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Preparation of 6-diallylamino-1,3,5-triazine-2,4-dithiol functional nanofilm by cyclic voltammetry on aluminum surface

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The functional polymeric nanofilm of 6-diallylamino-1,3,5-triazine-2,4-dithiol monosodium (DAN) was successfully prepared by cyclic voltammetry method in $NaNO_2$ supporting electrolyte on pure aluminum surface. Based on results of cyclic voltammetry and X-ray photoelectron spectroscopy (XPS), the mechanism of electrochemical polymerization was proposed, which indicated that radical polymerization took place during the electrochemical polymerization process. The obtained poly(6-diallylamino-1,3,5-triazine-2,4-dithiol) (PDA) functional nanofilm was also investigated by means of FT-IR spectra. The experimental results also showed that the structure of polymeric nanofilm was consisted of Al_2O_3 and PDA. It is expected that this technique will bring the direct joining between aluminum and rubber in the process of curing with the formed polymeric nanofilm.

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Keywords: triazinedithiol monosodium; aluminum; functional polymeric nanofilm; electropolymerization

1. Introduction

The pre-treatment of aluminum surface prior to painting or adhesive bonding is an essential technology in industrial fields. However, most of the pre-treatments are based on chromates, which are hazardous to environment and human health. Thus, much effort has been made to develop environment-friendly systems.

Since the publication of Mori K's results on the corrosion protection properties of triazinedithiols (TDTs) on copper surface [1], adsorption and polymerization of TDTs on metal surfaces have been receiving increasing attention, which could be used in corrosion-resistant in place of chromate-based treatment. Experimental researches showed that polymeric films prepared by different TDTs had a basic performance-anticorrosion property [2], with inhibition effciency ranging from 6.1 to 92.8 according to different structures of substituent groups. Thus, during the last decades, there were many studies about other applications of TDTs polymeric film, such as adhesion [3], lubrication property [4], dielectric property [5] and superhydrophobicity [6] on various metal substrates [7-15].

Monomer layer of triazinedithiols (TDTs) on metal surfaces can be polymerized mechanochemically [4], photochemically [16], thermochemically [7], electrochemically [8] or evaporatingly [17]. The electropolymerization process offers advantages of the simultaneity of adsorption and polymerization on metal surface in monomer-electrolyte solution, and the possibility of controlling their chemical and physical properties by changing electrochemical parameters (e.g. current density, potential, monomer concentration, supporting electrolyte, etc). The electropolymerization of TDTs, also referred to as polymer plating [10], on magnesium alloys [18], iron [8], cast iron [19] and copper surfaces [20] had been studied systematically. Poly(6-diallylamino-1,3,5-triazine-2,4-disulfide) (PDA) films on spheroidal-graphite cast iron [19] and magnesium/magnesium alloy [18] had been prepared successfully by means of electropolymerization. The former showed direct joining of acrylic rubber to the cast iron in the process of curing, and the latter exhibited excellent adhesion to ethylene-propylene-diene terpolymer (EPDM) in a peroxide curing system. High peel strength adherend of rubber/metal was obtained by the suitable film thickness and good quality of film under curing condition. In other words, the film thickness had considerable effect on peel strength and rubber coverage of adherends.

So far, adhesion research between rubber and aluminum treated with TDTs has not been studied and reported. Therefore, it is necessary to study the electrochemical polymerization parameters for preparing PDA film on aluminum surface to find the optimal conditions for future application of PDA film used for adhesion with rubber.

6-diallylamino-1,3,5-triazine-2,4-dithiol monosodium (DAN) has the reactivity to metals/metallic oxides with dithiol functional groups and the affinity to rubbers with allyl groups. In this work, the study on electropolymerization of 6-diallylamino-1,3,5-triazine-2,4-dithiol monosodium (DAN) on aluminum

plate was investigated by cyclic voltammetry and galvanostat methods. The polymerization mechanism was also proposed.

2. Experimental details

2.1 Materials

Test specimens (50 × 30 × 0.1mm) of pure aluminum (purity no less than 99.9995%) were prepared by cutting a large plate into pieces. All test plates were degreased by ultrasonic washing in acetone for 15min, then dried in nitrogen air. 6-diallylamino-1,3,5-triazine-2, 4-dithiol monosodium was synthesized by the reaction of 1,3,5-triazine-2,4,6-trichloride with diallyl amine and NaSH, according to the method described in the previous paper [10]. All of the chemicals were employed as analytical reagent (AR) without any further treatment. Distilled water was used as solvent, while $NaNO_2$ (pH=7.17), Na_2CO_3 (pH=10.25) and Na_2SO_3 (pH=6.32) were applied as supporting electrolytes. The concentrations of DAN and supporting electrolytes were kept constant at 5 mM and 0.15 M, respectively.

2.2 Preparation of polymeric film

The electrochemical polymerization of DAN was performed by using electrochemical measurement apparatus (Hokuto Denkou Co.Ltd., HD-3000). The electrolytic cell was equipped with working electrode (aluminum plates), Pt counter electrode, and reference electrode (saturated calomel electrode, SCE), then was filled with electrolytic solution containing DAN in distilled water. Cyclic voltammograms was carried out at a sweep rate $|dE/dt| = 10 mVs^{-1}$. Galvanostatic electropolymerization of current density was 0.2 $mAcm^{-2}$. The whole process was conducted at 298K without any stirring.

2.3 Characterization

Electronic balance with measurement accuracy of 0.01mg (CP225D, Sartorius) was used to examine the polymeric film weight before and after electropolymerization. Polymeric film thickness was measured by using JASCO M-150i ellipsometer (Jasco Tokyo Japan). FT-IR spectra were carried out at a resolution of 4 cm^{-1} using JASCO IR-5500 (Jasco Tokyo Japan) by high-performance reflection absorption spectroscopy (RAS). A reflection attachment was used at an incident angle of 80° together with a wire grid polarizer. Contact angles of pure water on the treated aluminum plates were determined using Elma goniometer contact angle measuring apparatus (Elma-type G-1). X-ray photoelectron spectroscopy (XPS) was performed to determine the elemental composition of aluminum surface. Spectra were obtained by using ULVAC PHI-5600 spectrometer equipped with monochrome Al Kα radiation (1,486.6 eV). The pressure in preparation chamber was less than 10^{-7} Torr and less than 4×10^{-10} Torr in analysis chamber. Samples were examined over an 800 × 2,000 μm area, and photoelectron spectra were recorded with a take-off angle of 45°.

3. Results and discussion

3.1 Effect of supporting electrolyte on electropolymerization

In order to find the optimal electrolyte for electropolymerization on aluminum surface, the FT-IR spectra obtained after galvanostat polymerization were analysed (Fig. 1). The results were totally different for three kinds of electrolytes. As for $NaNO_2$, absorption bands centered at 1481 cm^{-1}, 1536 cm^{-1} and 1566 cm^{-1} were assigned to C=N and C-N groups of triazine ring [8]. Bands at 2927 cm^{-1}, 2860 cm^{-1} and 2968 cm^{-1} were assigned to CH_2 and CH groups of allyl chain. Bands at 1645 cm^{-1} and 3090 cm^{-1}, 2975 cm^{-1} were assigned to C=C and $=CH_2$ groups. It is well known that aluminum is easily oxidized to form Al^{3+} species and the Al^{3+} encounters water to form a thin, stable, insulated and protective Al_2O_3 oxide film on the surface. The band at 960 cm^{-1} proved the presence of Al_2O_3 film. However, typical absorption bands of triazine ring and allyl groups could not be observed from FT-IR spectra with Na_2CO_3 and Na_2SO_3 supporting electrolytes. Besides, there were even no absorption bands of Al_2O_3 while Na_2SO_3 (pH=6.32) was used as electrolytes, which owed to the acidity reacting with Al_2O_3 and Al. In addition, the change of pH values before and after polymerization in Na_2CO_3 (10.25 ~ 10.31), and Na_2SO_3 (6.32 ~ 7.61) electrolyte was slight, while pH of $NaNO_2$ electrolyte solution varied from 7.17 to 9.28.

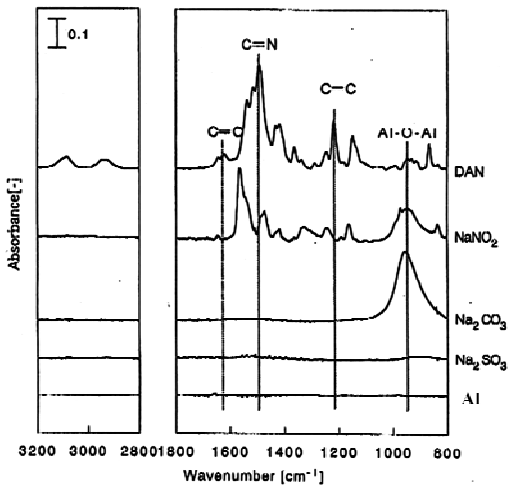


Fig. 1. FT-IR spectra of electropolymerized aluminum plates using 0.15 M various electrolyte solutions containing 5 mM DAN at a current density of 0.2 $mAcm^{-2}$.

The above results indicated that $NaNO_2$ was the ideal supporting electrolyte for electropolymerization of DAN on aluminum surface.

3.2 Electropolymerization of DAN by cyclic voltammetry (CV)

The conventional CV is regarded as a large potential amplitude technique. Additionally, it is still a very convenient tool that provides a general view of electro-chemical reaction process. Qualitative differences in the shape of CV curves of electrodes may provide useful information on the impact of the changes on electrochemical response[21]. Therefore, cyclic voltammetry was carried out to understand the polymerization mechanism of DAN in $NaNO_2$ solution. The aluminum electrode was polarized in 0.15 M aqueous $NaNO_2$ solution with/without DAN monomer between open circuit potential (E_{ocp}) and 1.70 V in positive direction then back to -0.70V in negative direction.

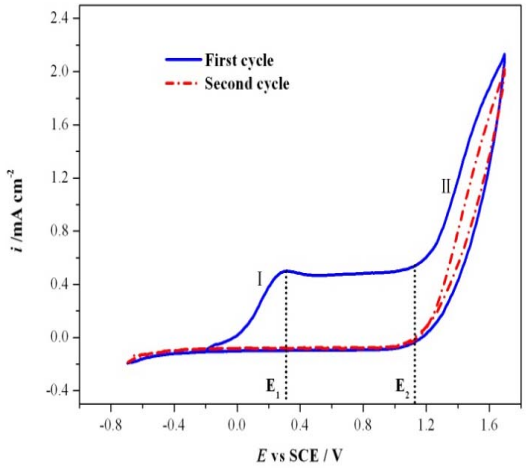


Fig. 2. Cyclic voltammetry on aluminum surface in 0.15M $NaNO_2$ aqueous solution without DAN monomer, T=298K , | dE/dt |=10mVs^{-1}.

The two cycles of reference experiment were recorded during the polarization of aluminum in 0.15M $NaNO_2$ aqueous solution without DAN monomer (Fig. 2). The open circuit potential (E_{ocp}) was -0.23V. With the scanning potential changing from -0.23V to 1.70V, the weaker current was firstly observed at -0.23 V and gradually become bigger to a high current peak at E_1 (0.32V), related to the oxidation of aluminum, which covered throughout the entire potential range and formed a broad peak remarked as peak□. In $NaNO_2$ solution, the aluminum plate was positively polarized by the reactions of electrochemical dissolution. The process was considered as follows (Eqs.(1) - (3)) [22]:

$$Al(ss) + OH^- \rightarrow Al(OH)_{ads} + e^- \quad (1)$$

$$Al(OH)_{ads} + 2OH^- \rightarrow Al(OH)_{3,ads} + 2e^- \quad (2)$$

$$Al(OH)_{3,ads} + OH^- \rightarrow Al(OH)_4^- + ss \quad (3)$$

where 'ss' in equations represented the bare surface site of aluminum.

Then, a sharp rise of current was observed at E_2(1.11V) and remarked as peak□, due to the oxidation of the OH^- and NO_2^-. The reaction equations were showed as follows [23]:

$$NO_2^- \rightarrow NO_2 + e^- \quad (4)$$

$$H_2O + NO_2^- \rightarrow NO_3^- + 2H^+ + 2e^- \quad (5)$$

$$2NO_2^- \rightarrow NO_3^- + NO + e^- \quad (6)$$

$$2NO_2^- \rightarrow 2NO_2\bullet + 2e^- \rightleftharpoons N_2O_4 \quad (7)$$

$$4OH^- \rightarrow 2H_2O + O_2\uparrow + 4e^- \quad (8)$$

In this process, there could be several possible reactions. NO_2^- could be oxidized directly with generating NO_2 or NO_3^-. NO_3^- and NO could also be generated from disproportionation reaction of two equivalents NO_2^- (Eq (6)). Nitrogen dioxide intermediate ($NO_2\bullet$) produced by oxidation of NO_2^- could dimerize to produce N_2O_4 (Eq (7))[24]. The $NaNO_2$ electrolyte could hydrolyze in water with OH^- being generated. Therefore, reaction (8) occurred due to the supply of OH^- [25]. Lots of bubbles could be observed on aluminum surface and irritant gas could be smelt simultaneously. No reduction peak appeared when scanning was carried out in negative direction because of Al_2O_3 oxide film on the aluminum surface. In the second cycle, the current density decreased dramatically due to the passivating nature of the aluminum oxide layer formed in the first cycle.

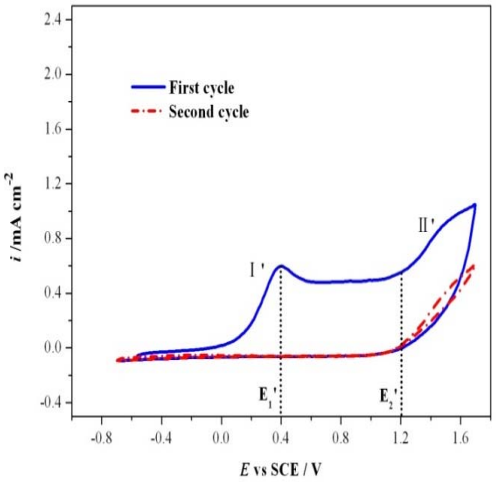


Fig. 3. Cyclic voltammetry on the aluminum in 0.15 M $NaNO_2$ aqueous solution with 5 mM DAN monomer,

T=298K, |dE/dt|=10mVs^{-1}

Two anodic peaks were also observed when the aluminum plate was polarized in the aqueous $NaNO_2$ solution with DAN monomer at a lower open circuit potential (E_{ocp}') -0.57V, which was different to E_{ocp} (Fig. 3). The peak□′at -0.57V was similar to the feature in the case of blank $NaNO_2$ solution, but E_1 (0.32V) shifted to higher potential E_1' (0.40V). It was considered that the reaction between aluminum ions and DAN produces thin monomer layer on the aluminum plate, depressing the oxidation of aluminum. Also, the maximum current density responding to E_1' increased from I_1 (0.49 mAcm^{-2}) to I_1' (0.61 mAcm^{-2}) (Fig. 4). It was supposed that the thin monomer layer was formed by the reaction between Al and DAN generating Al-DAN complexes slight white film after scanning from E_{ocp}' to 1.70V. The current density of peak□′ sharply decreased than that of the blank solution ($i_x'<i_x$, Fig. 4) and no bubbles could be seen on aluminum surface and no irritant gas could be smelt. It is suggested that the oxidation and polymerization of DAN took place [9], and the formation of PDA film inhibited direct electrolysis of OH^- and NO_2^-. No reduction peak appeared when scanning was carried out from 1.70 to -0.70V in negative direction. The absence of any reduction peak indicated that the depolymerization of polymer film on aluminum surface did not take place, since the PDA film was also insulated like Al_2O_3 film [8]. In the second cycle, the current density decreased more significantly than that of the blank due to the formation of PDA film and aluminum oxide layer formed in the first cycle, which proved to be an excellent barrier to inhibit electron transfer. The white film was observed on aluminum surface after the 1st scan, which revealed the obvious formation of PDA film .

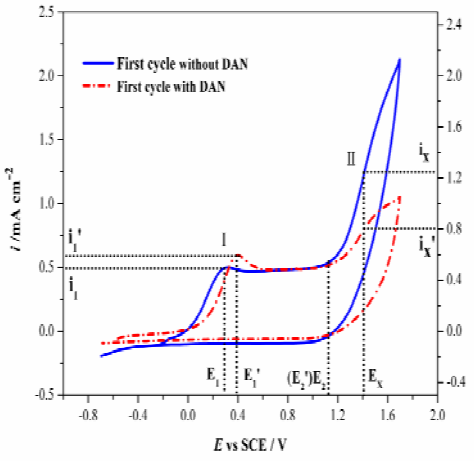


Fig. 4. Comparision of the first cycle with/without DAN in 0.15 M $NaNO_2$ aqueous solution.

In order to better understand the process of electropolymerization of DAN on aluminum surface, upper potential (2.10V) of CV was carried out (Fig. 5) and X-ray photoelectron spectroscopy (XPS) was also used to analyze the PDA film (Fig. 6 and Fig. 7).

A new strong peak □‴ started to appear at 1.75V with the upper limit of scan increasing, which did not appear under 1.70V scan potential (Fig. 3). It is attributed to the electrolysis of OH^- and NO_2^-, since lots of bubbles could be seen on aluminum surface and irritant gas could also be smelt at the same time. It was considered that Al_2O_3 film and PDA film inhibited electron transfer, namely, depressed the electrolysis of OH^- and NO_2^-. Peak□‴ and peak □‴ revealed the formation of the Al-DAN complexes and the PDA film, respectively. The obtained film was consisted of Al_2O_3 and PDA film. In the above anodization process, the polymerization potential played an important role in creating uniform and packed film, and the potential should be less than 1.75V.

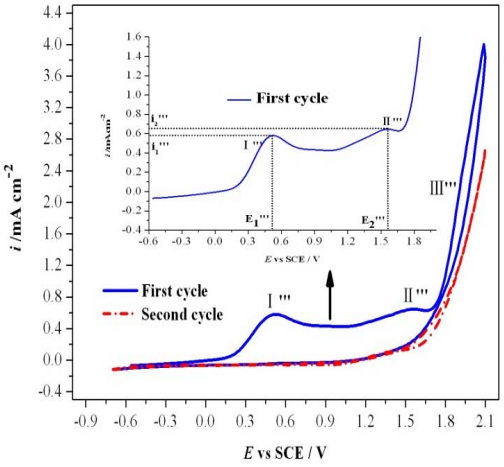


Fig. 5. Cyclic voltammetry for the aluminum in 0.15 M $NaNO_2$ aqueous solution with 5 mM DAN monomer at a higher potential, T=298K, |dE/dt|=10mVs^{-1}

XPS spectra were investigated to confirm the chemical structures of polymer film on aluminum surface. XPS spectra of samples covered with PDA film were compared to the blank aluminum. The XPS peaks corresponding to oxygen (O1s), nitrogen (N1s), carbon (C1s), sulphur (S2p, S2s) and aluminum (Al2p, Al2s) were analysed (Fig. 6). Only the peaks of C1s (285.0 eV), O1s (532.0 eV), Al2p (73.6 eV) and Al2s (119.7 eV) could be observed for the untreated aluminum plate, while the peaks of N1s (400.7eV), S2s (228.2 eV), S2p (163.6 eV) originated from the PDA film could be detected. The results also confirmed the formation of PDA film on aluminum surface. The atomic intensity for the relevant elements was different in the graphical representation. In the case of DAN treatment, there were increased amount of N (N1s), C (C1s) and S (S2s, S2p) and decreased amount of O (O1s) and Al (Al2p, Al2s) on the aluminum

surface.

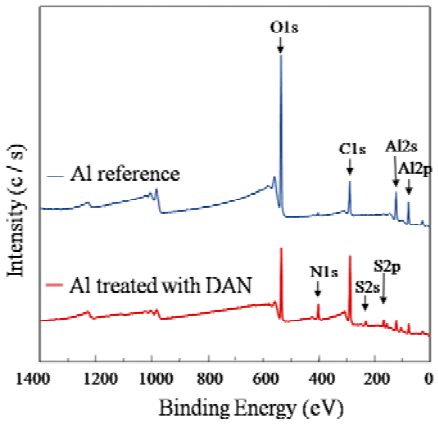


Fig. 6. XPS wide scan spectra of the untreated and DAN treated aluminum surfaces in 45°tilt degree. (X-ray anode: Al monochromated 2 nm filament; Aperture: 800 × 200 μm).

Fig.7 depicts the fitted S2p curves in the XPS spectra of polymer films on aluminum plate. The S2p peak was consisted of peaks assigned to S*–M (M: aluminum) group at 160.6 eV and C–S*–C groups at 163.4 eV, C–SS*–C groups at 163.9 eV. Peaks based on C–S*–Al groups indicated the reaction of SH groups and S^- with aluminum during electrochemical polymerization. Peaks based on C–S*–C groups suggested the reaction of SH groups with allylic groups. Peaks based on C–SS*–C groups revealed the electrochemical reaction of thiols. From the XPS data of S2p peak, the polymeric films formed on aluminum plate were confirmed to consist of PDA. Therefore, it could be concluded that PDA film was obtained by electrochemical methods of DAN on aluminum surface.

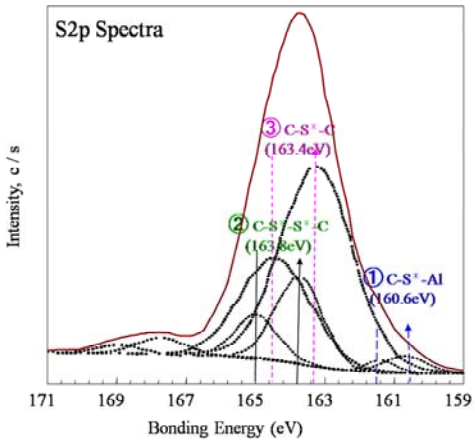
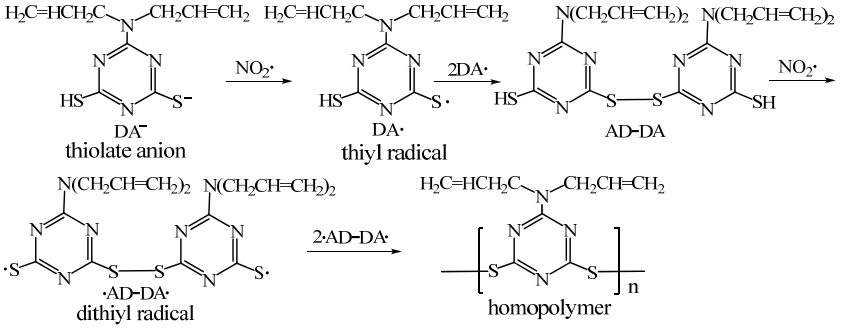


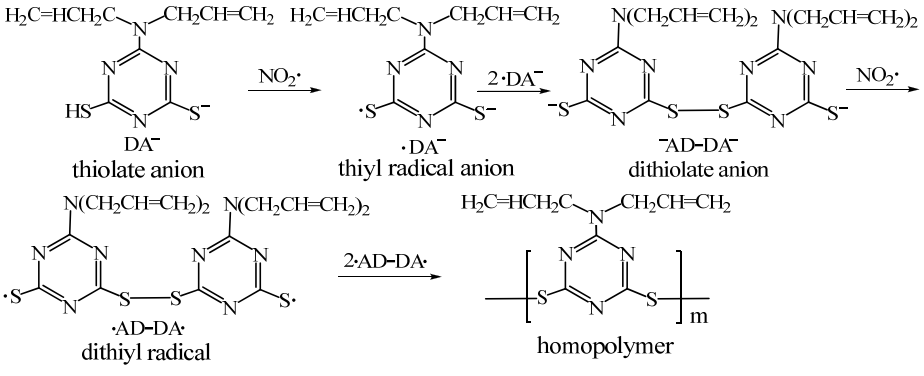
Fig. 7. S2p fitted curve of high resolution XPS spectra from polymeric film on aluminum plate in 45°tilt degree (X-ray anode: Al monochromated 2 nm filament; Aperture: 800 × 200 μm).

Based on the above experimental facts, the reaction mechanism is proposed as follows (Eqs.(9-13)):

$$2NO_2^- \rightarrow 2NO_2\bullet + 2e^- \rightleftharpoons N_2O_4 \tag{9}$$



(10)



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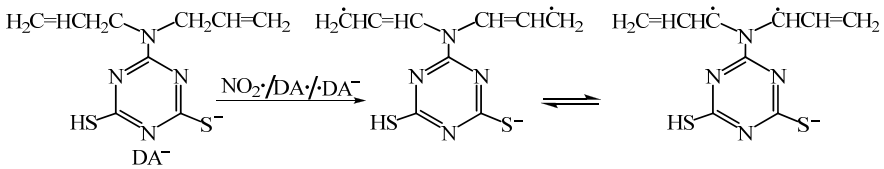
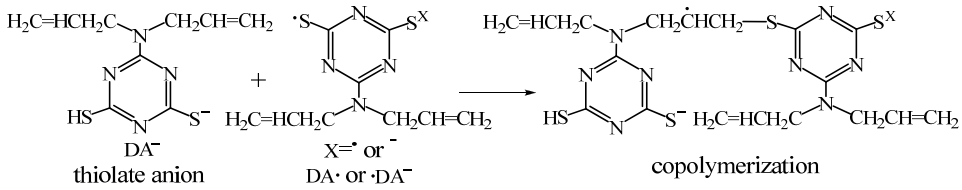


(12)



(13)

Scheme.1. Radical mechanism for the formation of triazinedithiol films on aluminum surface in the aqueous solution of DAN and $NaNO_2$ electrolyte

As shown in Scheme 1, the process involved electrochemical oxidation to generate N_2O_4 species followed by a chemical reaction to produce NO_2•. Free radicals (allyl radicals, NO_2•, DA•, •AD-DA•, •AD^-) generated by the electrochemical oxidation experienced chain growth reaction of DAN polymerization, then insoluble polymeric nanofilm was formed. Moreover, thiol group (AD-DA, intermediate of Eq.(10)) and dithiolate anion ($^-$AD-DA^-,intermediate of Eq.(11)) reacted with aluminum, which was similar to the reaction between triazinedithiols and copper/copper alloy [26]. Allyl radicals (a, b) reacted with each other or with other free radicals. Eq. (13) was just one of the possible reactions. Fig.8 showed the ideal structure of PDA film and newly formed chemical bonds. The dashed lines represented possible bonding sites. Bonding sites marked with different color (pink, green and blue) on the ideal structure of PDA polymer film were consistent with the results of XPS spectra.

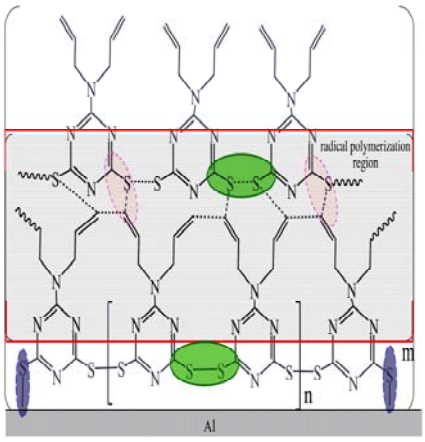


Fig. 8. Ideal structure of PDA film and possible bonding sites (dashed lines).

Monomer molecules are arranged on the substrate in an electric bilayer immediately following current application. Thiolate anions become instantly situated in the electric bilayer by polarization to form a two-dimensional plane. Polarization decreases with the distance to electrode surface. It becomes difficult for thiolate anions to enter the electric bilayer of polymer adhering to the electrode after 6 min polarization at 0.2mAcm^{-2} of current density. The arrangement extent of thiolate anions parallel to each other in lines and perpendicular to the aluminum surface is decreasing with the polymer growth. This arrangement is due to the diffusion of the thiolate anions and elctrode polarization .As a result, the outer layer of polymer film is composed of allyl group. Thus, the surface properties of DAN-treated aluminum could be potentially used for adhesion in future.

4. Conclusions

$NaNO_2$ proved to be the ideal supporting electrolyte for electropolymerization of DAN and their derivatives on aluminum surface. PDA film was successfully prepared on aluminum plate by cyclic voltammetry method. The obtained film was consisted of Al_2O_3 and PDA. Free radicals (allyl radicals, NO_2•, DA•, •AD-DA•, •AD^-) produced by the electrochemical oxidation, experienced reaction of radical polymerization, and insoluble polymeric nanofilm was obtained. The outer surface of nanofilm was composed of allyl groups, which had the affinity to rubbers. This technique was an environment-friendly method for promoting both adhesion and anti-corrosion of aluminum material.

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