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Influence of polyaniline nanoparticles on the corrosion protection properties of epoxy nanocomposite coating

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Abstract. In this study the anticorrosive properties of an epoxy coating loaded with polyaniline nanoparticles is investigated by means of Electrochemical Impedance Spectroscopy (EIS) and accelerated salt spray test. The blank epoxy coating was loaded with 0.1 wt % Polyaniline nanoparticles. Through the monitoring of open circuit potential, an ennoblement effect was detected for the systems in the presence of a 3.5 wt.% NaCl solution. Also, an increase in the impedance at low frequency range was occurred by adding polyaniline nanoparticles. The OCP and EIS results indicate that possibly a passive layer formed on the substrate surface. In addition the coating with polyaniline nanoparticles had better performance to salt spray media.

Keywords: Polyaniline Nanoparticles, Nanocomposite coating, TEM, EIS, Salt Spray.

1. INTRODUCTION

Polyaniline has emerged as one of the more promising conductive polymers for commercial applications. It is electrically conductive with good thermal and environmental stability. Its conductivity can be modified by the oxidation state of the main chain and degree of protonation. Polyaniline can be exploited in various applications such as microporous electrically conducting materials, anti-corrosion protection of metals, supporting material for catalysts, etc. [1, 2]. There have been many reports on the preparation of polyaniline microparticles via emulsion method focused on the contribution of micelles to the formation of the stable dispersions, morphology and the anti-corrosive properties [3], but the effect of polyaniline nanoparticles on coating anti-corrosive properties has not been studied by many research groups. Wessling et al. [4] studied the anticorrosive performance of nanostructure polyaniline product of Ormecom GmbH in an epoxy primer in combination with some other systems. L.G. Ecco et al. [5] have reported using polyaniline nanoparticles dispersion as an additive to make anti-corrosive alkyd coating. In recent years, corrosion protection of steel by conductive polymer pigmented coatings has been reported [4]. The advantage of protection by conductive polymer coatings is that the coatings have more tolerance to pinholes due to their passivation ability. As mentioned above there are some published studies in this field but it seems that there is still a long way ahead to achieve a profound insight into the effect of polyaniline nanoparticles on the anti-corrosive properties of the coating

Considering the above, this present work reports the anticorrosive behavior of epoxy polymer containing polyaniline nanoparticles. The study has been entirely carried out using steel coated panels with a single layer based on epoxy chemistry holding near 70 µm of thicknesses. Electrochemical Impedance Spectroscopy has been chosen in order to get understanding into the fundamental mechanisms through which polyaniline nanoparticles in

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promote corrosion protection of steel when inside the epoxy coating. Complementary characterization of the coated panels has been performed by means of the accelerated salt spray chamber test.

2. MATERIALS AND METHODS

2.1. Materials

The studied samples were formulated with an epoxy polymeric binder. Epoxy (EP) Epon Shell 1001 resin (Equivalent Weight (EEW): 500), and polyamide (H value: 190) hardener were used. The weight mixing ratio of resin to hardener was 10:4. Aniline (Ani) (analytical grade, Merck) was distilled twice under vacuum and stored under nitrogen in a refrigerator. Ammonium peroxydisulfate (APS) (analytical grade, Merck), phosphoric acid were used.

2.2 Synthesis of polyaniline nanoparticles

Aniline (4.44 g) was added to an aqueous solution containing 0.45 g of H3PO4 dissolved in 720 mL of distilled water, and the resulting solution was ultrasonicated for 15 min with a UIP 1000 HD ultrasonic instrument from Hielscher Ultrasound Technology Co. Then an aqueous solution containing 10.94 g of APS in 30 mL of water, was quickly added and the reaction medium was subjected to an ultrasound treatment for 5 min. The polymerization was carried out at room temperature for 6 h under static conditions. The dark green powder was poured into acetone, filtered and dried under vacuum. A Ziess Sigma VP Field Emission Scanning Electron Microscope (FESEM) was used to observe the dispersion of polyaniline nano particles.

2.3 Preparation of nanocomposite coating

Synthesis polyaniline nanoparticles were added to the resin and the mixture was stirred for 2 hrs in 2000 rpm. Prior to the application of the coatings, the sharp edges of mild steel panels of size 10 cm×7. 5 cm were filed down. The panel surface was then polished by sand blast and cleaned with gasoline. The hardener added to the mixture of resin and polyaniline nanoparticles. The mixture were then applied on the panels by air spraying and cured at room temperature for 10 days. There was no pinhole on the specimens selected for corrosion measurement. The transmission electron micrographs of polyaniline-epoxy nanocomposite films were obtained using a CM 30, Philips Co. Transmission Electron Microscope (TEM) instrument.

2.4 EIS Measurements

Glass tubes were attached to the paint-coated panels to form the electrochemical cells, in order to limit the measurable areas to 7.065 cm^2 . The cells were then filled with a 3.5% NaCl solution which served acting as corrosion medium. The test cells were maintained at 65° C and the NaCl solution was refreshed regularly during the whole test period. EIS data were collected using a Potentiostat/ Galvanostat (EG&G 273A) coupled with a HF frequency response analyzer Schlumberger SI 1255. The potentiostat was controlled by Powersuite Framework software. The EIS measurements were performed in 3-electrode mode, using a saturation calomel reference electrode (SCE) and a graphite counter electrode. All measurements were carried out on open-circuit potential (OCP), using 10 mV rms amplitude sinusoidal voltage, over a frequency range of 10^5–10^{-2} Hz. Prior to each experiment, the open circuit potential was monitored for 30 seconds. The impedance spectra were collected as a function of the exposure time. The times required to perform this test varied between 0 to 510 hrs for different samples.

2.4. Salt Spray Exposure

The corrosion resistance of the nano coating was studied in a salt spray test cabin ERICHSEN according to ASTM B117-09 [6]. The coated samples were exposed to a direct spray (with 0.7 bar pressure) of NaCl 5wt% solution at 35˚C for 720 hrs. The test plates after the exposure were evaluated from the points of view of the formation of osmotic blisters, the degree of surface corrosion and the degree in corrosion in the vicinity of the scribes.

3. RESULTS AND DISCUSSION

3.1. Characterizations of the PANI Nanoparticles

FESEM images (Figure 1) are used to view the morphology and size of the PANI nanoparticles. It was found that the PANI ES exhibited particular morphology without large agglomerates. Although size of spherical nanoparticles had uniform diameters in 60-100 nm, and few agglomerates could be observed. The TEM image (Figure 2) shows the dispersibility of the PANI nanoparticles in epoxy cured matrix.

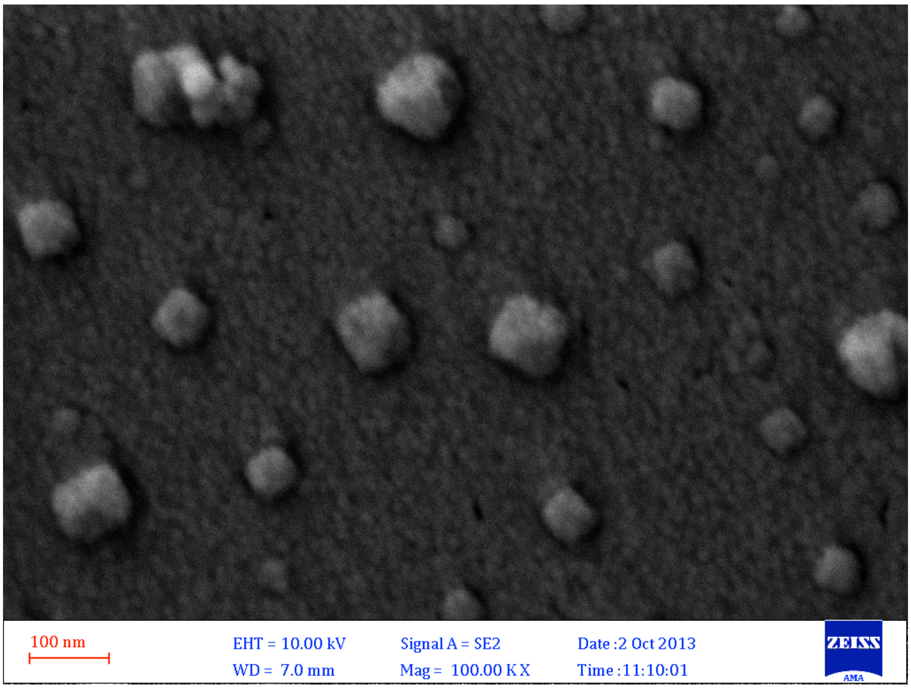


Figure 1. FESEM microg.raph of synthesize polyaniline nanoparticles.

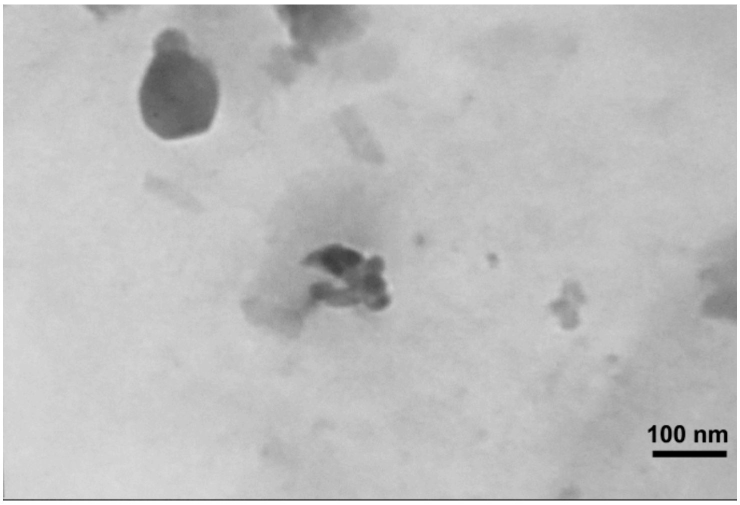


Figure 2. TEM micrograph of homogeneous polyaniline nanoparticles in epoxy coating.

3.2. Open circuit potential

In the case of the epoxy coating containing 0.1 wt% polyaniline (P10),the potential evolved as follows: OCP was first measured around −200 mV, followed by an oscillation toward more values and reached the maximum value, −100 mV, after 4 h. Afterwards, the potential was stable around to near −100 mV (Figure 3). The evolution of the OCP discussed has also been reported by other authors [7, 8]. According to them, when in contact with steel and in the presence of an electrolyte, the emeraldine salt of PAni is reduced to the emeraldine base leading to an oxidation reaction of iron to form the passive oxide layer. The presence of polyaniline in the coating favors oxidation of the ferrous ions to a stable passive iron oxide film at the pinhole region [9]. This shows that the polyaniline in the coating is able to passivate the steel surface in a 3.5 wt% sodium chloride solution after a longer exposure period. The OCP for epoxy blank (EP) coating showed decreasing with increasing of immersion times. when water and ions started to ingress into the coating layer toward the substrate, the potential reduced to −400 mV, approximately, between the 75 h and 100 h of immersion and reached near -550 mV at the end of immersion times.

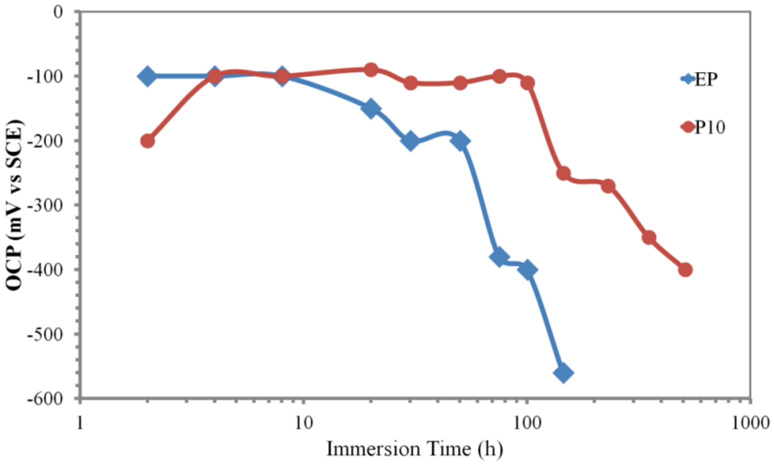


Figure 3. Variation of the OCP with time in 3.5% NaCl solution at 65°C for EP and P10 coatings.

3.3. EIS Evaluation

Electrochemical impedance spectroscopy (EIS) has been used with moderate success to monitor and predict the degradation of paint coatings [10-12]. However, the technique has limitations when the painting systems confer good protection since the impedance response is dominated by the capacitance of the paint. The time required to probe the paint resistance can be several months [13]. The above mentioned facts indicate that a procedure is still necessary in which the degradation is accelerated without compromising the results in real. This motivation led the current authors to raise the temperature of the solution in contact with the painted specimens and carry out EIS periodically.

The impedance spectra for the two coatings systems from initial condition and their evolutions after different time of exposure to 3.5 wt. % of NaCl are shown in Figures 4-5. Among all the information that EIS is able to provide, the value of the impedance at low frequency range (|Z|0.01Hz) are used as an estimation of the overall protection properties for organic coatings. In addition, it can be considered the sum of the contribution of the impedance related to the faradic process occurring at the interface metal/electrolyte plus the impedance of the organic coating itself [14]. Initially, there was approximately three orders of magnitude difference for the values |Z|0.01 Hz between the two coating systems samples . EP showed a rather poor barrier properties during the initial hours of analysis, with the values of impedance at low frequency near 10^5–10^6 Ω. cm^2. After 145 h of exposure (Figure 4), the values of |Z|0.01 Hz were found to be around 10^4 Ω.cm^2 for EP coating indicating its degradation.

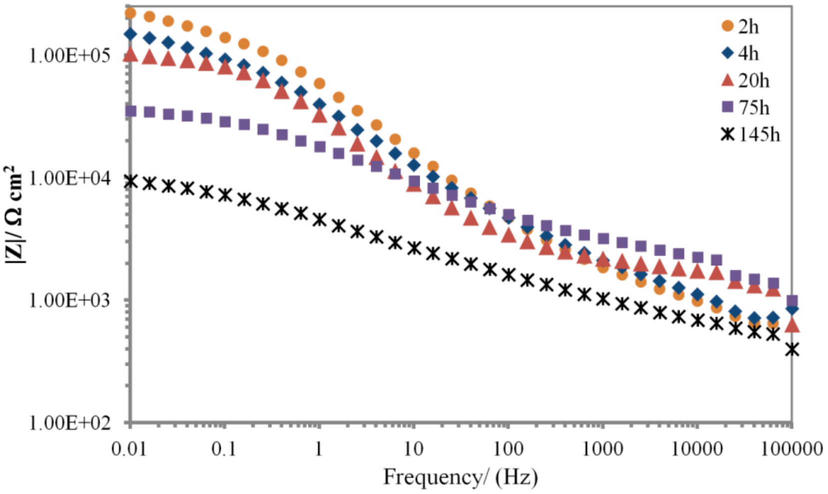


Figure 4. The Bode plots of the EP coating at different immersion times in 3.5% NaCl solution and 65°C.

In the case of P10, at the beginning of the test, the total|Z|0.01 Hz was first measured near to 10^8 Ω. cm^2 (Figure 5). After 4 h, the outline of the EIS spectra changed; the appearance of Figure 5 showed the increase of about one order of magnitude in the values of impedance at low frequency range. With increasing exposure times the |Z|0.01 Hz stabilized around 10^9 Ω. cm^2. For longer periods of exposure, the EIS evolution did not show significant changes. Making an allowance for the EIS evaluations verified to P10; the remarkable ennoblement shift in the evolution of OCP and the one order of magnitude raise of total |Z|0.01 Hz, even though not proved experimentally, it seems that the presence of 0.1 wt. % of polyaniline nanoparticles inside the epoxy coating are associated to the conversion or the formation of a passive layer upon the steel surface and, as a consequence, the anticorrosive properties of the epoxy coating are reinforced [15]. Both parameters showed important variations, approximately after 4 h of exposure; the potential has shifted toward higher values and |Z|0.01 Hz has raised about one orders. After 145 h immersion time the |Z|0.01 Hz decreased three orders of magnitude and stabilized at 510 h that showed the protective properties of P10 coating decreased.

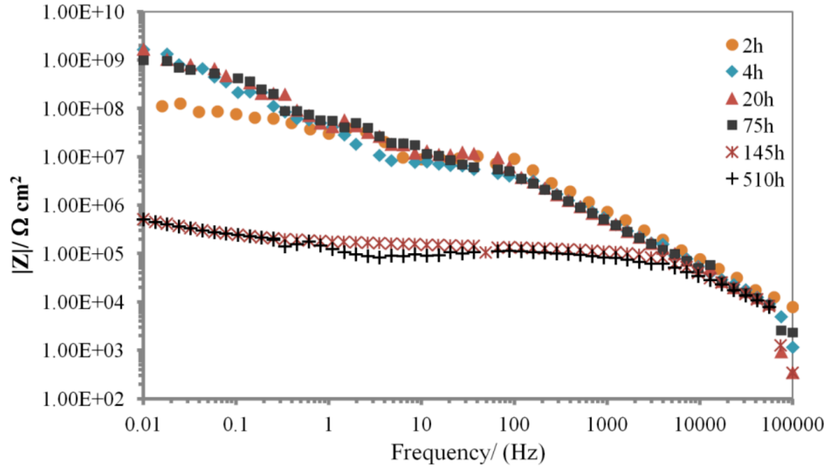
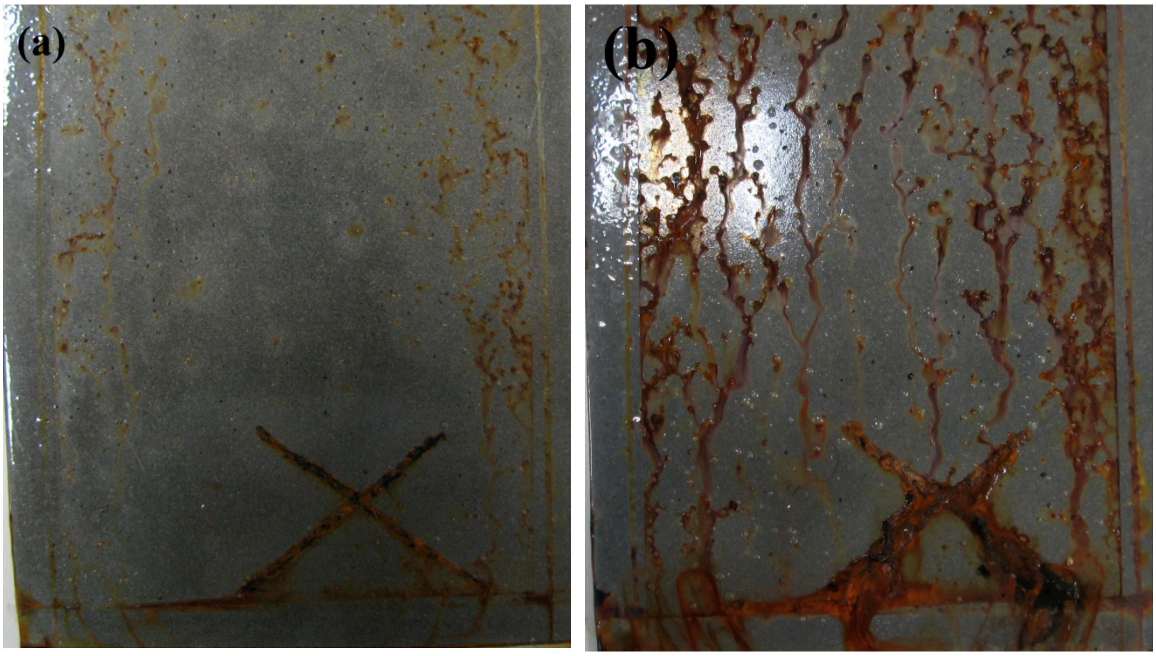


Figure 5. The Bode plots of the P10 coating at different immersion times in 3.5% NaCl solution and 65°C.

3.4. Salt spray test

The appearance of EP coated panel and P10 coated panel after salt spray test for 720 h is shown in Fig. 6. For coating EP, after 168 hrs as shown in Fig. 6 (a), a color contrast is observed which show disbonding has occurred around the scratched area and other area of the coating indicating poor adhesion of the EP coating that is not observed for the P10 coating (Fig. 6 (c,d)). It could also be seen that the EP coated panel suffered from aggravating corrosion in large-scale with red rust layers after 168 and 720 h (Fig 6(a,b)). For the P10 coating on the steel panel blister and corrosion were not observed and just a slight rust formation was found in the scribed areas after 168 h (Fig 6c). After 720 h just a little blisters around the scribed area were observed (Fig 6d). In general the coating with polyaniline nanoparticles had better performance to salt spray media that showed effect of nanoparticles on the coating.



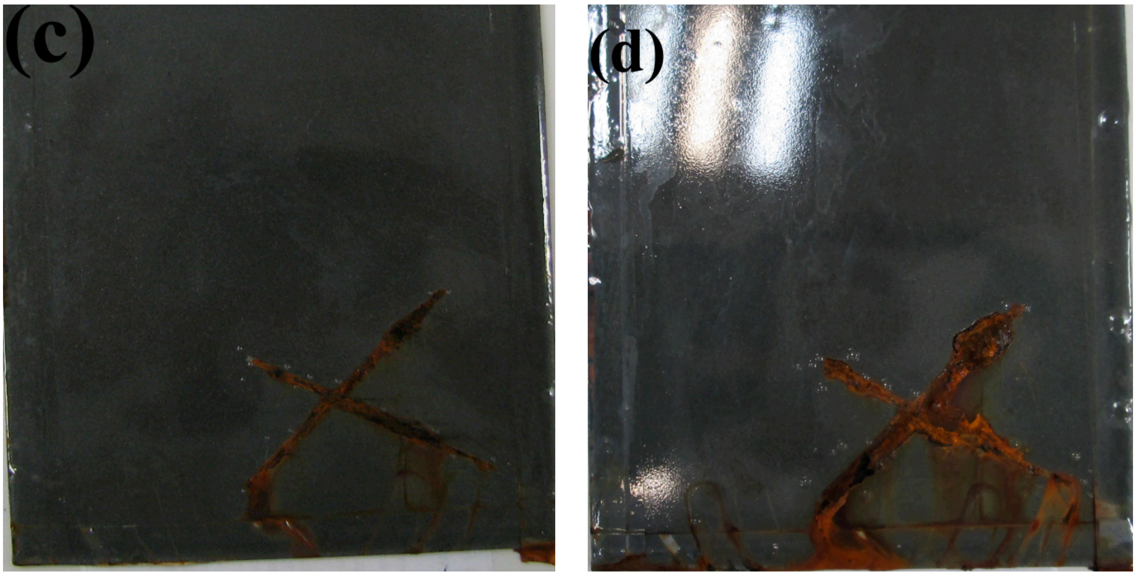


Figure 6: Surface appearances of the coated plates after exposing to salt spray for 168 hrs (a) EP (c) P10 and for 720 hrs (b) EP (d) P10 coatings.

4. CONCLUSIONS

The corrosion performance of polyaniline nanoparticles containing epoxy coating was studied in 3.5 % NaCl by EIS and accelerated salt spray test. Studies were shown that the presence of 0.1 wt% of polyaniline nanoparticles in the epoxy coating promoted anticorrosive protection of steel, where the efficiency of polyaniline inside the epoxy coating can be demonstrated by an increase in the open circuit potential. The effectiveness has been attributed to ennobling effect. However, an increase in the impedance at low frequency range was occurred by adding polyaniline nanoparticles. Moreover, as far as the accelerated salt spray test is concerned, the presence of blister has been significantly lowered in comparison with the epoxy blank coating.

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