



EIS Study of Epoxy Paints in Corrosive Environments with a New Filler: Rice Husk Ash

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ABSTRACT

In this paper, the corrosion behavior of the filled epoxy paint with the rice husk ash (RHA) on steel substrates in two different corrosive environments (natural sea water and 2M sulfuric acid) has been studied. Electrochemical impedance spectroscopy (EIS) was used to evaluate protective properties of different organic coating systems due to the different filler composition. RHA was prepared by heating rice husk at 700°C for 3 hours. By adding RHA, as a new and natural filler, to the epoxy paint, the resistance to penetration of the solution was increased in both environments. The best filler for the sea water was the white RHA (contained more silica) in 20% wt. due to increasing the corrosion resistance for 3 times with respect to the unfilled epoxy paint. The black RHA (contained more carbon) increased the corrosion resistance of the epoxy paint in sulfuric acid when added in 20% wt. Prog. Color Colorants Coat. 9 (2016), 53-60 © Institute for Color Science and Technology.

1. Introduction

Organic coatings are an efficient way to protect metal-based products from corrosion [1-5]. Using epoxy paints as internal or external coatings is one of the economical ways to protect bare steels against different corrosive environments [6]. Coatings based on epoxy resins have gained considerable importance in many areas of technology and daily life. This is due, on one hand, to the fact that epoxy resins can be processed relatively simply and safely and, on the other hand, to the good mechanical and chemical properties of cured epoxy resin molded materials. This versatility in formulation made epoxy resins widely applied industrially for surface coating, adhesive, painting

materials, potting, composites, etc [7, 8]. To enhance the properties of epoxy paint, ceramic particles such as silica are sometimes added [9]. The RHA is a cheap silica source as the rice husk is one of the major agricultural by-products and is available in the world [10]. Rice husk contains about 40% cellulose, 30% lignin group and 20% silica and hence its ash contains a large amount of silica. After burning RH, the RHA with approximately one-fifth of the initial weight is obtained as a by-product [11]. The RHA contains over 80% of silica and small proportion of impurities such as K₂O, Na₂O and Fe₂O₃. The cellular nature of the rice husk gives the cellular porous structure of the RHA

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texture [11, 12]. However, over the time, even in the absence of defects, sufficient amounts of ions may penetrate through the coating, resulting in corrosion at the interface [2, 3]. But more dangerous are defects in the coating which may be caused either by external attacks such as stones or scratches, or by production steps [2].

In the literature, the behavior of different coatings in corrosive media has been monitored by means of the EIS [4, 13]. Thus, the EIS is a good quantitative and sensitive tool to investigate the deterioration of coating on a metal. This method can be used for determining coating performance and the protection mechanism. Some electrochemical elements related to the corrosion process, such as coating capacitance, coating resistance, double layer capacitance, and charge transfer resistance can be determined via superposing experimental data and the results from equivalent electrical circuit (EEC) models. Many researchers have been reviewed and used this approach to analyze protective organic coatings performances [3, 4, 14, 15]. To better study the results of the EEC model, we need to use a non-linear least square-fitting algorithm program. The EEC is commonly used to interpret EIS studies of coating systems, but in some cases calculated data from EEC models are not always completely comparable with experimental data. Moreover, finding an exact fitted model is quite difficult [14, 15]. Thus coating materials should be controlled with appropriate techniques.

The aim of this paper is to determine the effect of adding the black and white RHA filler to epoxy paints on the corrosion stability of steel substrates in two different corrosive environments. The corrosion measurements were performed by electrical circuits via electrochemical impedance spectrometry (EIS).

2. Experimental

2.1. Materials

At first, the rice husk was washed. After it dried completely in air, the rice husk was heated at 700 °C for 3 hours to remove organic compounds in RHA. Then RHA was grinded to reach an acceptable ash size (Figure 1). As the burning of rice husk depends strongly on the amount of available oxygen and the surface of used crucible, the temperature and the time of the heat treatment in this experiment were fixed and the amount of primary material was changed to obtain

RHA with different compositions according to the ash color. For preparing white and black RHA, 12.5 and 50 g rice husk was used, respectively. A stainless steel crucible with an internal surface area of 40 cm² was used for burning the rice husk. It is clear that white rice husk ash has more silica and less carbon. Thus, two different types of RHA (white and black) were used in this study.

2.2. Preparation of painted specimens

The RHA was dispersed in the epoxy paint (10% and 20 wt%) with mechanical mixer and then applied on steel substrates. The thickness of the layer was less than 1 mm. To enhance the layer adhesion, steel surfaces were first polished and then washed with the acetone before applying the paint. The epoxy paint was complete dried after 48 hours in air.

2.3. The Electrochemical impedance spectroscopy (EIS)

For A.C. impedance measurements, coated samples were exposed to natural sea water (Persian gulf) for 1, 24, 36, 600 and 1200 hours and were exposed to sulfuric acid (2M) for 1, 24, 36 and 192 hours. A three-electrode cell arrangement was used in which the counter electrode was a platinum bar with a surface area considerably greater than that of the working electrode (about 3.14cm²). The reference electrode was an Ag/AgCl (saturated KCl) electrode. The impedance measurements were carried out in the frequency range of 100 kHz to 10 MHz using sinusoidal voltage with amplitude of 5 mV.

3. Results

The obtained RHAs were investigated using scanning electron microscope (SEM, Philips XL-30) in order to determine their particle size and shape. As shown in Figure 1, the diameter of filler particles was less than 50 micrometer. Also, the particle size of white ash was lower than that of black ash, which may be due to the presence of higher amount of small silica particles. The silica in the RHA had porous and laminated structure

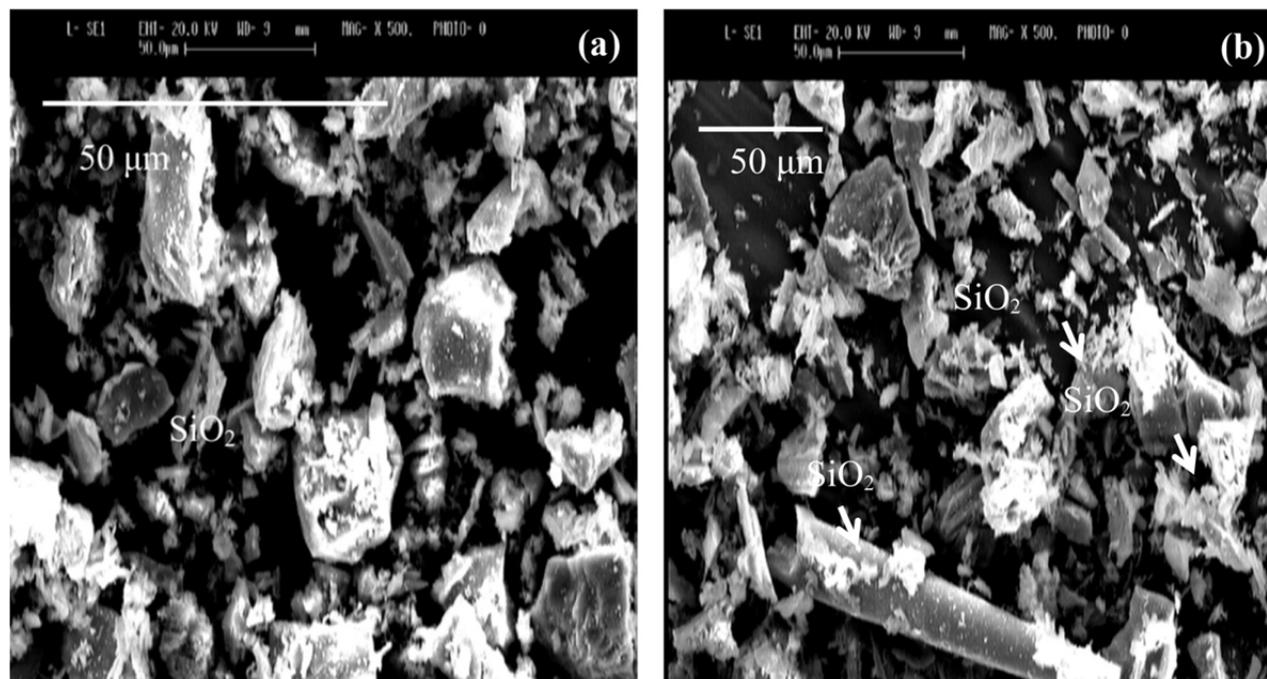


Figure 1: SEM images of RHA (1000x): (a) black ash, and (b) white ash.

EIS analysis of the coating was performed on the basis of Nyquist plots, as shown in Figures. 2 and 3 for the selective exposure time.

3.1. Sea water

By applying a layer of coating on steel substrates, the steel corrosion decreased about 103 times as shown in Figures 2(a) and (b) showed. When the exposure time increased to 25 days, the steel corrosion decreased (Figure 2(a)). Then, as the time increased to 50 days, the corrosion of steel increased relatively. However the oxide layer created on the surface of steel substrate, but this type of the oxide layer wasn't appropriate for preventing the corrosion occurrences. According to Figure 2(b), the resistance of unfilled epoxy paint

changed continually by increasing the time of exposure. The shape of plots became more complete (3 semicircle) which was due to the corporation of more electrical elements in the circuit. In general, by adding RHA to the epoxy paint, the coating resistance in the sea water, increased significantly. The white filler could be more beneficial in increasing the resistance of coating than the black one. When the amount of white filler was reached to 20 wt%, the resistance increasing became more obvious (Figure 2(c), 2(d)). The resistance increased about 2 times by increasing the amount of black filler to 20 wt% (Figure 2(e), 2(f)). Thus the coating containing 20 wt% white filler showed better resistance in all the exposure times in the sea water. In all, the resistance of filled epoxy paint coating increased by the exposure time to 25 days.

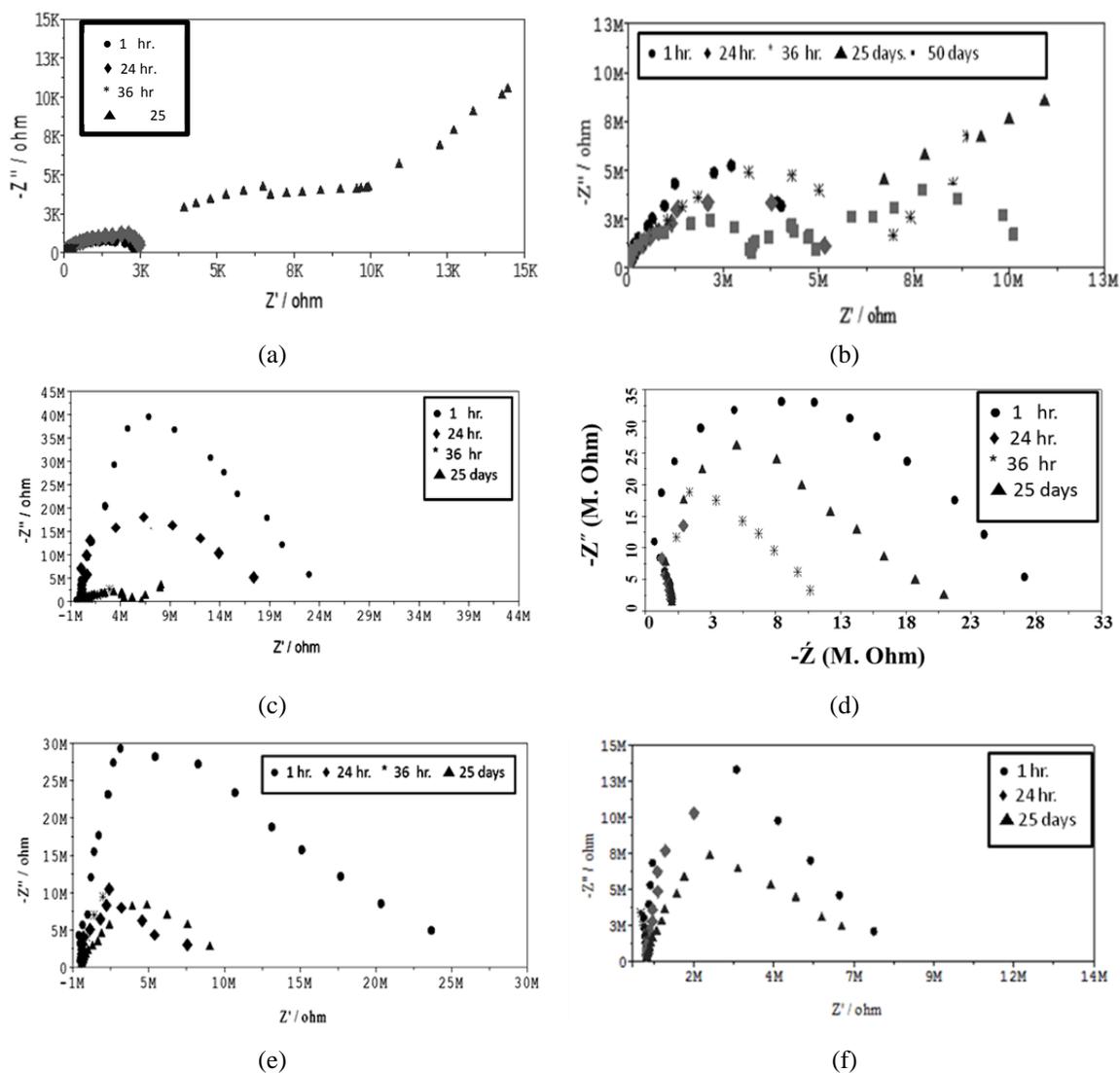


Figure 2: Nyquist plots for the selective exposure times in sea water for (a) steel, (b) pure epoxy, (c) epoxy-20% wt. white filler, (d) epoxy-10% wt. white filler, (e) epoxy-20% wt. black filler, (f) epoxy-10% wt. black filler.

3.2. Acidic solution

According to plots shown in Figures 3(a) and (b), the steel corrosion decreased 106 times after applying a layer of epoxy paint on steel substrate. By comparing Figures 2(a) and 3(a), it can be concluded that the steel corrosion in the acidic solution (2M sulfuric acid) was about 103 times more than in the sea water. In addition, by comparing Figures 2(b) and 3(b) it is evident that

the resistance of unfilled paint in the acidic solution (2M sulfuric acid) was about 4 times more than in the sea water. Thus, the epoxy paint was more beneficial in the acidic solution than the sea water. When the exposure time increased to 8 days, the corrosion of steel increased, although the oxide layer created on the surface of the steel substrate (Figure 3(a)).

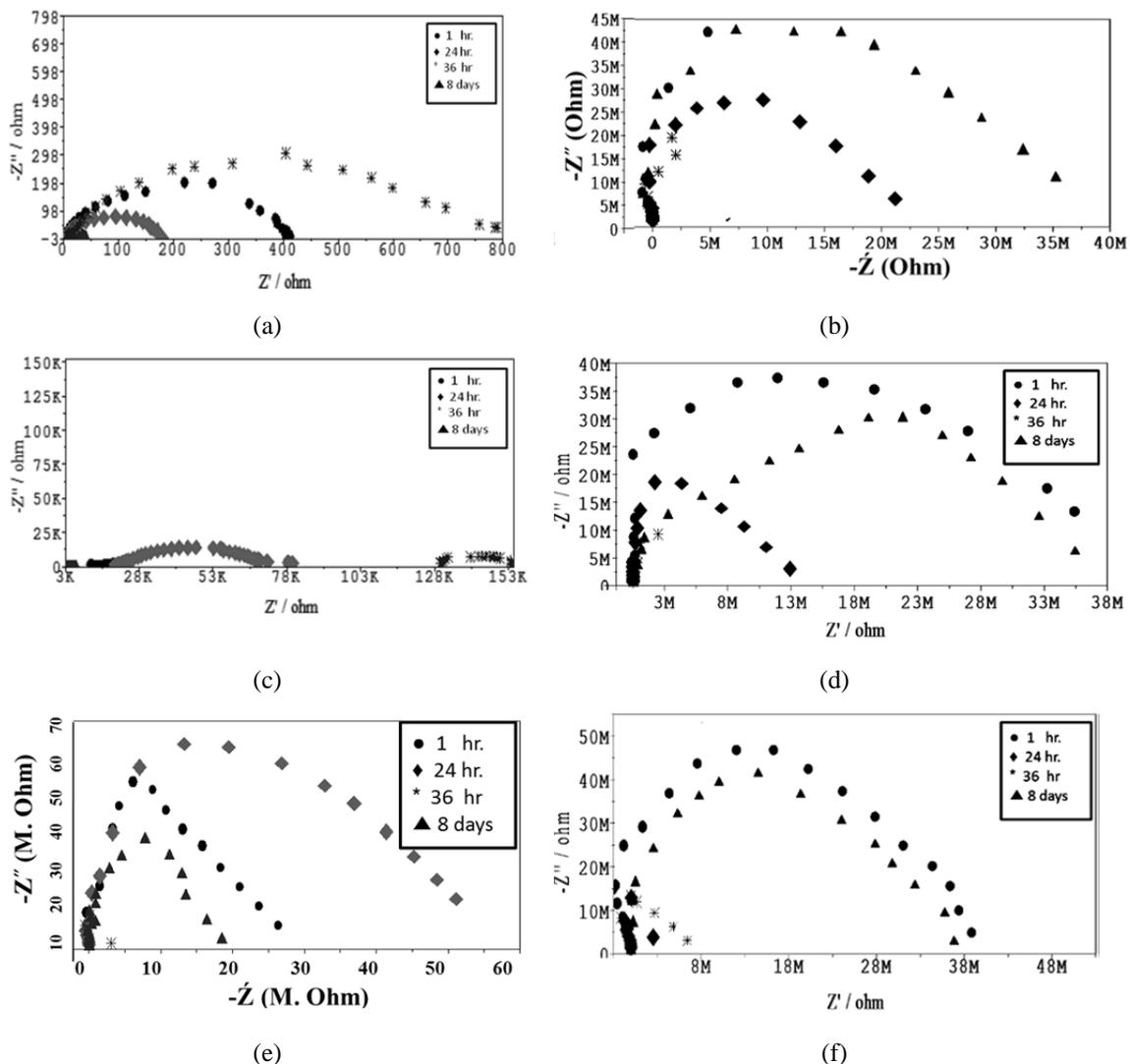


Figure 3: Nyquist plot for selective exposure times in acidic solution for (a) steel, (b) pure epoxy, (c) epoxy-20 wt% white filler, (d) epoxy-10 wt% white filler, (e) epoxy-20 wt% black filler, (f) epoxy-10 wt% black filler.

This barrier coating was unsuitable to prevent the solution penetration. The oxide layer was not stable in acidic solution by increasing the exposure time. By adding the white filler to the epoxy paint, the resistance of coating to penetration of acidic solution decreased and this resistance increased more significantly by adding 20 wt% white filler (Figure 3(c)). When the black RHA was added to the pure epoxy, the resistance of coating increased with respect to the unfilled paint. In general, after the primary exposure time (less than 36 hours) the resistance of the coating began to increase for all kind of coatings. The coating contained

20 wt% black filler showed the best resistance in all exposure times.

4. Discussion

The electrochemical properties of epoxy coatings on steel substrates were examined by EIS measurements. The fitting of experimental data obtained was accomplished using the equivalent electrical circuit [16]. The equivalent electrical circuit (model A) shown in Figure 4 was used to fit the impedance data for unfilled epoxy paints, where R_s is the solution

resistance, C_{dl} is the constant phase element which expresses the double layer capacitance, R_{ct} is the charge transfer resistance and R_w is the Randles resistance that showed the diffusion resistance. The equivalent electrical circuit (model B) shown in Figure 4, which is a typical model used frequently for the behavior of the filled epoxy paint in an electrolyte, was used to fit the impedance data, where R_s is the solution resistance, C_c is the constant phase element which expresses the coating capacitance and R_c is the coating resistance, C_{dl} is the CPE which expresses the double layer capacitance and R_{ct} is the charge transfer resistance of filled epoxy paints [13, 17].

For better discussion, the changes in the element amount in the equivalent electrical circuit for some samples are listed in Table 1. As steel adsorbs a lot of water, the amount of double layer capacitance was in the range of micro farad. The double layer capacitance decreased as the oxide layer was created on the surface of steel substrates.

The results shown in Table 1 supported the data in

agree with the Nyquist plot. When a layer of epoxy paint was coated on the steel substrate, the amount of double layer capacitance reached to Pico farad range after 25 days. After a long time (e.g. 50 days), coating capacitance increased to 10 milifarad that showed more water adsorption by the coating. According to the Nyquist plots, the resistance of the paint contained white filler increased with respect to the unfilled paint, the amount of coating capacitances decreased and the amount of coating resistance increased significantly.

The effectiveness of a coating depends on many factors. About 40 years ago, it was assumed that the mechanism by which coatings protected steel was by a barrier mechanism, whereby coatings kept water and oxygen away from the steel substrate. It is obvious that the coating must hinder the transport of the cathodic reactants toward the metal substrate and/or the removal of the corrosion products from the metal substrate. Additionally, the protective coatings are expected to strongly reduce the ingress of very corrosive anions such as chlorides within the film [4].

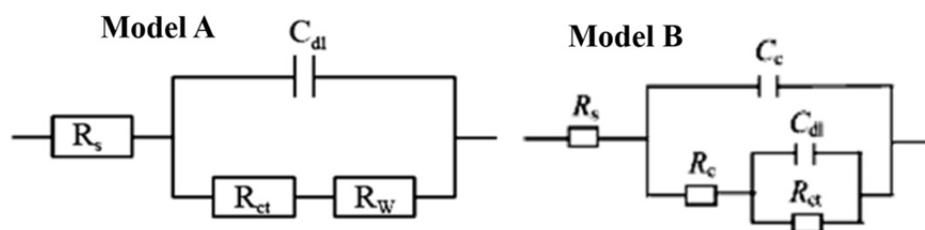


Figure 4: Equivalent electrical circuit of the organic coating/steel interface, epoxy paint (A) unfilled (B) filled.

Table 1: Electrical elements in the circuit for selective samples in sea water for different exposure times.

sample	C_{dl} (PF)	C_c (PF)	R_c (Mohm)	Time(days)
Bare Steel	-	50×10^6	25×10^{-3}	25
Pure Epoxy	2	100	12	25
Epoxy- 10 wt% black RHS	4	60	14	1
Epoxy- 10 wt% black RHS	5	70	7	25
Epoxy- 10 wt% white RHS	1	9	32	1
Epoxy- 10 wt% white RHS	4	7	22	25

Thus it seemed that, as no chemical reaction was happened in sea water, adding RHA to the epoxy paint could be barriers for the corrosion by different ways, for example they could increase cohesion between filler composition components or they can trap corrosive ions of solution. By adding more filler to paint, this barrier became stronger and as a result, less water absorption was happened. Thus, as the white filler had more porous silica content, it could be more effective in increasing coating resistance than black filler in the sea water. Similar results are reported in [19]. But in the acidic solution, chemical reactions are probable between filler and solution. Therefore, the precise composition of filler is very important. The impurities in RHA such as Fe_2O_3 and Zn could participate in reactions and had an effective role in corrosion behavior of filled epoxy paint. Thus, the carbonic group in black RHA filler had more effective role in increasing the coating resistance than the silica in white filler for acidic solution (2 M sulfuric acid).

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5. Conclusions

In this paper, RHA was used as a new, low cost and natural filler to optimize the corrosion behavior of the epoxy paint. The results showed that pure epoxy paint exhibited better resistivity in the acidic solution than in the sea water. By adding RHA with different compositions and concentrations (10 wt%. and 20 wt%.) to the epoxy paint, the coating resistance value in the sea water became as the same value for the coating resistance in acidic solution (2 M sulfuric acid). The result showed that the proposed corrosion mechanism was changed, as the filler was added to the epoxy paints. The 20 wt% white RHA could be the appropriate filler for the epoxy coating in the sea water but only 10 wt% black filler was effective in increasing the resistance of coating in the acidic solution. The reason for the later one may be related to the chemical reaction between the filler content and the sulfuric acid.

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