Undoped Polyaniline–Surfactant Complex for Corrosion Prevention

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ABSTRACT: Due to the strict regulations on the usage of heavy metals as the additives in the coating industries, the search for effective organic corrosion inhibitors in replacement of metal additives has become essential. Electrically conducting polymers have been shown to be effective for corrosion prevention, but the poor solubility of these intractable polymers has been a problem. We have explored a polyaniline–4-dodecylphenol complex (PANi–DDPh) to improve the dissolution, and it has been shown to be an effective organic corrosion inhibitor. With the surfactant, DDPh, PANi could be diluted into the coatings, and the properties of the coatings were affected. An emeraldine base (EB) form of PANi was also found to be oxidized by the hardener. The oxidized form of polyaniline provides improved corrosion protection of metals than that of emeraldine base since the value of the standard electrode potential for the oxidized form of PANi is higher than that of EB. Additionally, the surfactant improves the wet adhesion property between the coating and the metal surface. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2849–2856, 1999

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INTRODUCTION

Corrosion is a natural process that has troubled human beings ever since the use of metals. It occurs because metals tend to return to their more stable oxidized states; that is, the corrosion of a metal occurs when its potential has a value more noble than the reversible potential. Due to the strict regulations on the usage of heavy metals as the additive, the search of an effective organic corrosion inhibitor in replacement of those metal ones has become essential. For more than a decade, polyaniline (PANi) has been used in protecting metals because of its unique properties. PANi is unique in that it has a nitrogen heteroatom incorporated between phenyl rings along

polymer chain. This structure provides flexibility and allows the existence of three distinguished oxidation states that are leucoemeraldine, emeraldine, and pernigraniline. Leucoemeraldine and pernigraniline forms of PANi are not stable, and they will return to the state of emeraldine under the atmospheric environment. Figure 1 shows the structure of PANi. DeBerry[1] was the first one to report the capability of corrosion prevention of PANi and reported that the bare or anodically passivated type 410 or 430 stainless steel specimens became active within minutes after being placed in $0.1M$ sulfuric acid solution. On the other end, PANi-coated type 410 or 430 samples remained passive for at least 1200 h after immersion. Based on the above observation, it indicated that PANi immobilized on the alloy imparted a form of anodic protection, which stabilized the materials in mineral acids. Major research results were reported by a joint group from the Los

X	4-X	Name
4	0	leucoemeraldine (fully reduced)
2	2	emeraldine base
0	4	pernigraniline (fully oxidized)

Figure 1 The structure of polyaniline.

Alamos National Laboratory (LANL) and the National Aeronautics and Space Administration (NASA).[2] A high-performance coating was developed in order to protect the launch towers from acid vapor generated during space shuttle launches. It showed the performance of doped PANi, followed by an epoxy topcoat, was much better than that of an epoxy topcoat alone. The doped PANi imparted corrosion resistance to coated areas even after the doped PANi and epoxy topcoat were removed by scribing. It indicated doped PANi was an effective primer against acidic environment. Wei et al.[3–5] evaluated the performance of doped PANi and undoped PANi in various environments. The cold rolled steel (CRS) coated with undoped PANi or HCl-doped PANi had higher corrosion potential values than the uncoated CRS in $0.1M$ HCl solution. A similar trend was observed for CRS samples in the neutral environment. There was a significant decrease of the corrosion current for the CRS with undoped PANi, indicating that the undoped PANi offered good corrosion protection in aqueous NaCl medium, as evidenced by the increase in corrosion potential and by the decrease in corrosion current in comparison with the untreated CRS. This phenomenon was not only based on the barrier effect of the coating because nonconjugated, polymers such as polystyrene and epoxy, did not exhibit the same electrochemical behavior, but the electron transfer between the coating and the metal was to have an essential function on the behavior. Jasty and Epstein[6] evaluated undoped PANi and HCl-doped PANi as corrosion inhibitors with the X-ray photoelectron spectroscopy (XPS) analysis. The iron–polyaniline system was examined by XPS while the iron was exposed to the atmosphere with PANi as an undercoat. The undoped PANi passivated all surfaces of iron, and a passive oxide layer was formed at the interface of iron and the coating. On the other hand, the HCl-doped PANi did not provide effective corrosion protection for iron based on the XPS analyses. Wessling et al.[7–9] worked on the subject of corrosion prevention of

mild steel. Samples of mild steel with undoped PANi and with an epoxy topcoat exhibited corrosion rates slightly slower in 3.5% NaCl solution and 100 times slower in $0.1N$ HCl solutions than those of samples coated with epoxy alone. Based on the experimental results, they showed a passive oxide layer of mainly γ-Fe_2O_3 was formed at the interface between the metal and the PANi coatings. McAndrew et al.[10] investigated the corrosion prevention of the carbon steels and showed that the undoped PANi performed well as a corrosion resistant coatings, while conductive, protonated PANi showed virtually no effects.

In our study, the corrosion prevention of cold rolled steel (CRS) with undoped PANi in polyacrylic-based thermoset has been studied. Factors that influence the performance of the protective coating, such as the characteristic of conducting polymer, the role of the surfactant, and the role of the hardener were investigated.

EXPERIMENTAL

Polyaniline was synthesized by 1,4 coupling polymerization of aniline.[11] It was polymerized in acidic environment (pH 1), and a violet brown precipitate, emeraldine base (EB) was obtained after the dedoping reaction using ammonium persulphate solution. The viscosity is 0.72 dL/g in 1-methyl-2-pyrrolidone (NMP) at 25°C measured by the Ubbelohde viscometer. 4-dodecylphenol (DDPh) and 1,6-hexamethylene diisocyanate (HDI) were obtained from Aldrich Co.; dodecylbenzenesulfonic acid (DBSA) was obtained from TCI Co.; and ammonium hydroxide, chloroform, and n-hexane were obtained from EM Sciences. All chemicals were used as received without any further purification. The PANi–DBSA complex was prepared by mixing PANi with DBSA in a 1-to-4 weight ratio and mixing the components at 90°C for 4 h under effective stirring. A dark green protonated emeraldine salt was then dissolved in chloroform to yield 3 wt % solution and filtrated. PANi–DDPh was prepared by mixing PANi with DDPh in 1-to-10 weight ratio at 90°C for 4 h under effective stirring. The blue EB complex was dissolved in n-hexane to yield 3 wt % solution and filtrated. A polyacrylic-based formula was received from Akzo-Nobel Co.; hereafter, it is referred as the coating itself. The coating is composed of the binder part and the hardener part and was cured by mixing of 77.4 wt % of the binder with 22.6 wt % of the hardener under the ambient environment for two weeks. Force-curing was also applied at 80°C for

Figure 2 The corrosion test of various samples after 2000 h.

2 h. The binder is a mixture of polyacrylic acid, polyol, and acrylate-styrene copolymer, while the hardener is mainly 1,6-hexamethylene diisocyanate. Samples of coating with various amount of PANi–DBSA or PANi–DDPh were prepared by blending of the binder with appropriate amount of PANi–DBSA or PANi–DDPh. The main advantage in our approach is that with the use of the surfactants, we can apply dilute solutions of PANi in doped or undoped forms. The mixtures were then cast on the glass slides, and the cold rolled steels after the appropriate amounts of hardener were added. The cold rolled steel was provided by the Akzo Nobel Company, and it was sanded and degreased with methanol and acetone. The coated samples were cured under the ambient environment for 2 weeks.

The salt spray test was performed by the D/L Laboratories (in New York City) according to the ASTM B-117. The alkaline solution for the im-

mersion and corrosion test is an equal volume mixture of 3.5% $NaCl_{(aq)}$ and 0.1% $NaOH_{(aq)}$ with pH 12.4. The neutral solution is a 3.5% $NaCl_{(aq)}$ with pH 5.3, and the acidic solution is a 0.1M $HCl_{(aq)}$ with pH 1.06. The thickness of the coating was controlled between 1 to 3 mil. The Tafel plot, a potentiodynamic measurement that measures the corrosion current (i_{corr}) and the corrosion potential (E_{corr}) of the system, was done for us by Professor Wei from Drexel University. An ultraviolet–visible spectrometer (UV–visible) DMS-100 from Varian Co. was used to monitor the oxidation process. The adhesion test and the immersion test were designed for the investigations of the adhesive properties and the corrosion prevention capabilities of there additives. The contact angle was measured by the Contact Angle Goniometer made by the Ramé-Halt, Inc. The image was captured by a Sony CCD-IRIS color video camera and then sent to the computer for data processing by the NIH Image version 1.57 image processing software.

RESULTS AND DISCUSSIONS

The adhesion test and corrosion test were performed for evaluating of the effectiveness of PANi–DBSA and PANi–DDPh as the corrosion inhibitor in alkaline, neutral, and acidic environments. The corrosion test in our laboratory after 200 h shows

Figure 3 The salt spray test (total area of failure) of various samples after 100 and 200 h.

coating without any additives   coating with 0.3 wt.% PANi/DBSA   coating with 1 wt.% PANi/DBSA

Figure 4   The performances of coatings with various amounts of PANi–DBSA after 200 h of the salt spray test.

that there is no sign of corrosion of coating with 20 wt % PANi–DDPh, mild corrosion of coating with 10 wt % PANi–DDPh, and severe corrosion of coating with 1 wt % PANi–DBSA and coating without any additives in the alkaline solution. Figure 2 shows the images of the corrosion test in the alkaline so-

coating without any additives   coating with 0.1 wt.% PANi/DDPh   coating with 0.3 wt.% PANi/DDPh

coating with 1 wt.% PANi/DDPh   coating with 5 wt.% PANi/DDPh   coating with 10 wt.% PANi/DDPh

Figure 5   The performances of coatings with various amounts of PANi–DDPh after 200 h of the salt spray test.

Figure 6 The performances of coatings with various amounts of PANi–DDPh after 200 h of the salt spray test.

lution. The coating without any additives and coating with PANi–DBSA exhibit very poor performance in area of failure, while coating with PANi–DDPh shows excellent performance in total area of

failure. Figure 3 shows the performance of area of failure of coatings with 5, 10, 15, 20, 25, and 30 wt % PANi–DDPh, respectively. According to Tseng's study,[12] there is 0.4 wt % PANi, 9.6 wt % DDPh,

Figure 7 The salt spray test (distance from scribe) of various samples after 100 and 200 h.

Figure 8 The contact angle measurements of various samples.

Table I   The Potentiodynamic Measurements of Various Coating Samples

Sample	E_{corr} (mV vs. SCE)	i_{corr} (μA)
Cold rolled steel	−648	10.0
Coating itself without any additives	−597	9.8
Coating with 10 wt % PANi–DDPh	−520	9.2
Coating with 20 wt % PANi–DDPh	−492	9.0

and 90 wt % coating in a formula of coating with 10 wt % PANi–DDPh. It demonstrates that the real amount of PANi in the coating is quite small. As the overall area of failure shows significant rusting for the control sample without PANi (grade 5–6), with PANi, hardly any corrosion could be observed (grade 9–10). These results show clearly that the corrosion prevention improves with the increased amount of PANi. There is no significant improvement of the performance when coatings containing more 20 wt % PANi–DDPh. The images of cold rolled steels coated with different coatings after a 200 h salt spray test are shown in Figures 4–6. Similarly, the distance from the scribe for the observed corrosion decreased from 14 to 2 mm with PANi. This is shown in Figure 7. It was found that the coating with PANi–DDPh exhibits better adhesion than the coating with PANi–DBSA in both acidic and neutral environments. As DDPh lowers the surface tension, the wetting of coating on the metal surface will improve. In the neutral environment, all films adhesive well, and there are no apparent differences in the wet adhesive properties. In the alkaline and acidic environments, PANi–DDPh exhibits again much better wet adhesion than that of PANi–DBSA.

The adhesion between two surfaces is determined by the following two factors: (1) the intermolecular or atomic attraction forces, such as ionic bond, covalent bond, metallic bond, dipole-dipole forces, hydrogen bond, and (2) the surface energy of the interface. The surface energy that determines the wet adhesion of different surfaces can be measured by contact angle measurement. Better wet adhesion property means the coating spreads better on the surface of the substrate. A proper formulation of mixing the coating with the surfactant results in the better wet adhesion property between the interface. Figure 8 shows the contact angle measurement of the coating with DDPh and PANi–DDPh. The introduction of 10 wt % DDPh into the coating decreases the contact angle from 53.6 to 47.5°. Similarly, intro-

ducing 10 wt % PANi–DDPh decreased the angle to 46.5 and to 43.3° with 20 wt % PANi–DDPh. It indicates DDPh is an effective surfactant and improves the wet adhesion between the coating and the surface of cold rolled steel. The results of the salt spray test also suggest DDPh alone can exhibit excellent performance in the distance from scribe.

Table I shows the measurement results of cold roll steel, cold rolled steel coated with coating itself, coating with 10 wt % PANi–DDPh, and coating with 20 wt % PANi–DDPh, respectively. The potentiodynamic measurements show a positive potential shift and a reduction in the corrosion rate when the cold rolled steel is coated with coating with PANi–DDPh. It means the cold rolled steel is more noble when coated with coating with PANi–DDPh, as by the measurement of E_{corr} of different samples. The values of E_{corr} and i_{corr} for bare steel are −648 mV and 10 μA, re-

Figure 9   UV–vis analysis of the coating with various amounts of PANi–DDPh.

Figure 10   The coating side, of the adhesion test in the alkaline solution after 2000 h.

spectively. When coated with polyacrylic-based thermoset, the values of E_{corr} and i_{corr} are changed to -597 mV and 9.8 μA, respectively. The value of E_{corr} is increased to -492 mV, and i_{corr} is reduced to 9.0 μA for coating with 20 wt % PANi–DDPh. As a result, PANi passivates the surface of cold rolled steel, and the effectiveness of PANi as a corrosion inhibitor is of electrochemical nature; that is, there is charge transfer between PANi and the steel.

Figure 9 shows the UV–vis analysis of the coating with various amounts of PANi–DDPh. The emeraldine form of PANi has two characteristic peaks at 330 and 630 nm, which represent the π–π^* transition of benzenoid rings and the exciton absorption of the quinoid rings, respectively. According to the study of Masters et al.,[13] the peak at 630 nm will diminish to zero for the fully reduced PANi, and it will be shifted to 530 nm gradually for fully oxidized PANi. The peak at 330

nm, however, basically remains at the same position. Figure 9 shows that the 630-nm peaks of coatings with 1, 5, and 10 wt % PANi–DDPh all shifted to 530 nm. This indicates that PANi has been oxidized during the coating. Meanwhile, the color of the coating changed from blue to purple and stayed purple for more than 1 year, indicating that the oxidized form of PANi was stable in the polyacrylic-based thermoset.

The samples used for adhesion test were also used for the evaluation of corrosion test. Both sides of steel coupons coated with various amounts of PANi–DDPh in the alkaline environment are shown in Figures 10 and 11. Extensive rusting is observed on both sides of coating without any additives and coating with 5 wt % PANi–DDPh. Localized pitting is observed on the back side of the coupon for coating with 10 wt % PANi–DDPh, showing evidence of local passivation. Very interestingly, there is no sign of rust on the

Figure 11   The reverse side, of the adhesion test in the alkaline solution after 2000 h.

reverse side coating with 20 wt % PANi–DDPh. These corrosion tests done at our laboratory confirm the previous data from the ASTM results and also confirm Professor Epstein's earlier results on the corrosion prevention through the useful SPE meeting, in Toronto, during May 1997. Based on the above observations and discussions, coatings with 20 wt % PANi–DDPh perform well against alkaline and neutral environments, while PANi–DDPh also exhibits the best adhesion.

CONCLUSIONS

Several important conclusions could be obtained from the above observations and discussions. PANi–DDPh is an effective organic corrosion inhibitor against neutral and basic environments. An optimum formulation of polyacrylic-based thermoset blends with 20 wt % PANi–DDPh exhibits excellent performance in the salt spray test. The hardener acts as both the curing agent for the thermoset and an oxidant for PANi. The oxidized form of PANi is stable in the coating. DDPh acts as the surfactant, which reduces the surface tension, which results in a better wet adhesion property between the coating and the surface of the cold rolled steel.

The reasons why PANi–DDPh is an effective organic corrosion inhibitor are due to the facts the following.[14]

1. PANi contributes the formation of a metal oxide layer between PANi coatings and metal surfaces.
2. PANi enhances the formation of a dense and adherent coating, which restricts the diffusion of water and oxygen, the two critical components for corrosion, from the environment onto metal surfaces.
3. PANi forms an electric field at the interface, and it restricts electrons transfer from metal to the oxidant.

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