Short Communication

Anticorrosion properties of Epoxidized Palm Olein/Epoxy Resin as Coating Materials on Low-Carbon Steel in 3.5% NaCl

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Epoxy resins are valued for their excellent toughness and adhesive strength, which are contributing factors in determining a coating lifespan in aggressive environments. With new challenges in the oil and gas industry, polymers derived from petrochemical-based definitely have become major concern to the affected industry. Using epoxididized palm olein (EPO) is one of the alternative in the epoxy resins as minor substitution. This project aims to study the effects of mixing EPO into the conventional epoxy in terms of corrosion resistance. Coating performance was evaluated by comparing conventional epoxy and EPO using low-carbon steel as sample. Electrochemical impedance spectroscopy (EIS) and immersion test was conducted using 3.5% NaCl to study the effect of corrosion and weight loss on the low-carbon steel. The results indicated that a small amount (20%) of the EPO is still acceptable in terms of cost optimization but reduced the coating performance. However, too much of EPO (40%) had led to accumulation which hinder the coating performance and increased dry film thickness. Furthermore, the resistance against corrosion was affected with additional amount of EPO at 16% reduce (20% EPO) and 95% reduce (40% EPO) with respect to the conventional epoxy. In terms of cost optimization, the overall cost could be reduced by 13%.

1. INTRODUCTION

In order to ensure sustainable development for current and future society, renewable sources of energy are emerging as ways to reduce environmental pollution [1]. As most conventional polymers derived from petroleum resources are resistant to degradation, industrial interests in the development of eco-friendly materials have propelled the environmentally benign agricultural resources as feedstocks of the polymers industry [2].

Polymers obtained from the renewable resources such as lignin, protein, cellulose, wool fibers or vegetable oils can reduce the usage of petroleum resources as all polymer structures contain carbon as their backbone. As a starter, epoxidized vegetable oil not only improves the stability of the oil but also provides adequate reactivity to form chemical linkages with other polymer chains [3]. In addition, palm oil is by far the highest yielding natural source of oil-based hydrocarbons and is significantly more efficient than any other commercial oil crop [4]. This might have opened new possibilities for palm olein to be used in other industries as well and not only limited to biofuel applications.

Epoxy is widely used in coating industry such as piping, steel plate, boiler and electrical appliances [5]. It exhibits excellent abrasion resistance, toughness and corrosion resistance. The steel structures that are continuously exposed to an electrolyte could be successfully protected using the combination of cathodic protection and organic coatings. Furthermore, polyester based materials could contribute to health problem towards human if not handle properly. Previous research showed that polyester composites could contribute to fire risks and smoke hazards of fire [6, 7]. In addition, emission of carbon monoxide and carbon dioxide percentage was higher when it degrades [8].

Among various sustainable resources, palm olein has the potential to be used as anti-corrosive coatings [9]. It can act as natural biomaterials with excellent bioactivity, biodegradability, biocompatibility, nontoxicity with multi-functional groups. Apart from its being a renewable source, it can be used as substitution in the coating system such as epoxy. Besides that, research up to date often used palm oil as biofuels to produce clean energy for environment apart from coating systems.

Epoxidized palm olein (EPO) will be used as a minor substitution in petroleum-based epoxy (epoxy) formulations. In this project, different ratio of EPO and epoxy will be tested to analyze the performance between epoxy and a ratio of EPO/Epoxy. A key objective in this project is to prove whether the EPO can be used to produce a lower cost coating system and have the same performance or improvement as compared to conventional petroleum-based epoxy to act as protective and anticorrosion coating system.

2. MATERIALS AND METHODS

Ingredients in the conventional epoxy consist of polyamide, epoxy resin, organic and inorganic pigments. The pigments usually determined the epoxy color. Ketone, ester and aromatic hydrocarbon was used for the solvent. For mixing ratio, the manufacturer suggested to mix in a ratio of 4:1 (Binder:Hardener) in order to give out the best performance of the coating formulation. Density of the paint was approximately between 1.40-1.50 (kg/litre) with viscosity of 75 10 KU at 27 °C. The epoxy has a drying time of 5 hours and curing time of 6 days for heavy abrasion service.

The sample used in this experiment was commercially available low-carbon steel plates. Table 1 indicates the chemical composition of the low-carbon steel which are used as working electrodes.

Table 1. Chemical composition of the low-carbon steel

Composition (%)	
Iron	98.81 – 99.26
Carbon	0.16-0.18
Manganese	0.70-0.90
Silicon	0.40
Sulphur	0.05
Phosphorus	0.04

The low-carbon steel was ensured dry and free from rust, millscale, dirt, grease and other contaminants before coating takes place. All samples were cleaned based on standard ASTM G1-03. The working electrode was polished using wet grinded with 120, 180 and 240 grit silicon carbide paper until previous coarse scratches and corrosion product were removed. Then, sample was rinsed and dried. For immersion test, similar low-carbon steel was used with different dimension (8 cm width x 7 cm height x 8 mm thickness). Finally, the entire sample was sand blast to remove the remaining corrosion product.

All the coating formulations were prepared according to Table 2. The number shown indicates its ratio during mixing depending on the volume needed when experiment has been conducted. Four samples were prepared for this project for each of the experiments including control (sample with no coating).

Table 2. Coating Formulation applied on the low-carbon steel samples

	Coating 1	Coating 2	Coating 3
Epoxy resin	80%	60%	40%
Epoxididized palm olein (EPO)	0	20%	40%
Hardener	20%	20%	20%

The formulation was applied directly on the low-carbon steel samples after it was stirred for about 5 minutes and left 6 days for curing.

All samples were weighted to obtain their initial weight and immersed in 3.5 % NaCl solution. Coating 2 was immersed together with the control while Coating 1 was immersed with Coating 3 in one container. Water bath was used to increase temperature inside the container to 50 °C to enhance corrosion. The samples were periodically taken out, wiped, dried out and weighted again before immersing them back to the solution. In addition, the samples were rated for changes in color, blistering, etc. Evaluation of the samples should not take more than 10 minutes after removal from the

NaCl solution. These steps were conducted for 30 days to investigate any weight loss or water permeability and will follow ASTM D870 standard for exposure sample.

EIS used to track the condition of a coated metal sample as it changes. It generates quantitative data that relates to the quality of a coating on the samples by studying the nature of change of impedance of the surface coating. An electrochemical impedance instrument consists of a potentiostat will supply AC voltage and measure the impedance.

This experiment shall follow ASTM G106-89 standard in order to perform the test and analyze the data especially the impedance value (Autolab ver. 4.9.7 model). The impedance response was measured over a range of frequency from 10 kHz to 0.1 Hz. A beaker with a capacity of 1000 ml was used and 3.5 % of NaCl as electrolyte solution was used to encourage the corrosion with the area of exposure of 1 cm^2 for 30 days. The system configuration consists of three electrodes, namely the working electrode, the auxiliary electrode and the reference electrode. The sample acted as working electrode while silver/silver chloride was used as the reference electrode. The auxiliary electrode chosen in this experiment was stainless steel, which acted as the counter electrode.

3. RESULTS AND DISCUSION

The property of the EPO changed from transparent color into concentrated white color before the experiment was conducted. This happened due to the container was stored in a cupboard below the room temperature. The temperature significantly increased the viscosity of the EPO which hinder the movement of EPO. Besides that, temperature also can lead to a destabilization of the EPO interfacial bonds and change solubility in bulk phase. The EPO can still be used but the container must be immersed in warm water (40 °C - 60 °C) to change it back to transparent color and thus decreasing its viscosity. To prevent the same incidents from happening; the container will be placed above room temperatures (27 °C to 30 °C). This will enhance the EPO performance at its based condition when mixing with the epoxy.

When conventional epoxy and EPO were mixed together, the EPO tend to lump the epoxy, which had resulted in the reduction of Dry Film Thickness (DFT). This happened due to the EPO still had the characteristics of normal cooking oil which hinder the movement of the epoxy. Furthermore, the spreading of the coating formulations on the low-carbon steel became difficult, as the percentage of EPO increases and the sample had to be repainted again to ensure the sample was coated completely without having a pit hole or area that was not covered by the coating.
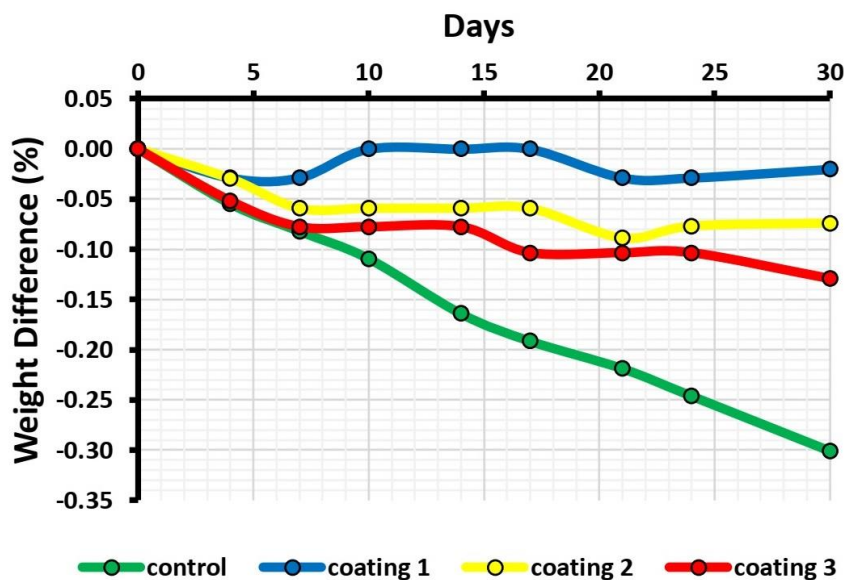
Figure 1. Weight difference as a function of immersion days for the coating formulations at NaCl concentration of 3.5% and temperature of 50 °C.

Figure 1 shows the weight difference as a function of immersion days for the coating formulations. It can be seen that the highest weight loss happened for the control part, where no coating was applied. It is expected that corrosion can occur more quickly without any coating. Furthermore, the corrosion was induced at NaCl concentration of 3.5% and temperature of 50 °C which results in corrosion of pitting on its surface.
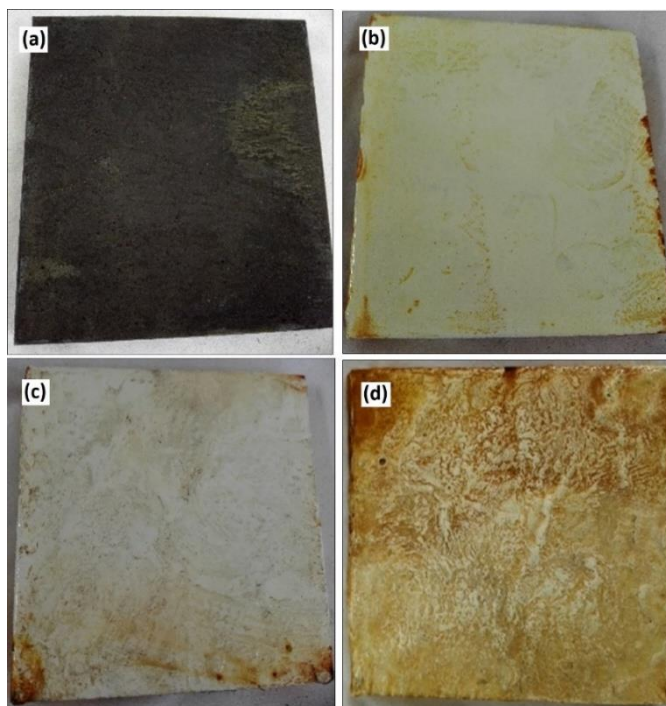

Figure 2. Visual inspection of the low-carbon steel after 30 days for: (a) control; (b) coating 1; (c) coating 2; (d) coating 3 in 3.5% NaCl environment at temperature of 50 °C.

For coating 1-3 samples, two processes may occur as a result of the immersion test; the processes of permeation and blistering, which took place simultaneously. In permeation process, water and corrosive ions could infiltrate into the pore structure of the coating, which leads to positive value in the weight difference as shown in the Figure 1. In addition, blistering might happen and results in weight loss for the affected coating system. The solutions also might solve some component of hydrophilic EPO or epoxy and weaken/break some bonds of the binders, thus damaging the corrosion resistance [10, 11].

Figure 2 shows visual inspection of the low-carbon steel after 30 days in 3.5% NaCl environment. As shown in Figure 2a, metal loss happened rapidly in the control sample which can be attributed to the major corrosion as discussed earlier. Furthermore, the pitting corrosion is clearly visible due to the presence of corrosion products. All the coating samples are still intact except for coating 3 which show a sign of blistering as shown in Figure 2d. Moreover, coating 1 sample still retains its shiny surface except for a minor corrosion that happened due to some surfaces may not be completely covered by the coating especially on the sides. Coating 2 had similar characteristic like coating 1 but did not have shiny surface. The performance for coating 2 indeed showed the performance reduction in terms of surface observation.
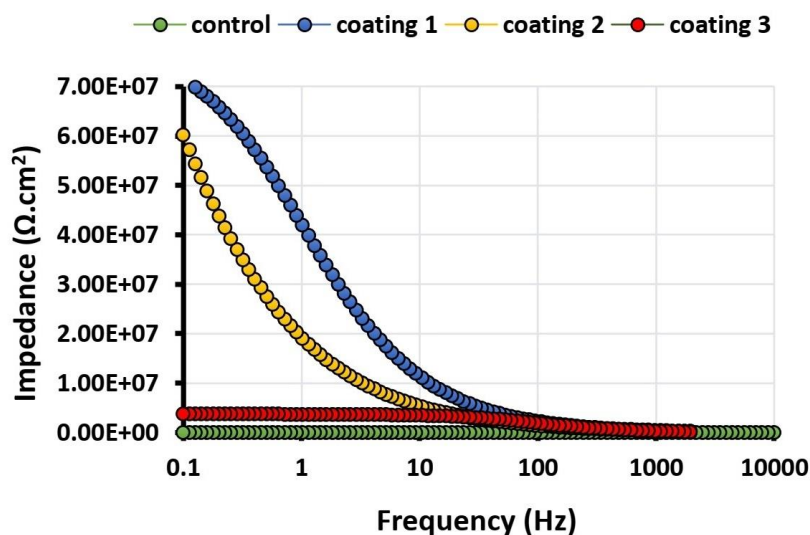

Figure 3. Bode plot of different samples immersed in the 3.5% NaCl after 30 days.

Figure 3 and Figure 4 show the impedance spectra corresponding to the coated samples immersed in the 3.5% NaCl after 30 days. After 30 days, the coating was expected to reduce its resistance due to blistering or 'holiday'. As shown in Figure 3, coating 1 resisted more corrosion at 0.1 Hz compared to coating 2, coating 3 and control. To make comparison between coating 2 (20% EPO) and coating 3 (40% EPO), the EPO percentage indeed plays a vital role in determining the coating performance. High percentage of EPO leads to easy occurrence of blistering and inducing corrosion. Furthermore, the spreading of the coating became difficult with the increase in the EPO, thus, coating 3 introduced more surface which were not covered by the coating system. The high value of the resistance in the order of 10^7 Ω cm^2 obtained confirm that there was no contact between the electrolyte solution and the samples which suggested that the EPO (coating 2 and coating 3 samples) provide

corrosion protection to the steel surfaces. The excellent corrosion resistance offered by coating 1 may be attributed to the inherent hydrophobic nature of alkyl pendant groups present in the silicone moiety that gives coating films with excellent resistivity to chemicals, solvents, electrolyte and inorganic acid [12].

The impedance at low frequency corresponds to the polarization resistance of the coatings and therefore can be used to estimate the corrosion protection. Moreover, the impedance values at low frequencies denote that the coating 1-3 samples presented the best corrosion protection as it had the highest absolute total impedance value [13]. The impedance of Fig. 6 based on 0.1 Hz and an alternative parameter for the evaluation of the protective properties of the coatings. This parameter is defined as the impedance modulus of the low-carbon steel-coating system at frequency 0.1 Hz. Hence, high values of impedance at 0.1 Hz are associated to a high protection capacity of the coating while low values of impedance at 0.1 Hz represent coatings with poor anticorrosive protection.
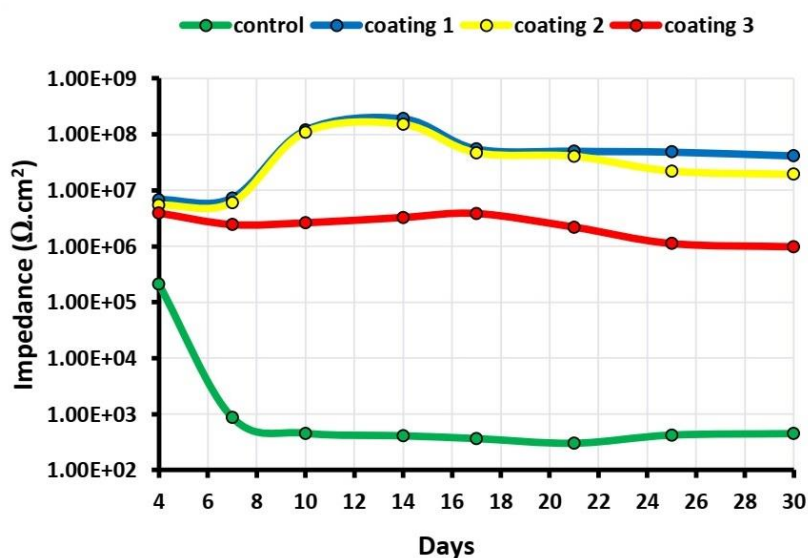

Figure 4. Impedance modulus of the samples in different immersion times at frequency of 0.1 Hz and 3.5% NaCl concentration.

As shown in Figure 4, the impedance modulus of the recorded spectra increases from day 7-10, constant from day 10-14 and decreases from day 17-30. This indicates that EIS is sensitive to the changes that occur in the samples during the solvation and migration process. Furthermore, in any coated metal samples, the high frequency interval is usually related to dieleletric properties of organic coatings, while the low frequency range corresponds to the metal response during corrosion process [14].

4. CONCLUSION

The ability to replace petroleum-based product with renewable resources is becoming a worldwide issue, as it will result in reducing the use of petroleum-based materials. This project

emphasized on using EPO in the conventional epoxy to produce a new type of coating systems against corrosion. Based on the results and discussion, it is proven that with a small amount of EPO, the performance of the coating indeed reduced the coating performance. However, too much of the EPO will lead to accumulation which hinder the coating performance and DFT will increase. Two processes occurred during the immersion test, which were permeation and blistering. Based on the Bode plot at 0.1 Hz, coating 2 sample reduced its performance by 16% while coating 3 sample reduced by 95% with respect to coating 1 sample. The impedance after 14 days showed a decline, which suggests the coating experienced blistering and introduced 'holiday' on the low-carbon steel surface and further enhance the corrosion.　In terms of cost optimization, industry could save up until 13% by implementing this type of formulation.

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