Journal of Physics: Conference Series

PAPER • **OPEN ACCESS**

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To cite this article: M S Noor Idora *et al* 2017 *J. Phys.: Conf. Ser.* **890** 012062

IOP Conf. Series: Journal of Physics: Conf. Series **890** (2017) 012062 doi:10.1088/1742-6596/890/1/012062

Effect of tannin from Rhizophora apiculate as corrosion inhibitor for epoxy paint on mild steel

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Abstract. There is a great concern to protect the steel surfaces from corrosion phenomenon in seawater environment. Several approaches have been proposed to introduce alternative new compounds in the paint which are green sources that can reduce environmental risks. The aim of this investigation was to enhance the protection properties of epoxy paint by providing an anticorrosive inhibitor for the paint. In this approach, the abilities of mangrove tannins, extracted from Rhizophora apiculata bark were studied. The inhibitive properties of mangrove tannins were evaluated by weight loss measurement, electrochemical impedance spectroscopy (EIS) and scanning electron microscope (SEM). Results shows the addition of mangrove tannin in the coating boosted the anticorrosive properties of the paint and represents valuable environmentally friendly of inhibitor.

1. Introduction

Mild steel has been used as the structural materials for marine applications due to the availability, excellent mechanical properties and low cost [1]. The major problem of using mild steel is its high rates of corrosion process in seawater and it requires regular maintenance. Corrosion can cause dangerous and expensive damage or loss to the structure [2], [3]. Intense efforts have been undertaken all over the world for the protection against corrosion phenomenon such as organic coating. The protection mechanism in controlling the corrosion rate of the steel is associated to the barrier effects added to the action of anticorrosive pigments present in the coating. Pigments in paints can enhancing their chemical or physical strength and increasing the resistance of the metal surfaces to corrosion as well as improving the barrier properties of the coating [4]. Besides, it seems that the recent research has been focused on the environmental friendly corrosion inhibitors after the strict environmental legislations and increasing ecological awareness [5]. The use of corrosion inhibitors is the most practical and economical method for corrosion protection and prevention even though the metal is in aggressive environment mainly in aqueous solution [6].

Some of the epoxy paints containing zinc chromate as paint pigment provide the most effective corrosion protection. However, the usage of chromates is being progressively prohibited throughout industries, since they are toxic, environmentally harmful and risk to human health [7]. The toxicity of the inhibitors can be reduced by lowering the amount of metal ion to the seawater [8]. Inhibitive pigments are introduced in organic coating to control corrosion. Meanwhile, the commercial paint based on zinc phosphate as a paint pigment becomes widely used due to the relatively good performance and low cost. Besides, it is known as an environmental friendly pigment compared to chromate pigment [9].

The ability of zinc phosphate to prevent the corrosion process is the same level or better that the zinc chromate which has been banned [10].

There has been increased interest in employing plant extracts as corrosion inhibitors for the metals in paint application. The plants serve as incredibly rich sources of naturally phytochemical that are environmentally acceptable, inexpensive, readily available and renewable source of materials [11]-[13]. Mangrove bark tannin is quite economical due to large quantity production and are disposed indiscriminately by charcoal industries. The antioxidant property of tannins in the mangrove bark is contributed through their polymeric structure which act as reducing agent and inhibit the oxidation process. The antioxidant property of tannins enables them to be used as alternative steel corrosion inhibitor [14].

In the present work, the mangrove tannins extracted from Rhizophora apiculata mangrove bark were investigated for their inhibition action to sustain the corrosion problem of mild steel. Besides, the effectiveness of tannin in paint was established as natural anticorrosive pigment based on the amount of tannin in paint formulation.

2. Experimental procedures

2.1 Materials

Mild steel specimens [of composition Carbon-0.22%; Manganese-1.30%; Sulfur-0.035%; Silicone-0.35%; and Phosphate-0.035%] were used in this study. The specimens were polished by using power tool cleaning equipped with wire cup brushes (SSPC-SP3). Then, the specimens were degreased using thinner and washed with distilled water (SSPC-SP1). The tannin was extracted from mangrove (Rhizophora apiculata) barks by total immersion of finely ground bark in 70% aqueous acetone for 72 h at room temperature. The extract was filtered and the filtrate was evaporated using a rotary evaporator at 40ºC. Then, powder tannin was produced by freeze-drying the aqueous solution, yielding 25-27% weight of the dry barks. The solubility of tannin was reduced by adding 200 ml of 1M zinc nitrate (Zn(NO3)2) in 800 ml of distilled water containing mangrove tannin. During the mixing process of the solutions, 0.5 M NaOH was added to adjust the solution pH to 4.0. The mixture was then left within 24 h to achieve saturation conditions before drying the solids compound in the oven at 50 ± 5ºC to produce zinc "tannate" (TZn) [15], [16].

2.2 Preparation of coatings

In this study, the epoxy high solid zinc phosphate primer, Paralux P268HS was obtained from Kansai Paint Co., Ltd. The paints were prepared by adding the hardener with an epoxy/hardener ratio of 4:1 and fractioned in 5 portions with different quality of TZn (2 g, 4 g and 6 g). Every portion of paint and TZn mixture were dispersed by using stirrer for 1 h to allow chemical reaction [17]. Finally, the prepared paints were applied on the polished specimens and cured in an oven at 35ºC for 3 h. For corrosion test specimens, X-scribed was made through the coated surface with dry film thickness of 160 ± 5 µm before immersion test. This procedure was employed to expose the underlying metal to the aggressive environment (ASTM D1654-92). Scribed painted sheets were made with Hoffman Cutter.

2.3 Laboratory test

The immersion test was conducted by diluting 3.1 wt.% NaCl in 20 L of artificial seawater. The coated metals with different amount of TZn were hung in test solution (complete immersion) for 3 months at room temperature.

2.4 Weight loss measurement

The initial weight of the specimens was weighed for original weight (W_o) after painted with epoxy paint with different amount of TZn. At the end of the corrosion test, the corroded specimens were washed with distilled water and dried. Then, the specimens were immersed in nitric acid (HNO_3) for 2-3 min to get rid of the corrosion products. Finally, the specimens were washed with distilled water, dried and weighed again using an electronic balance to obtain the final weight (W_f).

The weight loss value (W_L) for the coated specimens and the inhibition efficiency percentage (IE %) were calculated using Equation (1) and (2) respectively,

$$W_L = W_o - W_f \tag{1}$$

$$IE(\%) = ((W_u - W_i)/W_u) \times 100 \tag{2}$$

where W_u and W_i are the weight loss values for the uninhibited and inhibited coated specimens.

2.5 Electrochemical measurement

All the electrochemical measurements were obtained using Autolab frequency response analyser (FRA) coupled with an Autolab potentiostat connected to a computer. The cell used is a conventional three electrodes with a platinum wire counter electrode (CE) and a saturated calomel electrode (SCE) as reference to which all potentials are referred. Mild steel sheets were served as working electrode. Seawater with 3.1 wt.% NaCl was used as an electrolyte for the electrochemical cell. The electrodes were immersed in the electrolyte for 30 min to obtain steady state open circuit potential.

The inhibition efficiency values were calculated from electrochemical measurement using Equation (3),

$$IE(\%) = ((R_{ct(i)} - R_{ct})/R_{ct(i)}) \times 100 \tag{3}$$

where R_{ct} and $R_{ct(i)}$ are the charge transfer resistance for the uninhibited and inhibited coated specimens, respectively.

3. Results and discussion

3.1 Weight loss measurement

The effect of adding different amount of tannin in the paint on the corrosion of mild steel in seawater was studied by weight loss measurements after 45 days of immersion period. The weight loss and the corrosion rate of the specimens are shown in Figure 1.

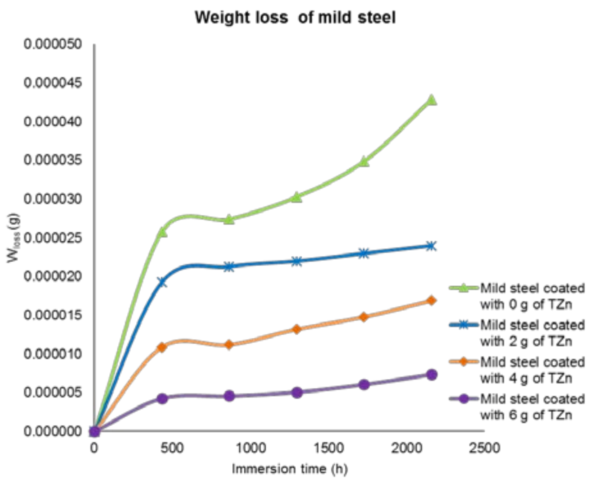

Figure 1. Weight loss of TZn at different amount during immersion in 3.1 wt.% solution up to 2160 h.

Due to the break down of layer at the specimens, the weight loss of specimens differed for each amount of tannin extraction. It can be seen the weight loss of the specimens with tannin is remarkably less than that of the specimen coated without tannin. Weight loss of mild steel increased with the decreasing of amount of tannin in the paint. This result suggests that tannin extract can be considered as an excellent inhibitor for mild steel in seawater by improving the corrosion-protective effect.

The aggressive Cl^- concentration in seawater influence the corrosion process by accelerating the corrosion rate of the mild steel. Figure 2 illustrates the corresponding trend of inhibition efficiency for various amount of tannin in the paint after seawater exposure. As expected, efficiency increases with increasing tannin content in the paint, with 83.86% at higher amount of tannin (6 g). The tannins in mangrove provide antioxidant properties and excellent corrosion inhibitor which reduce the cathodic reaction rate of hydrogen reduction [14].

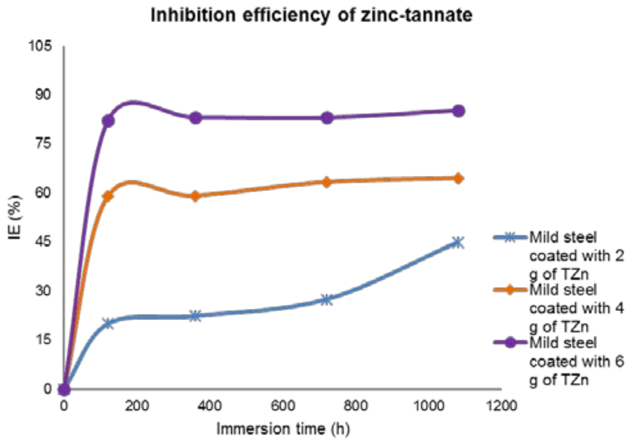

Figure 2. Inhibition efficiency of TZn at different amount during immersion in 3.1 wt.% solution up to 2160 h.

3.2 *Electrochemical impedance spectroscopy measurement*

The corrosion behavior of mild steel in seawater in the absence and presence of TZn, was investigated using impedance measurement through Nyquist plot in Figure 3. In Figure 3, single loop capacitive loop is shown, and the diameter of the capacitive loop increases with the increasing amount of inhibitor. In addition, the curves in the Nyquist plot are changed after adding the inhibitor indicating that the corrosion is mainly a charge transfer process [18]. It is suggested that TZn particle cut off the electrons-supplying path at the metal surface and transports them to the outside of the primer [19].

Generally, the paint separates the metallic substrate from the corrosive medium. It prevents more penetration of water and corrosive ions across the coating. The existence of zinc phosphate as a pigment in the paint inhibits the corrosion process at the metal. With the additional of TZn in the paint, it enhances the performance of the paint against metal corrosion. The inhibitor pigment improves the barrier properties of the coating and strengthens the protective layer [20]. It reduces the access of aggressive reagents to the metal surface and offers some kinds of electrochemical anodic and cathodic protection effect.

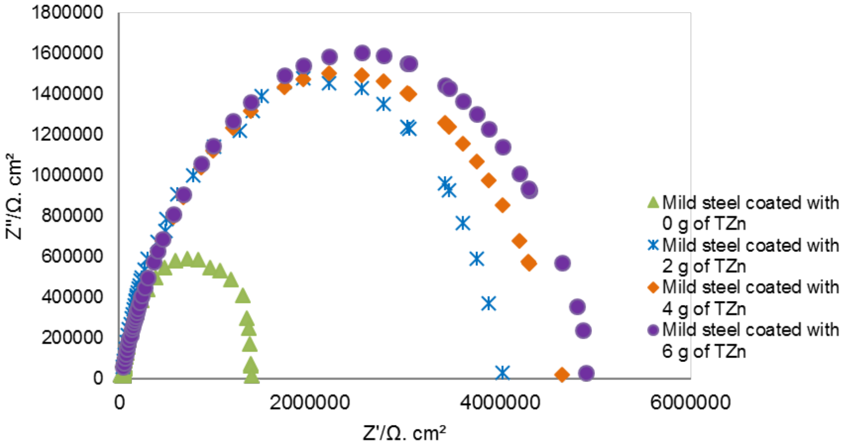

Figure 3. Nyquist plots of steel coated with absence and presence of TZn.

The electrochemical parameters calculated from the Nyquist plot are given in Table 1. As from Table 1, it was found that the value of charge transfer resistance, R_{ct} increases in the presence of TZn as compared to blank, thus increased the inhibition efficiency of TZn, IE%. The increase in R_{ct} value can be explained by the increasing in corrosion protection due to the anti-oxidation activity of tannin. The higher value of the coating resistance as well as R_{ct} could be considered as the key factor for effective coating [21]. Meanwhile, the values of double-layer capacitance, C_{dl}, decrease as the amount of TZn increases. This is resulting from local dielectric constant decrease and also increase of the thickness of protective layer at the metal surface. Thus, these parameters contribute to the enhancement of corrosion resistance and lower the corrosion rate of metal.

Table 1. Electrochemical parameters from impedance measurement of the coated mild steel immersed in the seawater.

Sample	R_{ct} (Ω cm^2)	C_{dl} (μF cm^{-2})	IE%
Blank	1.96 E+05	641.56	-
Epoxy paint with 2 g of TZn	1.83 E+06	184.23	89.3
Epoxy paint with 4 g of TZn	2.10 E+06	88.99	90.7
Epoxy paint with 6 g of TZn	3.23 E+06	41.88	93.9

3.3 *Surface analysis*

The surfaces of the specimens were characterized by scanning electron microscopy (SEM). Figure 4 displays surface morphology of the samples after the immersion in the seawater. SEM micrographs clearly show the existence of a porous and precipitate layer on the coated specimen. The specimen without inhibitor and contained lower amount of the inhibitor (2 g and 4 g) presented a wide porous film and damaged surface. The SEM micrograph depicted that cracks and pits were found on the surface of the coated specimen, which confirms the aggressiveness of seawater in attacking the surface. The damage appearance of coated specimen reduces as the amount of tannin in the paint increased. The specimen with 6 g of TZn showed different kind of patterns on the surface which could be attributed to high inhibition effect of the tannin compared to others. Figure 4d, shows much smoother surface image and it explains the higher amount of TZn in the paint provide higher protection surface. Thus, protective properties of paints over the mild steel increase as the amount of tannin in the paint increases.

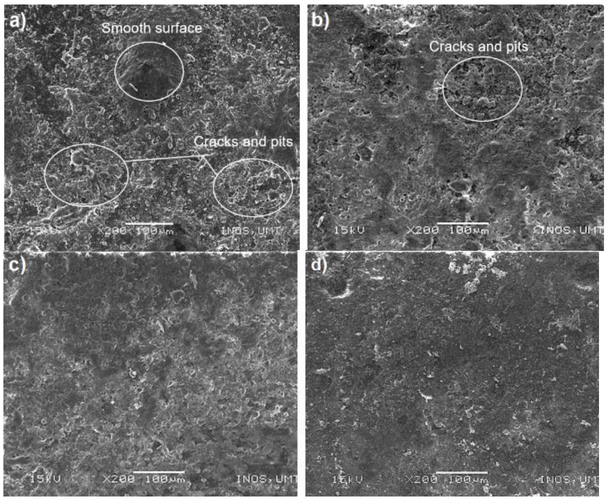

Figure 4. SEM micrographs of coated mild steel (a) paint without TZn (control), paint with (b) 2 g, (c) 4 g, (d) 6 g of TZn, after immersing the specimens in seawater in laboratory.

4. Conclusion

Modified epoxy paint with eco-friendly pigment from mangrove tannins was applied on mild steel specimens. The effect of the mangrove tannins towards the corrosion activities was investigated. The weight loss and electrochemical measurement indicated that the tannin reduced the weight loss of mild steel and increased the corrosion resistance of mild steel. The inhibition efficiency is increased until 93.9% at 6 g of TZn. The reduction in the deterioration of treated mild steel was successfully observed through the surface analysis.

Acknowledgement

This research was financially support by Universiti Teknologi Malaysia under research grant (Q.K130000.2643.14J65).

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