Enhanced Corrosion Resistance of Aluminium Alloy Using Hybrid Sol-gel Coating

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Abstract

Aluminium (Al) alloy has excellent corrosion resistance due to the oxide layer films generated on its surface. The applications of this material, therefore, normally relate to the utilization under corrosive environments, such as, offshore and marine industries. However, the protective film could be damaged by chloride and fluoride ions, and alkalinity environment. This study aimed to improve the corrosion resistance property of Al alloy A5083 by coating with inorganic-organic hybrid films. The hybrid films were prepared by sol-gel method containing an inorganic precursor, Tetraethyl orthosilicate (TEOS), and organic precursors, namely Octyltriethoxysilane (OTES) and Poly (methyl methacrylate) (PMMA). The surface structure, water contact angle, corrosion resistance and weathering resistance of the hybrid films were examined. Surprisingly, the film formed of TEOS and OTES in the ratio of 80:20 and PMMA 40% (40P) by volume showed the best corrosion resistance, around 0.37 x 10^{-3} mm per year. The corrosion resistance test was done by potentiodynamic technique in 3.5 wt % NaCl. While, the TEOS and OTES film with PMMA 20% (20P) presented lower corrosion resistance around 0.53 x 10^{-3} mm per year but the condition of the film was more stable. The QUV weathering resistance test exhibited that the 20P film had no defects up to 14 days, while the 40P film showed damaged surfaces within 7 days. In summary, the hybrid films composed of TEOS and OTES in the ratio of 80:20 and PMMA 20%. by volume was suitable to coat on Al alloy A5083 to increase corrosion resistance for marine environment applications.

Keywords: Sol-gel, Corrosion, Aluminium alloy, Inorganic/organic hybrid film

1. Introduction

Aluminium (Al) alloy is one of the most important materials used in a broad range spectrum of applications such as architecture, electronic, packaging, engine, aerospace, etc. It is due to the outstanding properties, i.e., light weight, anticorrosive, shape ability, strength to weight and weld ability [1]. Among many kinds of Al alloy, Al alloy 5xxx is generally used for marine applications, such as offshore industries, aerospace and transportations due to high corrosive resistance in marine environment, medium hard, easy to hardening and welding applications [2], [3]. The anticorrosive property of Al alloy oxide is benefit from oxide protective layers occurring after Al alloy surfaces react with oxygen in environment. In addition, this passive film can heal itself when the film is damaged [3], [4]. However, the passive film can be destroyed under the alkaline environment containing chloride and fluoride ions [2], [5]. Recently, there is a report that the total cost of corrosion on metal products is around $2.5 trillion or 3.4% of the Global Gross Domestic Product [6]. This cost is not only materials but also cost for protective coating, repairing, inspection and discharge of hazard waste [7]. To prevent or retard the corrosion on aluminium alloy, painting, surface treatment, coating, electrochemical, CVD or PVD are applied [7]. Those techniques are still having some limitation, for instance, expensive, size limitation, and toxic waste. However, sol-gel method is simple, low cost, low temperature working range [3], [7].

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The inexpensive approach to protect Al alloy from corrosion is coating with inorganic substances which generates the excellence anticorrosion film with over 1 µm thickness. Nevertheless, the inorganic coating on Al alloy needs 400-800°C for heat treatment, and obtaining films is fragile [7]. Inorganic-organic hybrid films are more interesting since the hybrid films are more flexible, lower temperature for curing, chemical inertness, good adhesion on the Al alloy substrate. In addition, the hybrid film requires thickness lower than 1 µm [3], [7]. The preparation of inorganic-organic hybrid films usually uses TEOS as the inorganic precursor. It is because the reactions are facile and cheap [8]. Organic precursors typically employ alkoxysilanes, for examples, AEAPS (3-(2-Aminoethyl) aminopropyl trimethoxysilane) GPTMS (3-Glycidoxypropyl trimethoxysilane) MTMS (Methyl trimethoxysilane) since they are mild reactions and mild conditions [7]. In sol-gel reactions, TEOS provides SiO_2 network that links with organic precursors. The anticorrosion ability of the hybrid films depends on many factors, for instance, the inorganic to organic ratios, the water contents and organic precursors [3], [9]. The study of A.H. Najafabadi *et. al.* found that the ratio of TEOS to GPTMS at 70:30 resulted in the highest corrosion resistance 17 $k\Omega/cm^2$, but increasing GPTMS to 50-82% reduced the corrosion resistance to 2-9 $k\Omega/cm^2$. In addition, the hydrophilic property reduces the corrosion resistance [3]. V. Purcar *et al,* [10] studied the effects of organic precursors to the hydrolytic resistance property of inorganic-organic hybrid films. It was found the film comprised of TEOS/OTES produced the highest hydrolytic resistance comparing to TEOS/VTES, TEOS/iTES, TEOS/MTES films, due to the increase of higher number of hydrophobic chains. In addition, PMMA was used in hybrid films to improve the corrosion resistance and promote metals to the hybrid film adhesion [11].

Our previous work was the study on the effects of the type and amount of organic precursors, where AEAPS, AMOE, GPTMS, MTMS and OTES were tested, and the water ratio on the corrosion resistance of inorganic-organic hybrid films. It was found that the hybrid film contains TEOS to OTES with 80 to 20%v/v and TEOS to water ratio 1:6 by mole generated the best corrosion resistance for 0.78×10^{-3} mm a year with 103.09± 0.35° of contact angle [12]. The aim of this project was to improve the corrosion resistance of TEOS/OTES hybrid film by adding PMMA with different ratios. The hydrophobic property and surface morphology of the film were determined. The anticorrosion was investigated in 3.5 wt% NaCl solution and the weathering resistance was also examined.

2. Experimental

2.1 Materials

Al alloy A5083 in this study was a commercial grade with 2 mm thickness purchased from Atlas Steels Company, Australia. The chemical compositions of the Al alloy were 92.35-94.05% Al, 0.40% Si, 0.40% Fe, 0.10% Cu, 0.40-1.00% Mn, 4.00-4.90% Mg, 0.05-0.25% Cr, 0.25% Zn, 0.15% Ti and 0.20% trace elements. Tetraethyl orthosilicate (TEOS, 98%) and Octyltriethoxysilane (OTES, 97%) were bought from Acros Organics. Poly (methyl methacrylate) (PMMA, 20%) was purchased from Figma-Aldrich. Nitric acid (HNO_3, 65%) was supplied by Merck. Propanol was purchased from Carlo Erba Reagents.

2.2 Aluminium alloy preparation

Al alloy was cut into 2 x 4 cm dimension and then was polished with sand papers no. 600, 800 and 1,000, respectively. Then, it was brought to clean with detergent, sonicated for 30 min in acetone, then cleaned with DI water and dried at 110°C in the oven for 20 min.

2.3 Hybrid films coating

The inorganic-organic hybrid films were prepared via sol-gel method. Tetraethyl orthosilicate (TEOS) and Octyltriethoxysilane (OTES) were mixed with the ratio 80:20 by volume, respectively, for 15 minutes at 400 ppm. After that, added 2.3 mL of DI water and pH was adjusted to 2 with 65% HNO_3. The mixture was continuously stirred with magnetic stirrer for 15 minutes. Then, propanol was added for 47 mL, continuously stirred for 3.5 hour and left for 2 days at room temperature without stirring. Adding 20% (Poly (methyl methacrylate); PMMA) in acetone at 10, 20,30 and 40 %v/v to the mixture, which were named 10P, 20P, 30P, and 40P, respectively. Al alloy A5083 was coated by the fresh solution via dip coating with 100 rpm speed. Let the samples dried at room temperature, incubated in the oven at 60ºC for 1 hour and 130ºC for 1 hour. In addition, the hybrid film without PMMA adding (806TOT) was prepared with the same condition for comparison.

2.4 Measurements

The surface roughness (SR) and the structures of the films were examined with an Atomic Force Microscope (AFM), Nanosurf NaioAFM. The water contact angle (WCA) of the films was measured using Contact angle meter, Data Physics OCA 20LHT.

The corrosion resistance was carried out by potentiometer in 3.5wt% NaCl solution on biological science instruments. The sample worked as the anode with 1.286 cm^2 working area and saturated calomel electrode (SCE) was used as a reference electrode. The polarization curve was used for determination of E_{corr} (the corrosion potential) and i_{corr} (corrosion current density) as shown in Fig. 1.

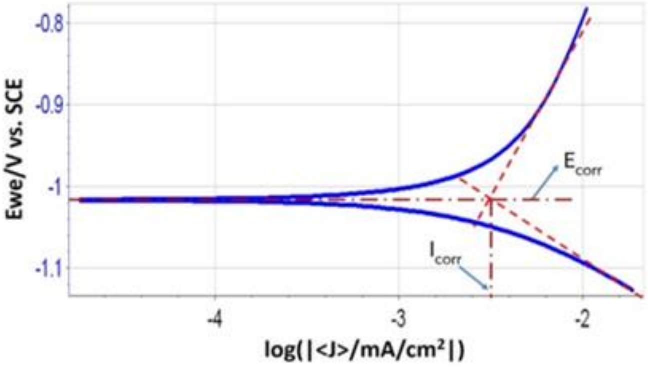


Fig. 1. Potentiodynamic polarization curves of Al A5083

The corrosion rate was calculated by using equation (1).

$$CR = K\frac{i_{corr}}{\rho}EW \qquad (1)$$

CR = corrosion rate (mm/year)
K = 3.27 x 10^{-3}
i_{corr}= current ($\mu A/cm^2$)

WE = 9.09 (equivalent weight of Al alloy A5083)
ρ = density of Al alloy A5083 (2.66 g/cm^3)

QUV accelerated weathering chamber (Q-LAB QUV/spray) was conducted to examine the weathering resistance of coated film. The testing condition was complied to ASTM D4587-11 with cycle No.4. The samples were irradiated with UVA lamp at 340 nm and 0.89 W/(m^2.nm) of intensity. The temperature was controlled in the cycles of 60±2.5°C for 8 h and 50±2.5°C for 4 hours. In this study, the samples coated with the hybrid films, 7 x 9 cm, were taken out at 7, 14, and 30 days. The microstructure of hybrid film morphology was scrutinized with Scanning Electron Microscopy (SEM) with a JEOL JSM-6610LV instrument.

3. Results and discussion

3.1 Surface Morphologies

WCA, surface appearance and SR of the coated and uncoated Al alloy A5083 with hybrid films were studied. The WCA of uncoated Al alloy A5083 (Al A5083) was compared to that of the Al alloy coated with TEOS/OTES film (806TOT) and coated with TEOS/OTES/PMMA in different ratios of PMMA (10P, 20P, 30P, and 40P) as shown in Fig.2. The bare Al alloy obtained the lowest WCA at 72.7° while the coated Al alloys had a higher WCA over 95°. The 806TOT showed 103.09° of the WCA but adding PMMA in TEOS/OTES film obtained a higher contact angle. The WCA of the TEOS/OTES/PMMA films increased with increasing the amount of PMMA. Mixing PMMA to TEOS/OTES film up to 20 %v/v resulted in the biggest WCA at 110.50°. On the other hand, loading PMMA more than 20 %v/v in the hybrid film resulted in a lower contact angle. At 30 and 40 %v/v loading of PMMA (30P and 40P, respectively) in TEOS/OTES film gave 102.82° and 99.93° WCA, respectively. Increasing of WCA was related to hydrophobic property since the hydrolysis reaction in sol-gel reactions was completed and obtained the dense hybrid network [11]. Then, the surfaces were prevented from water absorption [13], [14]. On the other hand, the higher or lower amount of PMMA brought to a lower WCA. This was because the decrease of WCA by 10%v/v of PMMA was due to the incompletion of polycondensation, however, adding PMMA over 20% rose up the amount of methoxycarbonyl groups ($PMMA\text{-}COOCH_3$). $PMMA\text{-}COOCH_3$ functional groups could rearrange slightly to carboxylic acid (-COOH) [15]. Consequently, the surface became more hydrophilic by hydroxyl groups.

The results of surface roughness examined by Atomic Force Microscope as shown in Fig.2. exhibited the rough surface of Al A5083 due to the polishing process. After coating with the hybrid film, the surfaces of 806TOT became finer and homogeneity. Adding PMMA, the surface structure became more inhomogeneity showing the different roughness between peaks. This can be explained by the thickness of the film since adding PMMA increased the concentration of the coating solvents.

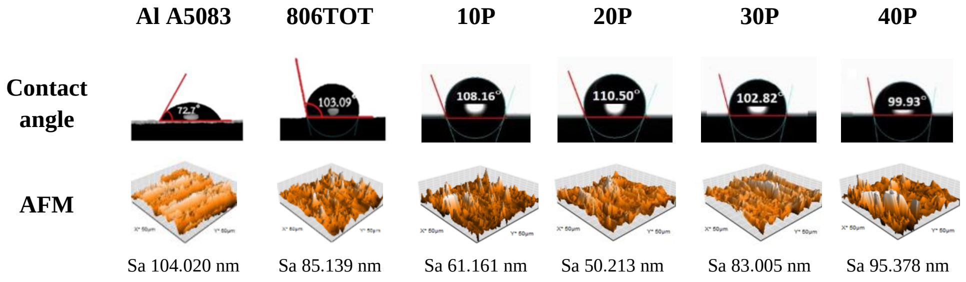


Fig. 2. Water contact angle (WCA) and surface morphology of Al A5083, 806TOT, 10P, 20P, 30P, and 40P

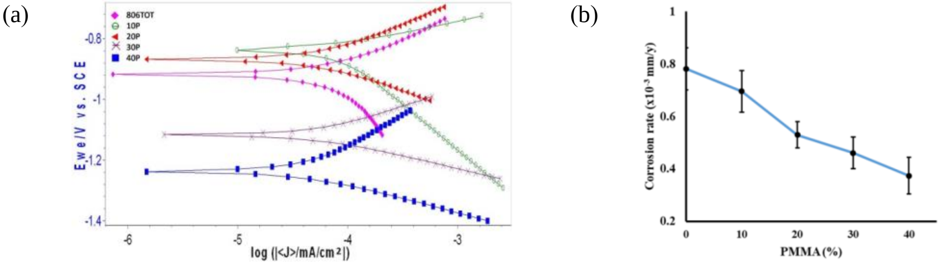


Fig. 3. (a) Potentiodynamic polarization curves and (b) the corrosion rate of the inorganic-organic hybrid films with various PMMA loafing on Al A5083

Table 1. Electrochemical parameters of Al A8053 and Al coated with the inorganic-organic hybrid film at different ratio of PMMA in 0.35 wt% NaCl solution

Sample's name	E_{corr} [mV]	i_{corr} [μA/cm^2]	Corrosion rate [×10^{-3}mm/y]
806TOT	-842.56	0.09	0.78 ± 0.08
10P	-834.63	0.08	0.70 ± 0.08
20P	-867.50	0.06	0.53 ± 0.05
30P	-1,116.22	0.05	0.46 ± 0.06
40P	-1,236.45	0.04	0.37 ± 0.07

3.2 Corrosion testing

The electrochemical technique was used to determine the corrosion resistance of the inorganic-organic hybrid film coating. The coated film was exposed in 0.35 wt% NaCl solution, imitating the marine environment. The potentiodynamic polarization curves were used to evaluate the E_{corr} and i_{corr} by mean of fitting with Tafel region showing in Fig. 3(a). The corrosion rate was calculated by equation 1 in term of millimeter per year (mm/y) as shown in Table 1. The results showed that the corrosion rate of the hybrid films reduced with increasing the amount of PMMA, as shown in Fig. 3(b). The TEOS/OTES film without PMMA (806TOT) had 0.78 x10^{-3} mm/y of the corrosion rate, while the hybrid films with PMMA had higher corrosion resistivity. The anticorrosion rate of the coated films with PMMA10, 20, 30 and 40%v/v on Al alloy was 0.70±0.08, 0.53±0.05, 0.46±0.06, and 0.37±0.07 mm/y, respectively. Reducing of the corrosion rate means better anticorrosion resistance. Increasing of corrosion resistance could be explained by the increasing the densification of silica networking, which resulted from the interconnection of the PMMA molecules [16]. In addition, PMMA increases the adhesion between the inorganic/organic film and Al alloy substrate [16], [17] then the initial corrosion at the interface is barrier [17].

3.3 Weathering resistance testing

The samples chosen for weathering resistance testing were considered from the results of corrosion rate. P20 and P40 were selected as their resulted corrosion rates are quite high, meaning they can protect the corrosion on the material surfaces. The results of corrosion rate of 20P and 30P were not significantly different, according to ANOVA-test.

The digital photographs of Al A5083, 806TOT 20P and 40P after exposing in the QUV chamber are shown in Fig. 4. All sample surfaces with the inorganic-organic hybrid film had clear surfaces. The appearance of the surfaces after testing over 4 weeks was the same for all coated samples, while the dark surface was occurred on Al A5083 since 1 weeks of explosion.

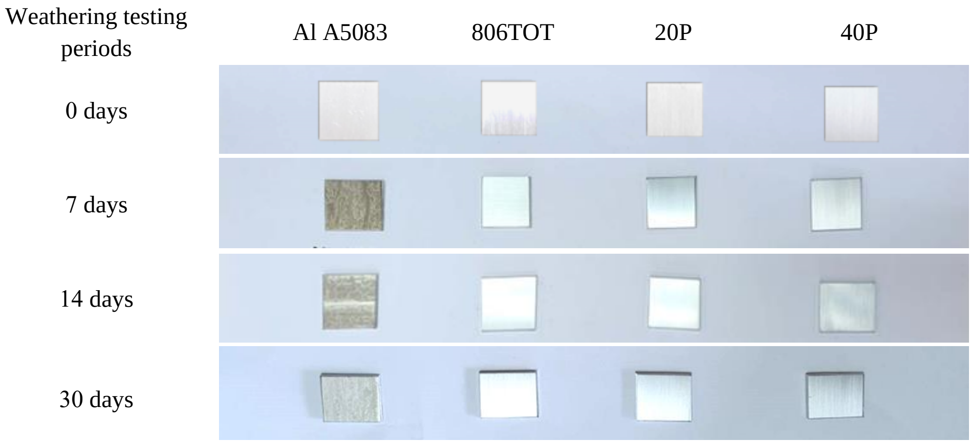


Fig. 4. QUV accelerated weathering testing of Al A5083, 806TOT 20P, and 40P for 7, 14, and 30 days

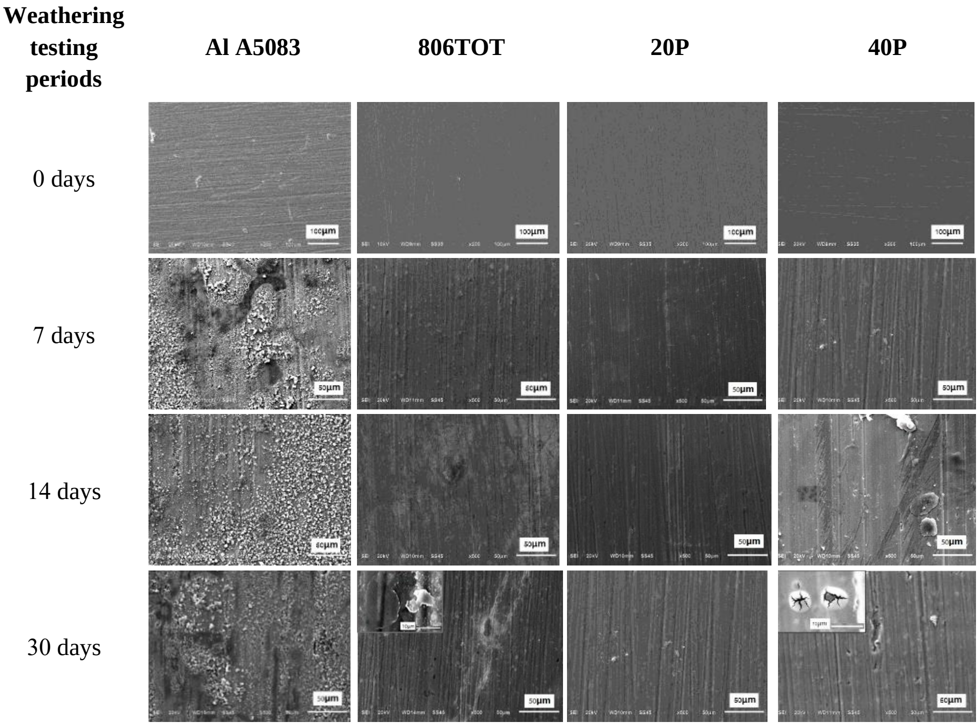
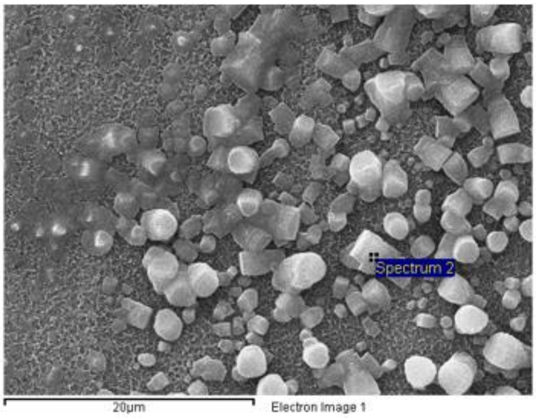


Fig. 5. SEM photograph of Al A5083, 806TOT 20P, and 40P curing in QUV accelerated weathering chamber for 7, 14, and 30 days

The microstructures of Al A5083 and Al A5083 coated with the inorganic-organic hybrid films are shown in Fig. 5. The Al A5083 surface was covered with corrosion product after being incubated for 7 days and after 30 days of exposure, pitting was generated in the surfaces. The EDX analysis in Fig. 6 illustrated the corrosion product on the uncoated sample was Al_2O_3 resulting from the condensation of $Al(OH)_3$. 806TOT and 40P started to bloat after curing in UV weathering chamber for 7 days. 20P (806TOT added with 20%v/v PMMA) was initial to swelling for 7 days in QUV chamber and there was no any changes on the surface of this sample up to 31 days. This could be possible since 20P had higher WCA, therefore water was



Element	Weight%	Atomic%
C K	3.21	5.29
O K	53.27	65.96
Mg K	0.75	0.61
Al K	37.52	27.54
Mn K	0.14	0.05
Ag L	0.42	0.08
Au M	4.70	0.47
Totals	100.00	

Fig. 6. The corrosion on the uncoated sample after 14 days

not able to penetrate through the coated film. The accelerated weather for 2,000 h which was equal to 1 year time (8,760 h) of natural weathering. So, the period of weathering testing can predict the real period of corrosion by multiplying the acceleration factor of 4.38 with the hours of testing. Therefore, the best weathering resistance of the inorganic/organic film was 31 days or around 4 months.

4. Conclusion

The hydrophobic property of TEOS/OTES films could be risen up by adding PMMA. The water contact angle increased with increasing the amount of PMMA, and the highest water contact angle was 110.5° generated from 20%v/v of PMMA loading. In addition, 20P had no damaged surfaces after exposing in a QUV chamber for 31 days, while other samples (coated and without coating) showed corrode surfaces within 7 days. However, the electrochemical testing in 3.5 wt% of NaCl exhibited that the hybrid film containing PMMA 40%v/v reduced the corrosion rate from 0.782±0.08 mm/y to 0.37±0.07 mm/y.

In conclusion, the inorganic/organic hybrid film with PMMA 40%v/v could be applied for marine applications, however, if the coating film was utilized on land where moisture and sun light directly contact, adding PMMA 20%v/v was more suitable.

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