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Coating of Polyaniline-Titanium Dioxide ($PAni-TiO_2$) Composite for Corrosion Protection in Low Carbon Steel

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Abstract. Carbon Steel is used as an industrial component and an electronic component that has a lifetime or a certain lifetime. Steel is not a rust-resistant material, so it can corrode over time, especially Indonesia is a tropical country that has high rainfall and humidity. Almost all industrial sectors have problems with corrosion. Problems that arise can be in the form of damage, age of use of goods that do not meet expectations until the security factor is inadequate. This study aims to investigate the inhibiting efficiency of coating on Low Carbon Steel with semiconductor materials and morphology changes on Low Carbon Steel. The semiconductor material used is a combination of $PAni-TiO_2$. Coating of $PAni-TiO_2$ composite on low carbon steel was carried out by electrodeposition method on acidic medium. The corrosion process is carried out with acid and salt media. Effectiveness is based on inhibition efficiency. The highest inhibition efficiency was produced on plate 3 with a composition of 10^{-2} M PAni-10^{-3} TiO_2 with a corrosion rate 0.003560 mpy. Uncoated specimens have a highest corrosion rate of 0.007359 mpy, so it suffers the most damage. From the results of visual observations conducted samples undergoing corrosion in the form of uniform corrosion.

1. Introduction

Steel is a metal (Fe) alloy with carbon as the main mixing material. In general, steel used as an industrial component and an electronic component that has a lifetime or a certain lifetime. Steel has properties that vary from the softest and easily made to the hardest and sharpest. One of the steels used in making industrial machinery is low carbon steel. However, Carbon steel is not a rust-resistant material so it can corrode over time. Corrosion is a serious problem and detrimental to the industrial sector in Indonesia, because Indonesia is a tropical country that has high rainfall and humidity. Corrosion is a decrease in the quality of metals due to electrochemical reactions with the environment that is directly related to opened air, often referred to as atmospheric corrosion [1]. Therefore, materials made of metal or alloys can be damaged due to corrosion [2]. Because corrosion is a big problem for buildings and equipment that uses metal base materials such as buildings, bridges, machinery, pipes, cars, ships, etc., so a method is needed for inhibiting corrosion.

Various methods have been carried out to reduce corrosion rates, one of which is by using an inhibitor. The use of corrosion inhibitors is intended to change the interface between metals and the corrosion environment by isolating one from the other. The inhibitors used are conductive polymers.

The use of conductive polymers as corrosion protective materials is one alternative that is being widely studied because conductive polymers have special features compared to other types of polymers.

The most popular conductive polymer is polyaniline. One study on the use of PAni is a study conducted by Yi et al. [3]. Yi et al reported that the inhibition of steel corrosion in 0.5 M HCl of efficiency increased with increasing concentration of PAni compounds. The inhibition efficiency obtained was 92.3% with a concentration of 40 mg / L. TiO_2 is an n-type semiconductor that can inhibit the reduction of oxygen in the mechanism of corrosion. Titania nanostructures in thin film layers act as important nanomaterials from a technological point of view in maintaining properties such as chemical and photoelectrochemical stability. TiO_2 has roles in several industries, including composite coatings for self-cleaning windows, electrolysis of water for energy conversion and anti-material corrosion.

Based on the ability possessed by polyaniline and TiO_2, the manufacture of polyaniline composites (PANi) -TiO_2 is expected to be an alternative corrosion protection material. The use of polyaniline as a composite matrix phase with TiO_2 as a fill phase can slow the rate of corrosion of metals with HCl as corrosion media [4]. Based on these problems, we need a study of the ability of composite polyaniline PAni-TiO_2 as carbon steel coating material, so this research will synthesize PAni-TiO_2 composites by electrodeposition method. PAni-TiO_2 composites are expected to have a high ability to suppress corrosion rates because they combine PAni which suppresses the oxidation rate and TiO_2 which suppresses the rate of reduction. This study varied the composition of nanocomposite PAni-TiO_2 to determine the effect of nanocomposite composition on the effectiveness of inhibitors. Material characterization was carried out before and after corrosion in the form of characterization of visual observations and pore morphology using Scanning Electron Microscope (SEM), while weight loss testing for analyzing Inhibition efficiency.

2. Method

Carbon steel protection is carried out by coating the surface of steel with PAni-TiO_2 composites through an electrodeposition process. This electrodeposition process is based on Abaci & Ness's research [5]. Steel plate samples that have been prepared, coated with PAni-TiO_2 composites are electrochemically carried out by electrode position on the sample for 10 minutes. The sample made amounted to 4 pieces, of which 1 piece was a sample uncoated, while 4 coated samples with composition variations of PAni-TiO_2. The electrolyte solution used is a solution of Sulfuric Acid and LiCl and set up in pH 2. After the sample is electrode positioned, the sample is weighed and recorded as the initial weight. Comparison of the composition of PAni-TiO_2 is presented in Table 1.

Table 1. Composition of PAni-TiO_2 for coating low carbon steel

Samples	PAni (M)	TiO_2 (M)	H_2SO_4
Uncoated Plate	0	0	250 mL
Steel Plate1	10^{-4}	10^{-1}	250 mL
Steel Plate 2	10^{-3}	10^{-2}	250 mL
Steel Plate 3	10^{-2}	10^{-3}	250 mL
Steel Plate 4	10^{-1}	10^{-4}	250 mL

The corrosion process carried out by immersing specimens (coated and uncoated) in sulfuric acid solutions and NaCl for 12 days. The weight of each specimen before and after immersion measured. The Inhibition Efficiency (IE) was calculated using the expression (loss weight method) [6]:

$$IE\% = \left[\frac{W_1 - W_2}{W_2}\right] x100\% \tag{1}$$

Where W_1 and W_2 are the corrosion rates in the absence and presence of the inhibitor, respectively

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3. Results and Discussion

Steel plate coating is carried out by electrodeposition when the electrodeposition process, at the anode and the cathode changes due to the potential there is a direct current of electricity. Solution electrolytes used in this study are sulfuric acid and LiCl a solution. Thin Layer of electrodeposition results is affected by some variables including meeting current, temperature, time of deposition, stirring, the acidity of solution (pH), solution concentration, electric potential, and substrate. Synthesis of Polyaniline is carried out by polymerization electrochemically produce products in the form of films covering the steel plate. Use of H_2SO_4 acid as a solution electrolyte also aim to accelerate polymerization. The addition of acid to the polymerization process will form aniline, acid which is more soluble in solution polymerization, creating an acidic atmosphere and acts as a dopant for polyaniline so many ions are formed SO_4^{2-} that can increase its electrical conductivity [7]. Visual comparison of steel plates without and with inhibitors ready for use presented in Figure 1 (a) to (e).

Figure 1 (a). Uncoated Plate

Figure 2 (b). Plate 1

Figure 3 (c). Plate 2

Figure 4 (d). Plate 3

Figure 5 (e). Plate 4

Based on observations, the samples that were the most severely corroded were Plat samples without inhibitors. This is because the uncoated plate, salt, and acid directly damage the surface. Additives in the form of organic compounds have an effect if the material adsorbs on the metal surface and does not have an affinity for water, resulting in a strong inhibitory effect. If organic additives adsorb metal surfaces and have an affinity for water, it will speed up the electrodeposition process. Therefore, the addition of organic compounds is more likely to have an influence in terms of accelerating the formation of deposits resulting in thicker deposits.

There are two factors influence the conductivity of PAni + TiO_2 composites. First, mobility in the composite depends on the concentration of H^+ and Cl^- which decreases dramatically with a decrease in PAni Concentration. The second factor is the length of the chain PAni. At lower PAni concentrations, conduction requires higher activation energy than higher concentrations, which can be attributed to an increase in energy barriers between different sites doing content as the content decreases [8].

Corrosion protection by layers depends on three aspects: (a) water uptake from the layers, (b) water transport in layers and (c) water accessibility to the layer/substrate interface [9]. One way to combat corrosion in an acidic environment is the application of corrosion inhibitors or coatings. This is evident from the results of research that, specimens uncoated has a corrosion rate of 0.007359 mpy. Corrosion is also inhibited by physical barriers in the presence of polymers on metal surfaces that inhibit access by corrosion of species [10]. Some reports suggest that hybrid organic-inorganic composite coatings can increase the corrosion resistance of metal substrates such as iron, aluminum, and magnesium. The percentage of inhibition efficiency is presented in Figure 2.

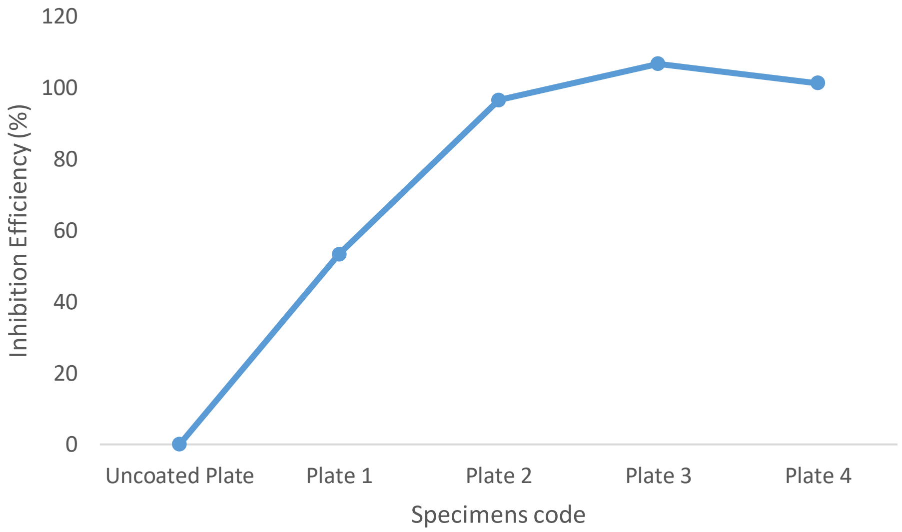

Figure 2. Inhibition Efficiency of Plates

After obtaining the Inhibition Efficiency of plates, each plate was characterized using SEM to see the morphology of the plate surface due to corrosion. PAni has various structures that can be granular, or nanofibers, nanotubes, nanospheres, microspheres, or flakes. the success of PANI / TiO_2 synthesis is characterized by granular and surface debris, in line with abaci's research [5] . Metalic cations interact with PAni imine nitrogen atoms and change the morphology and structure of PAni into compact groups that can greatly reduce the corrosion rate [11]. The PAni redox reaction can be increased significantly by adding metal oxide nanostructured materials. In the electrochemical method, PAni is obtained in the form of ordered thin films on the electrode surface. The morphology of specimens/plates after corrosion is shown in Figure 3 (a) to (e).

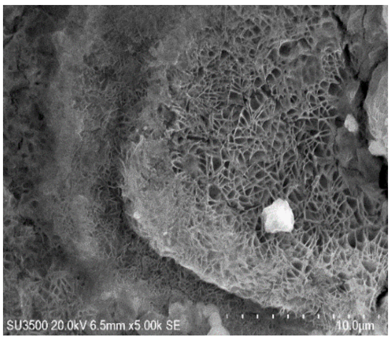

Figure 3 (a). Uncoated Plate

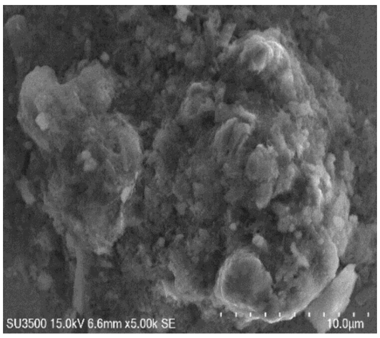

Figure 3 (b). Plate 1

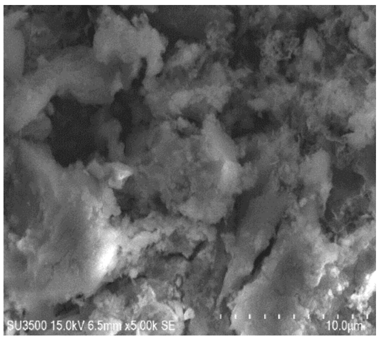

Figure 3 (c). Plate 2

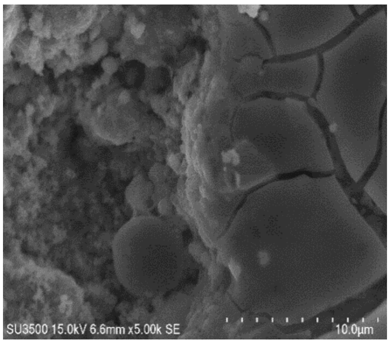

Figure 3 (d). Plate 3

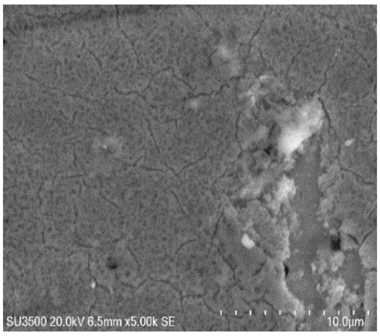

Figure 3 (e). Plate 4

Based on observations, the surface morphology of specimens without inhibitors appeared to have many holes compared to specimens with inhibitors. Corrosion that occurs is homogeneous corrosion. Homogeneous corrosion is caused by chemical reactions that attack uniformly across metal surfaces or in large areas of metal. The attacked metal will become thinner and brittle [12].

4. Conclusions

PAni-TiO_2 formed on the surface of specimens are granular and flakes. Based on visual observations conducted samples undergoing corrosion in the form of uniform corrosion. The addition of PAni-TiO_2 on specimens with the electrodeposition method was effective for inhibiting the corrosion rate. Uncoated specimens have a corrosion rate of 0.007359 mpy. The highest inhibition efficiency was produced on plate 3 with a composition of 10^{-2} M PAni-10^{-3} TiO_2 with a corrosion rate 0.003560 mpy. Uncoated specimens have a corrosion rate of 0.007359 mpy. Visually, PAni-TiO_2 coated specimens in the surface morphology are denser so they are more protected from corrosion. Further research needs to be done to improve the efficiency of PAni-TiO_2 coating inhibition

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