

Novel Composite Nanofilm of Electropolymerization and Self-Assembling on AA5052 Surface as Anticorrosion Coating

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ABSTRACT: Electropolymerization nanofilm was prepared by cyclic voltammogram with 6*N,N*-diallylamino-1,3,5-triazine-2,4-dithiol monosodium (DAN) on the AA5052 surface in 0.15*M* NaNO₂ at 10°C, then octyl-triethoxysilane (OTES) film was fabricated on the poly(6*N,N*-diallylamino-1,3,5-triazine-2,4-dithiol) nanofilm (PDA) covered AA5052 surface by self-assembling method to obtain the composite polymeric nanofilm (C-PDA/OTES). The composite polymeric nanofilm was characterized by means of FTIR spectra, scanning electron microscope (SEM),

contact angle, and potentiodynamic polarization. The results showed that the C-PDA/OTES covered surface was more homogenous, compact, hydrophobic compared with PDA covered surface and had excellent protection efficiency. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2906–2910, 2012

Key words: nanocomposites; electrochemistry; self-assembly; anticorrosion

INTRODUCTION

Nowadays, application of aluminum and its alloys has been extended to various fields, such as construction materials, automobile parts, aerospace industries, and so on. They are considered to be important as next-generation metallic materials due to their low cost, high mechanical intensity, easy machining, and good recycling efficiency.^{1–3} However, their expanding application has been seriously limited because of susceptibility to corrosion. To satisfy the increasing requirement for aluminum alloys, it is necessary to modify its surface especially for the corrosion protection. Different methods have been used to improve their corrosion resistance. Among them, pretreatment based on the chromates has been widely investigated. However, they have been classified as hazardous to environment and human health. Therefore, much effort has been made to develop environmental friendly alternatives. Organic nanofilms of metal/polymer assemblies^{4–9} have attracted considerable interest for their application

in industrial areas. Many researchers have been reported that the triazinethiols^{10–13} could react easily with metal surface to obtain nanofilms with ability to protect the surface against corrosion.^{14,15} These researches showed that the triazinedithiol polymer nanofilm had basic anticorrosion property without toxicity. Another important modification method is seen in the studies of aluminum treated with organosilane,^{16–18} which have currently been the subject of intensive research due to a viable and environmentally compliant alternative to the chromate technology in metal anticorrosion.^{19–21}

Since the nanofilm prepared by self-assembling of organosilane could not sufficiently inhibit the diffusion of corrosive species like O₂ and OH[−] and the electropolymerization nanofilm of triazine prepared by cyclic voltammogram was not thick and dense enough, we combine triazinedithiol with organosilane to prepare composite nanofilm on commonly used aluminum alloy (AA5052) surface in this article. So far, this kind of organic composite polymeric nanofilm has not been reported. The polymeric nanofilm of triazinedithiol was prepared by electropolymerization technique in the first step, and the further modification with organosilane was carried out by self-assembling technique.

EXPERIMENT

Material and reagents

AA5052 (Cu: 0.1%, Si: 0.2%, Fe: 0.4%, Mn: 0.1%, Mg: 2.8%, Zn: 0.1%, Cr: 0.3%, others: 0.15%) test samples

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(30 mm × 50 mm × 0.3 mm) were prepared by cutting pieces from a sheet of aluminum alloy plate; 6-diallylamino-1,3,5-triazine-2,4-dithiol monosodium (DAN) was synthesized by the reaction between 6*N,N*-diallylamino-1,3,5-triazine-2,4-dichloride and NaSH according to the method in the previous study.¹¹ Octyl-triethoxysilane (OTES) was purchased from the Aladdin Reagent Incorporation. The ratio of OTES/high purity water/ethanol was 3/7/90 (v/v/v). The pH of OTES solution was adjusted to 4.5 by adding acetic acid, followed by being stirred for 1 h, and aged at 30°C for 24 h²² to allow the sufficient hydrolysis of OTES. NaNO₂ was applied as supporting electrolyte for electropolymerization.

Fabrication of composite polymeric nanofilm

PDA film was fabricated on AA5052 surface by electropolymerization of DAN as the first step by cyclic voltammetry with the potential ranging from -0.7 to 5.0 V at the scanning rate of 10 mV/s using electrochemical work station (CHI660C). A three-electrode electrochemical system was applied, in which working electrode is AA5052, counter electrodes are stainless steel plates and reference electrode is the saturated calomel electrode, and the electrolyte solution is 0.15M NaNO₂ containing 5 mM DAN. Then, PDA covered AA5052 was silanized in hydrolyzed OTES solution for 10 min, followed by being rinsed with ethanol, dried in nitrogen air, and cured for 10 min at 120°C to form the composite nanofilm.

Characterization

FTIR was carried out by attenuated total reflection spectroscopy (Bruker TENSOR 37). The contact angle was measured by optical contact angle measuring instrument (OCA35, Dataphysics) at room temperature with 1 μL distilled water. The corrosion property was evaluated by potentiodynamic polarization test in 3.5% NaCl aqueous solution with Pt counter electrode at room temperature. The scan rate was 1 mV/s and the exposed area was 1.0 cm². The morphologies of the blank, PDA, and C-PDA/OTES covered AA5052 surface were observed by SEM (JSM-6360LV) at accelerating voltage of 20 kV.

RESULTS AND DISCUSSION

Electropolymerization of DAN

Information for the oxidation-reduction potential is essential for investigating electropolymerization reactions.^{23,24} Cyclic voltammogram processed in the 0.15M NaNO₂ with 5 mM DAN is shown in Figure 1. In the first cycle, three anodic peaks were observed when DAN monomer was electropolymerized.

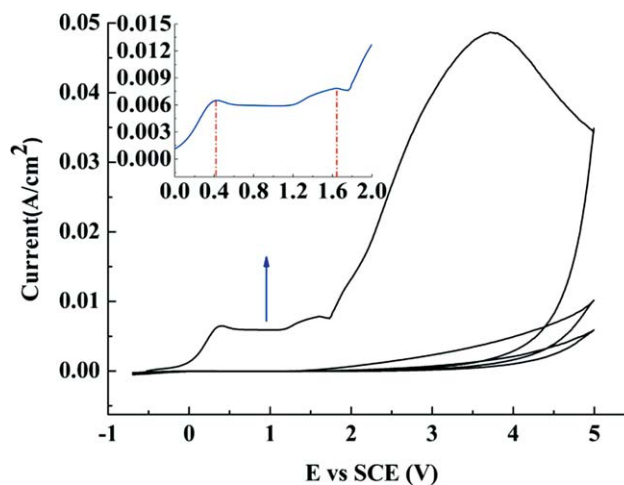


Figure 1 Cyclic voltammetry of AA5052 in 0.15M NaNO₂ aqueous solution with 5 mM DAN for three cycles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

A small peak was observed at 0.43 V, indicating that the reaction happened between aluminum and thiol functional groups of DAN to form the thin monomer layer. Another peak at 1.64 V suggested that DAN monomer was electropolymerized to obtain the PDA film on AA5052 surface. It was noted that a wide strong peak appeared at 3.75 V. At the same time, some bubbles could be observed on the electrode surface, which indicated that the electrolysis of water occurred. The peak was very wide due to the further formation of PDA film and alumina under the higher potential according to our previous study.²³ No reduction peak appeared when the scanning was carried out in the negative direction. In the second and third cycles of cyclic voltammogram, the current density decreased significantly. The decrease of current density and the absence of reduction peak indicated the insulation of PDA film, and the depolymerization of the PDA film did not take place.

FTIR analysis of PDA and C-PDA/OTES film

FTIR spectra measurement was performed to study the chemical structures of PDA and C-PDA/OTES film (Fig. 2). In the Figure 2(a), the presence of triazine ring was confirmed by the absorption peaks at 1464 cm⁻¹, 1535 cm⁻¹, and 1563 cm⁻¹ due to >C=N- bonds. Diallyl amino groups were confirmed by the absorption peaks at 2780 cm⁻¹ and 2736 cm⁻¹ due to C-H symmetric stretching vibrations of -CH₂ and -CH= as well as by the absorption peaks at 2959 cm⁻¹ and 2927 cm⁻¹ due to C-H asymmetric stretching vibrations of -CH₂ and -CH=. At the same time, the absorption peak of alumina at 938 cm⁻¹ was also observed. It is

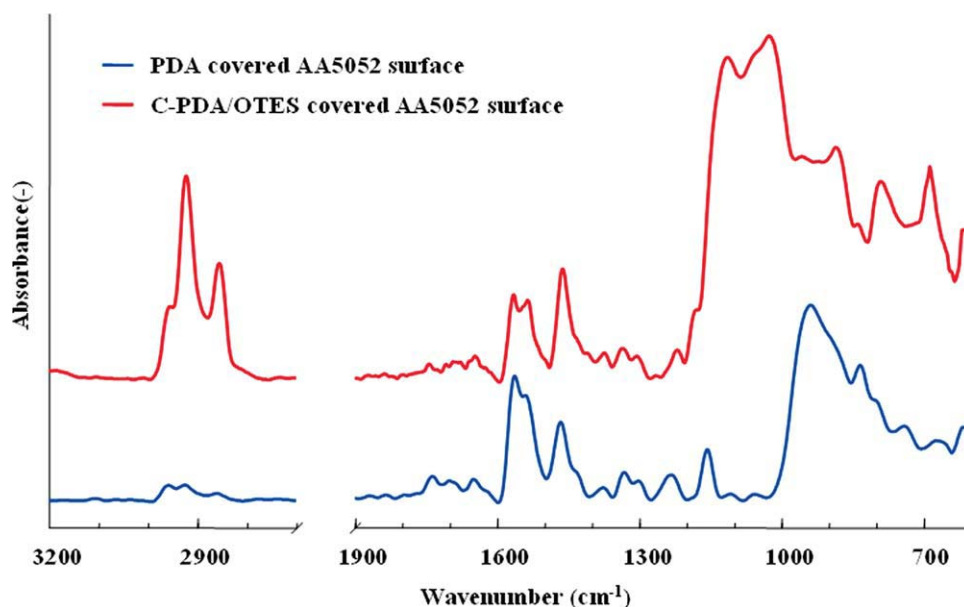


Figure 2 FTIR spectra of the PDA and C-PDA/OTES film on AA5052 surface. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

indicated that the electropolymerization of DAN and oxidation of aluminum occur simultaneously. In the Figure 2(b), the peaks at 2956 cm^{-1} , 2924 cm^{-1} , and 2855 cm^{-1} due to C—H stretching vibrations of $-\text{CH}_2$ existed in the C-PDA/OTES film were far stronger than that in the PDA film. The results indicated the formation of OTES self-assembled nanofilm on AA5052 surface. Also, some new peaks appeared in the range of 1200 to 800 cm^{-1} . Among them, the absorption peak at 1112 cm^{-1} was due to the Si—O—Si stretching and the peak at 1025 cm^{-1} was attributed to the formation of Si—O—Al bonding.⁵ These peaks indicated that the self-assembled nanofilm of OTES formed on the AA5052 surface and the condensation reaction of hydrolyzed OTES occurred to obtain the $-\text{Si}-\text{O}-\text{Si}-$ network structure, which could inhibit the corrosion species diffusion to the AA5052 substrate. The peak at 884 cm^{-1} suggested that the unreacted $-\text{Si}-\text{OH}$ existed in the C-PDA/OTES film.

Contact angle

Figure 3 shows the contact angles of blank, PDA, and C-PDA/OTES covered AA5052. The contact angle of the blank AA5052 is 89.9° , suggesting that the substrate has the weak hydrophobicity due to the natural aluminum oxide film. As for the PDA covered AA5052 surface, the contact angle increases to 102.2° , indicating that DAN is electropolymerized on AA5052 surface to form the polymeric nanofilm. The contact angle of the C-PDA/OTES covered AA5052 increases to 137.9° significantly, which suggests that a condensation reaction occurs between

the polar groups on the PDA covered AA5052 surface and the Si—OH groups of hydrolyzed OTES to obtain the network self-assembled nanofilm. The results indicated the formation of hydrophobic C-PDA/OTES nanofilm on AA5052 surface. Humid environment is one reason of aluminum alloy corrosion, and the hydrophobic surface of substrate is benefit for the protection of aluminum alloy. Therefore, the anticorrosion property of C-PDA/OTES covered AA5052 will be enhanced as the hydrophobicity of surface has been improved.

SEM analysis

The surface morphologies of blank, PDA, and C-PDA/OTES covered AA5052 were observed by SEM (Fig. 4). As shown in Figure 4(a), the scratches with

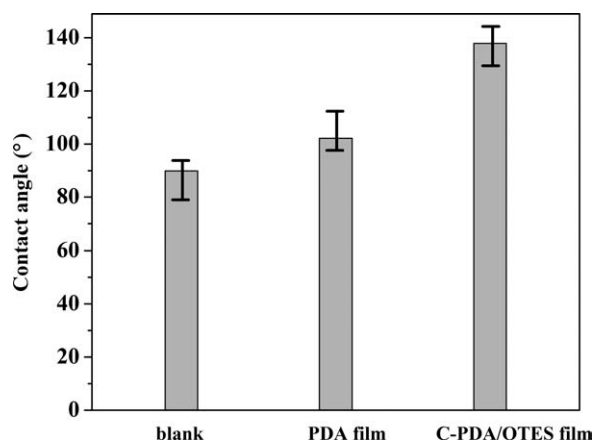


Figure 3 Contact angle of blank, PDA, and C-PDA/OTES covered AA5052.

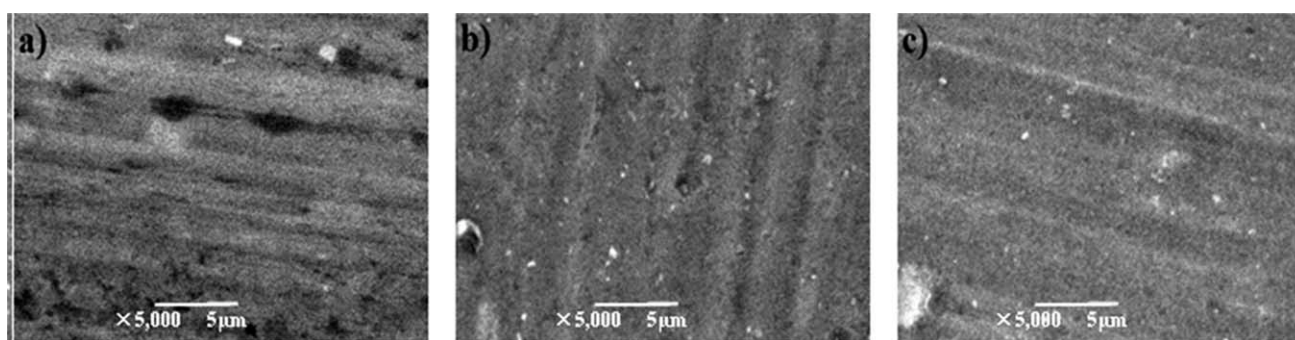


Figure 4 SEM images of AA5052 surface. (a) Blank; (b) PDA covered; (c) C-PDA/OTES covered.

the rolling process could be clearly observed on the blank AA5052. Fine intermetallic particles which are aligned along the rolling direction can be seen, distributing all over the surface. As for PDA covered surface [Fig. 4(b)], original morphology of AA5052 surface can hardly be seen. However, some pores and comparatively large fine intermetallic particles could still be observed. It is deduced that the pores are mainly caused by the hydrogen bubbling during anodic dissolution of aluminum, and the hydrolysis process may destroyed the film to some extent. However, the surface pores and large fine intermetallic particles can not be seen for the C-PDA/OTES covered AA5052 [Fig. 4(c)]. The surface is more homogenous, compact, and the film coverage is high. It is concluded that the composite technique of electropolymerization and self-assembling treatment could modify the AA5052 surface effectively.

Corrosion tests

Figure 5 displays the potentiodynamic polarization curves of blank and C-PDA/OTES covered AA5052

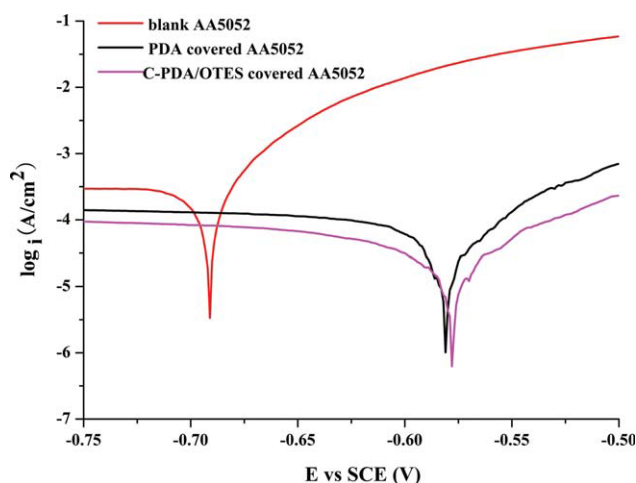


Figure 5 Polarization curves of the AA5052 in 3.5% NaCl after 1 h exposure: (a) blank, (b) PDA covered, (c) C-PDA/OTES covered. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in 3.5% NaCl aqueous solution. It can be seen that the corrosion potentials (E_{corr}) of blank, PDA, and C-PDA/OTES covered AA5052 are -0.691 V, -0.581 V, and -0.578 V, respectively. The corrosion current density (I_{corr}) decreases from 8.811×10^{-4} A/cm² of blank aluminum to 1.769×10^{-4} A/cm² for PDA covered surface. As for C-PDA/OTES covered surface, the change is even more notable with the I_{corr} reducing to 7.804×10^{-5} A/cm², exhibiting favorable inhibitive effect. The protection efficiency (PE) of PDA and C-PDA/OTES film can be calculated by the equation below:

$$\text{PE}(\%) = 100 \times [1 - (i/i_0)]$$

where i and i_0 are the I_{corr} of treated and blank AA5052, respectively. The protection efficiency is 79.9% for PDA covered AA5052 surface, while 91.1% for C-PDA/OTES covered surface. The right shift of E_{corr} and decrease of I_{corr} indicate that the corrosion of AA5052 is considerably suppressed by the C-PDA/OTES film. It can be concluded that the C-PDA/OTES covered AA5052 demonstrates excellent anticorrosion property.

Figure 6 shows the surface morphologies of blank, PDA, and C-PDA/OTES covered AA5052 after corrosion test. For the blank AA5052 [Fig. 6(a)], it can be seen that many severe corrosion spots appear after corrosion test. As for the PDA covered one [Fig. 6(b)], only little corrosive regions are clearly observed. In the case of the C-PDA/OTES covered AA5052 [Fig. 6(c)], the corrosion spots are almost invisible, which shows effective corrosion protection. All the above results showed favorable anticorrosion performance of C-PDA/OTES nanofilm on AA5052 surface.

CONCLUSIONS

The C-PDA/OTES film was successfully obtained on AA5052 surface by combining electropolymerization of DAN with self-assembling of OTES. The contact angle of C-PDA/OTES covered AA5052 was up to

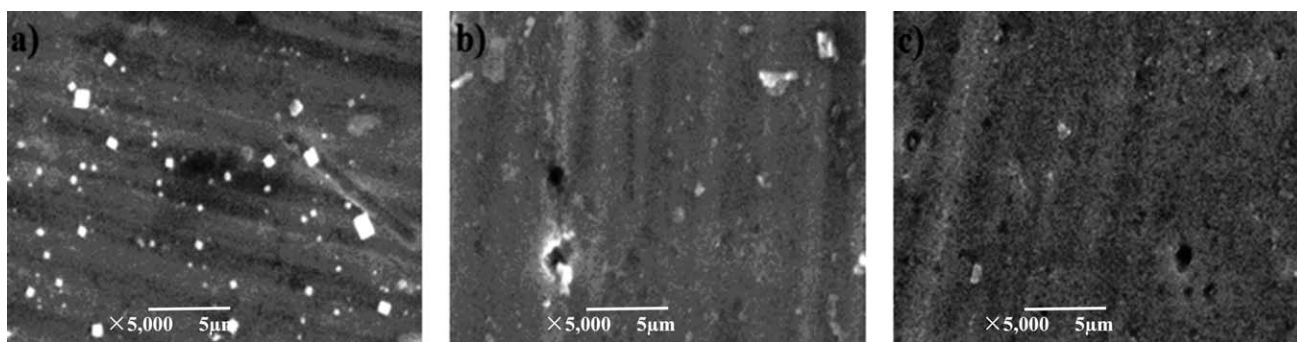


Figure 6 SEM images of AA5052 surface after corrosion test. (a) blank; (b) PDA covered AA5052; (c) C-PDA/OTES covered AA5052.

137.9°. The C-PDA/OTES film was homogenous, compact, hydrophobic, and had an excellent protection efficiency of 91.1%. It is expected that this technique can be applied in fabrication of hydrophobic and anticorrosion-protective surface on metal surface.

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