Corrosion Protection of Mild Steel with Nanofibrous Polyaniline-Based Coatings

Sude Ma,[1] Guolin Song,[2] Ningbo Feng,[1] Pei Zhao[3]

[1]School of Materials Science and Engineering, Xihua University, Sichuan Chengdu, 610039, China
[2]Institute of Advanced Materials, Graduated School at Shenzhen, Tsinghua University, Guangdong Shenzhen, 518055, China
[3]School of Human Settlement & Civic Engineering, Xi'an Jiaotong University, Shaanxi Xi'an, 710049, China

ABSTRACT: Polyaniline (PANI) nanofibers were successfully synthesized by a modified rapid mixing method, that is, by the rapid mixing of solutions of aniline and ammonium peroxydisulfate in either hydrochloric acid or filtrates of oxidative polymerization of aniline. Scanning electron microscopy examination showed that nanofibrous PANI products were achieved in all cases; this indicated that the initially presented excessive anions and cations had no evident effect on the formation of nanosized PANI. The nanofibrous PANI exhibited excellent dispersability in both water and organic solvents, and an ultraviolet–visible spectrum was successfully recorded by dispersion in cyclohexanone. Composite coatings were fabricated with the dispersions of nanofibrous PANI and solutions of epoxy. Greatly enhanced corrosion protection performances were demonstrated by the coatings loaded with a small quantity of nanofibrous PANI. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1601–1605, 2012

Key words: coatings; nanofiber; polymer synthesis and characterization

INTRODUCTION

The corrosion of materials, in the most common cases of metallic materials, is a thermodynamically driven and irreversible reaction with the environment. Tremendous economic losses are caused every year by corrosion. For example, it has been reported that approximately 3–4% of the gross domestic product of developed countries is spent for corrosion and corrosion control every year.[1] Furthermore, many safety risks and much environmental pollution is also brought about by corrosion. Because it is hardly possible to completely stop the corrosion of materials, many strategies have been employed to control or prevent corrosion. Generally, five different principles can be used: appropriate materials selection, changes to the environment, suitable design, electrochemical (cathodic and anodic) protection, and the application of coatings.[2] Among these, the application of coatings is one of the most commonly used and most cost-effective ways of providing practical protection to easily corrodible metallic structures and objects.[3]

Typically, the practically used corrosion protection coatings are often multiple-layer systems.[3] A primer coating, which is designed to provide corrosion protection to the substrates, is coated at first, and a second layer, named the *topcoat*, is applied on the primer to provide a barrier effect against environmental attacks, such as weathering and UV rays, and to provide decoration. In some cases, a conversion coating, with the aim of promoting adhesion between the metal substrate and the primer coating, is also used. Because the pure barrier effect of a polymeric coating is very limited, various kinds of additives are added to the primer coating. Although high corrosion protection effectiveness has been demonstrated by inhibitors, such as chromates, phosphates, and molybdates, these materials are poisonous, and these substances pose significant health and environmental hazards in their handling and disposal in corrosion protection. In some countries, government regulations have been established to limit the use of these materials. For instance, both the Environmental Protection Agency and the Occupation Safety and Health Agency of the United States continue to restrict the use of hexavalent chromium as a corrosion protection component.[4] It is, therefore, necessary to exploit some novel, effective, and nontoxic corrosion inhibitive materials.

Conducting polymers are one of the mostly studied novel materials for metallic corrosion protection.[5] These versatile materials exhibit not only the electrical

conductivity of semiconductors but also the general behaviors of polymers. They can be either electrochemically deposited on a substrate to form a pure film or blended with matrix polymers and then coated to form composite coatings. Generally, the preparation of composite materials of conductive polymers is considered the most effective way to process and practically apply these polymers for their intractability. Recently, nanofibers of polyaniline (PANI),[6–8] one of the most extensively investigated conducting polymers, have been successfully prepared by several kinds of template-free methods by chemical oxidative polymerization. In comparison with traditionally prepared larger sized PANI powders, one of the remarkable characteristics of PANI nanofibers is their easy dispersability. The nanostructures can be facilely dispersed in water and other organic solvents to form uniform dispersions. With these dispersions as the testing samples, the ultraviolet–visible (UV–vis) spectra of PANI, in both the doped and dedoped states, can be recorded. Motivated by these works, in this stud, we synthesized PANI nanofibers by a modified rapid mixing polymerization and then incorporated them into an epoxy coating to form PANI-nanofiber-based composite coatings. The corrosion protection performance of the composite coatings for mild steel in simulated saline water was examined.

EXPERIMENTAL

Materials

Aniline, ammonium peroxydisulfate (APS), hydrochloric acid (30 wt %), ammonia water (25 wt %), acetone, ethanol, cyclohexanone, and n-butanol were all analytical grade and were purchased from Xi'an Chemical Reagents Co. (Xi'an, China). Aniline was doubly distilled *in vacuum* to eliminate oxidation impurities and stored in the dark at 0°C. The commercial products epoxy resin E-44 (a bisphenol A epoxy resin with an epoxy value of 0.44 mol/g) and curing agent T-31 (an aromatic polyamine) were from Blue Star New Chemical Materials Co., Ltd. (Beijing, China). Mild steel slices (C = 10 wt %, Mn = 45 wt %, S = 3.5 wt %, and P = 6 wt %; $100 \times 20 \times 1.5$ mm^3) were carefully polished with emery paper (800 grit) and washed with deionized water and ethanol before coating or electrochemical testing. All other reagents were used as received.

Synthesis of the PANI nanofibers

PANI nanofibers were synthesized by a modified, rapid mixing polymerization with 0.25 mol/L aniline. Specifically, 9.31 g (0.1 mol) of aniline and 11.4 g (0.05 mol) of APS were dissolved in 200 mL of hydrochloric acid (1.0M) separately. After the mixtures were brought to 20°C, the two solutions were poured into a beaker with a volume of 500 mL and left without any disturbance. The reaction temperature was kept at 20 ± 2°C by cooling water around the beaker. With 0.5 h of reaction, the polymer was separated by filtration, and the filtrate was collected and divided equally into two parts. With the filtrate as the reaction medium for dissolving the same amount of aniline (0.1 mol) and APS (0.05 mol), the aforementioned synthesis procedure was repeated two times. After we took a very small quantity of sample from all three batches of the products for morphological examination, the rest of the products were put together and mixed with 600 mL of ammonia water (10%), stirred vigorously for 1 h, filtered, and washed with deionized water until the filtrate became neutral. Dedoped emeraldine base form of PANI was obtained and dried in vacuum at 50°C.

Preparation of the PANI nanofiber composite coatings

First, 10 g of epoxy resin was added to 40 g of mixed solvent (a mixture of cyclohexanone and n-butanol with a weight ratio of 1); these were stirred to form a homogeneous solution. Second, varied amounts (0.2, 0.5, 1.0, 1.5, and 2.0 g) of dedoped PANI nanofibers were added to 40 g of mixed solvent and ultrasonicated for 1.5 h to form a uniform dispersion of PANI nanofibers. Third, the solution of epoxy resin and the dispersion of PANI nanofibers were mixed and mechanically stirred for 1.0 h. Finally, half of the dispersion was thoroughly mixed with 2 g of polyamide 650 and brushed onto the surfaces of pretreated mild steel coupons ($100 \times 20 \times 1.5$ mm^3). With the evaporation of the solvent and curing at room temperature for 2 days, the other half of the dispersion was mixed with the same amount of polyamide 650 and brush-coated. The sample was then left for a week at room temperature before electrochemical testing.

Characterization

The UV–vis spectrum was recorded on a U-2100UV–vis spectrophotometer (Hitachi, Japan) with a dispersion of dedoped PANI nanofibers in water and cyclohexanone. Morphological examination was performed with field emission scanning electron microscopy (SEM; JSM 6700 F, JEOL, Japan) of the doped samples. Corrosion testing of the bare mild steel and coated coupons in a 3.5 wt % aqueous NaCl solution was performed on a DJS-292 potentiostat (Leici Instrument Factory, Shanghai, China) at room temperature with a three-electrode electrochemical cell, in which the working electrode, counter electrode, and reference electrode were the coated or uncoated steel coupons (1.5×3.0 cm^2), platinum foil (1.5×2.0 cm^2), and an Ag/AgCl reference electrode, respectively. The exposure surface of the working
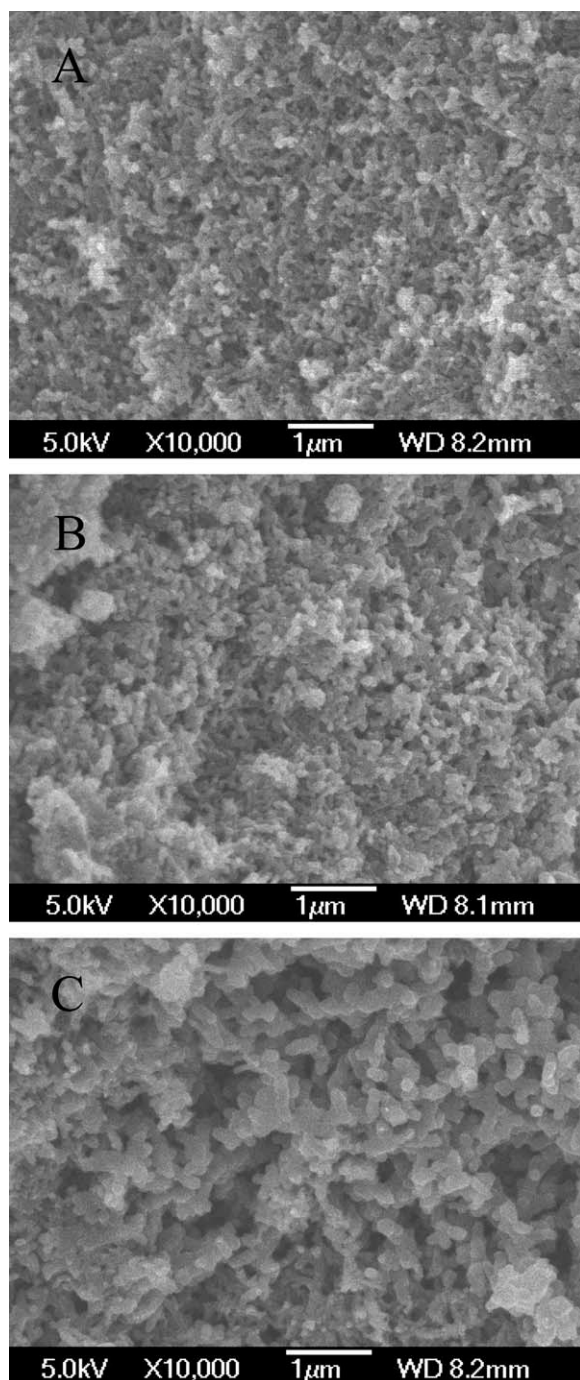
Figure 1 SEM images of PANI nanofibers synthesized in (A) hydrochloric acid, (B) the first filtrate and (C) the second filtrate.

electrode was 10×15 mm^2, with the rest of the part in water sealed with a mixture of rosin and paraffin (weight ratio = 1 : 1).

RESULTS AND DISCUSSION

Polymerization

When the hydrochloric acid solution of aniline and APS were mixed, the color of the mixture gradually turned from colorless to pale green; this indicated the formation of PANI molecules inside the mixture. After about 3 min, the color of the solution started to change green, sap green, and then purple blue over about 10 min; this revealed the formation of more and more PANI molecules. With 30 min of reaction, the mixture was filtered by gravity filtration to isolate the polymer. Morphological examination [Fig. 1(A)] revealed that nanofibrous PANI with a diameter of 50–100 nm was achieved. The result was in agreement with those reported by some other groups[9,10] because all of the monomers were consumed quickly to form the primary PANI nanofibers, and no secondary growth followed; this led to the formation of nanofibrous PANI.[9]

By mixing the solution of aniline and APS in the filtrates obtained the first and second times, we observed a similar color changing process from dark to darker, except the initial color of the mixture was some kind of purple or dark purple instead of the transparent color mentioned previously. After 30 min of reaction, the polymers were isolated in the same manner. By taking a very small quantity of the as-prepared PANI for morphological study, the rest of the products from all three polymerization procedures were mixed and treated with an excessive amount of ammonia to prepare the dedoped form of PANI. The products achieved in the second and third polymerization procedures were all nanofibers, and no significant difference was observed (Fig. 1), although there were some slightly increases in the sizes of the nanofibers. This indicated that the initially presented additional anions (SO_4^{2-}) and cations (NH_4^+) had little effect on the formation of the PANI nanofibers. The main reasons might have been the intrinsic properties of PANI,[11] the instantaneous consumption of the reactants,[9] and the concentration of the reactants.[6] The finding will be of great importance for the synthesis of nanofibrous PANI,
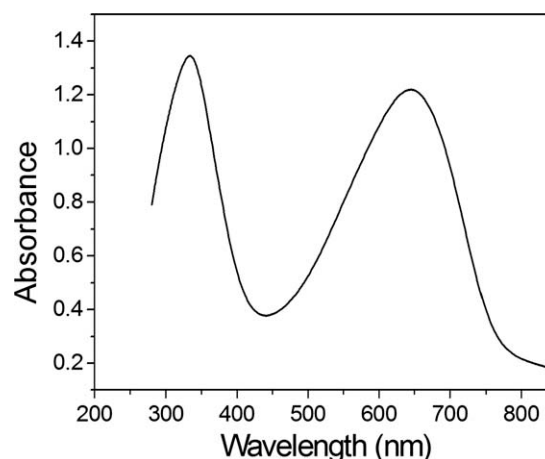

Figure 2 UV–vis spectrum of the dedoped PANI nanofiber dispersion in cyclohexanone.
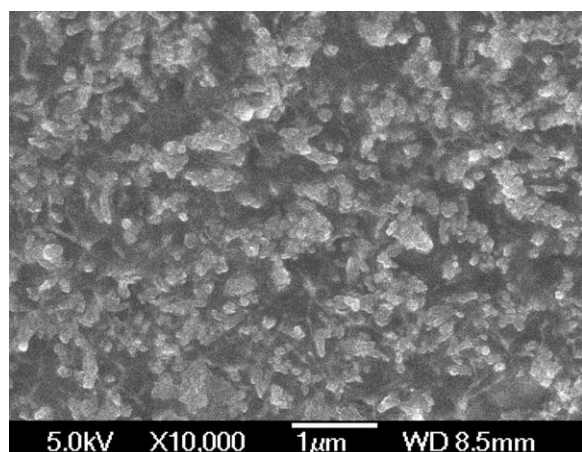
Figure 3 SEM image of the composite with a PANI nanofiber loading of 12.5 wt %.

especially on an industrial scale, because the amount of water will be reduced significantly.

Dispersion

Because of the intractability of PANI (i.e., it is insoluble in most common organic solvents and infusible), one of the most significant and most important advantages of nanofibrous PANI over traditionally prepared irregular PANI particles is its greatly enhanced dispersability because the nanosized PANI can be easily dispersed into matrix materials and achieve PANI-based functional composites; this is now accepted as one of the most practical and feasible methods for the large-scale application of PANI. By ultrasonicating mixtures of a small quantity (ca. 0.1 g) of the dedoped PANI nanofibers with 40 mL of water or cyclohexanone for 0.5 h, we achieved light blue uniform dispersions of PANI in both water and cyclohexanone. The dispersions were used for the successful recording of UV–vis spectra of dedoped nanofibrous PANI (Fig. 2), which indicated the excellent dispersability of the as-prepared PANI nanofibers. In preparing the nanofibrous PANI-based composite coatings with various PANI loadings, we increased the time for the ultrasonication of PANI in the mixed solvent (a mixture of cyclohexanone and n-butanol with weight ratio of 1) to 1.5 h to ensure that the nanosized PANI was completely and uniformly dispersed in the solvent. Morphological examination of the composite coatings showed that all of the PANI nanofibers were well
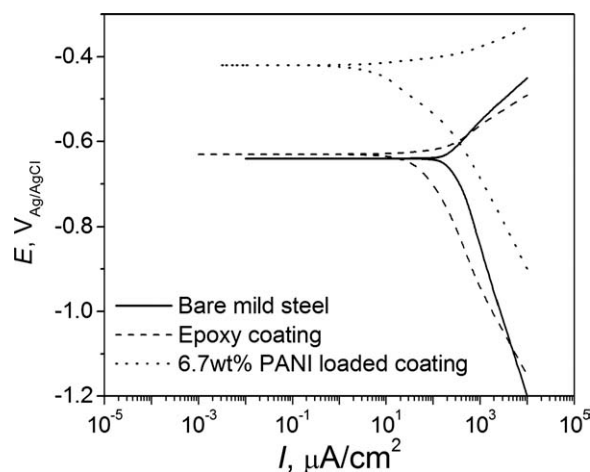

Figure 4 Tafel curves of bare mild steel, epoxy coating, and 6.7 wt % PANI nanofiber composite coating protected samples.

dispersed inside the epoxy matrix, regardless of the PANI loadings (1.4, 3.5, 6.7, 9.7, and 12.5 wt %) in the coatings (Fig. 3).

Corrosion protection

The potentiodynamic polarization curve is one of the most convenient ways to evaluate the corrosion protection efficiency of a coating, from which the corrosion potential and corrosion current density can be easily identified. Generally, the higher the corrosion potential and the lower the corrosion current density are, the better the corrosion protection performance of the coating will be. The potentiodynamic polarization curves of the bare mild steel and coated samples with varied PANI loadings are shown in Figure 4, and the corresponding corrosion potentials and corrosion current densities are tabulated in Table I. With the addition of nanosized PANI into the epoxy coatings, the corrosion potentials increased from -0.63 V for the pure epoxy coating to -0.42 to -0.44 V for the PANI-nanofiber-loaded coatings, whereas the corrosion current densities decreased from 80.25 $\mu A/cm^2$ for the pure epoxy coating to 14.86 to 29.81 $\mu A/cm^2$ for the coatings with PANI loadings lower than 6.7 wt %. However, with further increases in the PANI loadings to 9.7 and 12.5 wt %, no increase in the corrosion potential was observed, and the corrosion current density increased slightly compared with the coatings with PANI loadings lower than 6.7 wt %. The

TABLE I
Corrosion Potential (E_{corr}) and Corrosion Current Density (I_{corr}) Values of the Samples

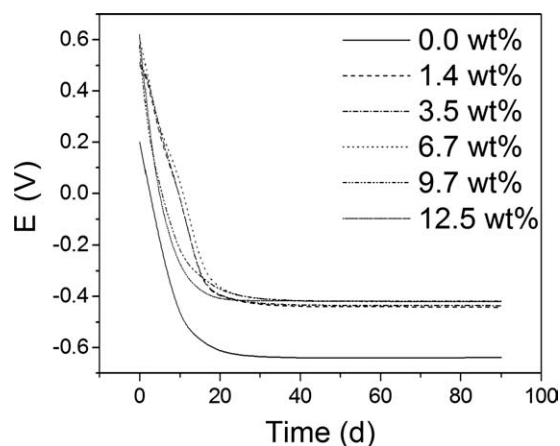|	Uncoated	Epoxy coated	1.4 wt %	3.5 wt %	6.7 wt %	9.7 wt %	12.5 wt %
E_{corr} (V)	−0.648	−0.634	−0.441	−0.436	−0.420	−0.418	−0.418
I_{corr} ($\mu A/cm^2$)	209.56	80.25	29.81	22.16	11.23	12.55	14.86

Figure 5 Corrosion potentials of the coatings with different PANI nanofiber loadings.

enhanced corrosion protection performance with the addition of nanosized PANI was attributed to the effective formation of a passive layer on the surface of the mild steel with the reaction of the nanosized PANI. However, because the formation of a passive layer and the penetration of corrosive ions such as Cl^{-1} are two competing processes, excessive loading of PANI nanofibers would lead to easier permeation of the corrosive ions and water molecules to the surface of mild steel; this would lead to increased corrosion current densities.

All of the samples were continuously immersed in Cl^{-1} containing neutral solutions separately, and the corrosion potentials were recorded. With increasing immersion times, the pure-epoxy-coated samples failed first, as indicated by both an earlier decrease in the corrosion potentials (Fig. 5) and the brown corrosion product formed in the immersion solutions after only 1–2 weeks. After 3 months of immersion, the corrosion potentials of the samples coated with PANI loadings lower than 6.7 wt % showed no decrease, whereas a slight decrease in the corrosion potential was exhibited by samples coated with PANI loadings higher than 6.7 wt %. The surface color of the samples with no decrease in corrosion potential was silver white after the coatings were peeled off; this indicated the passivation of the steel surfaces,[12] whereas the surfaces of the samples with a decrease in corrosion potential and the pure-epoxy-coated samples were corroded to various degrees. The results show that significantly enhanced corrosion protection performance can be achieved with the addition of a small quantity of nanosized PANI into the commonly used epoxy coating because of the effective anticorrosive performance of the nanosized PANI. However, an adverse effect was achieved with excessive loadings of nanosized PANI because of the facilitated permeation capability of the coating to corrosive ions.

CONCLUSIONS

Nanofibrous PANI was successfully prepared by the rapid mixing of solutions of aniline and APS in either hydrochloric acid or filtrates of oxidative polymerization of aniline. The initially presented excessive anions and cations had no evident effect on the formation of nanosized PANI. The nanofibrous PANI exhibited excellent dispersability in both water and organic solvent. Nanofibrous-PANI-filled epoxy coatings were facilely prepared with the dispersions of nanofibrous PANI and solutions of epoxy. Greatly enhanced corrosion protection performances were demonstrated by the coatings loaded with a small quantity of nanofibrous PANI, but adverse protection performance was achieved with further increases in the PANI loading.

References

1. Bardal, E. Corrosion and Protection; Springer: Berlin, 2004; p 1.
2. Bardal, E. Corrosion and Protection; Springer: Berlin, 2004; p 237.
3. Bierwagen, G. P. Organic coatings for corrosion control; American Chemical Society: Washington, DC, 1998; p 1.
4. Cohen, S. M. Corrosion 1995, 51, 71.
5. Tallman, D. E.; Spinks, G.; Dominis, A.; Wallace, G. G. J Solid State Electrochem 2002, 6, 73.
6. Zhang, D. H.; Wang, Y. Y. Mater Sci Eng B 2006, 134, 9.
7. Anderson, R. E.; Ostrowski, A. D.; Gran, D. E.; Fowler, J. D.; Hopkins, A. R.; Villahermosa, R. M. Polym Bull 2008, 61, 563.
8. Yang, X. G.; Li, B.; Wang, H. Z.; Hou, B. R. Prog Org Coat 2010, 69, 267.
9. Huang, J. X.; Kaner, R. B. Angew Chem Int Ed 2004, 43, 5817.
10. Li, D.; Kaner, R. B. J Am Chem Soc 2006, 128, 968.
11. Huang, J. X.; Kaner, R. B. Chem Commun 2006, 367.
12. Fahlman, M.; Jasty, S.; Epstein, A. J. Synth Met 1997, 85, 1323.