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The Performance of Bee Wax Propolis Inhibitor on the Ductile Cast Iron (DCI) in Saline and Acidic Environment

Femiana Gapsari¹, Hastono Wijaya¹, Andoko², Agus Suprpto³

Abstract – The Bee Wax Propolis (BWP) has an inhibition effect on the corrosion of Ductile Casting Iron (DCI). This effect has been observed in 3.5% NaCl and 1M H₂SO₄ solution. FTIR spectroscopy, HPLC, and electrochemical measurement have been used to examine the performance of BWP. The inhibition efficiency increases with the addition of BWP inhibitor both in 3.5% NaCl and 1M H₂SO₄ solution. Electrochemical studies have revealed that the BWP has acted as a mixed-type inhibitor. The surface morphologies of the DCI specimens have been observed by optical microscopy. Based on polarization method, the inhibition efficiency of BWP in 3.5% NaCl and 1M H₂SO₄ solution are 99.97% and 49.82 %, respectively. The EIS test has also showed that the inhibition efficiency of BWP in 3.5% NaCl and 1M H₂SO₄ solution is 79.37% and 22.3%, respectively. **Copyright © 2019 Praise Worthy Prize S.r.l. - All rights reserved.**

Keywords: BWP, Corrosion, DCI, Inhibition, Mixed Type Inhibitor

Nomenclature

CR	Corrosion rate, [mmpy]
E_{corr}	Corrosion potential, [V]
I_{corr}	Corrosion current density of absence inhibitor, [A/cm ²]
$I_{corr(i)}$	Corrosion current density of presence inhibitor, [A/cm ²]
IE	Inhibition efficiency, [%]
T	Temperature, [K]
β_a	Cathodic tafel slopes, [V/dec]
β_c	Anodictafel slopes, [V/dec]
ASTM ads	The American Society for Testing and Materials Adsorption
NaCl	Sodium Chloride
Cdl	Capacitance double layer
CE	Counter Electrode
DCI	Ductile Cast Iron
FEI	Field Electron and Ion
FTIR	Fourier Transform Infrared
H ₂ SO ₄	Sulphuric Acid
OCP	Open Circuit Potential
R_{ct}	The charge transfer resistance of the specimens immersed in the solution without inhibitor
$R_{ct(i)}$	Charge transfer resistance of the solution containing an inhibitor
RE	Reference Electrode
OM	Optical Microscope
WE	Working Electrode

I. Introduction

Ductile Cast Iron (DCI) is a ferrous metal, which is in the group with cast iron [1]. DCI is also well known as nodular cast iron [2]. DCI has strong and ductile

properties and a good machinability. Its carbon structure is nodular graphite which is formed by the addition of Mg and Ce. The addition of Mg and Ce can decrease the sulfur content cast iron. In addition, the high content of those alloys can change the graphite shape to a nodular shape. However, if its percentage is low, graphite will have flake shape. Si also plays a role as graphite stabilizer in the formation of graphite shape in DCI.

Another factor that affects the formation of DCI is carbon equivalent (CE); it is the percentage value of carbon, silicon, and phosphor (%C+1/3(%Si+%P)) [1].

DCI has superior properties for design and manufacture compared to steel. Gears, camshafts, connecting rods, crankshafts, front wheel spindle supports and truck axles are some of the application areas of ductile iron in automotive industry [3]. As known, these machine parts and many others are often subjected to fluctuating loads in service [2]. Corrosion behavior of metals in aqueous solutions is usually caused by dissolved salt and oxygen [4]. The characteristic of cast iron corrosion is strongly influenced by two anions. Both of them are chloride and sulfate ions [5]. Cast Iron in sulfuric acid is more corrosive at room temperature than at higher temperatures. The low corrosion rate often found for cast iron in hot concentrated sulphuric acid is due to a passivation of the cast iron [6]. The corrosion resistance of DCI is formed with the formation of the passive layer from silica oxide on the metal surface.

Some studies control corrosion in DCI by using inhibitors. Some of the inhibitors that have been used are ethanolamines [7], [8], NaNO₂ [8]. Previous studies have discussed that the inhibitor used in DCI are inorganic and mixed inhibitors. For this reason, this research has tried to use BWP extract as a corrosion inhibitor of DCI metal.

The application of organic inhibitor is well known for

protecting the metal from corrosion. The previous studies have shown that Bee Wax Propolis (BWP) has a good performance as an inhibitor whether in acid (sulfur and hydrochloric acid), seawater (3.5% NaCl) an environment [9]-[13]. Another name of Bee wax is Cera Flava (CF).

This inhibitor is produced from the waste of honeybee comb, which has a wax contain. There is still lack of study that uses bee wax propolis as a corrosion inhibitor.

Hence, it is proposed to observe the inhibition of BWP extract in the NaCl and H₂SO₄ solution for protecting DCI from corrosion.

Section II describes the materials and the methods of how the preparation of DCI has been used. The characteristics, the identification of BWP and the parameter of corrosion test with electrochemical method have been used. Section III provides the results, the discussion of the study, the correlation among the tests conducted and the supporting data of the study. Next, Conclusion of the study is presented in Section IV.

II. Materials and Method

II.1. Materials

The DCI specimen is the result of the casting process.

The chemical composition of DCI is presented in Table I. The dimension of cylinder specimen is 4.55 cm in length with the diameter of 0.63 cm. The specimens have been mounted and then covered using epoxy resin, with an uncovered area of 1 cm² as exposed area. Before they have been tested, the specimen surfaces have been polished using SiC paper grade 400 to 2000.

TABLE I
CHEMICAL COMPOSITION (% WT.) OF DCI

Element	Fe	Si	C	S	P	Mn	Cr
%wt.	93.98	2.37	3.54	0.025	0.03	0.32	0.02

II.2. Inhibitor Characterization

The inhibitor characterization is based on the previous study. BWP has been extracted according to the liquid-liquid method. The chemical grafting of bee wax propolis has been characterized by Fourier Transform Infra-Red (FTIR, Shimadzu IR Prestige -21) spectroscopy and High Performance Liquid Chromatography (HPLC). From the FTIR and HPLC characterization, it is shown that the BWP inhibitor has O-H aromatic functional group (flavonoid) and quercetin compound [9].

II.3. Electrochemical and Corrosion Tests

ASTM G-31 standard has been used as the reference method for this measurement. One batch of NaCl 3.5%wt. and 1M H₂SO₄ solution and other batches adding inhibitor BWP 2000 ppm have been prepared.

The concentration of bee wax propolis inhibitor of 2000 ppm based on previous studies [9]-[14] has been chosen. The best efficiency of BWP inhibitor has been achieved at a concentration of 2000 ppm. The

electrochemical test has been done at room temperature 298 K. The electrochemical properties have been considered by potentiodynamic polarization test and electrochemical impedance spectroscopy (EIS) using Autolab PGSTAT 128N. A three-electrode cell has been used for electrochemical measurement which consists of the as- prepared specimen, platinum rod and Ag/AgCl (KCl 3M) electrode as working electrode (WE), a counter electrode (CE), and a reference electrode (RE), respectively. The test has been recorded after immersion for 30 minutes. Then, the polarization curve has been plotted by sweeping the applied potential from -1V to +1V with respect to OCP at a scan rate of 0.001 V/s. The inhibition efficiency can be calculated with Equation (1) [9], [15], [16]:

$$IE (\%) = \frac{I_{corr} - I_{corr(i)}}{I_{corr}} \times 100 \quad (1)$$

where I_{corr} is corrosion current density in blank solution (i.e 3.5% NaCl and 1M H₂SO₄) and $I_{corr(i)}$ is current density in 3.5%wt. NaCl and 1M H₂SO₄ solutions with inhibitor addition. The EIS tests have been carried out in the frequency range of 1000 to 1 Hz with AC amplitude of 15 mV at OCP. Then the inhibition efficiency has been calculated as follows [4], [17]:

$$IE (\%) = \frac{R_{ct(i)} - R_{ct}}{R_{ct(i)}} \times 100 \quad (2)$$

Here, R_{ct} is the charge transfer resistance of the specimens immersed in the solution without inhibitor, and $R_{ct(i)}$ is charge transfer resistance of the solution containing an inhibitor.

II.4. Optical Microscopy (OM)

Surface specimens have been analyzed using OM. All specimens have been immersed in 3.5%wt.NaCl and 1M H₂SO₄solutions. Magnification is taken at 400×. The lenses used are Tamron SD macro lens.

III. Result and Discussion

III.1. Potentiodynamic Polarization Measurement

Fig. 1 shows the potentiodynamic polarization curve of specimens tested in 3.5%wt. NaCl and 1 M H₂SO₄ solution. The curve with black color is the specimen without inhibitor, while the curve with the red color is a specimen with inhibitor. The electrochemical parameters obtained from polarization curves are presented in Table II. Based on the previous study, it is known that the optimum BWP addition at 2000 ppm on 304SS [9]-[11], API 65X L [12] in various solutions. The polarization curves obtained have been extrapolated to calculate corrosion parameters such as I_{corr} , E_{corr} , βa , and βc [18].

The corrosion rate of blank specimen in sulfuric acid solution is greater than in sodium chloride.

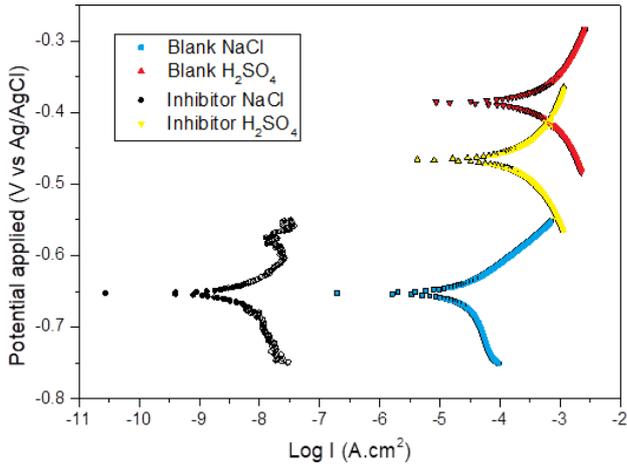


Fig. 1. Polarization curve of the DCI

TABLE II
SPECIMENS POLARIZATION PARAMETERS

Media	System	β_a (V/dec)	β_c (V/dec)	E_{corr} (V)	I_{corr} (A/cm ²)	Corrosion rate (mm/year)	IE (%)
NaCl	Blank	0.258	0.086	-0.652	4.22×10^{-5}	0.4703	0
	Inhibitor 3.5% 2000ppm	-0.645	0.072	-0.653	1.15×10^{-8}	0.00013	99.97
H ₂ SO ₄	Blank	0.728	0.657	-0.466	1.15×10^{-3}	16.85	0
	Inhibitor 1M 2000ppm	0.092	0.081	-0.388	3.88×10^{-4}	4.32	74.36

The E_{corr} of blank specimen that has been immersed in 3.5% NaCl is about -0.652 V vs. Ag/AgCl with a corrosion current density (I_{corr}) of about 4.22×10^{-5} A/cm².

It is seen that the E_{corr} values do not change much within inhibitor addition of 2000 ppm; the average value is -0.6525 V. In addition, it is also observed that with the present of inhibitor the curve shifts to lower I_{corr} (1.15×10^{-8} A/cm²). Both anodic and cathodic Tafel slopes have changed by incorporation of BWP inhibitor to the system. In the cases of the β_c and β_a values, their absolute value of β_a , larger than β_c (Table II), suggests that the anode is more polarized. This is due to type other BWP inhibitor, which acts like kind of mixed type inhibitor [9]. The performance of BWP inhibitor for protection DCI in 1M H₂SO₄ is also observed. DCI corrosion rate in 1M H₂SO₄ solution is greater than in 3.5% NaCl solution. Fig. 1 shows that the addition of BWP to the blank solutions (1M H₂SO₄) causes the corrosion potential (E_{corr}) shifts in a positive direction as shown in Table II. Electrons in solutions polarize DCI to the anode. The negative molecule of quercetine (the main compound of BWP) [9] causes the reduction of the current density of the oxidation process, so, the density of corrosion current (I_{corr}) decreases. Tafel plots in H₂SO₄ show the similar trend with the plot in NaCl media. The E_{corr} values shift to potentials that are more positive from -0.466 V to -0.388 V, with a remarkable decrease of I_{corr} (7.58×10^{-4} A/cm²). The noble shift of E_{corr} accompanying with the decrease of I_{corr} , suggests that BWP inhibitor can form the protective layer over the DCI. The β_c and β_a values are similar to each other ($\beta_c=0.154$ V/dec and $\beta_a= 0.202$ V/dec), but the value of

β_a is larger. This evidence shows the same condition with the measurement in NaCl solution. Table II also shows the percentage inhibition efficiency (IE) values. It is seen that adding of BWP inhibitor, the IE values increase dramatically. In previous studies, the BWP inhibitor would form physical adsorption on the surface of tested specimen [9]-[11]. In the NaCl environment, the interaction molecule of BWP just involves Cl⁻ anions, which have positively charged with the metal surface via electrostatic interaction at the metal or electrolyte interface [19]. Meanwhile in an acidic environment, in this case, in H₂SO₄ solution, the π - electron interaction from protonated species is not stable enough [20].

Therefore, the IE of BWP in the saline environment (99.97%) is higher than in the acidic one (74.36%). The adsorption process of molecules in quercetin can form a protective layer and it is a type of physical adsorption [9], [10]. The molecules in the inhibitor are physically bounded to a metal surface molecule. This type of adsorption is multilayer, since each molecule forms a layer above the previous layer, with the coating suitable for the inhibitor concentration.

IV. EIS Measurement

The corrosion behavior of DCI in the saline and acidic solution in absence of the BWP inhibitor has also been investigated by EIS. The Nyquist curve is shown in Fig. 2 and Table III. The EIS results have been simulated using the Randles equivalent circuit shown in Fig. 3. The circuit consists of the solution resistance (R_s), the charge-transfer resistance (R_{ct}) and the capacitance double layer (Cdl). It is clear that the addition of the inhibitor has caused a change in the impedance of the DCI. The impedance of the inhibited DCI increases with respect to the addition of the inhibitor; this indicates that IE also increases (79.37% and 22.37%). The IE values obtained from EIS measurements have a good agreement with polarization results. The Nyquist semicircles have not been perfect; the diameter of the capacitive loop in the form of a depressed semicircle (Fig. 2) indicates that the metal has a layer packed on the surface.

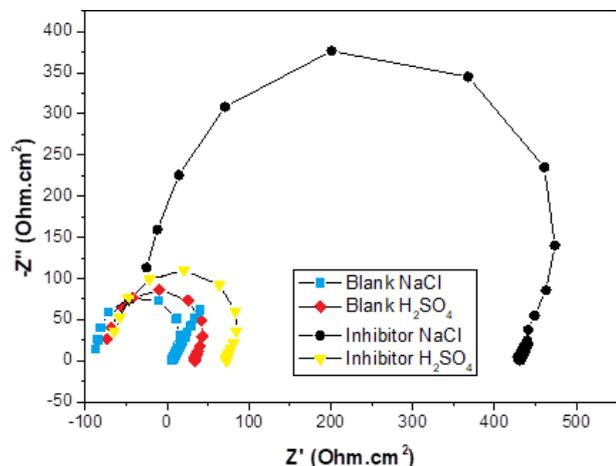


Fig. 2. Nyquist curve of DCI

TABLE III
EIS PARAMETERS OF SPECIMENS

Media	System	Cdl (nF)	Rs (Ω)	Rct (Ω)	IE (%)
NaCl 3.5%	Blank	6.206	-78.083	85.891	0
	Inhibitor 2000 ppm	1.2335	21.755	416.4	79.37
1 M H ₂ SO ₄	Blank	4.7301	-63.882	99.204	0
	Inhibitor 2000 ppm	3.5967	25.172	127.8	22.38

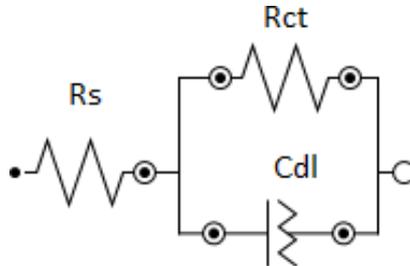


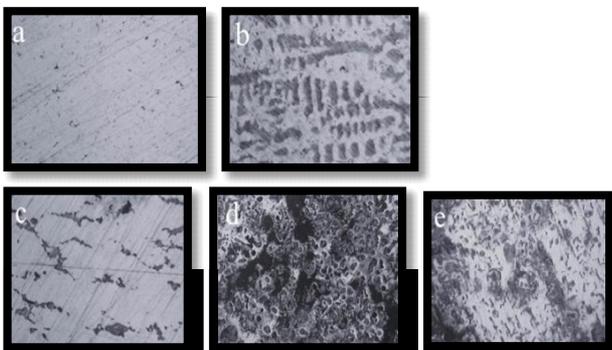
Fig. 3. Equivalent circuit model used for the EIS measurements

The diameter of the semicircles has increased with the addition of inhibitor and the *Rct* value has done, too. A large *Rct* assigns that the corrosion occurs in the slow process. The decrease of *Cdl* values is caused by the adsorption of the inhibitor molecules at the metal or solution interface increase [21].

V. OM Result

The effect of adding inhibitor into corrosion system is investigated by an optical microscope (OM). Figs. 4(b) and (d) show that the DCI surfaces have been damaged when immersed in the 3.5 % NaCl and 1M H₂SO₄ without adding inhibitor. The metal is dissolute in the corrosive solution. In Figs. 4(c) and (e), it is indicated that the dissolution of the DCI has been reduced and the DCI's surfaces have smoother appearing. It is seen that corrosion is higher than on other specimens' surface on DCI in H₂SO₄ without inhibitor. This is caused by the absorption of inhibitor molecules on the metal surface.

SpecimentH₂SO₄solution is darker compared to NaCl solution. This indicates that H₂SO₄ is more aggressive than NaCl. Surface analysis by OM has been in good agreement with the polarization and EIS techniques.



Figs 4. Topographies from DCI surface before immersion (a), without (b) and with (c) BWP inhibitor in 3.5% wt.NaCl, without (d) and with (e) BWP inhibitor in 1M H₂SO₄ in 200× zoom

VI. Conclusion

In this work, the corrosion inhibition performance of Bee Wax Propolis (BWP) extracts immersed in 3.5% NaCl and 1M H₂SO₄ solution have been investigated.

The BWP shows a good corrosion inhibitor for DCI in 3.5% NaCl. However, the performance of BWP inhibitor in sulphuric acid environment does not seem to work well. Polarization studies reveal that BWP also acts as a mixed-type inhibitor in DCI. The EIS study also has the same agreement with a polarization, which confirms that there is a formation of a protective layer on the DCI. The figure of OM supports the result of EIS and polarization measurement.

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