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Effect of mangrove bark condensed tannins (*Rhizophora apiculata*) as corrosion inhibitor for mild steel in simulated splash zone

W.B. Wan Nik [1,*], H. M. Hajar [1], M.S. Noor Idora [1], M.J. Suriani [1], A. Yabuki [2]

[1]*School of Ocean Engineering, University Malaysia Terengganu –Terengganu, Malaysia*
[2]*Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527, Japan*

Abstract: This study examined the effect of mangrove bark condensed tannins in epoxy paint for mild steel on corrosion resistance to simulate splash zone at room temperature. The weight loss, potentiodynamic polarization (PP) and electrochemical impedance spectroscopy (EIS) techniques revealed that the tannin lowered the corrosion rate of the mild steel. Through PP measurement, the corrosion rate for paint 2 g of tannin shown the corrosion rate is 0.00097 mm/year while paint with 6 g of tannin shown reading of corrosion rate is 0.00064 mm/year. The rate of corrosion of mild steel decreases as the amount of tannin in the paint increases. The results indicate that the mangrove bark condensed has potential as corrosion inhibitor for mild steel.

Key words: Corrosion; Electrochemical impedance spectroscopy (EIS); Potentiodynamic Polarization (PP)

1. Introduction

Corrosion is an electrochemical reaction based on universal laws of nature. All metallic structure can corrode (Shokry, 2009). This corrosion will directly destroy the original structure of the material as well as a high cost to repair the condition of the material to its original form. The existing of inhibitor can interrupt the chemical reaction between metals that can reduce the corrosion rate. Raja & Sethuraman (2008) said that inhibitors can be added to many systems. The use of inhibitors for the control of corrosion for metals and alloys which are in contact with aggressive environment is an accepted practice (Ameer and Fekry, 2011).

Inhibitor functions by absorption of ions or molecules onto metal surface. Plant extracts are low-cost and biodegradable, and so the study of plant extracts as corrosion inhibitors is an important scientific research field due to both economic and environmental benefits (Li et al., 2012).

Most of construction materials involve metals. The properties of the metals slowly destroyed due to the environment and lead to the higher cost of the maintenance.

Mild steel is the most versatile, least expensive and widely used engineering material which has found extensive application in various industries. However, the corrosion resistance of mild steel is relatively limited. This causes many corrosion problems to be arising in the maritime industries (Wan Nik et al., 2011). For an example, this issue has been established as the predominant factor which causes deterioration of construction structures especially in the coastal marine environment (Divyasree, 2014).

Metals Handbook [1990] had studied the super alloys reveal an outstanding strength and also surface stability (Singh & Manna, 2015). In addition, many metal and alloy which are used in difference human activities are susceptible to different mechanism of corrosion due to their exposure of difference corrosive media. Among these, mild steel is a very important structural material (Yaro et al., 2013).

Tannins, a class of natural, non-toxic, biodegradable organic compounds has been proposed to be a potential solution to this problem. Due to the currently imposed environmental requirements for eco-friendly corrosion inhibitors, there is a growing interest in the use of natural products such as leaves, seeds or bark extracts to get tannin (Shah et al., 2013).

The aim of the research is to investigate the corrosion performance on mild steel which coated with epoxy paint containing different amount of mangrove bark condensed tannin and being exposed to the splash zone in salt spray test. Therefore, in the present study, the coated mild steels with and without tannin were studied using potentiodynamic polarization, electrochemical impedance spectroscopy, weight loss and surface morphology analysis.

2. Methodology

2.1. Material preparation

* Corresponding Author.

In this study, mild steel grade of SS400 has been chosen. The specimens were cut into 25mm x 25mm x 4mm coupons and ground with wire cup brushes. Finally, after cleaning with thinner and drying with a blower, the specimens were then coated with epoxy paint, Paralux P268HS from Kansai Paint Co., Ltd. There are 5 types of specimens which are bare metal, paint 1 (paint without tannin), paint 2, 3, and 4. The paint was dilute with 2, 4, and 6 gram of tannin. The experiment was conducted for 40 days.

2.2. Salt spray test

The specimen were exposed to the salt mist and left in the chamber of salt spray cabin for 40 days. This test were conducted according to the Standard Salt Spray testing, ASTM B117.

2.3. Weight loss measurement

Before exposure to the salt spray test, the specimens were weighed to obtain initial weight (W_i). The corroded specimens were removed by immersing in nitric acid for 2-3 minutes and cleaned with distilled water, dried and weighed again in order to obtain the final weight (W_f). The experiment was conducted in fume cupboard at room temperature.

2.4. Electrochemical measurement

For electrochemical measurement, the Auto lab software was used. This device is connected to the computer to get the data. Two measurements which are General Purpose Electrochemical System (GPES) and Frequency Response Analyzer (FRA) were used for data analyzing. For potentiodynamic polarization (PP), the exposed area of the metal is 2.34cm2 which was immersed in the test solution (sea water) for measurement. The scanning rate 0.0101Vs-1 was set and the electrode potential was automatically changed from -0.5mV to +0.5mV to get the potential curve and potentiodynamic current. The output graph contains corrosion current (I_{corr}), corrosion potential (E_{corr}), anodic Tafel slope (ba), cathodic Tafel slope (bc) from the intersection of the linear anodic and cathodic branches of the PC as Tafel plots.

2.5. Scanning electron microscope

Scanning electron microscope was used to observe the surface morphology analysis of specimen at different amount of mangrove bark condensed tannin extract after the exposure test.

3. Result and discussion

3.1. Fourier transform infrared (FTIR)

Mangrove condensed bark extract contained catechin which is anti-oxidant that can act to inhibit oxidation molecules which can damage structure of metal. This is the main components which can be found in catechin structure. For instance, the main components can be found in mangrove extract are phenols O-H, esters C-O and alkenes C=C.

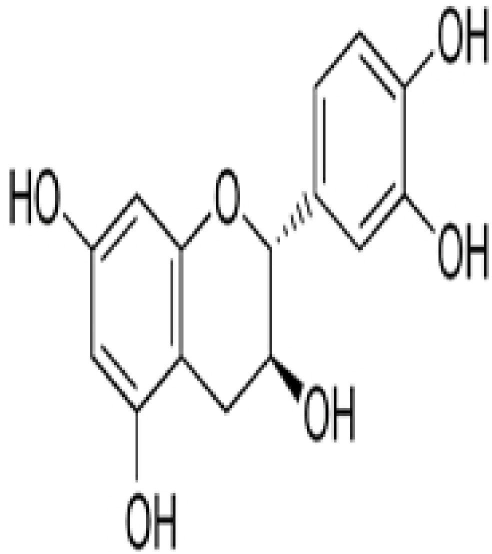

Fig. 1: Catechin molecular structure

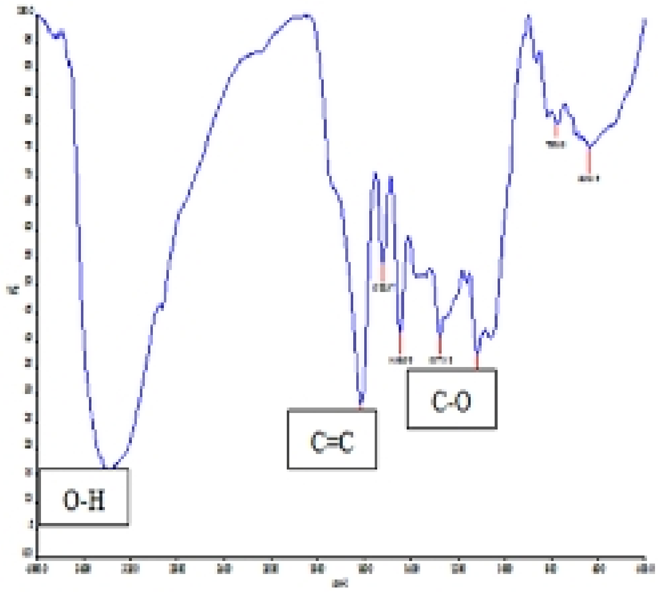

Fig. 2: IR Spectra for mangrove bark extraction by using Fourier Transform Infrared Spectroscopy (FTIR)

3.2. Weight loss measurement

Mild steel is one of the types of steel that have low copper component which is not strong and can be greatly influence their corrosion behavior in aggressive medium. The specimen was taken out every 15 days to investigate the weight loss in period of 40 days.

Fig. 3 illustrates the weight loss of coated mild steel in absence and presence of tannin. Increasing amount of mangrove bark tannin in the paint lead to decrease the weight loss specimen due to protective performance of mangrove bark tannin.

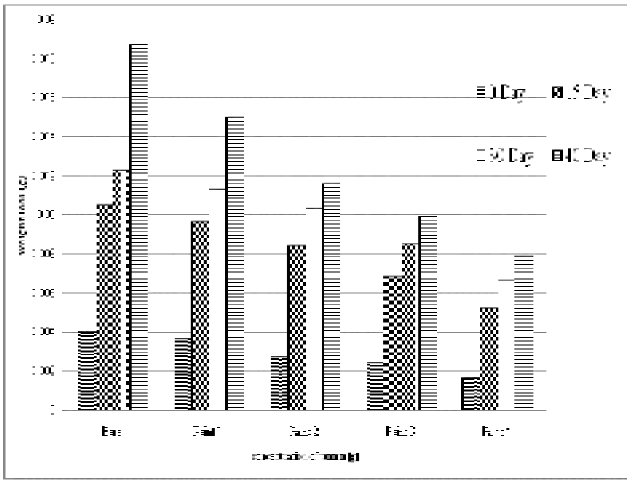

Fig. 3: Weight loss versus concentration of tannin

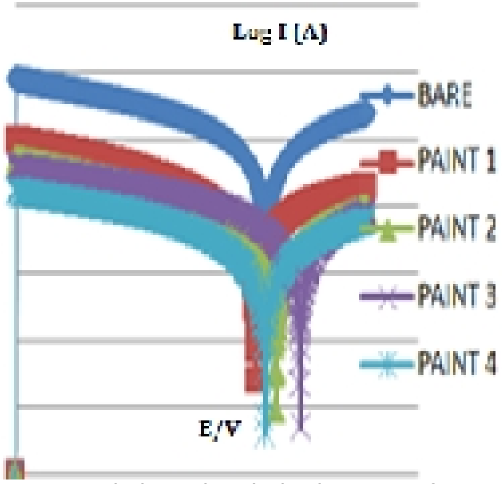

Fig. 4: Potentiodynamic polarization curves for 40 days exposed splash zone

3.3. Potentiodynamic polarization scan

From Fig. 4, the results show that the values of corrosion potential, E_{corr}, shifts to negative downward region as the concentration of mangrove condensed tannin extract becomes lower. For paint 1, the value of corrosion potential, E_{corr} is more negative compare to paint 4. The metal becomes more electronegative and it shows that the metal is becoming more anodic where high corrosion rate occurs. The low value of corrosion potential (E_{corr}) indicates higher corrosion rate. The corrosion potential (E_{corr}) is decrease as lowering the concentration.

Table 1 shows the value of anodic Tafel Slope (b_a), cathodic Tafel Slope (b_c) which markedly changed in the presence of mangrove condensed tannin. The result reflects the effect on both anodic and cathodic direction. Most commonly, corrosion inhibitors are classified as anodic, cathodic or mixed according to their influence on the electrochemical reaction involving metal, and their environment. Therefore, it could be concluded that mangrove act as mixed inhibitor.

Table 1: The electrochemical parameters of mild steel in simulated splash zone for 40 days

Paint type	I_{corr}, µA	b_a, V/dec	$-b_c$, V/dec	E_{corr} Mv	CR mm/year
Bare	7.47E-06	0.022	0.022	-0.615	0.03700
Paint 1	4.98E-07	0.019	0.015	-0.628	0.00250
Paint 2	4.78E-06	0.014	0.014	-0.604	0.00097
Paint 3	5.89E-06	0.013	0.013	-0.576	0.00097
Paint 4	7.12E-06	0.016	0.018	-0.617	0.00064

Addition of inhibitor increases the polarization resistance, R_p and decreases the corrosion rate of mild steel. Higher values of corrosion rate are due to the thin layer formed on metal surface to protect the metal from corrosion. The values of corrosion current density, I_{corr} decreased with increasing amount of mangrove condensed tannin in the paint.

3.4. Electro impedance spectroscopy (EIS)

The data is presented in the form of Nyquist plots. The x-axis indicates real impedance (Z') while the y-axis indicates imaginary impedance (-Z"). Fig. 5 shows size of semicircle decreases with decreasing inhibitor concentration and it indicates a high corrosion rate. From Fig. 5, small semicircle form shown the coupons becomes more active and high corrosion rate occurred indirectly.

Potential resistance (R_p) decrease and increase of double layer capacitance (C_{dl}) contributes to higher corrosion rate. Hence, the absence of the inhibitor decreases the potential resistance (R_p) and increases the double layer capacitance (C_{dl}). The values of the charge transfer resistance and double layer capacitance is showed in Table 2.

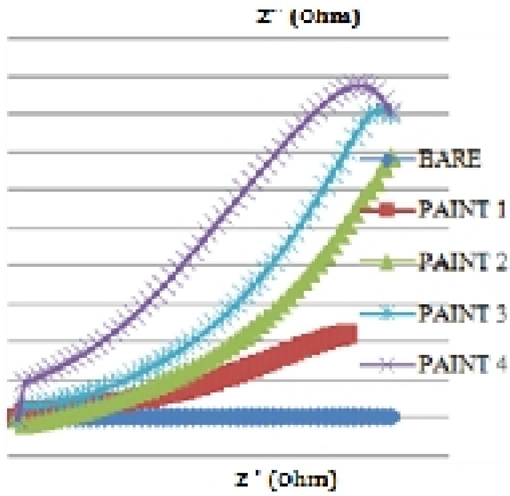

Fig. 5: Nyquist plot of coated mild steel for 40 days exposed in simulated splash zone

Table 2: R_p and C_{dl} values of coated mild steel in seawater obtained using impedance method

Type of paint	R_p (Ω)	C_{dl} (F)
Bare	4.4377	0.023756
Paint 1	5439.2	0.000293
Paint 2	10640	0.000150
Paint 3	11598	0.000137
Paint 4	33952	0.000047

3.5. Inhibition efficiency

The average values of inhibition efficiencies from electrochemical measurement are presents in Table 3. Inhibition efficiencies from values of polarization resistance (R_p) can be calculated where R_p' and R_p are the polarization resistance with and without the presence of inhibitor as Equation 1:

IE_{Rp} (%) = 100 (1- R_p/R_p') (1)

It can be seen from the table, the value of inhibition efficiency was increased as increasing of amount mangrove condensed tannin in the coated mild steel. It reveals the mangrove condensed tannin plays an important role in the corrosion resistance of mild steel. However, it should be noted that further research in this interesting phenomenon will be carried out in the near future in order to obtain the optimum amount of mangrove condensed tannin should be applied in the paint.

Table 3: Value of inhibition efficiencies, IE (%) for 40 days exposed in simulated splash zone

Type of paint	R_p	C_{dl}	IE(%)
Bare	4.4377	0.023756	-
Paint 1	5439.2	0.000293	-
Paint 2	10640	0.000150	48.88
Paint 3	11598	0.000137	53.10
Paint 4	33952	0.000047	83.97

3.6. Scanning electron microscope (SEM)

Scanning electron microscope (SEM) surface of mild steel after conducting electrochemical test in the absence and presence of mangrove extract are shown in Fig. 6 and 7 after 40 days exposed to splash zone in sea water. The analysis of SEM confirms the formation of precipitate of inhibitor on metal surface.

Fig. 6 shows the mild steel without the mangrove bark condensed tannin was observed. The surface was very rough and severely damage in the absent of the inhibitor while Fig. 7 shows the mild steel with presence mangrove bark tannin. The surface (Fig. 7) transformed into smoother, more uniform deposits in the presence of the mangrove bark tannin. Both Fig. 6 and 7 was compared at the same magnification and it was observed that the mangrove tannin extract more effective when its concentration increased.

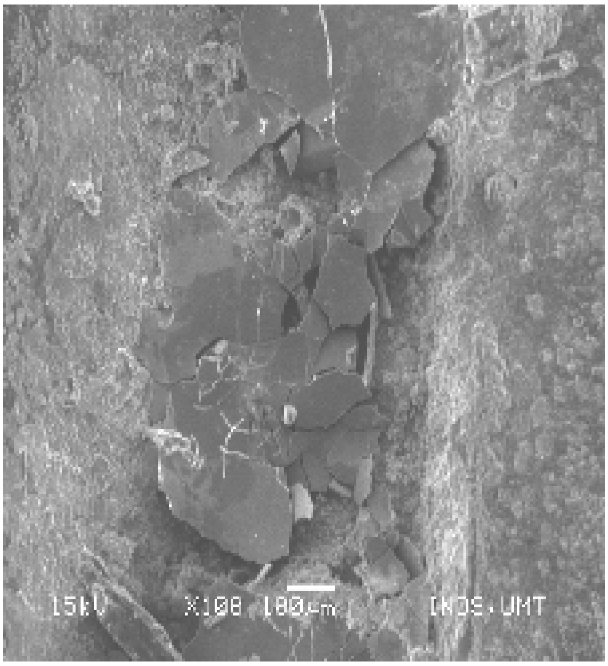

Fig 6: SEM micrographs of the surface of coated mild steel in simulated splash zone (without mangrove condensed tannin)

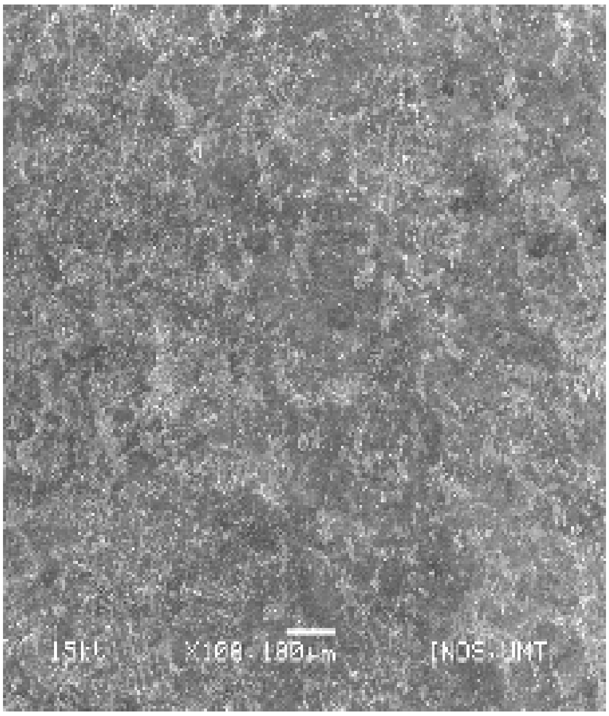

Fig 7: SEM micrographs of the surface of coated mild steel in simulated splash zone (with mangrove condensed tannin)

4. Conclusion

Mangrove condensed tannin was used as natural inhibitor to replace the synthetic inhibitor. The value of polarization potential resistance (R_p) decreasing with low protection of coated mild steel as there is presence of mangrove extract. The formation of thin film on metal surface at low concentration caused the low resistance polarization and increases the double layer capacitance (C_{dl}). Addition of inhibitor reduced the corrosion rate of coated mild steel. Catechin was found as the main component of mangrove extract that was analyzed by using FTIR. As a conclusion, mangrove bark can be used as natural inhibitor to replace the synthetic inhibitor.

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