



Full Length Article

Corrosion protection performance of waterborne epoxy coatings containing self-doped polyaniline nanofiber

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ABSTRACT

Self-doped sulfonated polyaniline (SPANi) nanofiber was synthesized by the copolymerization of 2-aminobenzenesulfonic acid (ASA) and aniline via a rapid mixing polymerization approach. The chemical structure of SPANi was investigated by the Fourier-transform infrared (FT-IR), Raman, X-ray photoelectron spectroscopy (XPS), UV–vis spectra and X-ray diffraction (XRD) pattern. The as-prepared SPANi nanofibers had 45 nm average diameter and length up to 750 nm as measured by scanning electron microscope (SEM) and transmission electron microscope (TEM). The self-doped SPANi nanofiber possessed excellent aqueous solubility, good conductivity (0.11 S/cm) and reversible redox activity, making it suitable as a corrosion inhibitor for waterborne coatings. The prepared SPANi/waterborne epoxy composite coatings exhibited remarkably improved corrosion protection compared with pure waterborne epoxy coating as proved by the polarization curves and electrochemical impedance spectroscopy (EIS). The passivation effect of SPANi nanofiber and the corrosion products beneath the epoxy coatings immersed in 3.5% NaCl solution as a function of time were also investigated in this study.

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1. Introduction

Metallic corrosion has a major impact on the cost and reliability of industrial facilities, environment and human safety [1]. Organic coatings are one of the most cost-effective means of providing practical corrosion applications. However, all organic coatings are not perfect barriers and they can be inevitably penetrated by water, oxygen, and ions to some extent, resulting in corrosion failures. Therefore, current organic coatings usually are incorporated with heavy-metal as corrosion inhibitors in the primer in order to provide high performance of corrosion protection. For years, the most effective corrosion inhibitors are those containing hexavalent chromium, lead, copper and zinc, which are toxic to the environment and human health [2]. Hence, it is desirable to develop novel corrosion inhibitors that are not only remarkably anti-corrosive but also environmental friendly [3]. During the last decade, the usage of intrinsically conducting polymers (ICPs) as nontoxic anticorrosion coating materials or additives has been received growing interest

both in academia and industry [4]. A variety of ICPs have been developed for corrosion protection including polyaniline (PANi), oligoanilines, polypyrrole, polythiophene, polydioxithiophene and polyvinylcarbazole [5].

Among all the conducting polymers, PANis are the most investigated conducting polymers owing to their facile synthesis, environmental stability and unique redox behavior [6]. It is generally accepted that polyaniline based coatings provided corrosion protections by suppressing permeation of corrosive agents and at the same time allowing the formation of passive oxide layer on the metal surface [7]. PANi can be directly electrodeposited onto the metal substrate as a protective coating by electro-chemical polymerization of aniline monomers [8,9], while it turned out that electrodeposited PANi coating showed limited practical applications owing to its porous structure and poor adhesion to metal substrate [10]. For an efficient corrosion protection, PANi was usually blended in polymeric resin as an additive to form composite coatings, combining the good adhesion and barrier properties of organic coatings and electroactive properties of PANis [11]. In this case, the effectiveness of the composite coatings relied on the solubility and dispersion of polyaniline in the coating matrices [12]. Several strategies have been employed with a view to improve the solubility of PANi, which include choice of suitable dopants

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[13], incorporation of functional group in side chain [14,15] and formation of dispersible nanoparticles or nanofibers [16].

Currently, the majority of PANi based anticorrosive organic coatings are solvent borne, containing a high relative content of toxic organic solvent. The increasing environmental concern and legislation on the emission of volatile organic compounds (VOCs) require the development of new coating technology that emits extremely low or no VOCs [17]. Accordingly, waterborne coating is a fast-growing technology for replacing solvent-borne coating. To get PANi based waterborne coatings with high anticorrosion performance, it is of great importance to improve the dispersion of PANi in aqueous solution. Recently, water-soluble polyaniline nanoparticles doped with anionic species have been attained great interest for anticorrosion applications. For instance, Perrin et al. [8] reported the preparation of bilayer coatings composed of a bottom layer of *n*-decylphosphonic acid (DPA) doped PANi nanocolloids. The efficient corrosion protection from the bilayer coatings was ascribed to the formation of a passive oxide layer by redox-catalytic reaction between PANi and metal and inhibitive properties of DPA. Chen et al. [18] employed phosphorylated polyvinyl alcohol as dopant for preparation of water dispersible PANi nanoparticles by chemical oxidative polymerization. The aqueous epoxy coatings containing resulting PANi nanoparticles offered high anticorrosion protection as confirmed by salt spray test and electrochemical impedance spectroscopy (EIS). Recently, we described an approach to the preparation of conductive PANi nanoparticles with 60–80 nm particle size by dispersion polymerization using H_3PO_4 as dopant and polyvinylpyrrolidone (PVP) as a stabilizer. The addition of water-soluble PANi nanoparticles to waterborne epoxy coating significantly improved the anticorrosion properties, based on polarization curves and EIS investigations [19].

Polyanilines with one dimensional nanostructures, such as nanofiber [20,21], nanotube [22] and nanorod [23], are well known to have various applications including chemical sensors, battery electrodes, supercapacitor and antistatic coatings [24] while there is no report on using aqueous dispersible polyaniline nanofiber as additive for waterborne anticorrosion coatings. In this work, we demonstrated the synthesis of conducting sulfonated polyaniline nanofibers by rapid mixing copolymerization of aniline and ortho-aminobenzene-sulfonic acid with equal molar ratio in 1 N HCl aqueous solution. Self-doped sulfonated polyaniline (SPANi) had been the most studied water soluble conducting polymer since it possessed unusual electro-physical properties, excellent processability and thermal stability [25]. Besides, it exhibited high conductivity, good electrochemical activity and good dispersibility in water, allowing for facile incorporation into waterborne epoxy to form composite coatings. The corrosion protective performance of water-borne epoxy coatings containing different amount of SPANi nanofibers were investigated by potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS). The corrosion products beneath the epoxy coatings after the immersion in 3.5% NaCl solution were also investigated by X-ray diffraction (XRD) and scanning electron microscope (SEM) in this study.

2. Experimental

2.1. Materials

Aniline, hydrochloric acid and ethanol (95%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ammonium peroxydisulfate and o-aminobenzenesulfonic acid were purchased from Aladdin Industrial Corporation. Epoxy resin (H228A) and curing agent (H228B) were purchased from Shanghai Jiuyou Chemical Technology Co., Ltd. The Q235 steel electrodes were degreased by ultrasonication in acetone repeatedly and then polished by the sand

papers of 400, 800, 1200 and 1500 grid. Finally, the electrodes were dried after being rinsed by distilled water and ethanol.

2.2. Synthesis of SPANi nanofiber

Sulfonated polyaniline (SPANi) nanofibers were prepared by using rapid initiation polymerization method (Fig. 1). Aniline (25 mmol, 2.33 g) and o-aminobenzenesulfonic acid (ASA, 25 mmol, 4.32 g) with equal molar ratio were dissolved in 250 mL 1 N HCl solution. The obtained solution was kept mechanically stirring for 1 h. Then 250 mL 1 N HCl solution containing ammonium peroxydisulfate (APS, 50 mmol, 11.40 g) was homogeneously mixed with the monomers solution for a few seconds. The reaction mixture was kept unstirring for 24 h at room temperature. After finishing the reaction, the polymer was collected by decompressed filter and washed with ethanol and distilled water as far as the pH of filtrate reached 5.0–6.0. It was then dried to constant weight in vacuum at 50 °C.

2.3. Preparation of SPANi/epoxy anticorrosion coatings

The composite coatings containing 0.5 wt%, 1 wt%, and 2 wt% of SPANi nanofibers were prepared. General procedure for preparation of SPANi/epoxy composite coatings is as follows. The precalculated epoxy curing agent, SPANi nanofibers and water were mixed by ultrasonic vibration. After water was removed via rotary evaporation, the curing agent (the weight ratio of curing agent and epoxy resin was 4:1) was added and mixed thoroughly. Then the coating material was painted on the Q235 steel electrode surfaces by a bar coater. The coating thickness was controlled by $20 \pm 2 \mu\text{m}$. For the purpose of comparison, pure epoxy coating was prepared in a similar way. The prepared coatings were cured for 96 h under room temperature before measurements.

2.4. Characterization

The Fourier-transform infrared (FT-IR) spectrum was recorded on a NICOLET 6700 spectrometer at a resolution of 1 cm^{-1} with 32 scans. The UV-vis spectra of SPANi fibers dispersed in deionized water and coatings were obtained with Lambda 950 spectroscope. The Raman spectrum was scanned by Renishaw inVia Reflex. The X-ray diffraction (XRD) pattern of SPANi was identified by X-ray powder diffractometer (D8 ADVANCE) at the scan range of 2θ from 10° to 50° and XRD pattern of rust layer on the steel substrate was established at the region of $2\theta = 5\text{--}90^\circ$. The X-ray photoelectron spectroscopy (XPS) spectrum was obtained by AXIS UTLTRA DLD. The scanning electron microscope (SEM) images of SPANi powders and coatings' section were taken by HITACHI S4800 and transmission electron microscope (TEM) images of samples after ultrathin sectioning (RMC PT-XL) prepared on Formvar-coated copper grids were taken by JEM2100. To investigate the conductivity of SPANi, its powder was pressed into a cake with the diameter of 13 mm and measured by four-point probe technique (CRESBOX). The cyclic voltammogram of SPANi was scanned by CHI-660E electrochemical workstation, and the electrochemical measurement of pure epoxy or SPANi/epoxy coatings on the Q235 electrodes was also tested with CHI-660E electrochemical workstation by using conventional three-electrode cell assembly in 3.5% NaCl aqueous solution: coating/Q235 electrode of 1 cm^2 area acts as the working electrode, the saturated calomel electrode (SCE) performs as the reference electrode, and the platinum plate of 2.5 cm^2 area as the counter electrode. The electrochemical impedance spectroscopy (EIS) data were collected in the range of 10^{-2} – 10^5 Hz using an alternating current (AC) signal with amplitude of 20 mV. The SEM images of

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