were marked as SPANI-0.5, SPANI-1 and SPANI-2, which pure epoxy coatings (marked as SPANI-0) were prepared for blank control samples. The prepared coatings were cured for 2 h at 60 °C to accelerate full curing after the coatings' surface was dry.

2.4. Characterization

The UV–vis spectrum of SPANI powder dispersed in ethanol was obtained with Lambda 950 spectroscopy. The Raman spectrum was scanned by Renishaw inVia Reflex. The X-ray diffraction (XRD) patterns of SPANI and corrosive products beneath the coatings were identified by X-ray powder diffractometer (D8 ADVANCE) using monochromatic Cu Kα radiation at a speed of 5°/min in the scan range of 2θ = 5–85° and 2θ = 10–90°, respectively. The X-ray photoelectron spectroscopy (XPS) spectra were measured by Kratos multifunctional X-ray photoelectron spectroscopy (AXIS UTLTRA DLD). Scanning electron microscopy (SEM) observations of SPANI and freely fracture surfaces for coatings were carried out on a field emission SEM (Hitachi S-4800) at an accelerating voltage of 4 kV and 6 kV, respectively. The morphologies of corrosive products on the metal substrate were observed by FEI-SEM (Quanta FEG 250).

2.5. Electrochemical measurement for coatings

The electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves for coatings on Q235 electrodes (1 cm^2) in 3.5 wt% NaCl solution were collected by CHI-660E electrochemical workstation equipped with a saturated calomel electrode (SCE) as the reference electrode and a platinum plate (2.5 cm^2 area) as the counter electrode. The parameters for EIS were frequency region of 10^{-2}–10^5 Hz and alternating current (AC) signal with amplitude of 20 mV. The polarization curves were scanned from cathodic direction to anodic direction ($E_{ocp} \pm 250$ mV) with the rate of 1 mV s^{-1}. The protective efficiency (PE) was calculated by the following Eq. (1) [25]:

$$PE = \frac{i_{corr}^{bare} - i_{corr}}{i_{corr}^{bare}} \times 100\%$$

(1)

where i_{corr}^{bare} and i_{corr} signify the corrosion current density in the absence and presence of coatings.

3. Results and discussion

3.1. Characterization of self-doping sulfonated polyaniline

The UV–vis spectrum of sulfonated polyaniline was shown in Fig. 2a. It exhibited two characteristic peaks at 330 nm and 645 nm attributed to the π–π* transition of the benzenoid ring and the polaron−π* transition of the quinonoid ring, respectively [26]. Raman spectroscopy offered an efficient method to certify the structural characteristics of sulfonated polyaniline as shown in Fig. 2b. The Raman spectrum of SPANI showed bands at 413 cm^{-1} and 518 cm^{-1} for the out-of-plane ring deformation, 575 cm^{-1} for phenoxazine-type units and 718 cm^{-1} mainly due to the amine deformation in bipolarons [27]. The peaks at 810 cm^{-1} and 1185 cm^{-1} reflected the benzenoid ring deformation and the C−H bending of the quinonoid/benzenoid ring, respectively [28]. The small peak at around 1250 cm^{-1} resulted from the C−N stretching vibration of amine form. The intense peak at 1339 cm^{-1} in relation to the stretching mode of the radical cation C ∼ N$^+\cdot$ was also named as the protonation band [29] which proved that SPANI was in its conducting form [30]. The C=C stretching

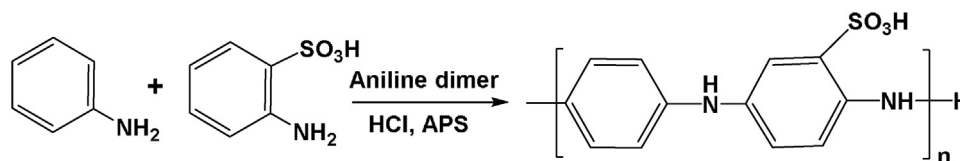**Fig. 1.** Scheme of copolymerization for aniline and 2-aminobenzenesulfonic acid.