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Analysis Of Corrosion Rate And Hardness Value Of Low Carbon Steel Coated With PAni-TiO_2 Synthesized By Electrodeposition

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Abstract

In the industrial world, carbon steel has been widely used. Corrosion of carbon steel cannot be avoided, so many studies have been carried out to overcome Corrosion. One of the efforts to overcome Corrosion is by coating. Low-carbon steel coating was done by combining TiO_2 and polyaniline (PAni), which was carried out by electrodeposition. A carbon steel specimen that has been coated is corroded by immersing it in an acid and salt medium. After Corrosion, the specimen is tested for hardness. The specimen without inhibitor has a hardness value of 131 kg/mm^2, while the specimen with the highest hardness value is a specimen coated with PAni 10^{-1} M and TiO_2 10^{-4} M at 336 kg/mm^2. Based on visual observation, the Corrosion that occurs is uniform.

Introduction

Metal is one type of material that is widely used in supporting equipment for human life. Steel is one of the most commonly used metal materials in the industry. One of the problems of using metal for industry i.e. Corrosion [1]. Some big companies provide a very high cost for anticipating corrosion problems in their products, such as companies engaged in automotive with the use of metal dominant, as well as the company engaged in the aircraft industry flying, power station, chemical industry, as well as concrete structure buildings and steel frame [2]. Corrosion is an electrochemical reaction between a metal and the environment that causes rust and reduces the quality of the metal. Corrosion is very dangerous, either directly or indirectly. The corrosion resistance of steel is influenced by the alloying elements contained in it [3]. The mechanical properties and corrosion resistance of steel depend on the chemical composition and the microstructure contained in it [4], such as nickel (Ni), chromium (Cr), and manganese (Mn). These three elements will impact the corrosion resistance properties [3]. Corrosion is damage or deterioration of metal caused by electrochemical reactions because the surrounding environment influences it. Corrosion is returning metallic materials to compounds found in nature [5]. Materials that cause Corrosion consist of acids and salts such as hydrochloric acid (HCl) and sodium chloride (NaCl) [6].

Metal protection technology has been widely used, including metal coating. The coating process aims to give specific properties to a workpiece surface. Technically these properties can be classified, among others, to improve the external appearance of the surface, Isolate the metal surface from interaction with the environment and provide unique properties on the metal surface, including properties complex, wear-resistant properties, high-temperature resistance properties, etc. [7]. Electroplating is a technique of metal plating to prevent Corrosion by deposition on the electrodes. The goal is to form a surface with different properties or dimensions of essential metals [8]. In electroplating coating, corrosion testing states that the higher the concentration of the solution and the longer the immersion time, the slower the corrosion rate [9].

The coating can be done using organic and inorganic polymers. The use of conductive polymers as anti-corrosion materials is an alternative that is being extensively investigated because of their unique properties compared to other types of polymers. The most popular conductive polymer is polyaniline [10] as an inhibitor. The use of PAni has been carried out by Yi et al. [10] to prevent corrosion. Yi et al. reported that the efficiency of corrosion inhibition of steel in 0.5 M HCl increased with increasing concentrations of PAni compounds. The inhibition efficiency obtained was 92.3% at 40 mg/L concentration. TiO_2 is an n-type semiconductor capable of inhibiting the oxygen reduction process in the corrosion mechanism. Nano-structured TiO_2 (titania) thin film acts as an important nanomaterial from the technological point of view due to its outstanding properties, such as good chemical stability, unique photoelectrochemical properties, biocompatibility, and high corrosion resistance [11]. Siregar et al. used TiO_2 to prevent corrosion. The corrosion rate obtained is 2.64 cm/year; 3,100 cm/year, where each temperature is 100, 150, and 200 ^{0}C [12]. The use of the PAni-TiO_2 combination as a coating for carbon steel has been carried out by Muzkantri and Kusumawati. The method used is to make a PAni-TiO_2/paint composite which is then used for coating. The most optimal decrease in corrosion rate was obtained on the PAni-TiO_2 coating with a 15% TiO_2 composition of 0.0015406 mm/year. PAni-TiO_2 is mixed with paint using a rotary mixer and then used to paint steel. The weakness of this method is that the painting is not uniform, so it requires polymerization using an electrodeposition process.

Based on the ability of Pani and TiO_2 as inhibitors, this research combines organic and inorganic inhibitors to increase their ability to coat carbon steel. The coating was carried /out by synthesizing PAni-TiO_2 with a different method, namely the electrodeposition method. PAni-TiO_2 composites are expected to have a high ability to suppress corrosion rates. The study was conducted on the hardness and corrosion rate of stainless steel ST37 in corrosive media. Corrosion testing was done by immersing the specimen in NaCl solution with various variations. The purpose of this study is to investigate the corrosion behaviour and hardness of ST37 after treatment. The value of the corrosion rate is obtained by the weight loss method. In addition, the hardness of the material is measured after immersion.

Experimental Method

Materials

The materials used in this study were carbon steel plate specimen, aniline, TiO_2, potassium persulfate, H_2SO_4, lithium chloride (LiCl), 37% HCl, distilled water, ethanol pa, NH_3, NaOH, NaCl, n-butanol, pertalite, Whatman paper, silica gel.

Instrumentation

The tools used in this research are: glassware, magnetic stirrer, Buchner filter, pH meter, analytical balance, sandpaper, soaking tub, petri dish, porcelain dish, muffle furnace, a set of electrodeposition tools, Scanning Electron Microscopy, steel specimen cutting tools, drilling machine and drill bit size 4 mm, woven grinding stone, polishing cloth, hair dryer.

Procedure

a. Steel Coating

Carbon steel protection was done by coating the steel surface with PAni-TiO_2 composites through an electrodeposition process. This electrodeposition process is based on Abaci & Ness's research [12]. PAni-TiO_2 coating was carried out by electrodeposition for 10 minutes Solution. The electrolyte used is a Sulfate acid solution and LiCl. Table 1 presents variations of electrolyte solutions in the electrodeposition process.

Table 1. Variations of electrolyte solutions in the electrodeposition process

Samples	**PAni (M)**	**TiO_2 (M)**	**H_2SO_4**
Uncoated specimen	0	0	0.25 L
Specimen A	10^{-4}	10^{-1}	0.25 L
Specimen B	10^{-3}	10^{-2}	0.25 L
Specimen C	10^{-2}	10^{-3}	0.25 L
Specimen D	10^{-1}	10^{-3}	0.25 L
Spesimen E	10^{-1}	10^{-4}	0.25 L

The corrosion process was 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 was measured. The Inhibition Efficiency (IE) was calculated using the expression (weight loss formula) [13]:

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

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

b. Hardness Testing Materials

Hardness testing materials was done by the Vickers method. The Vickers hardness test uses a diamond pyramid pounder with a square base. The angle between the faces of the pyramids that are facing each other is 136°. Because of the shape of the pyramid, this test is often called the diamond pyramid hardness test. The Vickers hardness number (VHN) is defined as the load divided by the surface area of the indentation. In practice, this area is calculated from microscopic measurements of the length of the diagonal of the trace. VHN can be determined from the following equation [3]:

$$VHN = \frac{1.854P}{L} \tag{2}$$

Where P= applied load (kg) and L = average diagonal length (mm).

Result and Discussion

Corrosion Rate

Electroplating is a process of electrodeposition of a metal layer on an electrode that aims to form a surface with one-dimensional properties that are different from the base layer. Plating is one way to cope with metals' Corrosion and functions as a material resistance, namely the hardness of the material [8]. In this study, the coating was carried out by polymerizing aniline (polyaniline) and TiO_2 as an inhibitor.

Polyaniline is used as an inhibitor in conventional organic coatings and is usually obtained by chemical synthesis. The chemical synthesis mechanism of polyaniline has been well studied and is related to oxidative radical polymerization. The first step is the formation of aniline cation radicals through the oxidation of aniline monomers, a reaction that requires a highly acidic environment as pH > 2 leads to the formation of various oligomeric forms [14]. So this study used PH 1 and 2. The next step involves dimer formation by coupling cationic radicals, followed by proton loss (deprotonation) and re-aromatization. More recently, the dimer is oxidized to form a dimer cationic radical, which reacts with other cationic radicals, resulting in chain growth [14]. The electrochemical polymerization of aniline produces a product in the form of a film that coats the steel specimen. The deposition time used in this study was 10 minutes. Using H_2SO_4 acid as an electrolyte solution also aims to accelerate polymerization. The addition of acid in the polymerization process will form aniline acids which are more soluble in the polymerization solution, create an acidic atmosphere, and act as a dopant for polyaniline so that many ions are formed, which can increase its electrical conductivity [15]. Acid addition polymerization process that aims to develop aniline-acid, which is more soluble in the polymerization solution, creates a sour atmosphere and acts as a dopant for polyaniline so that many ions are formed SO_4^{2-}, which can increase the conductivity of the electricity [16].

Inhibitors can slow down the corrosion process [17]: The inhibitor is adsorbed on the metal surface and forms a thin layer with a thickness of several inhibitor molecules; ecological influences (e.g., pH) cause inhibitors to precipitate and then adsorb on the metal surface and protect against corrosion. The precipitate occurs quite a lot so that the eye can observe the layers; inhibitors corrode the metal first and produce a chemical substance that then forms a layer passive on metal surfaces through the adsorption event of the corrosion product. Inhibitors remove aggressive constituents from their environment.

Coating systems in this study include primer and top coat because they contain intermediates or body coats. Primers usually contain inorganic compounds (this study used TiO_2) as corrosion inhibitors. In contrast, topcoats contain colour pigments and extenders that improve barrier performance and protect the coating from UV damage. The reaction mechanism that may occur is cathodic inhibitors; the inhibitor will react with the reduction of oxygen, OH-, forming a thin layer of inhibitors that block the entry of oxygen so as to protect the metal. Combining two types of combined inhibitors will complement each other's deficiencies of organic and inorganic inhibitors. This is because polyaniline is a semiconductor, and TiO_2 is an n-type semiconductor. On corrosion mechanism, which is polyaniline as p-type semiconductors, will hinder the transfer of electrons released by iron. While TiO_2, which is an n-type semiconductor, will inhibit the reduction of oxygen and the formation process of rust [18].

However, this type of inhibitor shows better results when comparing organic inhibitors (in this case, PAni) with higher concentrations. This is indicated by the corrosion rate in specimen D, having the lowest corrosion rate. This is following research [19]. Specimen D used the most PAni but not too much TiO_2. If too much of the TiO_2 composition is used, the electron transfer causing less corrosion can be inhibited by PAni. Figure 1 shows the corrosion rate of specimens.

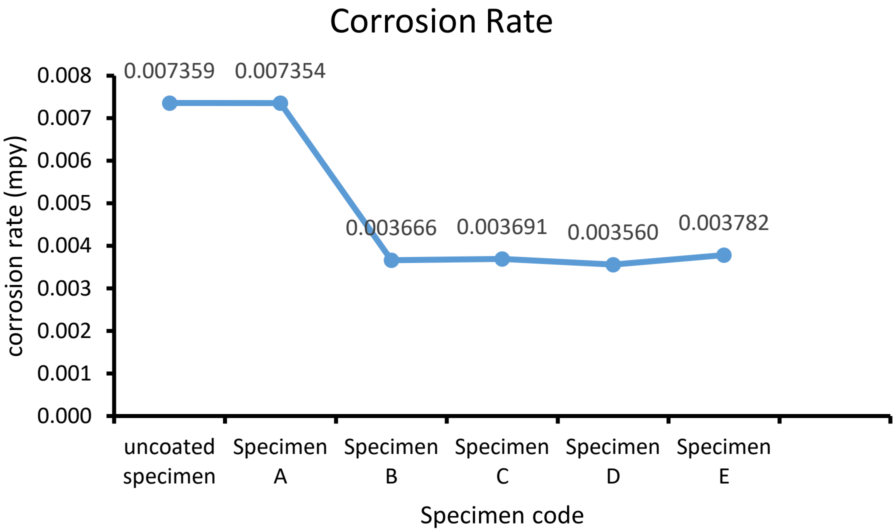
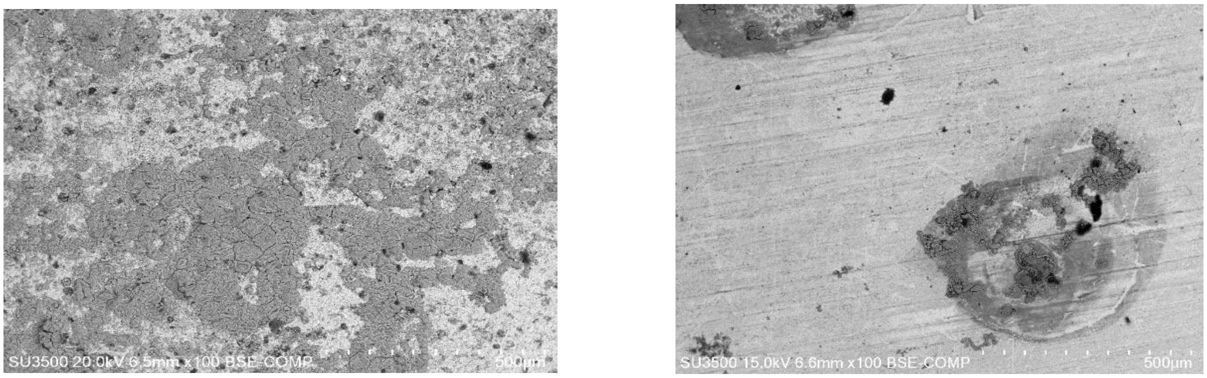
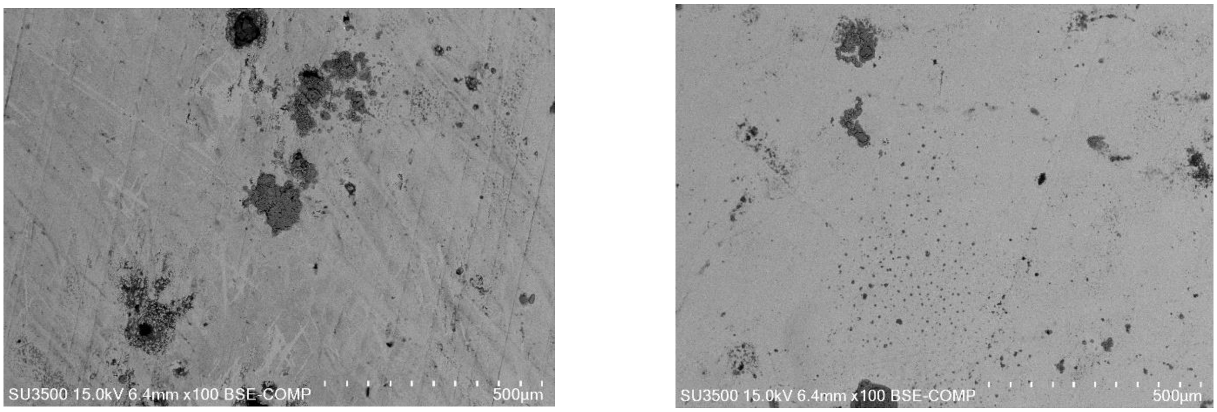


Figure 1. Corrosion rate of specimens

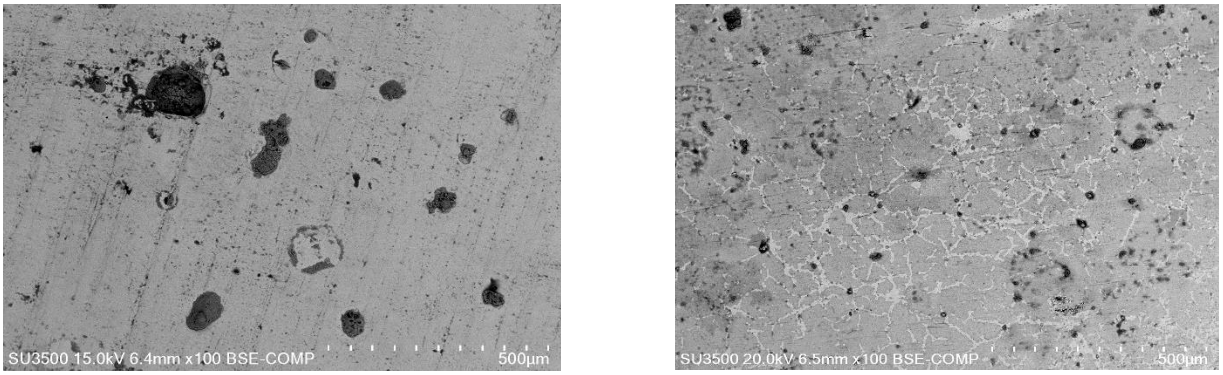
The corrosion rate was calculated to evaluate the corrosion protection ability of Polyaniline and TiO_2, and then the layer's appearance was analyzed after Corrosion. Based on Figure 1, it can be seen that the uncoated specimen has the highest corrosion rate. The coated specimens are still corroded and have a reasonably high corrosion rate. This happens on the surface of carbon steel that is not adequately coated or peeling. This is in line with Sumarji's research [20] that releasing the film layer on the surface causes corrosion at the anode, which makes the metal hygroscopic. Grain boundaries on the metal have higher energy than the medium grain, so if there is an electrolyte, the corrosion attack will start at the grain boundaries—pitting corrosion with a comprehensive and shallow orientation. This is because the water droplets stay longer on the surface, which can also be called a suitable mechanism. This is following the image shown by the results of surface morphology. The uncoated specimen has many holes indicating pores, accelerating the corrosion rate. Wider Fe or Ferrite (white) iron of carbon or pearlite (black). Because that is corroded only by iron Fe or Ferrite while carbon itself is not corroded. Figure 2 shows the results of microstructure testing.



Uncoated plate **Specimen A**



Specimen B **Specimen C**



Specimen D **Specimen E**

Figure 2. Observation Result of Surface Morphology of ST 37 in NaCl Media After Corrosion

Figures 2 show that the Corrosion that occurs in ST37 is generally uniform Corrosion because this Corrosion occurs evenly on the surface, causing a reduction in the dimensions of the metal. Usually, this Corrosion occurs on homogeneous steel and metal specimen. Uniform corrosion occurs in stainless steel when the passivation layer is entirely or partially destroyed part of the surface. Anodic and cathodic reactions occur on the same surface when there is constant movement. In an environment with constant temperature and chemical composition, Corrosion occurs at a steady rate. In addition to the uniform Corrosion showed in Figure 2, there is also a black hole, indicating that the sample's surface is some pitting [21].

Mechanical Properties

The hardness of a material is an important parameter that affects its mechanical properties of a material. Other mechanical properties include strength, hardness, stiffness, and plasticity. Mechanical characterization is done by testing the hardness of the material. The material's hardness test is a microhardness test (microhardness). The results of the material hardness test can be seen in Figure 3.

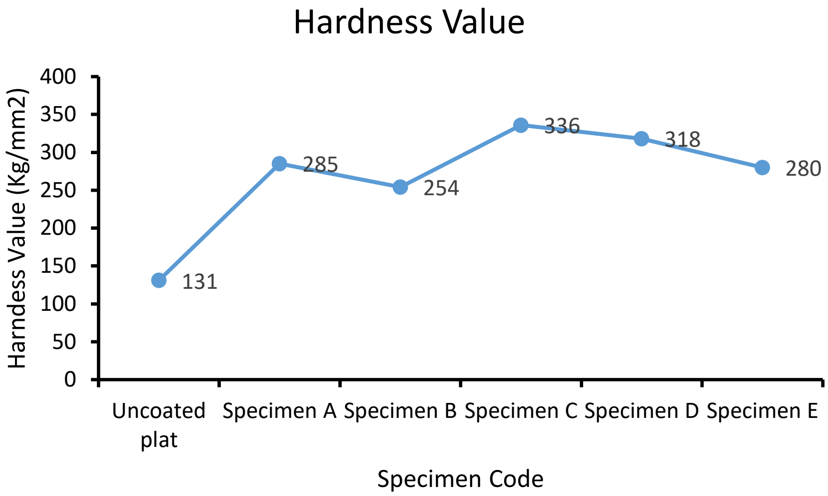


Figure 3. Material Hardness Value of Specimens

The hardness value of steel before being coated and not corroded was 165 kg/m². In the presence of corrosion, the hardness value decreases to 131 kg/m². This shows that the coating can increase the hardness value of the metal to be more corrosion-resistant [22]. The increase in hardness produced in this study was higher than the coating using Cu. Rakiman [23] coated low-carbon steel using Cu to produce a hardness value of 218 kg/m². Specimens with high corrosion rates have low hardness values. The hardness values of the coated samples were higher than those of the uncoated samples. This is because inhibition is usually caused by one or more of the following mechanisms: Adsorption process: In this mechanism, the inhibitor is adsorbed on the metal surface. The inhibition process usually depends on the inhibitory amount of the covering metal. This efficiency of inhibitor adsorption on metal surfaces can be improved by increasing the coverage area [24]. Thus, there is no damage in the metal specimen, so the hardness value is maintained. Corroded specimens become thin and brittle. The high corrosion rate causes some Fe ions to bind to H_2SO_4 and H_2O from the environment so that the Fe metal bonds are broken, and the structure inside the specimen becomes tenuous.

Conclusion

Based on morphological observations using SEM, the surface of the uncoated specimen has a high porosity. So, it has the fastest corrosion rate and lowest material hardness value. The lower the concentration of polyaniline used for coating, the higher the corrosion rate. The corrosion rate of coated specimens is 0.007354 mpy with a PAni 10^{-4} M - TiO_2 10^{-1} M. The higher the concentration of TiO_2 used for coating, the lower the corrosion rate.

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