

Enhanced Corrosion Protective Coating Based on Conducting Polyaniline/Zinc Nanocomposite

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ABSTRACT: Conducting polyaniline (PANI) is being explored as promising material for protection of metals against corrosion. It has the possibility of making smart coatings on metals, which can prevent corrosion even in scratched areas where bare metal surface is exposed to the aggressive environment. However, PANI coatings have poor barrier and mechanical properties. The barrier property of coatings can be enhanced by the addition of appropriate filler particles. Also it has been demonstrated that nanoparticulate fillers give much better barrier properties even at lower concentrations. In this study, the effect of zinc nanoparticles on the anticorrosive property of PANI coating on iron samples has been investigated. The PANI/Zn nanocomposite was synthesized by *in situ* polymeriza-

tion of aniline in the presence of Zn nanoparticles. The nanocomposite was characterized by using FTIR, conductivity measurement, cyclic voltammetry, and AFM techniques. Results showed that PANI/Zn nanocomposite coating has improved corrosion protection effect when compared with pure PANI coating. The corrosion current of PANI/Zn coated samples were found to be much lower than that of pure PANI coated samples. The results were referred to the good barrier properties of Zn nanoparticles and improvement in electrochemical corrosion protection of PANI coating in the presence of Zn nanoparticles. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2221–2227, 2010

Key words: nanocomposites; conducting polymers; coatings

INTRODUCTION

Metal-polymer composite materials have been the subject of intense studies in recent years because of their attractive fundamental science and potential applications.¹ These materials can be prepared by a variety of methods, such as, treatment of polymer films with metal vapors,² reaction of metal compounds in polymer solutions,³ *in situ* polymerization of monomers or comonomers in the presence of metals, and solution mixing.⁴ Various polymers can be used as matrix in metal-polymer composites and nanocomposites.⁵ Conducting polymers, such as, polyacetylene, polyaniline, polypyrrole, and polythiophene have gained considerable theoretical interest and practical applications in various fields, especially in the protection of metals against corrosion.^{6–10} These polymers offer a unique combination of electrical conductivity as metals with processability as polymers.^{11–13} Among all conducting polymers, polyaniline (PANI) is found to be the most

promising candidate because of its high electrical conductivity, ease of synthesis, low-cost monomer, better stability, and practical applications.^{14,15} PANI, as powder (inhibitor) and film (coating), has been used for protection of various metals against corrosion.^{16–19} The promising results, obtained from the using of PANI as anticorrosive coating, has motivated the studies dealing with its electrochemical deposition, chemical coating, and corrosion performance.²⁰ Conducting PANI coating not only prevents the access of corrosive materials to metal surface but also electrochemically reduces the corrosion rate of metals by making a smart coating.^{21–23} However, PANI coatings suffer from poor barrier and mechanical properties.²⁴ There are a number of methods to overcome these problems, such as, using of a top coat on PANI coating¹⁹ or application of a composite coating based on PANI.^{7,18} It has been reported that the mechanical and barrier properties of PANI coating can be improved using organic or inorganic fillers.^{25,26} However, filler particles may be the cause to the reduction of PANI conductivity and as a result, the electrochemical corrosion protection property of PANI coating can be adversely affected. It seems that, using conductive fillers, such as, metal particles, it is capable to prevent the conductivity reduction. Also, it has been demonstrated that using nanoparticulate fillers considerable improvement in

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matrix properties can be achieved even at low filler fractions.²⁷ Various metal nanoparticles have been used in the preparation of nanocomposites based on PANI matrix.²⁷ Nanocomposites of PANI with transition metal nanoparticles offer an attractive combination of metallic properties with unique interesting electrochemical behavior of conducting PANI.²⁸ These nanocomposites are intensively studied for applications in optoelectronic devices,²⁹ batteries,³⁰ sensors,³¹ electronic display devices,³² and corrosion protection.³³

Zinc, as a transition metal, has conducting and semiconducting properties together with potential ability to cathodic sacrificial protection of metals against corrosion.^{34,35} Zn acts like a sacrificial anode against the corrosion of mild steel.³⁶ It has been demonstrated that zinc particles can improve the barrier property of PANI coating on copper by the formation of voluminous zinc corrosion products within the pores of PANI coating.²¹ Also in cathodic protection of metals by zinc particles, the conducting PANI or polypyrrole can play the role of conductance between zinc particles and metal surface.²¹

The aim of this study is to analyze the anticorrosive property of PANI/Zn nanocomposite coating on iron coupons. The PANI/Zn nanocomposite was prepared, characterized, and evaluated as anticorrosive coating on iron coupons in various corrosive electrolytes and compared with pure PANI anticorrosive coating.

EXPERIMENTAL

Reagents and materials

Ammonium persulfate, sodium borohydride, zinc nitrate, sulfuric acid, sodium chloride, 1-methyl-2-pyrrolidone, and hydrochloric acid were all purchased from Merck Company and were used as received. Aniline monomer was doubly distilled before use. For chemical synthesis, double-distilled water was used.

Metal sample preparation

Iron coupons with 2 cm × 2 cm × 0.05 cm dimensions were used in corrosion studies. The chemical composition of the iron samples has been shown in Table I. To remove any existing passive films, the iron coupons were mechanically polished using 100 and 400 grade emery papers, followed by rinsing with distilled water and acetone, before coating and corrosion experiments.

Synthesis of PANI/Zn nanocomposite

An aqueous solution of zinc nanoparticles of 100 mL volume was prepared by the controlled reduction of

TABLE I
Chemical Composition of Iron Samples

Element	Percent (% w/w)	Element	Percent (% w/w)
Fe	99.521	Co	0.0131
C	0.0351	Al	0.0347
Si	0.0133	Cu	0.0481
P	0.0145	W	0.0022
Mn	0.2408	S	0.0158
Ni	0.0325	Sn	0.0005
Cr	0.0284		

zinc nitrate ($10^{-3}M$) using desired quantity of sodium borohydride. To this solution, 0.93 mL of aniline and 2 mL of HCl were added under vigorous stirring. Polymerization of aniline was processed by the addition of 2.28 g ammonium persulfate dissolved separately in 5 mL of deionized water. The oxidation agent was added dropwise over 2 h under vigorous stirring and the polymerization was allowed to proceed for 2 h at $-4^{\circ}C$ temperature. The nanocomposite powder was recovered as precipitate. The precipitate was filtered and washed with deionized water. The washing process was repeated until the pH under washing solution became neutral. Finally, the nanocomposite was dried in an oven for 24 h to achieve a constant weight. To compare the anticorrosive properties of PANI/Zn nanocomposite and pure PANI, the pure PANI was also synthesized using a similar procedure in the absence of zinc solution.

Coating of iron samples

The solution casting method was used to coat iron samples by a thin layer (100 μm thickness) of PANI/Zn nanocomposite or pure PANI. 1-Methyl-2-pyrrolidone (NMP) was used as solvent in solution casting. One gram of PANI/Zn nanocomposite was dissolved in 40 mL NMP. Five milliliter of the nanocomposite solution was casted on iron coupon (2 cm × cm 2 cm × 0.05 cm). Evaporation of solvent was performed in an oven at 60°C temperature for 12 h. For comparison, in an exactly similar method, pure PANI coated coupons were also prepared.

Corrosion tests

Throughout this work, Tafel plots were recorded using a conventional three-electrode electrochemical cell with platinum gauze as counter electrode and an Ag/AgCl as reference electrode. The working electrode was the iron sample (coated or uncoated). To measure the open circuit potential of the samples, a two-electrode electrochemical cell system was used with the iron sample as working electrode and an Ag/AgCl as reference electrode. The HCl (0.1M), H₂SO₄ (0.1M), and NaCl (3.5% w/w) solutions were used as corrosive environments.

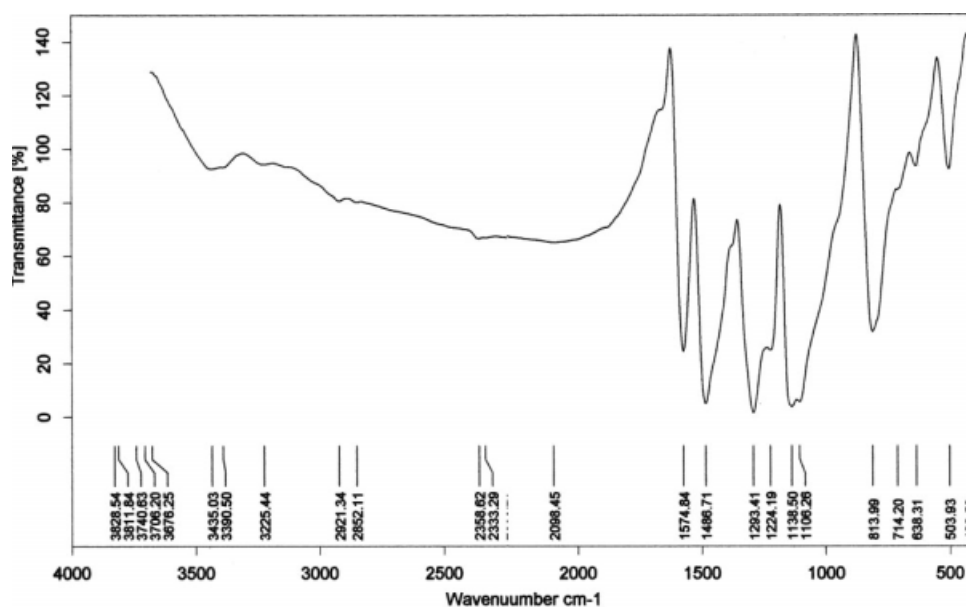


Figure 1 FTIR spectra of PANI/Zn nanocomposite with Zn content of 5% w/w.

RESULTS AND DISCUSSION

The PANI/Zn nanocomposite was synthesized chemically by *in situ* polymerization of aniline monomer in the presence of Zn nanoparticles using ammonium persulfate as initiator. Before the addition of initiator, Zn nanoparticles were synthesized in the monomer solution by the reduction of Zn^{2+} cations using sodium borohydride under vigorous stirring. PANI/Zn nanocomposite was characterized using FTIR technique. Figure 1 shows the FTIR spectra of PANI/Zn nanocomposite. The characteristic vibration bands of Zn are visible at 503.93 cm^{-1} , 638.31 cm^{-1} , 813.99 cm^{-1} , 2921.34 cm^{-1} , and 3435.03 cm^{-1} . The absorption peaks at 1138.50 , 1293.41 , 1488.71 , and 1574.84 cm^{-1} are the characteristic peaks for PANI. In this spectrum, the prominent absorption peaks at 1488.71 and 1574.84 cm^{-1} are attributed to the C=C stretching vibration bands of benzoid and quinoid rings, respectively. The peak at 1293.41 cm^{-1} is assigned to the C–N stretching of secondary amine group in PANI backbone. The peak at 1138.50 cm^{-1} can be assigned to an in plane bending vibration of C–H. Therefore, the incorporation of zinc nanoparticles into the PANI chains in PANI/Zn nanocomposite was confirmed.

To evaluate the particle size and the distribution of PANI/Zn nanocomposite, the contact atomic force micrograph (C-AFM) was recorded. Figures 2 and 3 show the C-AFM image and normalized particle size distribution of PANI/Zn nanocomposite, respectively. According to the results, the average size of the particles in nanocomposite was $\sim 80\text{ nm}$.

Electrical conductivity

To investigate the effect of Zn nanoparticles on the electrical conductivity of PANI, the electrical conductivity of PANI/Zn nanocomposite with various Zn contents (0–20% w/w) as free-standing film were measured and compared with the electrical conductivity of pure PANI film (Zn content = 0% w/w). Four-point probe technique was used to measure the electrical conductivity of PANI/Zn nanocomposite

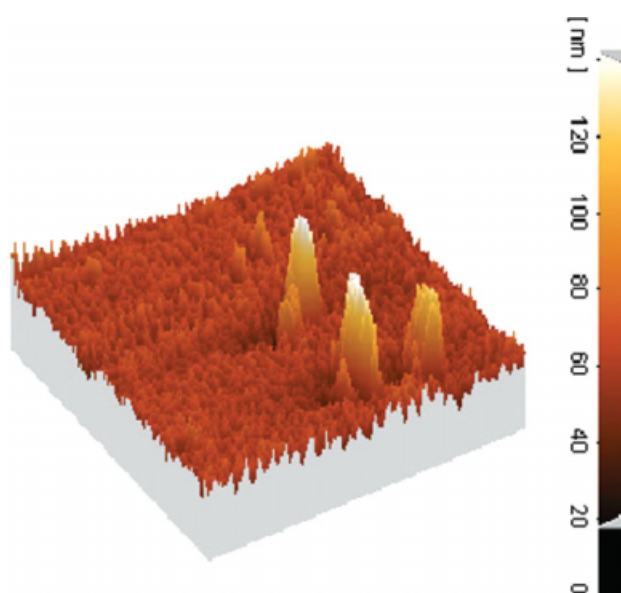


Figure 2 The contact atomic force micrograph of PANI/Zn (5% w/w) nanocomposite. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

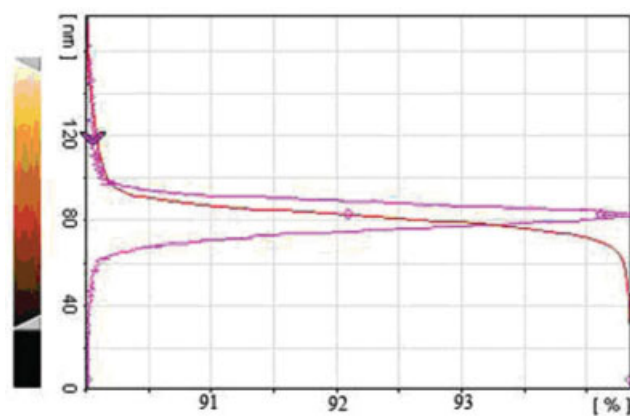


Figure 3 The size distributions of PANI/Zn (5% w/w) nanocomposite particles extracted from C-AFM results. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and pure PANI films. Free-standing films of nanocomposite and pure PANI with 15 μm thickness were prepared by a solution casting method, using NMP as solvent. Figure 4 shows the electrical conductivity of PANI/Zn nanocomposite films with different Zn content as well as pure PANI film (Zn content = 0% w/w). Unlike pure PANI, the electrical conductivity of PANI/Zn nanocomposite depends on the nature of both the host PANI and the guest Zn. Results showed that the electrical conductivity of PANI/Zn nanocomposite films are higher than pure PANI film. The better connection of PANI chains in the presence of conductive zinc nanoparticles is responsible for the high electrical conductivity of nanocomposite compared with the pure PANI. This connectivity can give rise to longer carrier pathways and causes to the better electrical conduction. Therefore, the electrical conductivity of the nanocomposite increases by the increasing of the Zn content in nanocomposite film. Also this can be due to the increasing of the structural order and crystallinity of PANI chains in the presence of Zn nanoparticles. However, by making saturation in the conductive pathways, a decrease in the rate of conductivity increased by Zn addition was observed (Fig. 4). High electrical conductivity values were obtained with the nanocomposites containing at least 5% w/w of Zn nanoparticles. The electrical conductivity measurement for each nanocomposite films (with different Zn content) or pure PANI film was repeated 10 times and the related relative standard deviation (RSD)% of measurements was calculated. The mean value of RSD% for conductivity measurements was obtained as 2.02%. It is obvious that the electroactivity and electrochemical anticorrosion effect of PANI/Zn nanocomposite are dependent to its electrical conductivity. Therefore, the next investigations on the electroactivity and anticorrosive properties of PANI/Zn nanocomposite

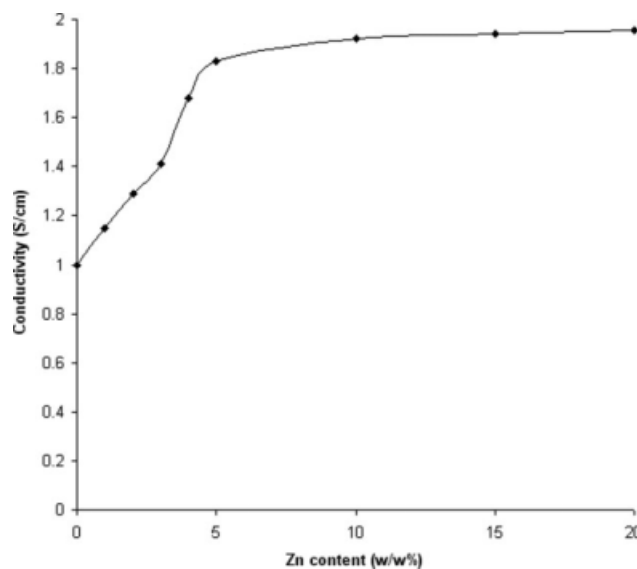


Figure 4 Electrical conductivity of PANI/Zn nanocomposite free-standing films with different Zn content prepared using *in situ* polymerization method.

were carried out using PANI/Zn nanocomposite with Zn content of 5% w/w, which have the maximum electrical conductivity.

Cyclic voltammetry studies

Cyclic voltammetry studies were carried out to investigate the electroactivity of PANI/Zn nanocomposite in comparison with PANI. A gold-electrode coated with a thin layer (15 μm thicknesses) of nanocomposite film with Zn content of 5% w/w was used as working electrode. Various solutions including HCl (0.1M), H_2SO_4 (0.1M), and NaCl (3.5% w/w) were used as electrolyte. Figures 5–7 typically show the

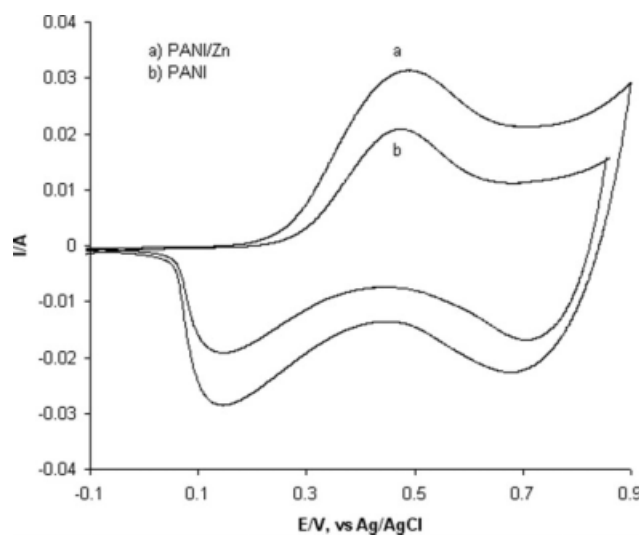


Figure 5 Cyclic voltammograms of PANI/Zn (5% w/w) nanocomposite and pure polyaniline in H_2SO_4 (0.1M) solution with potential scan rate of 100 mV/s.

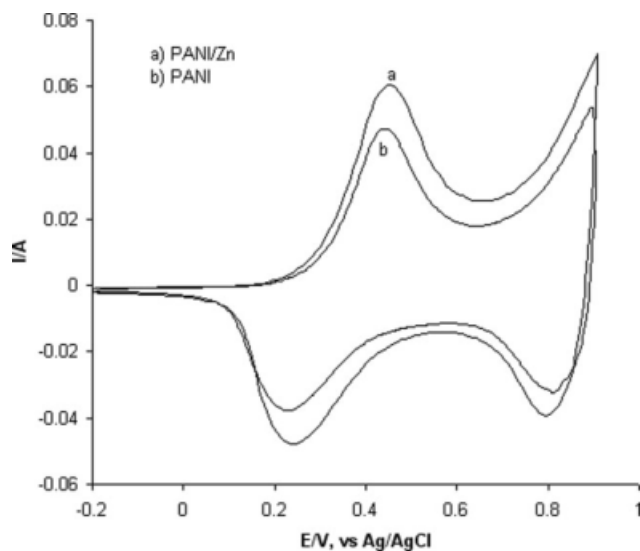


Figure 6 Cyclic voltammograms of PANI/Zn (5% w/w) nanocomposite and polyaniline in HCl (0.1M) solution with potential scan rate of 100 mV/s.

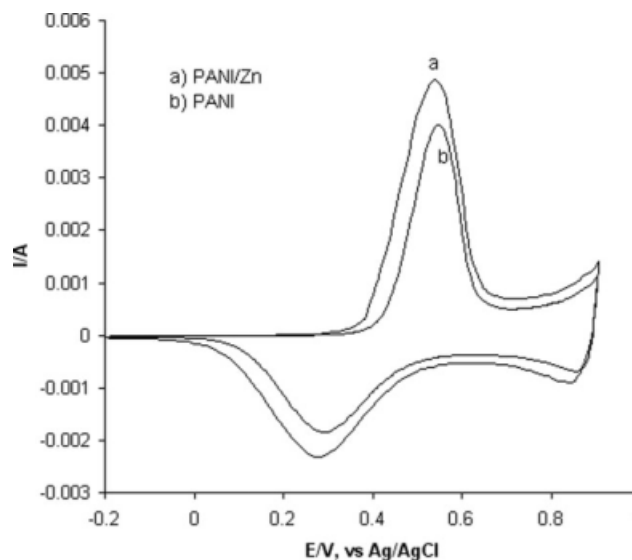


Figure 7 Cyclic voltammograms of PANI/Zn (5% w/w) nanocomposite and polyaniline in NaCl (3.5% w/w) solution with potential scan rate of 100 mV/s.

cyclic voltammograms of PANI/Zn (5% w/w) nanocomposite and pure PANI, respectively, in H_2SO_4 (0.1M), HCl (0.1M), and NaCl (3.5% w/w) electrolytes at potential scan rate of 100 mV/s. According to the results, it was found that PANI/Zn nanocomposite is electroactive similar to that of pure PANI, and there are two pairs of oxidation/reduction peaks in cyclic voltammograms. Also results showed that the electrochemical behavior of the nanocomposite in all of the mentioned electrolytes is completely reversible. In Figures 5–7, the high-current densities related to the cyclic voltammogram of nanocomposite film compared with pure PANI indicates that the presence of Zn nanoparticles in PANI matrix promotes the oxidation and reduction of PANI chains. Also the high-current densities obtained for nanocomposite in cyclic voltammograms are in good correlation to the high electrical conductivity of PANI/Zn nanocomposite films compared with the pure PANI film (Fig. 4). According to the results, the current density in cyclic voltammogram of nanocomposite in HCl solution is higher than that of H_2SO_4 solution, which is higher than in NaCl solution (Figs. 5–7). This phenomenon is related to the different ion activities in various solutions. Oxidation and reduction of PANI are together with the insertion and excretion of dopant anions into and out of the polymer backbone (doping and dedoping) and, therefore, the activity of ions (dopants) in electrolytes is affective on the current density in cyclic voltammograms.

Corrosion studies

Open circuit potential measurement

The corrosion protection performance of PANI/Zn nanocomposite coating on iron sample was investi-

gated. For this, thin films of the nanocomposite coatings with 100 μm thickness were applied on iron coupons (2 cm \times 2 cm dimensions) by a solution casting method. Open circuit potential of the iron samples, coated by PANI/Zn nanocomposite was recorded against time as well as uncoated and pure PANI coated samples. Figure 8 shows the open circuit potential of bare, PANI coated and PANI/Zn nanocomposite coated iron samples against time in various corrosive solutions. According to the results, in all electrolytes, the open circuit potential of iron

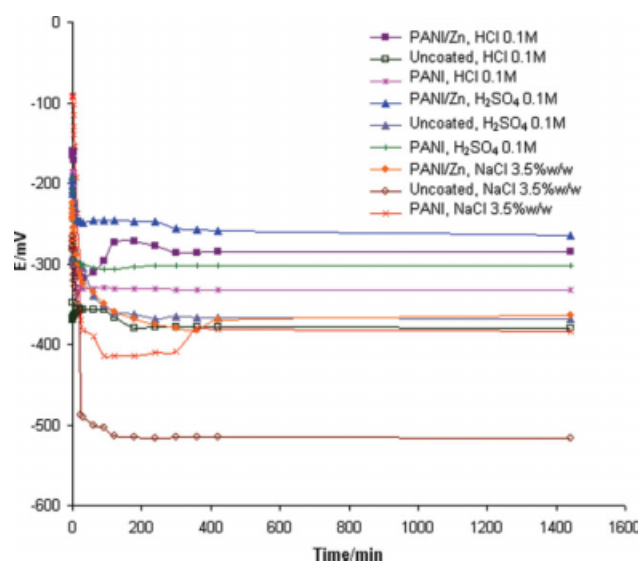


Figure 8 Open circuit potentials of bare, PANI coated, and PANI/Zn nanocomposite coated iron samples in various corrosive solutions against time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

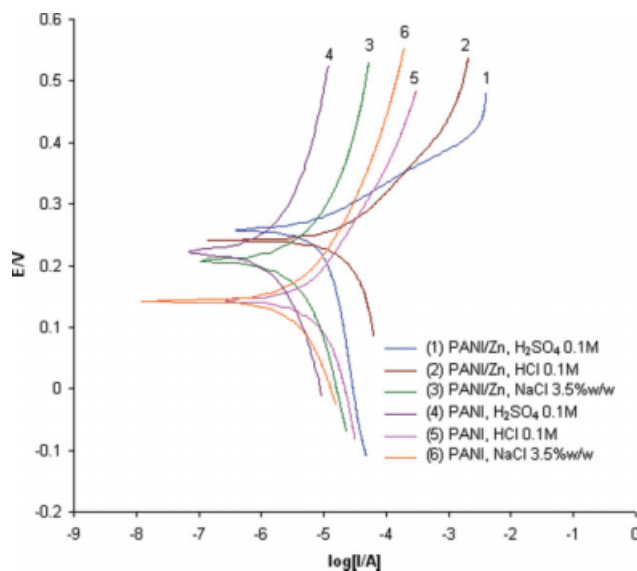


Figure 9 Tafel plots of PANI coated and PANI/Zn (5% w/w) nanocomposite coated samples in HCl (0.1M), H₂SO₄ (0.1M), and NaCl (3.5% w/w) as corrosive solutions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

samples coated with PANI/Zn nanocomposite is higher than pure PANI coated and uncoated samples. In other word, incorporation of zinc nanoparticles in PANI matrix causes to a positive shift in the open circuit potential or corrosion potential of the iron samples coated with the PANI/Zn (5% w/w) nanocomposite compared with the iron samples coated with pure PANI in various corrosive environments. Also the open circuit potential of pure PANI coated samples is higher than the bare iron samples in various corrosive environments. Therefore, the PANI/Zn nanocomposite coating thermodynamically has better corrosion protection effect compared with pure PANI coating. The presence of zinc nanoparticles in PANI matrix thermodynamically causes an improvement in the anticorrosion efficiency of PANI. This is due to the electrochemical corrosion

protection effect of zinc nanoparticles on iron coupons and also improvement of electrical conductivity and electroactivity of PANI in the presence of Zn nanoparticles. Also sacrificial oxidation of Zn in conjunction with iron can prevent the reduction of the iron potential as the cathode of a galvanic cell. This behavior of Zn is similar to PANI, and, therefore, Zn thermodynamically has a synergic effect on the corrosion protection behavior of PANI on iron.

Tafel plots

The electrochemical Tafel slope analysis was used to evaluate the anticorrosion performance of PANI/Zn (5% w/w) nanocomposite coating on iron samples. The Tafel plots for coated and uncoated iron samples were recorded by sweeping of potential from equilibrium potential toward negative and positive potentials against Ag/AgCl reference electrode in HCl (0.1M), H₂SO₄ (0.1M), and NaCl (3.5% w/w) electrolytes. The iron coupons were coated with 100 μ m coating of pure PANI and PANI/Zn (5% w/w) nanocomposite by the solution casting method using NMP as solvent. Figure 9 shows the Tafel plots for PANI and PANI/Zn (5% w/w) nanocomposite coated iron samples in HCl (0.1M), H₂SO₄ (0.1M), and NaCl (3.5% w/w) solutions. It can be seen that the corrosion current of PANI/Zn nanocomposite coated samples is much lower than the pure PANI coated samples in all of the corrosive environments. Therefore, it was found that the incorporation of Zn nanoparticles in PANI matrix, also kinetically promotes the anticorrosive efficiency of PANI/Zn nanocomposite coating on iron samples. Comparison of the corrosion rate for PANI/Zn nanocomposite and pure PANI coated iron samples showed that the corrosion kinetics of nanocomposite coated samples is much lower than the pure PANI coated samples (Table II). In addition to the thermodynamically synergic effect of Zn nanoparticles on the anticorrosive properties of PANI, they also causes the increase of the tortuosity of diffusion

TABLE II
Corrosion Current (I_{corr}) and Corrosion Rate (CR) for Bare, PANI Coated, and PANI/Zn Nanocomposite (5% w/w) Coated Iron Samples in HCl (0.1M), H₂SO₄ (0.1M), and NaCl (3.5% w/w) as Corrosive Solutions

Corrosive solution	Samples	I_{corr} (mA)	CR (mm/year)
HCl (0.1M)	Bare	1.550×10^{-3}	18.0604
	PANI coated	5.808×10^{-6}	0.0676
	PANI/Zn coated	7.438×10^{-7}	0.0087
H ₂ SO ₄ (0.1M)	Bare	1.493×10^{-3}	16.8713
	PANI coated	5.335×10^{-6}	0.0621
	PANI/Zn coated	2.989×10^{-6}	0.0247
NaCl (3.5% w/w)	Bare	1.221×10^{-3}	14.2225
	PANI coated	4.686×10^{-6}	0.0545
	PANI/Zn coated	2.232×10^{-7}	0.0025

pathway of corrosive agents, such as, oxygen gas, hydrogen, and hydroxide ions toward metal surface. Therefore, the addition of Zn nanoparticles to the PANI matrix increases the anticorrosive effect of PANI coating both thermodynamically and kinetically.

CONCLUSIONS

In situ production of Zn nanoparticles under vigorous stirring followed by *in situ* polymerization of aniline caused to the incorporation of Zn nanoparticles in PANI matrix and preparation of PANI/Zn nanocomposite. The electrical conductivity measurements showed that the PANI/Zn nanocomposite films are conductive with conductivities higher than the pure PANI film prepared in a similar method. The electrical conductivity was increased by increasing the Zn content of the nanocomposite and a maximum electrical conductivity was obtained for nanocomposite films with at least Zn content of 5% w/w. The reversible electroactive behavior for PANI/Zn nanocomposite was confirmed by cyclic voltammetry technique. Results of the corrosion studies showed that the anticorrosive property of PANI/Zn nanocomposite coating on iron samples is thermodynamically and kinetically much better than pure PANI coating. Therefore, Zn nanoparticles have a good synergic effect on the corrosion protection behavior of PANI matrix.

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