Application of polyaniline/nylon composites coating for corrosion protection of steel

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Abstract In this research, we investigated the corrosion inhibition properties of polished steel plates (low carbon) coated with a polyaniline (emeraldine base form) blend with nylon 66 (termed PANi/Ny) via cast method with formic acid as the solvent. Polyaniline (PANi) was prepared chemically from aqueous solution using aniline (0.2 M) as a monomer and ammonium persulfate (0.2 M) as an oxidant. The polymer powder produced was changed into emeraldine base (EB) form after treatment with dilute ammonia solution (0.5 M) in order to do further processing. The corrosion experiments were performed in the open circuit, exposing samples to different aggressive and corrosive conditions (e.g., NaCl, HCl). To produce a good comparison, the corrosion study was performed on both polymer-coated and bare-steel samples. Corrosion monitoring was performed by simple immersion tests and determination of the concentration of iron ions and metal weight loss in test solutions. It was found that PANi/Ny coatings can provide an anodic protection against corrosive environments in which the metals are exposed. The corrosion rate for the polymer coated steel was significantly lower than the bare steel $(\sim10-15 \text{ times}).$

Keywords Corrosion, Polyaniline, Nylons, Steel, Coating, Immersion test

Introduction

Corrosion is defined as the destructive attack of a metal by the environment, or by chemical or electrochemical processes. The corrosion problem is unfortunately

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widespread, costly, and has no easy solution. Every year, industries pay a huge price (more than 100 billions dollars) for corrosion, and that cost is rising. Many papers and documents are published each year about corrosion and corrosion protection of different metals. Among the metals investigated, most research about corrosion protection concentrates on iron, since iron and its alloys are the basis of modern industry. Despite the advent of composites—ceramics and polymers, which have become dominant in some fields—iron is still the most important construction material in modern industry. The most common origin of corrosion is the basic thermodynamic tendency for metal to react, as expressed in terms of the free energy of reaction. One of the most familiar corrosion processes is the oxidation of iron (rusting):

 $2Fe + 3/2O_2 \Leftrightarrow Fe_2O_3$ $\Delta G^{\circ} = -741.0 \text{ KJ} \text{mol}^{-}$ (1)

A negative ΔG° indicates that the elemental metal is unstable, and iron metal is spontaneously oxidized in the presence of O_2 and an aqueous electrolyte solution. In the natural environment, oxygen gas is a good oxidizing agent. Most metals have lower reduction potentials than O_2 , therefore they are easily oxidized in the presence of oxygen. Early in the history of corrosion, it was discovered that corrosion is basically an electrochemical process rather than a strictly chemical reaction. The type of corrosion mechanism and its rate of attack depend on the exact nature of the metal, media (e.g., air, soil, aqueous) and the environmental conditions in which the corrosion takes place.

Metals such as iron can be protected from corrosion in many ways. A common method involves the application of protective coatings made from paints, organic resins, plastics, or films of noble metals on the structure itself (e.g., the coating on tin cans). $1-3$ These coatings form an impervious barrier between the metal and the oxidant, but are only effective when the

coating completely covers the structure. Flaws in the coating have been found to produce accelerated corrosion of the metal. Within coating technology, there is increasing interest in the development of efficient anticorrosive coating that is able to replace the conventional inorganic anticorrosive pigments usually added to paints, which may have detrimental effects on both environment and health.

Researchers have invented a revolutionary corrosion control system using conducting electroactive polymers (CEPs) in the last two decades. $4-6$ Among the conducting polymers investigated in corrosion control or protection of metals, most of the previous researchers have been attracted toward polyaniline (termed usually as organic or synthetic metal) and its derivatives or composites $7-26$ $7-26$ —mostly due to its interesting electrical conductivity (metallic), unique electrochemical properties (involving both electron and mass transfer during reduction and oxidation, $26-29$ ease and simplicity of its synthesis (chemically) in aqueous solutions in bulk scale without the need for any special or expensive equipment, low cost of the monomer and oxidants, and high thermal and environmental stabil-ities.^{[30](#page-6-0)} CEPs undergo redox reactions at moderate potential to control corrosion. It has been found that interactions of PAni with metal surfaces leads to a beneficial anticorrosion effect. The metallic and electroactive nature of polyaniline (ES) have been proposed to explain the anticorrosion properties.

PANi exhibits four different oxidation states: Leocoemeraldine (LE) (reduced and base form, nonconductive), Emeraldine base (EB) (partially oxidized form), protonated emeraldine (ES) (salt form), and pernigraniline (base form, oxidized form). Out of these, only protonated (acid-doped) emeraldine base (salt form, ES) has been found to be conductive in nature $(0.01-100 \text{ S cm}^{-1})$. However; PAni-conducting polymers normally need acidic conditions to keep their electrical conductive state alive. In particular, polyaniline and its derivatives need a pH value of at least 1 to be reasonably electrically conductive. Conducting/ insulating interchange states with acid/base treatment can be simply shown as in Fig. 1.

Based on this feature of electrochemical corrosion protection, the conducting polymers must act as corrosive materials on the metals to be protected in the first place. However, this would only end up in increased metal dissolution, if the composition of the conducting polymer does not allow for a mechanism to form the protective oxide layer at some critical dissolution (corrosion) rate. Analyzing with SEM and XPS methods shows that there was no $Fe₃O₄$, but only a clean-gamma Fe₂O₃. Fe₃O₄ is the passivating layer composition formed by PAni.[4,16](#page-5-0) So, it can be concluded that PAni coatings on active metals like iron provide anodic protection, act as electronic, chemical, and physical barriers to inhibit anodic reaction, and maintain high resistance to ionic flow—thereby blocking the metal dissolution and providing excellent corrosion protection. Intrinsically conducting polymers

Fig. 1: Doping/dedoping processes in polyaniline

(ICPs) can also compete in price compared to common zinc-based coatings (galvanizing iron). Basically, such materials might be either chemically or electrochemically active as a protecting material.

Experiment

Preparation of samples

The coating solution was made from the base form of PANi (EB) and nylon 66 and nylon 6 (both woven and granulated forms) in formic acid with a concentration of 0.50 wt% separately. EB was prepared with a treatment of PANi salt (ES) with 0.5 M ammonia solution. Polyaniline was synthesized using 0.2 M freshly distilled aniline in HCl 1 M solution. Ammonium persulfate (0.2 M) was employed as chemical oxidant. Formic acid was used as solvent for dissolving of PANi and nylon 66 in order to solution processing. The details of preparing polyaniline and polyaniline/ nylon composites have already been published. 31

Commercial grade mild steel (St 37) samples were obtained from Khoozestan Steel Company (Ahvaz, Iran) with the following specifications: Iron (99.77%), Carbon ($\leq 0.17\%$), Phosphorus and Sulfur ($\leq 0.05\%$), and Nitrogen (6.009%) . The corrosion study was done on coated samples and bare steel was used as a reference. Upon exposure to a corrosive, acidic media, PANi coating film in base form was converted to a doped conductive salt form. The coating solution was made from the base form of PANi (EB form) and nylon 66 in formic acid with a concentration of 1%. EB was prepared after treatment of synthesized PANi (emeraldine salt, ES) with a dilute aqueous base solution (0.5 M NH_3) . The solvent allowed evaporation (at $50-60$ °C using an oven), leaving the substrate coated with a solid thin film with the approximate

desired thickness. The thickness of the coatings was measured using X-ray fluorescence (Dualscope FMP 100, Fisher Instrumentation, Germany).

Corrosion monitoring

In this research, corrosion tests were performed in an open circuit, exposing metal to different aggressive and corrosive conditions (immersion method). 32 Since corrosion is basically an electrochemical process, it can be monitored using electrochemical techniques, too. $33-35$ The immersion test is used extensively to generate uniform corrosion data for alloys used in the process industries under immersion conditions. In this method, small sections of the candidate material (termed as ''coupons'') are exposed to the test medium in a beaker and the loss of weight of the material is measured for a period of time. The following equation was used for evaluating the corrosion resistance behavior using the immersion method 32

Rate of corrosion $(CR) = (K \times W)/(A \times T \times D)$ (2)

where K is conversion constant (2.40×10^6) , W is the weight loss (g) or weight difference before and after corrosion, T is the time (hour), A is the area of the coupon (cm²), and D is density of the metal ($g/cm³$). The corrosion rate is then reported as milligrams per square decimeter per day (MDD) throughout the text, according to ASTM.^{[32](#page-6-0)} In order to reproduce data, similar areas (4 cm^2) of the metal coupons were exposed to an equal volume of corrosive solution in similar beakers (50 cc) .

Corrosion rate was also monitored from determination of total iron ions (Fe^{2+} , Fe^{3+}) entered into the test solution in the course of corrosion. The analysis was performed spectrophotometrically using a calibration curve prepared from standard solutions and Beers Law $(A = ebc)$. 1, 10 ortho-phenanthroline reacts with Fe(II) ions, producing strongly colored complexes $(\lambda_{\text{max}} = 510 \text{ nm}, \quad \varepsilon = 11100 \text{ M}^{-1} \text{ cm}^{-1}).$ Hydroxylamine (HCl salt) is added before the color is developed to provide a measure of the total iron ions present in solution. The pH is adjusted to a value between 6 and 9 by the addition of a sodium acetate buffer. A single-beam spectrophotometer (Perkin-Elmer) was used for analysis of iron ions in the solution. Two techniques used in this paper for monitoring corrosion (weight loss measurement and solution analysis for metal ion) are well established, standard methods. The corrosion data reported throughout the paper (as MDD) are the average of at least two or three measurements. Uncertainty or RSD for 3-replicate measurements were less than 5%. Some fluctuations in the data obtained might partly be due to the small difference in surface uniformity and trace composition of the steel samples used in this investigation.

Results and discussion

Effect of solvent

Due to the solubility of polyaniline in some solvents, these polymers have attracted special attention compared to the other conducting polymers—such as polypyrrole, which is insoluble in any solvent and infusible. N-methyl pyrrolidone (NMP) is the most famous solvent of PAni. However, it is an expensive solvent and its boiling point is high (bp = 202° C). So it does not seem to be a suitable solvent for coating of metal surfaces by PAni through the cast method, especially in bulk scale. We found that formic acid is a good alternative. It is an inexpensive and volatile solvent (bp = 105° C).

It is interesting to note that as our results have shown (Table 1), PANi coatings via cast from formic acid decrease the rate of corrosion of iron more than when PANi is coated via cast from NMP solvent. In the other words, formic acid seems to be a more suitable solvent than NMP for coating of steel by PANi via the cast method for corrosion control. As previous investigators have demonstrated, 4 ES can apply passivating and anticorrosion properties more than the EB form of PANi. The possible reason for this observation can be due to the partial doping of EB in formic acid $(K_a \sim 10^{-4})$. In the NMP solvent, doping of PANi does not occur. In our further studies in this paper, PANi and its composite solutions with nylons were prepared and casted from formic acid.

In a separate experiment, we examined the effect of formic acid on the corrosion of steel samples. It was observed that the corrosion of steel samples in formic acid 1 M for 1 h was less than 1.0 MDD. Corrosion of iron or steel is much less in the presence of weak organic acids in comparison to strong inorganic acids, such as HCl.

Corrosion control using PANi composites with some common polymers

In this experiment, we prepared composites of PANi with some common polymers such as nylon 6 and nylon 66, polyvinyl acetate (PVAc) and polyurethane (PU). The corrosion experiments were carried out in 1 M

a MDD stands for milligram per square decimeter per day

* G stands for granulate, F stands for Fiber form, and W stands for woven form of nylon 66, ES stands for emerldine salt form of PANi, B stands for uncoated plate, and CR stands for corrosion rate of metal as MDD. The weight proportion ratio of PANi and nylon in preparation of composite was 1:1

NaCl. The results obtained were compared with a bare steel sample (see Table 2).

As our results interestingly show (Table 2), the highest corrosion inhibition is observed when a woven form of nylon (commercial textile) is used for preparation of the PANi composite. The woven form of nylon also dissolves in formic acid more quickly than granulated forms. The small difference in the composition of the woven nylon might be the reason for this observation. However, the exact mechanism is not very clear to us. Our further investigations in this paper were carried out using this composite. The reaction scheme for the passivation of metals by polyaniline and amazing corrosion protection properties of PANi can be shown as the following equations (3) – (7) .^{[4](#page-5-0)}

Iron is directly oxidized to the ferric state, where ferric oxide is formed and acts as a passivating layer:

$$
2Fe(s) \rightarrow 2Fe^{2+} + 4e \quad (First step)
$$
 (3)

$$
2\text{Fe}^{2+} \rightarrow 2\text{Fe}^{3+} + 2\text{e}
$$
 (4)

$$
O_2 + 2H_2O \rightarrow 4OH^- + 4e \quad (Second step)
$$
 (5)

 $2Fe^{3+} + 6OH^{-} \rightarrow Fe_2O_3 + 3H_2O$ (6)

$$
ES + 4e + 4H^{+} \rightleftarrows LE \quad (Third step) \tag{7}
$$

This means that PANi oxidizes iron where it is reduced to LE. Further oxidation of iron ions lead to iron (III) oxide, and oxygen re-oxidizes the LE into ES form. This tells us that the mechanism of the corrosion protection by PANi is potentially shifted due to the noble metal properties of PANi and the redox catalytic properties of PANi, leading to the formation of a passive oxide layer. The metallic conductivity, electroactive nature (reversible redox behavior) and electrocatalytic properties of polyaniline (ES) are suggested to explain its anticorrosion properties. It has also been recently reported^{[25](#page-6-0)} that a coating of the nylon polymer on steel is not sufficient to prevent corrosion in a chloride medium—the underlying steel shows signs of corrosion after only three days in a neutral salt spray (NSS) environment. Open-circuit potential measurements indicate that the steel is corroding, forming soluble ferrous and ferric oxy-complexes. PANi by itself is also insufficient in inhibiting corrosion on steel. A synergy exists between an underlayer of PANi and a top layer of the nylon coating in minimizing corrosion.

In conclusion, polyaniline coatings on active metals like iron provide anodic protection, act as electronic,

Weight ratio (EB:Ny)	1:1	2:1	3:1	4:1
Corrosion rate (MDD)		9		

Table 4: Effect of polymer thickness on corrosion rates

chemical, and physical barriers to inhibit anodic reaction, and maintain high resistance to ionic flow, thereby blocking the metal dissolution and providing excellent corrosion protection.

The effect of composite/PANi ratio

To optimize the coating quality of steel by PANi/Ny, we changed the weight proportion ratio of PANi and Nylon 66, then measured the corrosion rate of the steel plates after exposing them in NaCl solution (1 M) for 1 h at room temperature (Table 3).

The best ratio was found to be a 4:1 weight ratio. EB and nylon also exhibited high protection, but their adhesions were not satisfactory. So, in our further experiments in this paper, we used PANi/Ny prepared with weight ratio of 4:1.

Effect of thickness

For performing this experiment, different thicknesses of polymer composite (EB/Ny66) were deposited on the steel plates by controlling the volume of polymer solutions taken for cast. The polymer-coated plates were then exposed to test solutions (1 M NaCl). The results of this investigation have been summarized in Table 4.

As our data in this investigation clearly show, to have protection against corrosion, the thickness of the polymer film on the metal surface (iron) should be at least 30 microns. It was also observed (using an adhesion test) that with increasing thickness more than 32 microns, adhesion of the coating is decreased.

Table 5: The effect of NaCl concentration on corrosion rates in MDD

Effect of concentration of NaCl

To find out the effect of salt concentration on corrosion rates, steel plates coated with PANi/Ny were exposed to NaCl solutions with different concentrations. Exposure time was 1 h at room temperature. The results have been summarized in Table $\overline{5}$.

Interestingly, our results show that with increasing concentrations of NaCl, corrosion rates in the case of polymer-coated plates decrease. According to the results (Table 5), the highest corrosion is observed in NaCl 1 M for both coated and bare steel samples. In general, the environment has a significant effect on corrosion rates. The important environmental factors are the oxygen concentration in the solution or atmosphere, the pH of the electrolyte, and the temperature, concentration, and nature of various salts in solution in contact with the metal. Chloride is an aggressive anion that normally accelerates corrosion of the metals. The usual role of chloride ions in the acceleration of corrosion rates are their property of dispersing protective film, formation of stable and soluble surface complexes with iron, and catalytic, adsorptive, and field effects.

Effect of solution temperature on the corrosion rate of steel

In this experiment, we investigated the effect of solution temperature on the rate of corrosion using PANi/Ny. Exposure time was 2 h and the concentration of NaCl was 1.0 M. The results have been collected in Table 6.

As our results show, high corrosion stability is the result of steel plates coated with PANi/Ny composite. Corrosion reaches a maximum at 70° C, then drops again for both coated and uncoated samples. This can be due to a decrease in concentration of oxygen in the water at elevated temperatures (Henry's law). The increased rate of chemical reaction achieved with increased temperature is balanced by a decreased cathodic depolarization reaction owing to the inverse solubility of oxygen in the solution.

Effect of pH

For performing this experiment, steel plates coated by PANi/Ny 66 with 4:1 ratio were exposed to a NaCl solution (1 M) for 2 h at different pH values. The pH of the solution was adjusted using dilute HCl and

Table 6: Effect of solution temperature on corrosion rate (CR)

Table 7: Effect of solution pH on corrosion rate of steel (as MDD)

NaOH solutions. As our results indicate (Table 7), the polymer-coated plates showed high resistance against the corrosion of steel samples in both acidic and basic conditions.

Corrosion of bare iron is promoted in both acidic and alkaline conditions, especially in the presence of complexing and oxidizing agents. However; there is some evidence that iron can be passivated under specific alkaline conditions, too.^{[35](#page-6-0)}

Effect of complexing agent

In general, it is well-established that metal corrosion or oxidation is accelerated in the presence of oxidative and complexing agents. So, in this experiment we examined the presence of EDTA, which is a popular complexing agent that forms stable complex ions with most of the metal ions. Experimental conditions were selected as before, and the metal samples were exposed to NaCl (1 M) and EDTA (0.01 M) for 2 h at room temperature. It was found that the corrosion rate for steel samples coated by PANi/Ny was much lower than the uncoated steel samples coated in a comparison of plates (\sim 8 times).

Effect of oxidation state of PANi

In this investigation, the steel plates coated with polymer composite (PANi/Ny) were treated with hydrazine sulfate (a reducing agent) to reduce the polymer and change it into reduced form before the

Table 8: Effect of salts on corrosion rate of steel samples (as MDD)

Salt	NaCl	NaNO ₃	Na ₂ SO ₄	
CR for coated plates	8	11	9	
CR for uncoated plates	220	255	223	

corrosion test. Then, the plates were exposed to NaCl 1 M for 2 h. It was observed that this treatment had no effect on the corrosion rate of the steel samples. On the other hand, corrosion stability can be achieved with the EB form of PANi, which consists of both reduced and oxidized units in its structure.

Effect of different corrosive salts

In this part of our research, polymer-coated steel plates were exposed to corrosive solutions containing constant concentrations (1.0 M) of different salts under the same conditions. The corrosion rate was then measured as described in the Experiment section. As our data show (Table 8), almost the same protection of metal plates was observed when the polymer-coated metals were exposed to the different salts used. In all cases, considerable corrosion prevention or control is observed.

General conclusions

It was found that PANi/Ny coatings can provide considerable protection, as well as a physical barrier against corrosive environments (e.g., NaCl, HCl) in which the metal are exposed. The corrosion rate for the polymer-coated steel was significantly lower than the bare steel (\sim 10–15 times). Metal passivation (formation of a thin, compact, adherent, and passive layer of $Fe₂O₃$ at the interface) may be due to the redox catalytic effect of PANi. Polyaniline conductive polymers have emerged as one of the most promising candidates for corrosion control applications providing superior corrosion resistance, cheaper protection, and environmentally friendly properties than the present techniques for steel corrosion prevention. Accepting these properties of conducting electroactive polymers, one can create corrosion protection materials that are environmentally promising as potential substitutes for highly toxic lead and chromium pigments.

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