



Anticorrosion properties of smart coating based on polyaniline nanoparticles/epoxy-ester system

Reza Arefinia^a, Akbar Shojaei^{a,*}, Homira Shariatpanahi^b, Jaber Neshati^b

^a Department of Chemical and Petroleum Engineering, Sharif University of Technology, P.O. Box 11155-9465, Tehran, Iran

^b Corrosion Department, Coating Research Center, Research Institute of Petroleum Industry (RIPI), P.O. Box 18745-4163, Tehran, Iran

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ABSTRACT

In this study, the anticorrosive effect of dodecylbenzenesulfonic acid-doped polyaniline nanoparticles [n-PANI (DBSA)] as a conductive polymer was investigated using electrochemical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS) techniques. Initially, the n-PANI (DBSA) were successfully synthesized via inverse microemulsion polymerization leading to the spherical nanoparticles with an average diameter less than 30 nm. Two coating systems including 1 wt% n-PANI(DBSA) blended epoxy ester (n-PANI(DBSA)/EPE) and neat epoxy ester (EPE) were coated on the carbon steel substrate. The anticorrosion performance of the prepared coatings was studied using EIS measurement in 3.5% NaCl solution during 77 days. The experimental data was modeled using Zview software according to the appropriate equivalent circuit model. The results clearly showed the better corrosion protection of the n-PANI(DBSA)/EPE coating compared to the EPE coating. This behavior was attributed to the ability of n-PANI(DBSA) in releasing dopant anion when the corrosion process is initiated on the metal substrate emphasizing the smart protection of n-PANI(DBSA)/EPE coating. Accordingly, the released dopant anions along with the iron cations provide a secondary barrier layer, which passivates the substrate.

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1. Introduction

Inherently conducting polymers (ICPs) have been extensively investigated due to their useful applications such as rechargeable batteries, antistatic shielding and anticorrosion coatings. Polypyrrole, polythiophene and polyaniline (PANI) are the most investigated ICPs over the three past decades [1–3]. Among these, PANI has attracted much attention due to its low cost, easy synthesis, good adhesion and environmental stability. In 1985, DeBerry [4] revealed corrosion protection of PANI film on the stainless steel. Thereafter, many researches have been concentrated on the corrosion inhibition behavior of PANI [5–7].

Actually, the mechanical properties of PANI aren't good enough to be used as a single constituent coating. Therefore, it is often incorporated into thermoplastic [8,9] and thermosetting [10–12] polymers for anticorrosion applications with two different forms including emeraldine base (EB) and emeraldine salt (ES). The EB form is itself nonconductive in nature but it can be transformed into the ES form with conductive nature through the protonation process in an acidic environment.

Many research activities have been focused on the corrosion properties of EB filled polymer coating onto various metallic substrates [13,14]. The results have emphasized the positive protection effects of the EB possibly due to its good adhesive property toward the metal substrate and proper interfacial interaction with polymer matrix restricting further diffusion of corrosive ions through the coating. Therefore, the corrosion protection behavior of the EB is mainly considered as barrier or inactive mechanism [15,16]. Practically, the polymeric coatings are not completely impermeable against diffusion of corrosive ions due to presence of micro-pores or mechanical defects created during service life. Consequently, the corrosion occurrence will be unavoidable.

Contrary to the EB acting as an inactive constituent, the ES promotes an active protection mechanism against metal corrosion. Indeed, the ES contains inhibitor anions (dopant) on its structure which can be released through the oxidation–reduction reaction with metal surfaces [17,18]. The reaction between the released dopant anion and metallic cations leads to the formation of a second barrier layer suppressing the corrosion process [19–21]. It is important to be mentioned that the inhibitor releasing process is attributed to the conductivity nature of the ES form. Therefore, to ensure about active protection function of the ES, its conductivity should be retained in the coating. This situation is not always met properly, in particular for the basic environment (PH > 7) where ES form losses its conductivity through the conversion to EB form

* Corresponding author. Tel.: +98 21 66166432; fax: +98 21 66166432.

E-mail addresses: rarefinia@yahoo.com (R. Arefinia), akbar.shojaei@sharif.edu (A. Shojaei), shariatpanahih@ripi.ir (H. Shariatpanahi), neshatj@ripi.ir (J. Neshati).

[22]. For example, epoxy as a thermosetting resin has wide coating applications because of its high chemical resistance, good mechanical properties and easy curing process. Amine curing agent is often used for epoxy coating at room temperature; however, it facilitates the transformation of the ES into the EB state. Thus, epoxy/amine system is not suitable to be used as an active protection coating based on ES.

The ES form has been commonly incorporated into the thermoplastic resins in the coating applications [9,23–25]. The solidification of these polymeric resins is often air drying at room temperature which has no chemical effect on the ES transformation state. Nevertheless, the chemical resistance of these coatings is often less than thermosetting resins such as epoxy.

Epoxy-esters (EPEs) are a type of thermosetting resins which are produced through the reaction of epoxy groups of epoxy resin with carboxylic groups of fatty acids in high temperature [26]. The chemical resistance of EPE resins is often considered approximately between thermoplastic and epoxy resins, while their curing mechanism (air drying) leads to robust coating process and no significant effect on the deprotonation of ES form.

There is little study about the coating applications of EPE resins [27]. Recently, anticorrosion and mechanical behaviors of EPE resin filled with ES particles as a coating on the steel substrate have been investigated by Kalendova et al. [28]. It is believed that the ES particles can be able to protect substrate smartly in which the ES can be activated upon the initiation of corrosion reactions. Such an observation has not been reported for EPE resin filled with dodecylbenzenesulfonic acid-doped polyaniline nanoparticles [n-PANI(DBSA)], to the best knowledge of the authors, while the focal point of the present work is to take into consideration such a behavior in this system. To do this efficiently, the corrosion mechanism was investigated in deep details using electrochemical impedance spectroscopy (EIS), and the results are used to demonstrate the corrosion mechanisms by suitable equivalent circuit models (ECMs).

2. Experimental

2.1. Synthesis and characterization of n-PANI(DBSA)

The n-PANI(DBSA) was successfully synthesized according to the reported procedure in literature [29] via inverse microemulsion polymerization method. Briefly, DBSA as both surfactant and doping agent received from local company was added into the hexane (Merck, 99%) and then was mixed for 15 min. Then aniline (Merck, 99.5%, previously distilled under reduced pressure) as monomer, at concentration of 0.1 M in the hexane, was introduced dropwise into the solution for about 30 min leading to a homogeneous milky solution indicating micelle formation in the reaction medium. At the end, oxidative chemical polymerization was initiated by dropwise addition of ammonium peroxydisulfate (APS) (Merck, extra pure) as oxidant dissolved in 10 ml of deionized water for 45 min. The molar ratio of aniline to DBSA and APS were 1:2 and 1:0.8, respectively. In all of the polymerization steps, the reaction temperature was kept at 0 °C and the mixture was well sonicated to synthesis PANI particles in nano scale. Green color of the final mixture was an indication of conductive form of PANI, i.e. n-PANI(DBSA). The unreacted materials and byproducts were removed from the n-PANI(DBSA) through three times washing-filtering process with methanol, ethanol, acetone and distilled water. Finally, the green purified n-PANI(DBSA) particles were dried at 40 °C for 24 h.

The morphology and size of n-PANI particles were observed by transmission electron microscopy (TEM, Leo 912 AB, 120 kV). The chemical structure of synthesized n-PANI(DBSA) was characterized using FT-IR (PerkinElmer model spectrum 400) of dry powders

and UV–vis (Cary model 50 Conc. spectrophotometer) spectrum of diluted powders in hexane solution.

2.2. Preparation of n-PANI(DBSA)/EPE coating

The n-PANI(DBSA)/EPE coating was prepared by dispersion of 1 wt% of n-PANI(DBSA) in the solvent based EPE (35 wt% of resin in the solution) (ALE 381 × 50, Saman Chem. Co.) as binder. To do this, the n-PANI(DBSA) was gradually incorporated into the EPE during 15 min and the suspension was continuously mixed by sonication leading to a uniform and stable suspension for a long time.

Prior to coating application, carbon steel plaques (SAE 1020) of size 100 mm × 150 mm × 2 mm were sand blasted with a profile of about 30 μm and then degreased with acetone. Afterwards, the n-PANI(DBSA)/EPE and neat EPE coatings were applied onto the treated surface of carbon steel followed by a room temperature curing process for about 10 days. The average thickness of the coatings was measured using Minitest 2000, which was found to be 50 ± 10 μm.

2.3. Measurement of anticorrosion behavior

Anticorrosion behavior of n-PANI(DBSA)/EPE and EPE coatings were carefully studied using EIS in 3.5% NaCl solution. EIS measurements were carried out using an Autolab potentiostat/galvanostat PGSTAT30 instrument. To do this, a three-electrode cell including surface area of coating exposed to the electrolyte (12.56 cm²) as working electrode, saturated calomel electrode as reference electrode and a platinum mesh as counter electrode was utilized. The EIS spectra were recorded over a frequency range from 100 kHz to 0.01 Hz with an AC amplitude of 10 mV for all of the measurements up to 77 days. The recorded spectra of EIS were precisely analyzed by Zview software according to appropriate ECMs.

Additionally, the chemical composition of underlying steel surface for n-PANI(DBSA)/EPE coating was analyzed using X-ray photoelectron spectroscopy (XPS, VG Microtech, Twin axle, XR3E2 X-ray source) technique. For this purpose, the n-PANI(DBSA)/EPE coating was exposed to the 3.5% NaCl solution for about 14 days and then the coating was mechanically removed to record XPS spectrum in the binding energies range from 0 up to 1200 eV.

3. Results and discussion

3.1. Characterization of PANI nanoparticles

Fig. 1 represents TEM image of the synthesized n-PANI(DBSA) containing spherical shape with a particle size less than 30 nm. This morphological characteristic is mainly dominated by the shape and size of micelles formed during polymerization [30]. Fig. 2 shows FT-IR spectrum of n-PANI(DBSA) which is in good agreement with the other observations reported in the literature [31,32]. The characteristic peaks at 1560 cm⁻¹ and 1475 cm⁻¹ correspond to the quinoid (N=Q=N) and benzenoid (N-Q-N) ring stretching, respectively. The peaks at 1290 cm⁻¹ and 1230 cm⁻¹ are due to the C–N stretching while the broad peak around 1100 cm⁻¹ is assigned to the sulfonic acid group. Fig. 3 exhibits the UV–vis spectrum of diluted n-PANI(DBSA). Existence of three major peaks at wavelength of about 340 nm (π – π^* transition of benzenoid rings), 430 nm (polaron– π^* transition of quinoid rings) and 720 nm (π –polaron transition of quinoid rings) demonstrates the conductive nature of the synthesized n-PANI(DBSA) particles [29].

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