Anti-Corrosive Performances of Natural Products on Al-Mg-Si Alloy

R. Rosliza, and W. B. Wan Nik

***Abstract*—** The anti-corrosive performances of aluminum and its alloys is the subject of considerable technological importance due to the increased industrial applications of these materials. This paper reports the results of the linear polarization (LP) and electrochemical impedance spectroscopy (EIS) measurements on the corrosion inhibition of Al-Mg-Si alloy in seawater using natural products (natural honey, vanillin and tapioca starch) as an inhibitor. The results show that the anti-corrosive performances increases with the increasing of natural products concentration. The energy dispersive spectrometer (EDS) studies elucidated that the breakdowns of Al_2O_3 after exposed to seawater decreased with the presence of natural products. In all cases, the anti-corrosive performances can be given in the following increasing order: Natural honey < Vanillin < Tapioca starch.

***Keywords*—** Aluminum alloy, Corrosion inhibitors, Polarization, Adsorption.

I. Introduction

The demand for aluminum (Al) and its alloys are increasing year by year due to wide ranges of industrial applications such as construction, transportation, food, electric industries and are commonly used in marine applications as well. The most popular aluminum alloys for used in corrosive environments, such as seawater are the 5XXX and 6XXX series alloys. The 6XXX alloys contain Mg and Si as main alloying elements with others elements such as Cu and Mn for improving mechanical properties [1].

Corrosion inhibitors play a very important role in protecting engineering of metal materials and corrosion science, and in recent years, many new corrosion inhibitors are been developed [2]-[4]. Though many synthetic compounds showed good anticorrosive activity, most of them are highly toxic to both human beings and environment. The safety and environmental issues of corrosion inhibitors arisen in industries has always been a global concern.

Honey has recently reported as effective corrosion inhibitor for copper [5], carbon steel [6] and tin [7] in various solutions. However, no published information is available on these natural products as corrosion inhibitors for Al and its alloy in seawater. The aim of the present work is to compare the anti-corrosive performances of natural honey (NH), vanillin (VL) and tapioca starch (TS) on the corrosion inhibition of Al-Mg-Si alloy in seawater using LP and EIS measurements and to clarify their anti-corrosive performances.

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II. Materials and methods

A. Materials

The experiments were performed with Al-Mg-Si alloy (25 × 25 × 3 mm coupons) specimens with the following chemical composition (wt): Si (0.40%), Fe (0.7%), Cu (0.15%), Mn (0.15%), Mg (0.80%), Cr (0.04%), Zn (0.25%), Ti (0.15%) and Al (remainder). The samples were mechanically polished using 400, 500 and 600 emery papers and lubricated using distilled water. The polished samples were cleaned with acetone, washed using distilled water, dried in air and stored in moisture-free desiccators prior to use.

The test solution used for the investigation was seawater collected from Pantai Teluk Kalong, Kemaman, Terengganu (port area). The inhibitors used were NH, VL and TS with the concentration range from 200–1000 ppm. NH was collected freshly from the bee hive, meanwhile VL and TS were obtained from local market.

B. Methods

Al-Mg-Si alloy specimens for each concentration were immersed in a 100 mL beaker containing the respective solution for 30 minutes. All the electrochemical measurements were obtained using Autolab frequency response analyzer (FRA) coupled to an Autolab potentiostat connected to a computer. The. The LPR measurements were carried out from −10 mV to +10 mV vs. E_{corr} at scan rate of 1 mV s^{-1}. Impedance measurements were conducted over a frequency range of 5 x 10^5 Hz down to 5 x 10^{-3} Hz. The EDS spectra were used to determine the elements presence on the Al-Mg-Si alloy surface after 60 days exposure to the uninhibited and inhibited seawater.

III. Results

The values of R_p determined by LP method are summarized in Table I. Fig. 1 shows the inhibitor concentration of natural products versus the values of R_p for each studied inhibitor. The values of R_p and double layer capacitance, C_{dl} from EIS measurement for Al-Mg-Si alloy at various concentrations of NH, VL and TS are tabulated in Table I. The values of IE (%) from the PP, LPR and EIS tests are also shown in Table I.

Table II displays the percentage of passive film, Al_2O_3 obtained from the analysis of the EDS spectra.

TABLE I
THE ELECTROCHEMICAL PARAMETERS AND IE (%) FROM LP AND EIS OF AL-MG-SI ALLOY IN ABSENCE AND PRESENCE OF DIFFERENT CONCENTRATIONS OF NATURAL PRODUCTS

Inhibitor	c_{inh} (ppm)	LP R_p (kΩ cm^2)	LP IE (%)	EIS R_p (kΩ cm^2)	EIS C_{dl} (µF cm^{-2})	EIS IE (%)
Blank		11.71		11.76	23.98	
	200	34.78	66.34	33.1	8.11	66.18
	600	55.06	78.73	57.12	5.16	78.46
NH	1000	112.72	89.61	119.84	2.31	90.36
	200	35.28	66.81	39.04	7.06	70.55
	600	57.13	79.5	60.27	4.39	81.69
VL	1000	145.05	91.93	155.84	1.95	91.85
	200	41.29	71.64	40.73	7.3	69.56
	600	81.67	85.66	79.23	3.37	85.96
TS	1000	177	93.38	166.09	0.99	95.87

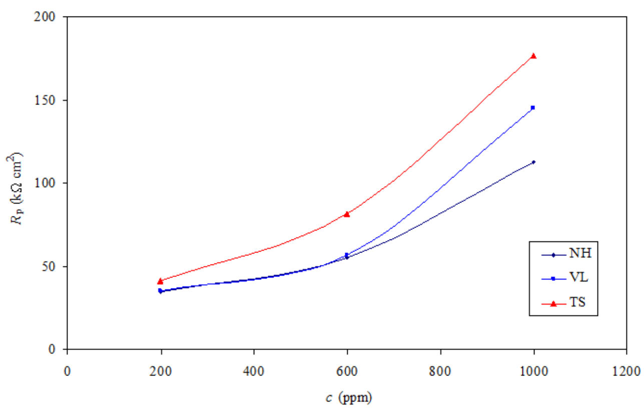

Fig. 1 R_p versus concentration of the studied inhibitors

IV. Discussion

A. Linear Polarization (LP)

The data in Table 1 shows that addition of the examined corrosion inhibitors causes increase in R_p of Al-Mg-Si alloy. A higher of R_p indicates the lower of the corrosion rate. A higher of R_p is directly proportional to a higher of the anti-corrosive performances. The values of R_p obtained by LP measurement were compared between the studied inhibitors. The inhibitor concentration of natural products was plotted against the values of R_p for each studied inhibitor (Fig. 2). The results show that the values of R_p after addition of inhibitor increase with the following sequence: NH < VL < TS.

A. Electrochemical Impedance Spectroscopy (EIS)

The results of EIS in Table I show that the R_p values increase with the addition of corrosion inhibitors when compared with those without corrosion inhibitor. Furthermore, the values of R_p are observed to increase with the increasing corrosion inhibitor concentration, which can be attributed to the formation of a protective over-layer at the metal surface. It becomes a barrier for the charge transfers.

The values of R_p for the alloy in inhibited solution with NH were enhanced up to 10 times higher as compared to that of the value of R_p in uninhibited solution. Meanwhile, VL and TS have shown better performance in improving the value of R_p for Al-Mg-Si alloy in studied aggressive solution, where the values were increased up to 13 and 14 times higher, respectively.

TABLE II
THE PERCENTAGE OF PASSIVE FILM, AL_2O_3 OBTAINED FROM THE ANALYSIS OF THE EDS SPECTRA.

Inhibitor	Concentration (ppm)	Compound Al_2O_3 (mass%)
Blank		48.28
NH	200	52.67
	600	60.86
	1000	75.22
VL	200	55.23
	600	65.96
	1000	80.21
TS	200	57.09
	600	67.57
	1000	85.96

Plain Al_2O_3 = 96.06%

It should be noted that while R_p values increase with the addition of corrosion inhibitor, the capacitance, C_{dl} values decrease indicating the formation of a surface film. Thus, effective corrosion resistance is associated with high R_p and low C_{dl} values [8]. Increase in R_p values and decrease in C_{dl} values by inhibitors are related to the increased degree of protection of Al-Mg-Si alloy in seawater. The capacitance decrease as the corrosion inhibitors coverage increases since the capacitance is inversely proportional to the distance between the charges. It can be concluded that the increasing order of the anti-corrosive performance toward corrosion on Al-Mg-Si alloy is NH < VL < TS.

B. Inhibition Efficiency

The calculation of the inhibition efficiency, IE (%) was as previously reported [8]. The data in Table I reveal that IE (%) for all studied inhibitors increase with the inhibitor concentrations ranges from 200 to 1000 ppm. It can be seen that the IE (%) for all measurements for the studied inhibitors obtained from the two different methods; LPR and EIS are in good agreement. In all cases, the increasing order of inhibition efficiency is: NH < VL < TS.

C. Anti-corrosive mechanism

Based on the surface observation in the current study and literature to date [9]-[11], the nature of surface film was proposed as shown in Fig. 2a. The protection mechanism after addition of these inhibitors is schematically shown in Fig. 2b.

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In the absence of inhibitors, the solution is in contact with the metal surface and the porous surface film. In the presence of inhibitors, the open locations in the porous layer are blocked due to precipitation of studied inhibitors.

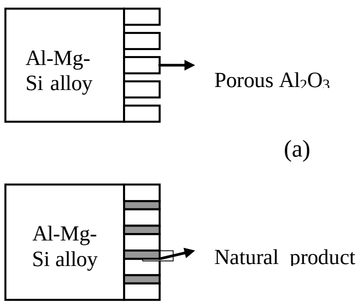

Fig. 2 Schematic diagrams of surface film (a) nature and (b) after the presence of inhibitors

The anti-corrosive mechanism of NH could be explained as follows: Fourier transform infrared (FTIR) spectrum in Fig. 3a demonstrates that honey is a mixture of various compounds containing carbon (C), oxygen (O), nitrogen (N) and sulphur (S) which all can be adsorbed on the corroded metal. The adsorption of NH onto the surface of Al-Mg-si alloy may take place through all these functional groups. The simultaneous adsorption of the four functional groups forces the natural honey molecule to be horizontally oriented at the on the surface of Al-Mg-Si alloy [10]. As the inhibitor concentration increases, the area of the metal surface covered by the inhibitor molecule also increases, leading to an increase in the IE. As previously reported by Et-Etre [5] and Rodojcic *et al*. [7], the adsorption of inhibitor molecules onto metal surface is due to the presence of oxygen, nitrogen and sulphur containing in NH.

The anti-corrosive mechanism of VL could be explained as follows: FTIR spectrum illustrate that VL is an aromatic aldehyde containing carbonyl, methoxy, and hydroxyl groups arranged around the aromatic ring (Fig. 3b). The adsorption of VL onto the surface of the Al-Mg-Si alloy may take place through all these functional groups. Similar to the findings reported previously [12], [13] the adsorption of vanillin mechanism is related to the presence of carbonyl, methoxy, and hydroxyl groups arranged around the aromatic ring in their molecular structures.

FTIR spectrum of TS (Fig. 3c) shows that TS is composed of mixture of two molecular entities (polysaccharides), a linear fraction, amylase and highly branched fraction, amylopectin. Both of them are polymers of glucose. Amylose is constituted by glucose monomer units joined to one another head to tail forming alpha-1, 4 linkages; these are linked with the ring oxygen atoms all on the same side. Amylopectin differs from amylase in that branching occurs, with an alpha-1, 6 linkages every 24–30 glucose monomer units. Amylopectin has phosphate groups attached to some hydroxyl group. The adsorption of TS on Al-Mg-Si alloy surface would take place through all these functional groups. As the concentration of corrosion inhibitor increases, the part of the metal surface covered by the corrosion inhibitor molecule also increases, leading to an increase in the IE.

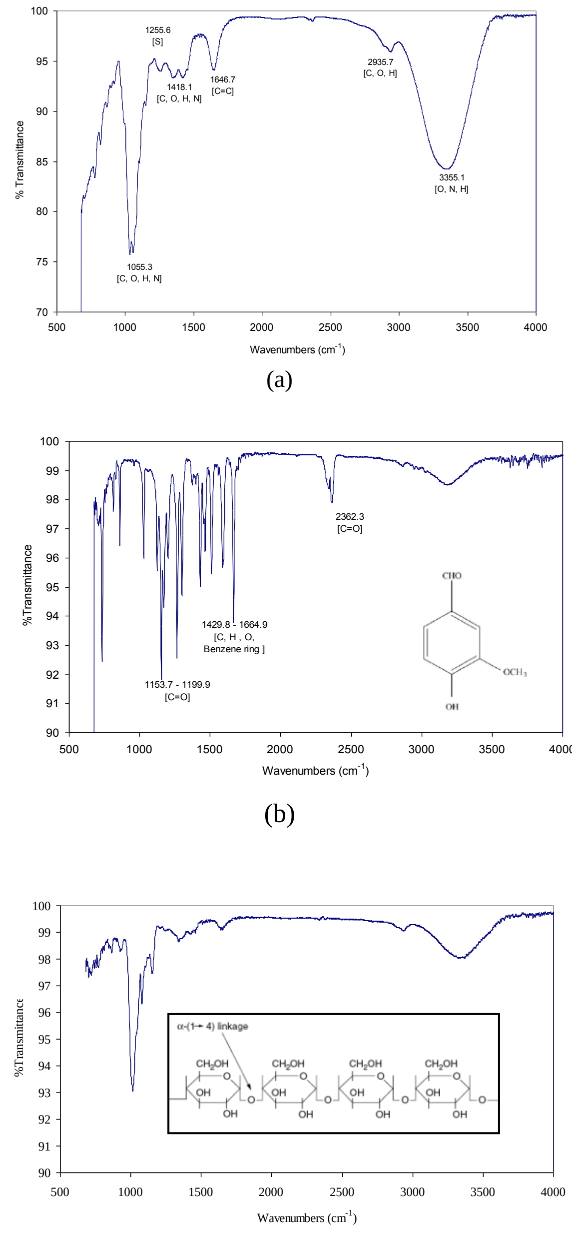

Fig. 3 FTIR spectrum of (a) NH, (b) VL and (c) TS

D.Energy Dispersive Spectrometer (EDS)

The EDS analysis of plain sample in Table II indicated that only Al and oxygen were detected, with ratio of about 2:3, which indicated that the passive film contained only Al_2O_3. The data show that plain surface of unexposed specimen consists of 96.06% Al_2O_3. The EDS analysis of exposed specimen indicated that 50% of passive film, Al_2O_3 was breakdown after exposed to seawater. The data also indicate that the breakdowns of Al_2O_3 percentage for three studied inhibitors were decreased with the increasing of inhibitor concentrations of NH, VL and TS; hence decreased the dissolution of Al-Mg-Si substrate. It means the NH, VL and TS acts as anti-corrosive film for Al-Mg-Si alloy from the aggressive solution. The protective film coverage is increased with the increasing of inhibitor concentration.

V. Conclusions

The anti-corrosive performances of some natural products on Al-Mg-Si alloy have been carried out at room temperature using seawater and the results indicate that NH, VL and TS performed very effectively anti-corrosive behavior for Al-Mg-Si alloy in seawater. The values of R_p increase with addition of inhibitor whilst, the values of C_{dl} decrease indicating the formation of a surface film. The EDS studies elucidated that the breakdowns of Al_2O_3 after exposed to seawater decreased with the presence of natural products. In all cases, the increasing order of the anti-corrosive performances is: NH < VL < TS.

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