Electrodeposition and Radical Polymerization to Prepare Cross-linked Film of Triazinethiol on Aluminum Surface

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Electrodeposition and radical polymerization technique were applied to fabricate triazinedithiol cross-linked film on aluminum alloy surface. The heterocyclic monomer containing fluorine substituent of 6-(N-allyl-1,1,2,2-tetrahydroperfluorodecyl)amino-1,3,5-triazine-2,4-dithiol monosodium (AF17N) was first electrodeposited on aluminum alloy surface by two-step potentiostat technique. Then 6-N,N-diallylamino-1,3,5-triazine-2,4-dithiol monosodium (DAN) was further polymerized on the electrodeposition film covered aluminum surface to fabricate the cross-linked film for ameliorating its anticorrosion efficiency. The wettability of samples was studied by contact angle. The film compactness was carried out by cyclic voltammograms method in 0.1% H_2SO_4 solution. The corrosion inhibition property of the film was demonstrated in 0.5 mol/L NaCl aqueous solution by potentiodynamic polarization and salty water test. Surface morphologies of aluminum before and after immersion tests were observed by scanning electron microscopy (SEM). All results show that the corrosion inhibition efficiency of electrodeposition film and cross-linked film covered aluminum substrates increases markedly. Compared to electrodeposition film, the cross-linked film has better effect for protecting aluminum from corrosion.

1. INTRODUCTION

The lightweight metal material-aluminum alloy is a key point for several industries especially for aerospace, since structural weight reduction is an efficacious means of improving aircraft performance [1-2]. However, like all other alloys, aluminum alloy is subjected to corrosion, which results in the formation of an oxide or salt layer on its surface. These materials exhibit poor corrosion resistance, suffering several types of degradation, such as pitting, exfoliation and intergranular

corrosion. The moisture, oxygen and other species migration of the environment transit the metal surface leading serious corrosion, especially the rain and high temperature. These are limitations to its more widespread use in hostile environments [3].

Therefore, it is necessary to develop protection film to improve the anticorrosion property of the aluminum alloys. The corrosion study of aluminum has a long and substantial history. Various methods of the protection film on aluminum alloys have been reported. In early stage, the phosphate and chromate passivation (the formation on the metallic surface of a thin layer of oxide or hydroxide that protects the metal surface against further corrosion) were employed as surface treatment method, but chromates are toxic and carcinogenic [4-6]. During the last decade, nitriding is also a surface treatment technique used to introduce nitrogen into metallic materials to improve their surface hardness, mechanical properties and corrosion resistance [7]. Moreover, polymer films have been also suggested to be a promising alternative and most organic inhibitors generally protect the metal from corrosion by forming a film on the metal surface [8-9]. Many authors' attention has been focused on the corrosion resistance of polymer coatings, particularly aromatic polymers, such as propylene derivative [10], polyaniline [11-14], polypyrrole [15-16], polythiophene, polyindole [17] and plasma polymers [18]. In recent years, some organic compounds, which contain the functional electronegative groups and π-electron in triple or conjugated double bonds, play an important role in corrosion inhibition process [19]. These hetero-atoms, such as sulfur, phosphorus, nitrogen, and oxygen, together with heterocyclic or conjugated aromatic, are known to be excellent complex or chelate forming substances with metals of transition series. Furthermore, the most synthesized compounds are the nitrogen-heterocyclic compounds. Mori had studied the corrosion protection properties of triazinedithiols on the various metal substrates by the adsorption and electrochemical polymerization [20-22]. The researches showed that polymeric nanofilms prepared by different triazinedithiols had basic anticorrosion property. The chemistry of aromatic and heterocyclic compounds containing fluorine substituents has developed rapidly now. It has become a large division of the chemistry of intermediate products which are widely used for synthesizing pesticides, drugs, dyes and monomers for polymeric materials. Fluorinated polymers exhibit a unique combination of high thermal stability, chemical inertness (to acids, bases, solvents and petroleum), low water absorptivities, excellent weatherability and a good resistance to oxidation and ageing, etc. And the cladding that contains a fluorinated group can provide good hydrophobicity [23].

In this paper, the heterocyclic monomer containing fluorine substituent of 6-(N-allyl-1,1,2,2-tetrahydroperfluorodecyl)amino-1,3,5-triazine-2,4-dithiol mono- sodium (AF17N) was polymerized by electrochemical deposition on aluminum alloy 5052 substrate surface (AA5052), and then the electrodeposited film (PAF) covered substrate were chemically modified by radical polymerization of 6-N,N-diallylamino-1,3,5-triazine-2,4-dithiol monosodium (DAN) using potassium persulfate as initiator to form cross-linked film (PAF/PDA). The performance of film on aluminum surface was evaluated by contact angle, scanning electron microscope and potentiodynamic polarization.

2. EXPERIMENTAL

2.1 Materials and reagents

The aluminum alloy used in this study was AA5052. The chemical composition is given as follows: Cu: 0.1%, Si: 0.2%, Fe: 0.4%, Mn: 0.1%, Mg: 2.8%, Zn: 0.1%, Cr: 0.3%, others: 0.15% and Al balance (mass fraction). It was in the form of sheets with 30×50×0.3 mm dimensions ultrasonically degreased with acetone for 15 min. 6-(N-allyl-1,1,2,2-tetrahydroperfluorodecyl)amino-1,3,5-triazine-2,4-dithiol monosodium (AF17N) was prepared by reaction between 6-(N-allyl-1,1,2,2-tetrahydroperfluorodecyl)-amine-1,3,5-triazine-2,4-dichloride and NaSH. 6-N,N-diallylamino-1,3,5-triazine-2,4-dithiol monosodium (DAN) was synthesized by 6-N,N-diallylamino-1,3,5-triazine-2,4-dichloride and NaSH, according to the previous study [24]. The molecular structures of AF17N and DAN are shown in Fig.1. Sodium nitrite ($NaNO_2$) was applied as supporting electrolyte in the electrochemical polymerization. Potassium persulfate ($K_2S_2O_8$) was used as initiator for radical polymerization.
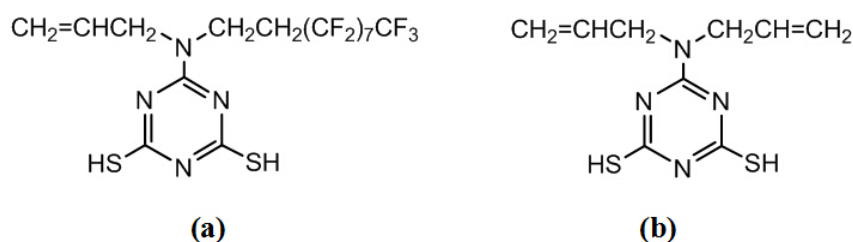
Figure 1. The molecular structures of AF17N and DAN

2.2 Preparation of cross-linked triazinedithiol film

The electrochemical polymerization was carried out in a three-electrode system at room temperature. The working electrode was AA5052. A rectangular stainless steel plate was used as counter electrode and saturated calomel electrode (SCE) as reference electrode. In this work, all of the potentials were versus to SCE. AF17N monomer was electropolymerized on AA5052 surface by two-step potentiostat method using electrochemical workstation (CHI 660C). The two-step potentials were 1.6 V and 7 V, respectively. The electrochemical polymerization time was 30s and 10s, respectively. After the electrodeposition, the working electrode was removed from the electrolytic cell and immediately rinsed by distilled water and acetone, then dried in nitrogen. The electrodeposited film covered substrate surface was further modified by radical polymerization in the solution of 1.5 mmol/L DAN and 0.12 mmol/L $K_2S_2O_8$ for 40 min, followed by being rinsed with acetone, dried in nitrogen and cured at 100°C for 10 min, forming the cross-linked triazinedithiol film on aluminum alloy surface. The above experimental condition derived from our orthogonal tests.

2.3 Characterization

The wettability of aluminum surface was measured by contact angle instrument (SL100) with double distilled water at room temperature. The open circuit potential (E_{ocp}) of aluminum electrode was monitored in 0.1% H_2SO_4 solution for 10 min. Then the film compactness was tested by cyclic voltammograms in 0.1% H_2SO_4 solution at a scanning rate of 10 mV/s between the potential region of -1.0~2.0 V. The potentiodynamic polarization studies were carried out from cathodic potential of -1.1 V to an anodic potential of 0.2 V to study the anticorrosion performance of electropolymerized film and cross-linked film at a sweep rate of 5 mV/s. The exposed area was fixed at 1.0 cm^2. The saline immersion test was carried out for 5 months at room temperature. The standard aggressive medium was 0.5 mol/L NaCl aqueous solution with a pH value of 7.0. The surface morphologies of blank, electropolymerized film and cross-linked film covered aluminum were characterized by scanning electron microscopy (SEM, JSM-6360LV) with an acceleration voltage of 20 kV.

3. RESULTS AND DISCUSSION

3.1 Open circuit potential (OCP) study

The change of the open circuit potential (E_{ocp}) of blank and film covered aluminum electrodes in 0.1% H_2SO_4 solution aqueous solution was monitored in open circuit conditions for 10 min, and presented in Fig. 2. Immediately after immersion of the blank electrode, the open circuit potential shifted steeply towards the positive direction suggesting the dissolution of the native oxide layer and aluminum.
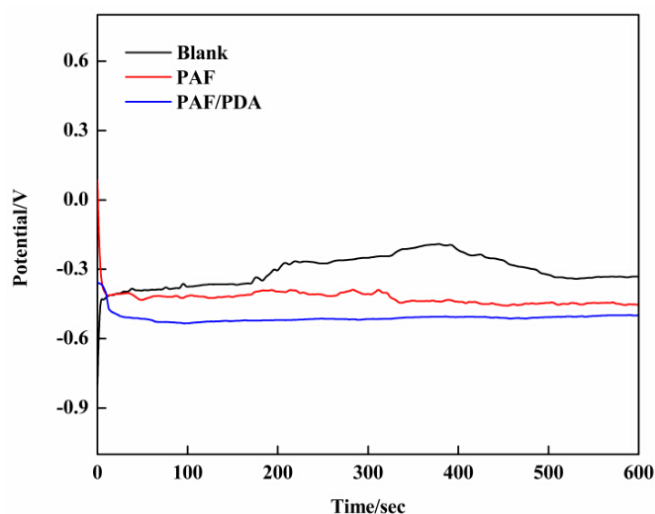

Figure 2. Open circuit potential change of aluminum alloy 5052 electrodes surface

Beyond 8 min immersion, the open circuit potential remained practically constant and ranged between 0.374 and 0.368 V. In contrast, it was observed that the open circuit potential shifted towards

the negative values for the PAF film and PAF/PDA cross-linked film covered aluminum electrodes. This behavior can be attributed to the protective effect of the electrodeposited film or cross-linked film on the aluminum surface which slows down the cathodic reaction. And the open circuit potential for PAF/PDA cross-linked film covered electrode is more negative and constant than that of only PAF electrodeposited film covered electrode. It was assumed that the allyl groups in the PAF film could react with allyl groups in DAN monomer by radical polymerization to form the PAF/PDA cross-linked film. The result suggests that the PAF/PDA cross-linked film on the aluminum surface has better protective effect for AA5052.

3.2 Wettability

To understand the formation of films, the wettability of blank, PAF film and PAF/PDA cross-linked film covered specimens were studied by contact angle, shown in Fig.3. It can be seen that the contact angle increases from 89.9° for the blank specimen to 134.7° for PAF-covered specimen and reaches to 141.2° for PAF/PDA-covered sample, which suggests that the PAF film and PAF/PDA cross-linked film on AA5052 surface is more hydrophobic. The results could be attributed to the existence of fluorine substituent in PAF film or PAF/PDA cross-linked film which reduced the surface free energy. Furthermore, PAF/PDA cross-linked film has stronger hydrophobility than that of PAF electrodeposited film. The hydrophobic property is also believed to be due to the presence of cross-linked geometric structure at the micro-/nano-meter scale. Due to the existence of moisture and polluting ions in environmental conditions, the corrosion of metallic materials can't be suppressed completely. Moreover, the higher hydrophobility, the higher blocking effect for the corrosive medium to protect AA5052 from corrosion. According to the contact angle data, it was proposed that PAF/PDA cross-linked film would have more excellent anticorrosion for AA5052.
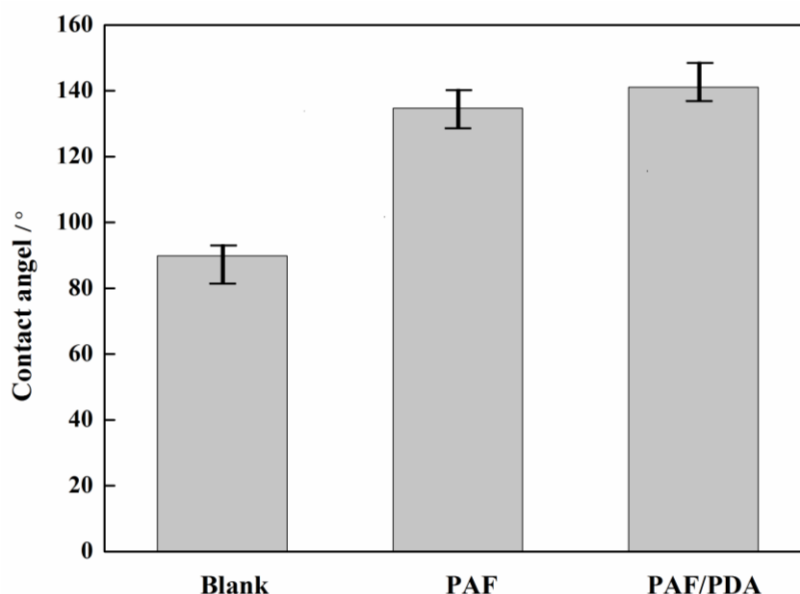
Figure 3. Contact angle of aluminum alloy 5052 electrodes surface

*3.3 Surface morphology-SEM studies for films*

To further investigate the performance of the films, the surface morphologies of PAF electrodeposited film and PAF/PDA cross-linked film were observed by SEM, shown in Fig. 4. It can be seen that the blank aluminum surface (Fig. 4(a)) has the vertical production traces and some defects, while the surface morphology of AA5052 covered by PAF electrodeposited film (Fig. 4(b)) is uniform. Compared to blank aluminum, the vertical production traces and some defects on AA5052 surface were shaded by PAF film to some extent though a little rolling trace could still be observed. It is inferred that the appearance is mainly caused by the imperfect coverage of electrodeposited film for the relative larger steric hindrance of AF17N molecules and the hydrogen bubbling during anodic dissolution of aluminum. Fig. 4(c) showed that the image of AA5052 surface covered by PAF/PDA cross-linked film was more compact. The surface texture could hardly be seen which was due to the increased thickness of PAF/PDA cross-linked film. Therefore, it is concluded that the composite technique of electrodeposition and radical polymerization could modify the aluminum alloy surface effectively.
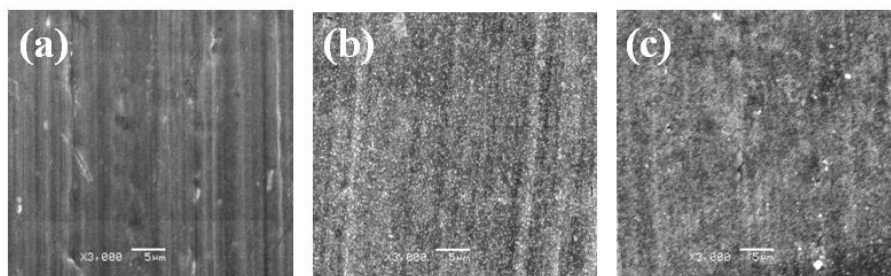
Figure 4. Surface morphology of aluminum alloy 5052 electrodes

3.4 Cyclic voltammetry measurement

The cyclic voltammograms curves of AA5052 electrodes obtained by the electrochemical workstation in 0.1% H_2SO_4 solution are presented in Fig. 5, with the scanning potential ranged from -1.0 V to 2.0 V, the current density of the blank aluminum changed significantly from 0 to 0.65 A/cm^2, which indicated that the surface stability of the blank was poor and apt to be corroded. In the sweeps of PAF-covered and PAF/PDA-covered aluminum electrodes, the current density varied only a little compared to the blank. This might be associated with the significant inhibition of the PAF or PAF/PDA film, which was characteristic of the non-conductive polymer film. In fact, the aluminum surface is covered by pale thin film which can be seen by naked-eye. It could block corrosive electrolyte particle through the surface of aluminum electrodes and played a protective effect for metal materials. From the enlarged partial picture of cyclic voltammograms curves for PAF and PAF/PDA film covered aluminum, the current density of PAF/PDA cross-linked film covered electrode was smaller than that of PAF film. The electrochemical behavior showed that the PAF/PDA cross-linked film could provide better protection of AA5052 from corrosion.
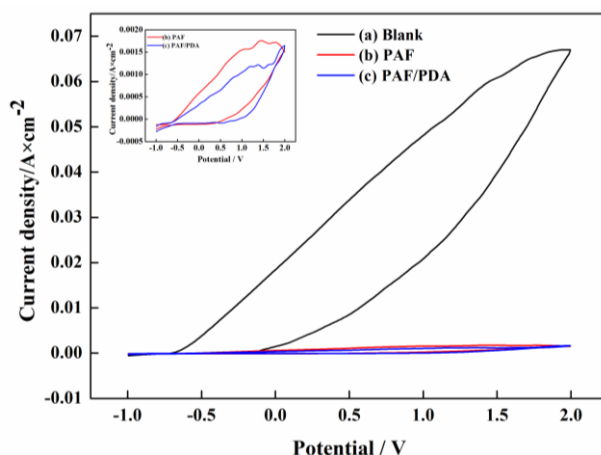
Figure 5. Cyclic voltammograms of aluminum alloy 5052 electrodes in 0.1% H_2SO_4 solution

3.5 Potentiodynamic polarization

To confirm the protective property of PAF electrodeposited film and PAF/PDA cross-linked film for AA5052, the potentiodynamic polarization were measured in standard three electrode system with a scan rate of 5 mV/s, shown in Fig. 6. The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) which was determined by the anodic/cathodic tafel slopes, were presented in table 1. The curve shapes nearly vary, indicating that electrochemical corrosion behaviors are similar. It was clearly observed that the corrosion potential (E_{corr}) corresponding to the PAF or PAF/PDA film modified aluminum alloy shifted significantly towards positive potential, which indicated that the PAF electrodeposited film and PAF/PDA cross-linked film could suppress the cathodic reactions, and therefore inhibit the surface corrosion process in the system. The corrosion current density (I_{corr}) of blank AA5052 was 4.073×10^{-4} A/cm^2, and that decreased to 8.656×10^{-5} A/cm^2 for PAF film covered aluminum. As for PAF/PDA cross-linked film covered substrate, the change was even more notable with the I_{corr} deeply reducing to 2.939×10^{-5} A/cm^2. During the potentiodynamic polarization of blank aluminum alloy, some small bubbles could be observed and visible partial damage took place. But no visible damage happened for the films covered substrates, especially for PAF/PDA cross-linked film covered AA5052. Based on the approximate linear polarization at corrosion current density, the protection efficiency (PE) was calculated by the following equation [25].

PE (%) = 100 × [1-i/i$_0$]

Where i and i$_0$ are the corrosion current density of films covered and blank AA5052, respectively. From the above formula, the PE was 78.8% for PAF film covered aluminum and 94.1% for PAF/PDA cross-linked film covered specimen. The results show that the PAF film prevents the penetration of corrosive medium into the interface between the film and substrate, making an improvement in corrosion resistance. The hydrophobicity of PAF/PDA cross-linked film is further improved, which can hinder the dispersion and migration of the Cl$^-$ from solution to the substrate. Therefore, the cross-linked film plays a role in protection and leads to a further improvement in corrosion resistance.
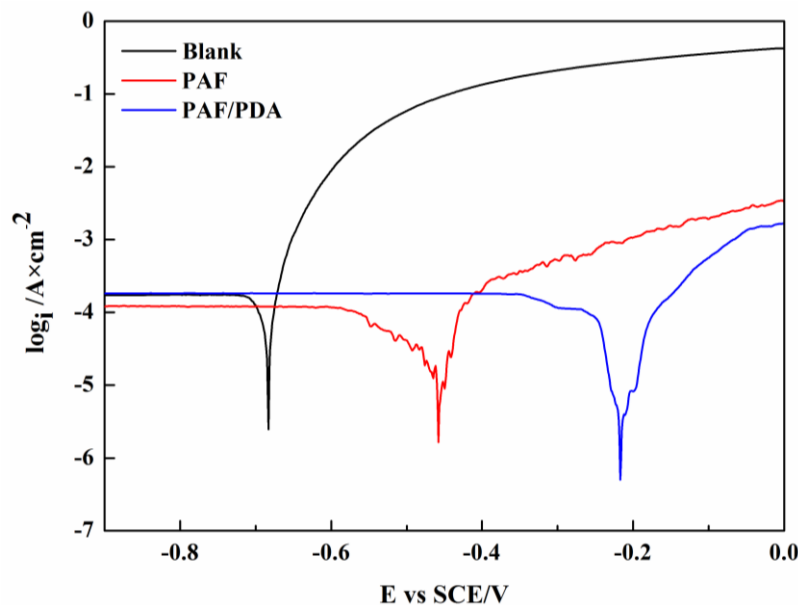
Figure 6. Potentiodynamic polarization behaviour of aluminum alloy 5052 electrodes in 0.5 mol/L NaCl aqueous solution

Table 1. Electrochemical parameters after 30 min exposure in 0.5 mol/L NaCl solution

Sample	E_{corr} vs SCE (V)	i_{corr} (A/cm^2)	PE (%)
Blank	- 0.683	4.073×10^{-3}	-
PAF	- 0.458	8.656×10^{-5}	78.8
PAF/PDA	- 0.217	2.939×10^{-5}	94.1

3.6 SEM-for salty water test

The morphologies of the aluminum alloy surface were also observed after being immersed in 0.5 mol/L NaCl aqueous solution for five months. In the Fig. 7, some white precipitates NaCl crystals were observed because of strong particle adsorption and insufficient surface rinsing. It was clearly seen that the surface of blank aluminum (Fig. 7(a)) was corroded heavily and appeared some pores due to the salty water corrosion, where the aluminum had been destroyed badly. For PAF film covered aluminum (Fig. 7(b)), the corrosion was suppressed and the pores were nearly observed on substrate surface, which indicated less attack of salty water to the surface. But some larger white precipitates were still existed, which would lead to the occurence of corrosion. In Fig. 7(c), the substrate surface was almost intact, which suggested that PAF/PDA cross-linked film could inhibit the corrosive particle adsorption or penetration of corrosive medium into the interface to provide better protection for retarding corrosion.
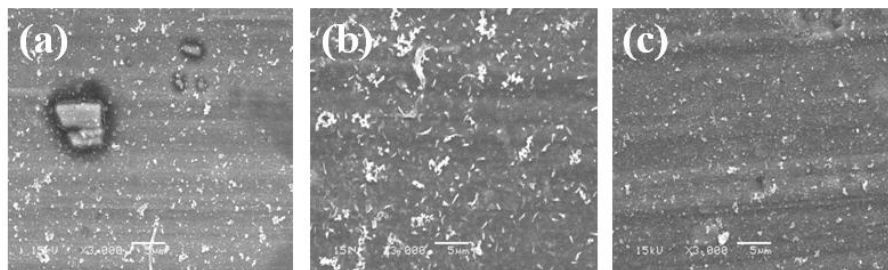
Figure 7. Surface morphology of aluminum alloy after 5 months salty water test

4. CONCLUSIONS

The PAF film and PAF/PDA cross-linked film were successfully fabricated on aluminum alloy surface based on the combination of electrodeposition and radical polymerization methods. The contact angle proved the high hydrophobility of the PAF and PAF/PDA films. Surface morphologies also evidenced the formation of compact PAF/PDA cross-linked film. Open circuit potential, cyclic voltammograms, potentiodynamic polarization and salty water test suggested the superior inhibitive property of cross-linked film. The cross-linked film plays a role in corrosion resistance and is expected to be applied in the metal protection fields.

References

1. F. Wang, YN. Li, Q. Wang, Y. Wang, *Int. J. Electrochem. Sci,* 6 (2011) 113
2. A. Seth, W. Van Ooij, P. Puomi, Z. Yin, A. Ashirgade, S. Bafna, C. Shivane, *Prog. Org. Coat,* 58 (2007) 136
3. U. Bardi, S. Caporali, M. Craig, A. Giorgetti, I. Perissi, J. Nicholls, *Surf. Coat. Technol,* 203 (2009) 1373
4. P. Marcus, *Electrochim. Acta,* 43 (1998) 109
5. N. Akmal, AM. Usmani, *Polym. News,* 28 (2003) 143
6. R. Racicot, R. Brown, SC. Yang, *Synthetic. Met,* 85 (1997) 1263
7. DC. Wen, *Appl. Surf. Sci,* 256 (2009) 797
8. ZX. Kang, K. Mori , Y. Oishi, *Surf. Coat. Technol,* 195 (2005) 162
9. T. Ishizaki, R. Kudo, T. Omi, K. Teshima, T. Sonoda, I. Shigematsu, M. Sakamoto, *Electrochim. Acta,* 62 (2011) 19
10. K. Shah, Y. Zhu, JO. Iroh, O. Popoola, *Surface. Engineering,* 17 (2011) 405
11. K. Shah, J. Iroh, *Advances. in. Polym. Tech,* 23 (2004) 291
12. DE. Tallman, Y. Pae, G. Chen, GPB. Brent, *Conductive polymers and plastics in industrial applications*. Larry Rupprecht (1999)
13. S. Ghoreishi, M. Shabani-Nooshabadi, M. Behpour, Y. Jafari, *Prog. Org. Coat,* 74 (2012) 502
14. N. Nam, J. Kim, Y. Lee, Y. Son, *Corros. Sci,* 51 (2009) 3007
15. M. Trueba, SP. Trasatti, DO. Flamini, *Adv. Mat. Res,* 138 (2010) 63
16. J. Martins, T. Reis, M. Bazzaoui, E. Bazzaoui, L. Martins, *Corros. Sci,* 46 (2004) 2361

17. D. Sazou, M. Kourouzidou, E. Pavlidou, *Electrochim. Acta,* 52 (2007) 4385
18. Y. Chan, Q. Yu, *J. Vac. Sci. Technol. A,* 23 (2005) 991
19. H. Ju, ZP. Kai, Y. Li, *Corros. Sci,* 50 (2008) 865
20. K. Mori, Y. Okai, H. Horie, H. Yamada, *Corros. Sci,* 32 (1991) 1237
21. K. Mori, H. Sasaki, I. Kobayashi, *J. Adhes. Sci. Technol,* 14 (2000) 791
22. F. Wang, K. Mori, Y. Oishi, *Polym. J,* 38 (2006) 484
23. F. Wang, HY. Luo, JG. Wang, Q. Wang, *Molecules,* 14 (2009) 4737
24. F. Wang, K. Mori, ZX. Kang,Y. Oishi, *Heteroatom. Chem,* 18 (2007) 60
25. KV. Subramaniam, MD. Bi, *Corros. Sci,* 52 (2010) 2725