Anticorrosive Properties of Epoxy Resin Coatings Cured by Aniline/*p*-Phenylenediamine Copolymer

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ABSTRACT: Aniline/*p*-phenylenediamine copolymer [poly(ANI-*co*-*p*-PDA)] was prepared by chemical oxidative polymerization. FTIR and ^{1}H-NMR analysis indicate that the poly(ANI-*co*-*p*-PDA) is oligomer with end-capped amino groups, which can cure epoxy resin. The anticorrosion performance of carbon steel (CS) samples coated by epoxy resin coating cured with poly(ANI-*co*-*p*-PDA) and epoxy resin coating cured with triethylenetetramine exposed to 5 wt % NaCl and 0.1 mol/L HCl aqueous solution is studied by the potentiodynamic polarization and electrochemical impedance spectroscopy. The results show that the CS coated by epoxy resin coating cured with poly(ANI-*co*-*p*-PDA) has more excellent corrosion protection than that of epoxy resin coating cured with triethylenetetramine. Raman spectroscopy analysis indicates that the surface of CS coated by epoxy resin coating cured with poly(ANI-*co*-*p*-PDA) forms passive layer, which is composed of α-Fe_2O_3. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1988–1993, 2009

Key words: conducting polymers; coatings; electrochemistry; epoxy resin; corrosion protection

INTRODUCTION

Corrosion of the metals is one of the most serious problems that mankind has to face.[1,2] Three approaches are commonly used to reduce the rate of corrosion: (1) cathodic protection, i.e., charge is donated to the metal from a sacrificial material; (2) anodic protection, i.e., surface passivation of metals; and (3) barrier protection.[3]

Conducting polymer as either film-forming corrosion inhibitors or in protective coating has attracted more and more attention because of the excellent anticorrosion ability and environmental friendship.[4] Among all conducting polymers, polyaniline (PANI) families are generally recognized to be one of the most important conducting polymers, because of their ease of preparation and excellent environmental stability.[5–7] Moreover, unlike other conducting polymers, the PANI can be doped to a highly conducting regime in acidic media, without removing electrons from the backbone.[8] This ability also enables PANI to act as a versatile polymer in anticorrosion studies.

Many papers have been published on the use of PANI for the protection of metals against corrosion.[9–26] Mengoli et al.[10] found that the paints containing PANI offer high corrosion-resistant coating. Wessling and Posdorfer[11,12] reported that the corrosion potential for PANI-coated metals significantly shifts toward noble potentials and corrosion current decreases. Wrobleski et al.[13] showed that the doped PANI films on steel with epoxy top coat are able to offer protection in 3.5 wt % NaCl and 0.1 mol/L HCl. Kinlen et al.[15] found that the PANI coatings passivate the pinholes and defects. Sathiyanarayanan et al.[18] reported the corrosion performance of PANI-pigmented vinyl acrylic coating on steel in acid, neutral, and alkaline media. Palaniappan et al.[19] studied the curing kinetics of the epoxy resin with PANI by the DSC technique. Ahmad et al.[21] found that the emeraldine base coating on steel offers good protection in HCl. Alam et al.[24] reported that the PANI/ferrite nanocomposite dispersed alkyd coatings were able to effectively protect steel from corrosion in acid, alkaline, and saline. These results are indeed very encouraging.

In this article, the aniline/*p*-phenylenediamine copolymer [poly(ANI-*co*-*p*-PDA)] with end-capped amino groups is synthesized by chemical oxidative polymerization. We demonstrate that the copolymer

not only cures epoxy resin but also epoxy resin coating cured with the copolymer can offer good corrosion protection for carbon steel (CS).

EXPERIMENTAL

Materials

Aniline (analytical grade) was purchased from Shanghai Chemical Reagent Corp and distilled under vacuum before use. Ammonium persulfate (analytical grade) was purchased from Shanghai Lingfeng Chemical Reagent Corp and was purified by the recrystallization from ethanol. Epoxy resin (E-44V95, Epoxy equivalent 213–244) was purchased from Wuxi Resin Factory of Bluestar New Chemical Materials Corp (China). p-Phenylenediamine (p-PDA), hydrochloric acid, ammonia, triethylenetetramine, and other reagents were analytical grade and used without further purification.

Synthesis of aniline/p-phenylenediamine copolymer

An amount of 1.86 g (20 mmol) of aniline and 8.64 g (80 mmol) of p-PDA were injected to 200 mL of 1 mol/L HCl with constant stirring. A total of 22.8 g (100 mmol) of ammonium persulfate (dissolved in 100 mL deionized water) was dropped into the above solution. The polymerization was allowed to proceed for 24 h at 5°C. Reaction product was filtered and washed with deionized water, afterward dried at 60°C for 48 h under vacuum to obtain a protonated aniline/p-phenylenediamine copolymer [doped poly(ANI-co-p-PDA)]. The protonated poly(ANI-co-p-PDA) was immerged to 10 wt % ammonia solution for 24 h in order to dedoped. After drying, deprotonated poly(ANI-co-p-PDA) powder was obtained.

The preparation of epoxy resin coating cured by poly(ANI-co-p-PDA)

A total of 1.5 g of deprotonated poly(ANI-co-p-PDA) was put into 30 mL of N-methyl-2-pyrrolidone and sonicated for 2 h, which provided a solution. Then, 1.7 g epoxy resin and 0.1 g commercially leveling additive (BYK-354, BYK Chemie, Germany) were added to this solution and stirred for 4 h to obtain a homogeneous solution. After filtrating, the epoxy resin coating cured by poly(ANI-co-p-PDA) was obtained.

Carbon steel samples preparation

The square (20 mm × 20 mm × 2 mm) and CS samples, that the content of carbon is 0.25–0.45% were polished by emery paper 600 grit, and under ultra-sonic all CS samples were pretreated in acetone and ethanol solution to degrease before coating.

Carbon steel samples coated by poly(ANI-co-p-PDA)/epoxy coatings

Epoxy resin coating cured by poly(ANI-co-p-PDA) was brushed on all sides of the CS plates and was cured at 60°C for 96 h. The dry thickness of coating is ∼ 80 μm, which was measured with a Fischerscope Multi Measuring System.

Control samples

An epoxy resin coatings cured by triethylene-tetramine was air-sprayed on all sides of the CS plates and was cured at room temperature for 7 days. The dry thickness of coating about 80 μm was measured with a Fischerscope Multi Measuring System.

Measurements

The FTIR spectra of samples were obtained on a Nicolet 5700 spectrophotometer. The PANI and poly(ANI-co-p-PDA) were applied in the form of KBr pellets (compressed powder), and the epoxy resin coating cured by poly(ANI-co-p-PDA) was applied directly by daubing onto a KBr pellet and then was cured at 100°C. ^{1}H-NMR spectrum of CDCl$_3$ solutions was recorded on an AVANCE 500 spectrometer. Scanning electron microscopy inspection was taken with a JEOL JSM–6360 instrument. The film surface was coated with a gold vapor. The passive layers of CS were determined by Raman spectra on a Renishaw inVia-Reflex using a CCD detector and a 50 mW He–Ne laser operating at 514 nm.

The triethylenetetramine/epoxy and poly(ANI-co-p-PDA)/epoxy coatings were applied by brush on all sides of tinned iron strips (50 mm × 120 mm × 0.3 mm) for determination of pencil hardness (GB/T 6739), impact resistance (GB/T l732), and flexibility (GB/T l731).

The electrochemical corrosion measurements were carried out in a three-electrode electrochemical cell with a Pt counter electrode and a saturated calomel reference electrode (SCE). The potentiodynamic polarization curves (Tafel plots) were obtained by scanning potential from below 300 to above 300 mV the corrosion potential (E_{corr} in V vs. SCE) at a sweep rate 10 mV/min. Electrochemical impedance spectroscopy was carried out for a frequency range of 10^5–0.1 Hz with an ac amplitude of 5 mV for different immersion time. Electrochemical corrosion measurements were performed in 5 wt % NaCl and 0.1 mol/L HCl aqueous solution at room temperature and in open air with a CHI760C model electrochemical analyzer.
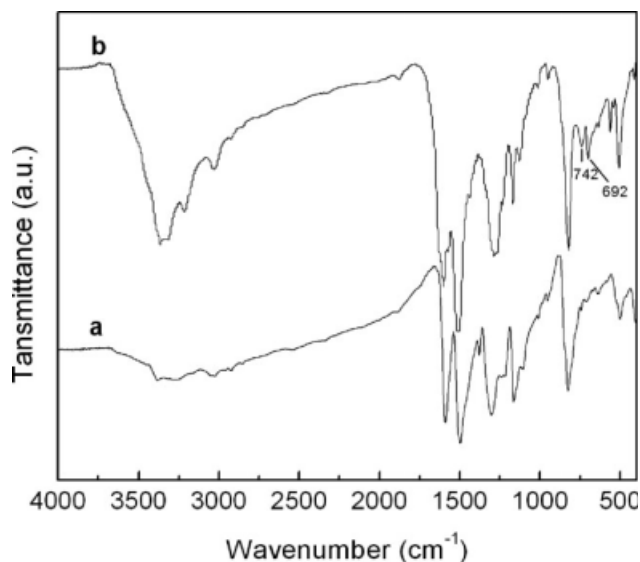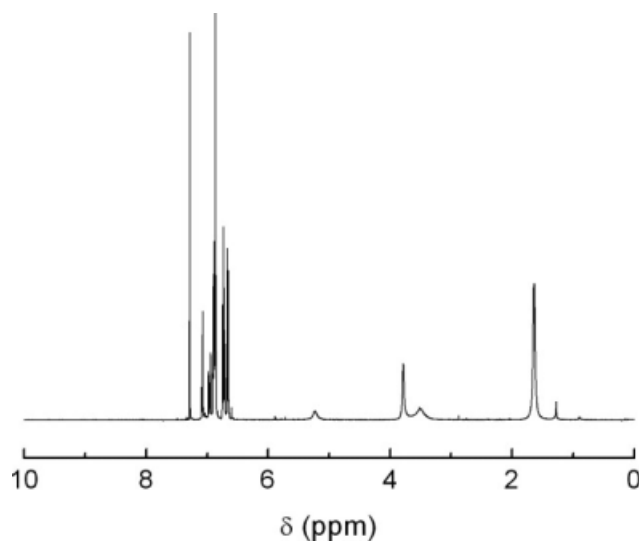
Figure 1 The FTIR spectra of (a) PANI and (b) poly(ANI-*co-p*-PDA).

RESULTS AND DISCUSSION

Characterization of poly(ANI-*co-p*-PDA)

Figure 1 shows the FTIR spectra of deprotonated PANI and poly(ANI-*co-p*-PDA), respectively. The main characteristic bands of the dedoped PANI are assigned as follows: the band at about 3350 cm^{-1} is attributable to N—H stretching mode, and C=C stretching mode for the quinoid and benzenoid rings occur at 1583 and 1492 cm^{-1}, whereas the band at 820 cm^{-1} is assigned to the C—H out-of-plane bending vibration of the 1,4-disubstituted benzene rings.[27] Curve b in Figure 1 indicates that the main characteristic bands of PANI appear in poly(ANI-*co-p*-PDA). It suggests the presences of PANI segment in the copolymer. It can also be found that the band of N—H stretching mode is obvious different in the FTIR

Figure 2 The ^{1}H-NMR spectrum of poly(ANI-*co-p*-PDA).
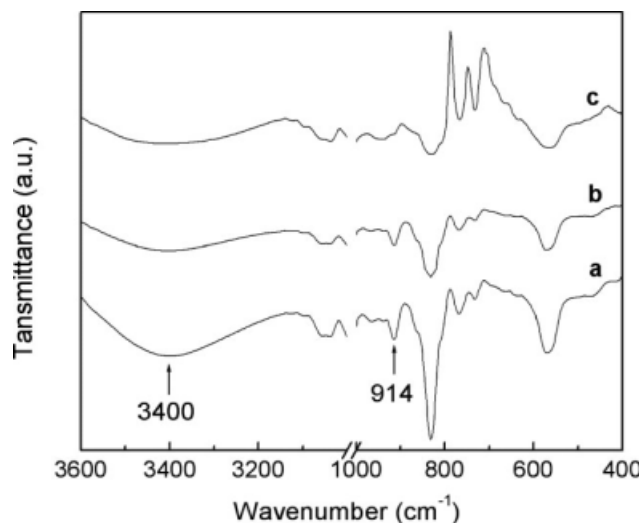
Figure 3 The FTIR spectra of epoxy resin cured by poly(ANI-*co-p*-PDA): (a) before cured, (b) 2 h, and (c) 24 h.

spectra of PANI and the copolymer. When the band at 820 cm^{-1} is used as inner criterion, the band of N—H stretching mode (about 3350 cm^{-1}) in copolymer is stronger than in PANI. This implies that poly(ANI-*co-p*-PDA) contains more end-capped amino groups. In addition to, the bands at about 742 and 692 cm^{-1} are observed in poly(ANI-*co-p*-PDA), which are related to the presence of aniline/*p*-phenylenediamine oligomers.[28,29]

Figure 2 shows the ^{1}H-NMR spectrum of deprotonated poly(ANI-*co-p*-PDA). The peaks between 6.6 and 7.4 ppm correspond to the aromatic protons. Two peaks at 3.5 and 3.8 ppm are assigned to —NH— and —NH$_2$, respectively. This indicates that poly(ANI-*co-p*-PDA) contains end-capped —NH$_2$ groups, which can cure epoxy resin.

Cure effect of poly(ANI-*co-p*-PDA) to epoxy resin

The FTIR spectra of epoxy resin coatings cured by poly(ANI-*co-p*-PDA) for different cure times were given in Figure 3, respectively. In Figure 3, the band at about 914 cm^{-1} is attributable to epoxy group, and the band at 3400 cm^{-1} is assigned to N—H stretching mode. From Figure 3(b,c), it can be found that two bands at 914 and 3400 cm^{-1} become weak.

TABLE I
The PhysicoMechanical Properties of Triethylenetetramine/Epoxy and Poly(ANI-*co-p*-PDA)/Epoxy Coatings

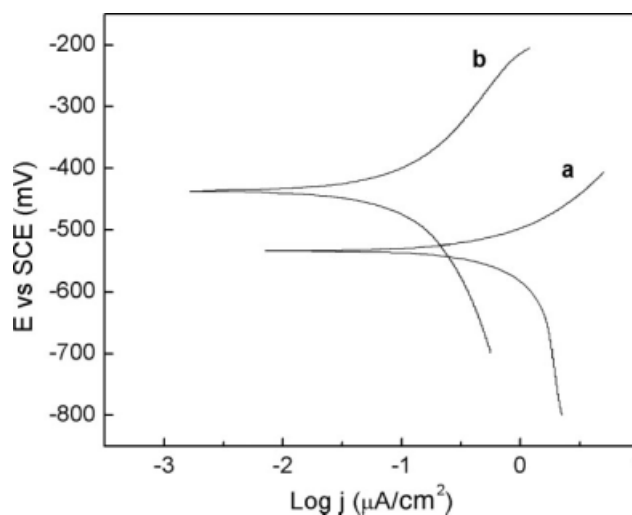| Samples	Pencil hardness	Impact resistance (kg cm)	Flexibility (mm)
Triethylenetetramine/ epoxy	4H	15	4.0
Poly(ANI-*co-p*-PDA)/ epoxy	4H	25	1.0
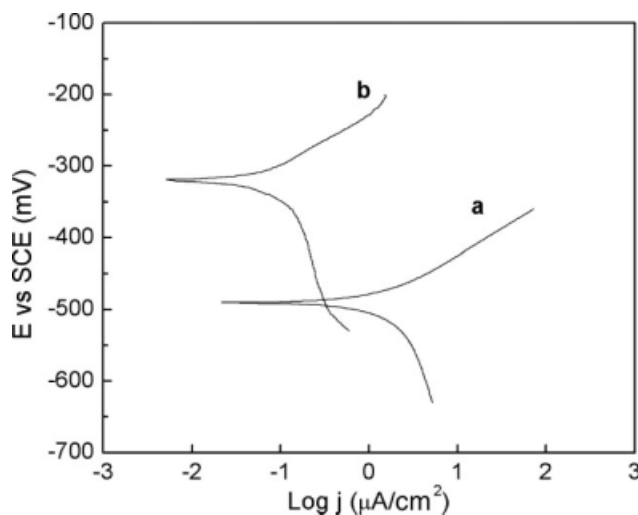
Figure 4 Tafel plots of carbon steel samples coated by different coatings in 5 wt % NaCl aqueous solution: (a) epoxy resin cured by triethylenetetramine and (b) epoxy resin cured by poly(ANI-*co-p*-PDA).

Figure 5 Tafel plots of carbon steel samples coated by different coatings in 0.1 mol/L HCl aqueous solution: (a) epoxy resin cured with triethylenetetramine and (b) epoxy resin cured with poly(ANI-*co-p*-PDA).

Especially, the band at 914 cm^{-1} almost disappears after cured for 24 h. However, weakening of the band at 3400 cm^{-1} is not obvious, because of the effects of epoxy resin itself and cured offspring. The result implies that cure reaction occurs between the poly(ANI-*co-p*-PDA) and epoxy resin, and a hardness membrane was formed after cured.

Physicomechanical properties

The physicomechanical performance of triethylene-tetramine/epoxy and poly(ANI-*co-p*-PDA)/epoxy coatings is given in Table I. The pencil hardness of poly(ANI-*co-p*-PDA)/epoxy film was found to be 4H as triethylenetetramine/epoxy film, which was attributed to the curing effect of the poly(ANI-*co-p*-PDA) on epoxy resin. It was also found that the impact resistance increases from 15 kg cm in case of triethylenetetramine/epoxy to 25 kg cm in poly (ANI-*co-p*-PDA)/epoxy. Likewise, the flexibility of poly(ANI-*co-p*-PDA)/epoxy was higher than that of triethylenetetramine/epoxy coating. The poly(ANI-*co-p*-PDA) curing agent has longer chain structure than that of triethylenetetramine, resulting in the formation of considerable molecular weight of the poly(ANI-*co-p*-PDA)/epoxy film that ensures better

flexibility in comparison to triethylenetetramine/ epoxy. Moreover, the excellent physicomechanical properties of the poly(ANI-*co-p*-PDA)/epoxy film also correlated to its morphology (see Supp. Info. S1). The poly(ANI-*co-p*-PDA) uniformly distributed in epoxy resin and the agglomerate is not observed.

Electrochemical corrosion measurements

The potentiodynamic polarization curves for CS/epoxy resin cured with poly(ANI-*co-p*-PDA) and CS/ epoxy resin cured with triethylenetetramine in 5 wt % NaCl and 0.1 mol/L HCl solution are shown in Figures 4 and 5, respectively. The corrosion current (i_{corr}) and corrosion potential (E_{corr}) were determined by extrapolating a straight line along the linear portion of the cathodic and anodic curves to their point of intersection (see Table II). Compared with CS/ epoxy resin cured with triethylenetetramine, the corrosion potential of CS/epoxy resin cured with poly(ANI-*co-p*-PDA) in 5 wt % NaCl and 0.1 mol/L HCl solution increased about 169 and 96 mV, respectively. The corrosion current of CS/epoxy resin cured with poly(ANI-*co-p*-PDA) reduced 20 and 12 times, respectively. The results indicate that the epoxy resin coating cured with poly(ANI-*co-p*-PDA)

TABLE II
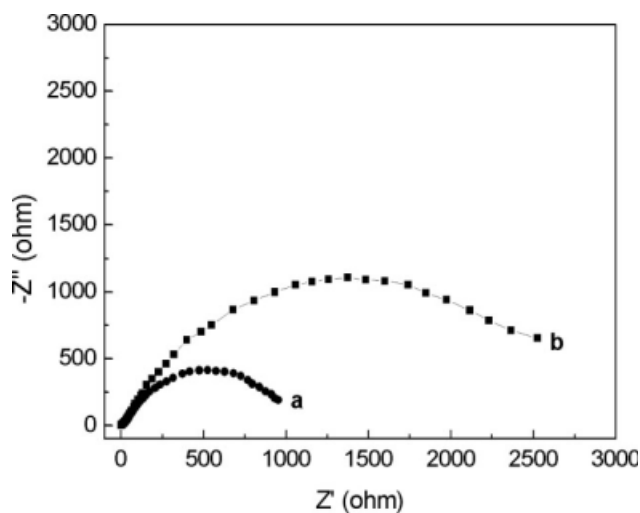**Corrosion Parameters of Carbon Steel Samples Coated by Different Coatings**

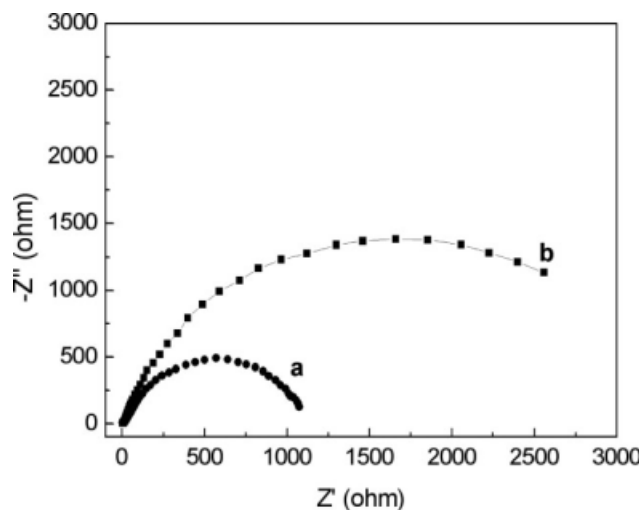| Samples	0.1 mol/L HCl		5 wt % NaCl	
	$I_{corr}/\mu A \cdot cm^{-2}$	E_{corr}/mV	$I_{corr}/\mu A \cdot cm^{-2}$	E_{corr}/mV
Epoxy resin cured with triethylene-tetramine	1.99	−489	0.72	−532
Epoxy resin cured with poly(ANI-*co-p*-PDA)	0.10	−320	0.06	−438
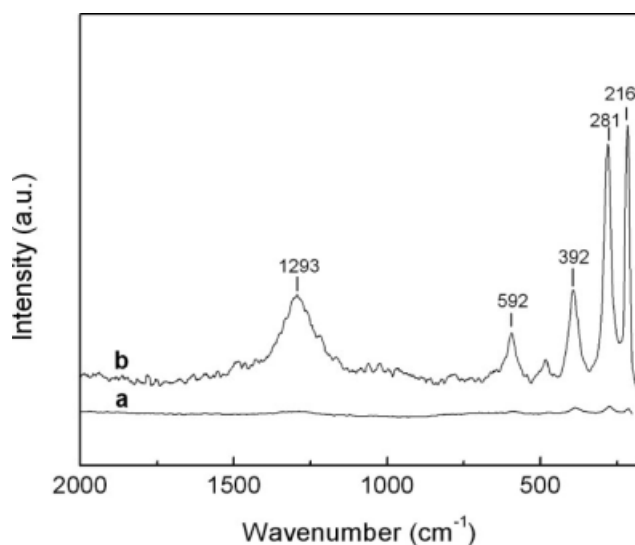
Figure 6 Raman spectra of the surface for carbon steel coated by different coatings immerged for 2 days in 5 wt % NaCl aqueous solution: (a) epoxy resin cured with triethylenetetramine and (b) epoxy resin cured with poly(ANI-*co-p*-PDA).

has better corrosion protection to CS than that of coating cured with triethylenetetramine exposed to the severe corrosion environments of dilute HCl and NaCl, and the level of corrosion protection depends on the nature of corrosion environment. This is because the poly(ANI-*co-p*-PDA) cured epoxy resin to form a three-dimensional structure, which reduces the infiltration of corrosive media, thus effectively protects the metal substrate. Moreover, the metal substrate is passivated and passive film is formed because of inherent electric activity of the poly(ANI-*co-p*-PDA).[30]

Figure 8 Nyquist plots of carbon steel coated by (a) triethylenetetramine/epoxy and (b) poly(ANI-*co-p*-PDA)/epoxy in 5 wt % NaCl aqueous solution for 720 h.

The presence of the passive layer was determined by Raman spectra. As shown in Figure 6(a), the bands on bare surface of CS coated by epoxy resin cured with triethylenetetramine immerged for 2 days in 5 wt % NaCl aqueous solution were very weaker. However, the bare surfaces of CS coated by epoxy resin cured with poly(ANI-*co-p*-PDA) after immersion in 5 wt % NaCl for 2 days exhibited stronger bands. The bands at about 216, 281, and 1293 cm^{-1} are assigned to α-Fe_2O_3 [Fig. 6(b)].[31] This indicates that the surfaces of CS coated by epoxy resin cured with poly(ANI-*co-p*-PDA) formed passive layers, which are composed of α-Fe_2O_3.
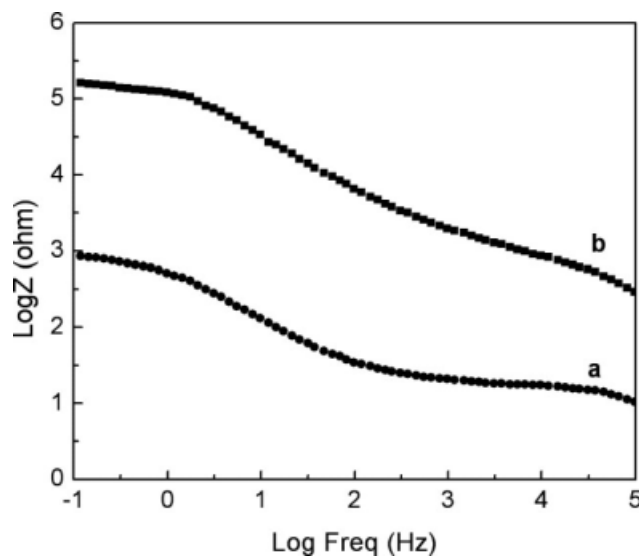

Figure 7 Nyquist plots of carbon steel coated by (a) triethylenetetramine/epoxy and (b) poly(ANI-*co-p*-PDA)/epoxy in 0.1 mol/L HCl aqueous solution for 720 h.
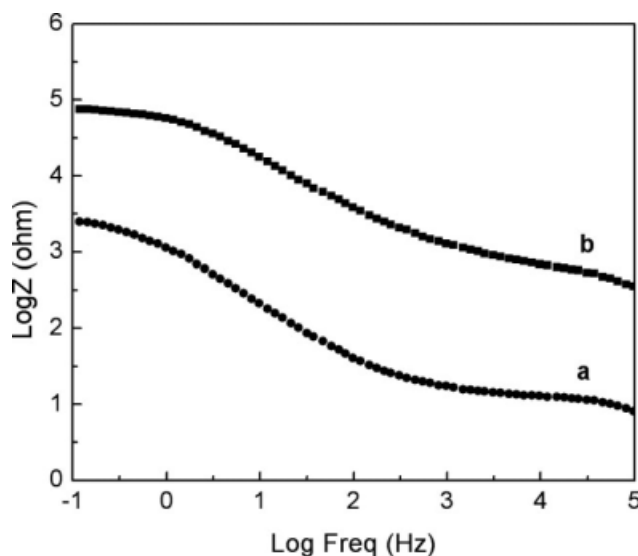

Figure 9 Bode plots of carbon steel coated by (a) triethylenetetramine/epoxy and (b) poly(ANI-*co-p*-PDA)/epoxy in 0.1 mol/L HCl aqueous solution for 720 h.

Figure 10 Bode plots of carbon steel coated by (a) triethylenetetramine/epoxy and (b) poly(ANI-*co-p*-PDA)/epoxy in 5 wt % NaCl aqueous solution for 720 h.

Figures 7 and 8 show the Nyquist plots recorded for CS coated by triethylenetetramine/epoxy and poly(ANI-*co-p*-PDA)/epoxy immerged for 720 h in 0.1 mol/L HCl and 5 wt % NaCl aqueous solution, respectively. The feature of Nyquist plots was a semicircle. The charge transfer resistance (R_p) values are equal to the diameters of the semicircles. The R_p values for CS coated by poly(ANI-*co-p*-PDA)/epoxy are higher than that of triethylenetetramine/epoxy. This can be explained by the formation of passive layer on the surface of CS in poly(ANI-*co-p*-PDA)/epoxy coating system. This indicates that poly(ANI-*co-p*-PDA)/epoxy can provide significant corrosion protection to CS exposed to the severe corrosion environments of 0.1 mol/L HCl and 5 wt % NaCl.[31]

Bode plots of logZ–log frequency for CS coated by triethylenetetramine/epoxy and poly(ANI-*co-p*-PDA)/epoxy immerged for 720 h in 0.1 mol/L HCl and 5 wt % NaCl aqueous solution are given in Figures 9 and 10, respectively. For CS coated by poly(ANI-*co-p*-PDA)/epoxy, a high impedance at low frequency was measured compared with the CS coated by triethylenetetramine/epoxy. This also indicates that the poly(ANI-*co-p*-PDA)/epoxy coating has better protective effect than that of triethylenetetramine/epoxy coating.

CONCLUSIONS

The poly(ANI-*co-p*-PDA) was prepared by chemical oxidative polymerization, and the spectrum analysis determines that the poly(ANI-*co-p*-PDA) has the end-capped $-NH_2$ structure. Results of FTIR spectra show that the cure reaction occurs between the poly(ANI-*co-p*-PDA) and epoxy resin. The electrochemical corrosion measurements indicate that the epoxy resin coatings cured by poly(ANI-*co-p*-PDA) can provide significant corrosion protection to CS samples exposed to the severe corrosion environments of 0.1 mol/L HCl and 5 wt % NaCl. Further, this corrosion protection is caused by the formation of a passive layer, and presence of the passive layer was determined by Raman spectra.

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