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Novel Technique of Two-step Potentiostatic Polymerization to Fabricate Triazinedithiol Polymeric Nanofilm on Aluminum Surface

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The polymeric nanofilm of 6-dihexylamino-1,3,5-triazine-2,4-dithiol monosodium (DHN) was prepared on aluminum surface by novel two-step potentiostatic polymerization technique. The chemical structures of polymeric nanofilm were characterized by Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). The results indicated that the chemical structure of polymeric nanofilm was poly(6-dihexylamino-1,3,5-triazine-2,4-dithiol) (PDH). The morphologies of PDH were observed by atomic force microscopy (AFM). It was suggested that the optimal process for two-step electrochemical polymerization was polymerized at 1.6 V for 60 s in the first step, then at 10.0 V for 30 s in the second step. The optimal electrochemical polymerization temperature was 10℃. It is expected that this technique will provide a novel method for preparation of triazinedithiol polymeric nanofilm on various metal surfaces.

Keywords: Aluminum surface, polymeric nanofilm, potentiostatic electropolymerization

1. INTRODUCTION

Aluminum is used in various industrial applications especially in architecture, aerospace and automobile industries due to their low cost, high mechanical intensity, low density and good recycling efficiency. However, their application has been limited because of susceptibility to corrosion. Corrosion inhibition of aluminum materials has attracted the attention of many researchers. One approach is the use of pre-treatments based on chromates, which are hazardous to environment and human health. Therefore, many researches have been carried out to develop environmental-friendly system [1-3].

Since the publication of researches on the anticorrosion properties of triazinedithiols (TDTs) on copper surface [4], adsorption and polymerization of TDTs on metal surfaces have been receiving much attention in the past few years. The researches showed that polymeric nanofilms prepared by different TDTs had basic anticorrosion property [5, 6].

Thus, during the last decade, there were many studies on other applications of TDTs polymeric film on various metal substrates. Silikas [7] investigated the performance of TDTs primers on clinically relevant metal substrate for dental adhesion application. Mori studied the lubrication property of TDTs polymeric nanofilm during steel wire drawing [8, 9], and concluded that this technique would be possible to use for unifying metal processing and surface treatment. Wang [10] investigated the dielectric property of polymeric nanofilm obtained by 6-(N-allyl-1,1,2,2-tetrahydroperfluorodecyl)amino-1,3,5-triazine-2,4-dithiol monosodium on aluminum plate, which showed that the dielectric constant were the highest reported for organic dielectrics to date. Kang [11] studied the superhydrophobic property of some TDTs polymeric nanofilm on pure copper plate, indicating that the polymeric film on rough copper surface exhibited superhydrophobic property.

The triazinedithiol polymeric nanofilm could be electrochemically polymerized by cyclic voltammetry [6, 12, 13] or galvanostatic [14] methods in the previous studies. These two electrochemical methods had been studied systematically. However, the polymeric nanofilm obtained by the techniques was too thin to apply in more fields. Therefore, new technique to fabricate ideal thicker and denser triazinedithiol polymeric nanofilm is necessary. The two-step potentiostatic polymerization will provide the possibility to prepare the ideal polymeric nanofilm of triazinedithiol as an emerging technology.

In this study, we focused on this technique and the influencing factors including electrochemical polymerization potential and temperature for the two-step potentiostatic method to obtain excellent polymeric nanofilm, which is expected to be applied in wider fields.

2. EXPERIMENTAL SECTION

2.1. Materials

Test specimens (50 × 30 × 0.1 mm) of pure aluminum were prepared by cutting a large plate into pieces.

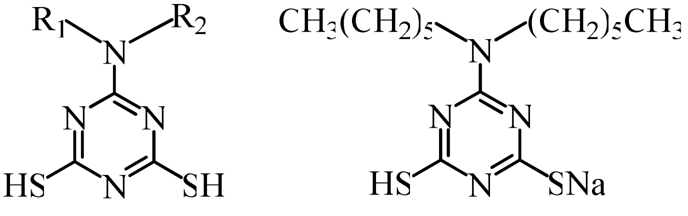


Figure 1. Structure of TDTs and DHN

All test plates were degreased by ultrasonic washing in acetone for 15min, and dried in nitrogen air. 6-dihexylamino-1,3,5-triazine-2,4-dithiol monosodium (DHN) (Fig. 1) was prepared by the reaction between 6-dihexylamino-1,3,5-triazine-2,4-dichloride and NaSH, according to the method described in the previous study [15]. All of the chemicals were employed as analytical reagent (AR) without further purification. Distilled water was used as solvent and sodiumnitrite ($NaNO_2$) was applied as supporting electrolyte [12]. The concentrations of DHN and $NaNO_2$ were kept at 5 mM and 0.15 M, respectively.

2.2. Preparation of polymeric film (PDH)

Electrochemical polymerization of DHN was performed by 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 filled with electrolytic solution containing DHN in distilled water. The potential of 1.6 V was used as the first step potentiostatic potential, then the higher potential (2, 6, 8, 10 V) was applied for the second step. Here, the potentials higher than 10 V were not chosen since the polymeric nanofilm obtained by the first step will be broken down when the potential exceeded 10 V. Electrochemical polymerization time was 60 and 30 s for the two steps, respectively. To obtain the favorable polymeric nanofilm, the effect of polymerization temperature was also investigated.

2.3. Characterization

FT-IR was carried out by high-performance reflection absorption spectroscopy (JASCO IR-5500). A reflection attachment was used at an incident angle of 80° together with a wire grid polarizer. 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 the preparation chamber was less than 10^{-7} Torr and less than 4×10^{-10} Torr in the analysis chamber. The samples were examined over an area of $800 \times 2,000$ μm, and the photoelectron spectra were recorded with a take-off angle of 45°. The treated surfaces were observed by atomic force microscopy (AFM) (Nanoscope III Scanning Probe Microscope, Digital Instruments, Veeco Metrology Group) with contact mode to characterize their morphologies.

3. RESULTS AND DISCUSSION

3.1. Effect of the second-step potential on polymeric nanofilm

Fig. 2 shows FT-IR spectra of polymeric nanofilm obtained by electrochemical polymerization of DHN on aluminum plate under different second step polymerization potentials. In the FT-IR spectra, the presence of a triazine ring is confirmed by absorption peaks at 1,481, 1,536 and 1,560 cm^{-1}

due to >C=N- bonds. Dihexyl amino groups are confirmed by absorption peaks at 2,872 and 2,853 cm^{-1} due to C-H symmetric stretching vibrations of CH_3- and -CH_2- as well as by absorption peaks at 2,962 and 2,938 cm^{-1} due to C-H asymmetric stretching vibrations of CH_3- and -CH_2-. The peak at 956 cm^{-1} was also observed due to the alumina. It is suggested that the electrochemical polymerization of DHN and oxidative reaction of aluminum occur simultaneously.

It was also noted that absorption intensities of >C=N- , C-H and Al-O for the polymeric nanofilm prepared at 10 V were the strongest, which indicated that the thickest nanofilm could be obtained at 10 V.

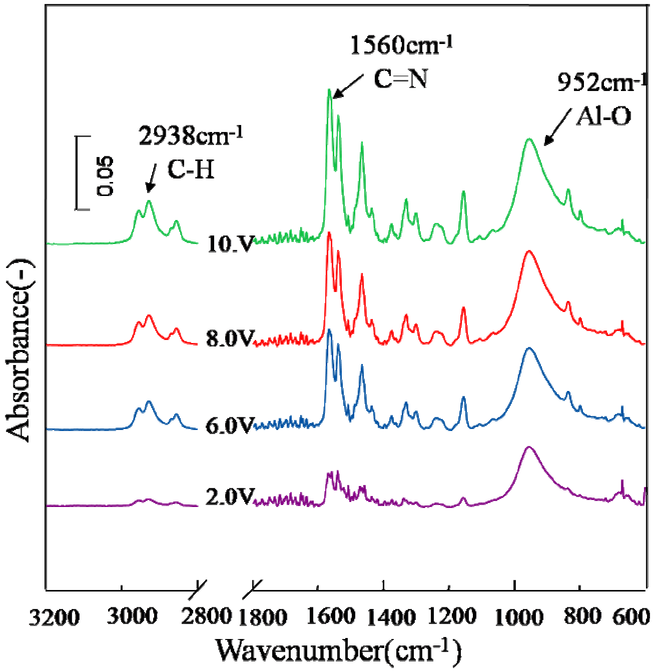


Figure 2. FT-IR spectra of PDH films obtained by electrochemical polymerization at different second step potentials

The atomic concentrations of PDH nanofilm obtained by different second step potentials were investigated by XPS (Fig. 3). The peaks corresponding to oxygen (O1s), nitrogen (N1s), carbon (C1s), sulphur (S2p, S2s) and aluminum (Al2p, Al2s) were analyzed. The peaks of C1s (285.0 eV), O1s (532.0 eV), Al2p (73.6 eV) and Al2s (119.7 eV) could be observed obviously at 2 V, while the peaks of N1s (400.7 eV), S2s (228.2 eV) and S2p (163.6 eV) were invisible. In the case of polymerization at 6, 8 and 10 V, an increased amount of N (N1s), C (C1s) and S (S2s, S2p) and decreased amount of O (O1s) and Al (Al2p, Al2s) could be detected on aluminum surface.

Table 1 shows the XPS results of PDH film polymerized at different second step potentials. It can be seen that the atomic concentrations of C1s, N1s and S2p increase, while that of Al2p and O1s decrease on aluminum surface at the higher polymerization potentials, which is consistent with the conclusion from FT-IR spectra. It is indicated that the continuous formation of polymeric nanofilm at the higher potential takes place. The results showed that the optimal second step potential was 10 V.

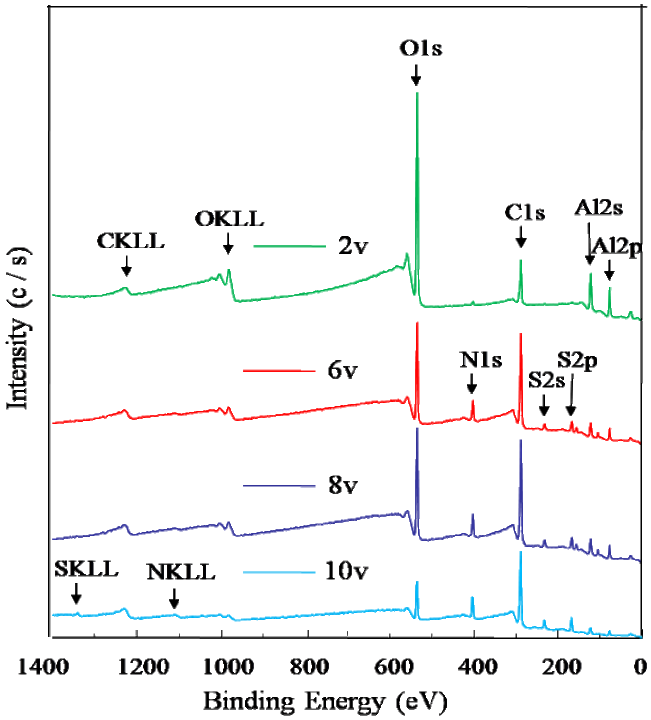


Figure 3. XPS analysis of PDH films obtained by electrochemical polymerization at different second step potentials

Table 1. Atomic concentration (%) of PDH polymerized by different second step potentials

Potential(V)	C1s (%)	N1s (%)	S2p (%)	Al2p (%)	O1s (%)
1.6V60s+2.0V30s	25.31	1.13	0.55	22.06	50.95
1.6V60s+6.0V30s	57.94	6.75	3.21	8.92	24.03
1.6V60s+8.0V30s	57.74	8.13	3.88	8.86	21.39
1.6V60s+10.0V30s	62.98	11.54	5.53	5.68	14.27

Based on the results of FT-IR and XPS spectra, the morphologies of PDH nanofilm prepared at 6, 8, 9 and 10 V were also investigated by AFM (Fig. 4). It can be seen that the aluminum surfaces (b, c, d, e and f) were covered by PDH nanofilm compared to Al reference (a). The fringes of aluminum surface became to disappear gradually due to the formation of polymeric nanofilm from (a) to (f), and the coverage of aluminum surface became higher. The fringes could be hardly observed when the potential was 8.0 V. Island domain was uniformly distributed at 10 V. All of the results demonstrated the continuous formation of polymeric nanofilm on aluminum surface at a higher polymerization potential, and confirmed that the optimal second step potential was 10 V.

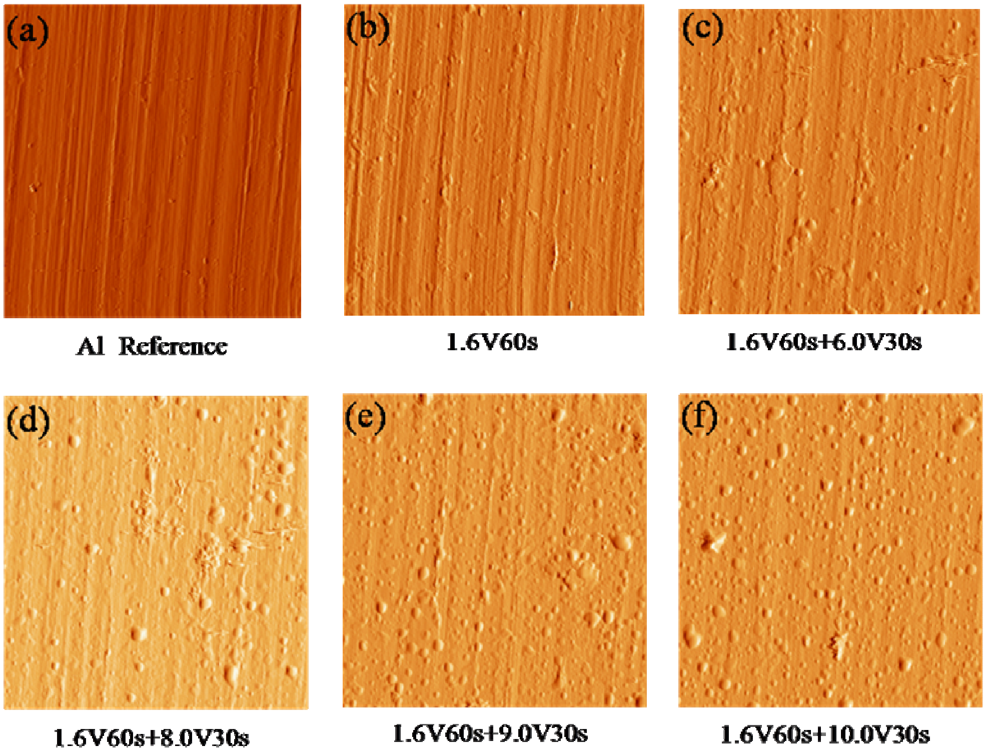


Figure 4. AFM images (25×25μm) of PDH films prepared under different second step potentials

3.2. Effect of polymerization temperature on polymeric nanofilm

FT-IR spectra of PDH films fabricated by different electrochemical polymerization temperature are shown (Fig. 5).

It can be seen that when the electrochemical polymerization temperature is over 10 ^{o}C, the intensities of >C=N-, C-H and Al-O absorption peaks become decreased. The oxidative reaction and stripping of aluminum electrode could be accelerated with the polymerization temperature increasing, which led to the formation of alumina layer and pinhole. It was assumed that the alumina layer was insulated, hindering the further polymerization of triazinedithiol monosodium. Also, the two dimensional morphologies of the aluminum surface by different temperature were studied by AFM (Fig. 6). It can be seen that the aluminum surfaces are covered by PDH nanofilm. Island domain is uniformly distributed at 10 ^{o}C, which also reveals that the optimal electrochemical polymerization temperature is 10 ^{o}C.

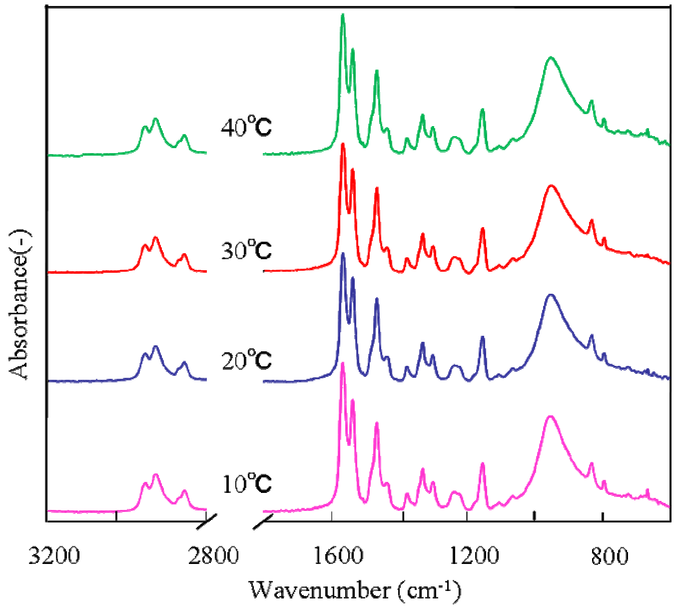
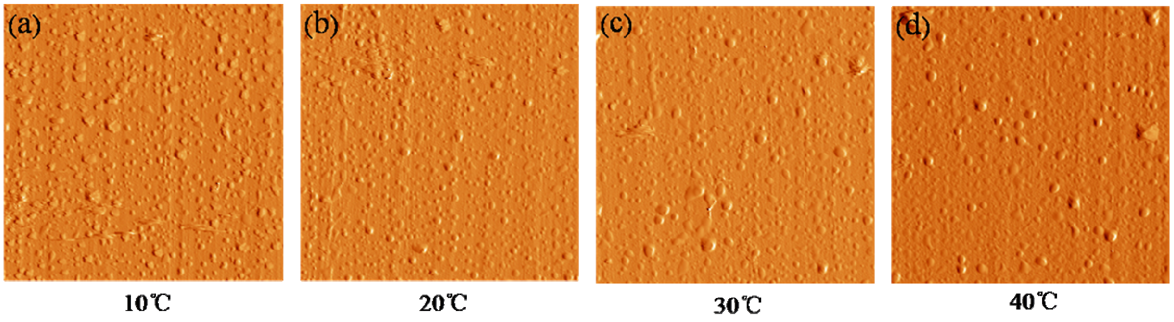


Figure 5. FT-IR spectra of PDH films obtained by different temperature from 10 to 40 □ at 1.6 V 60 s and 10.0 V 30 s



10℃ 20℃ 30℃ 40℃

Figure 6. AFM images (25×25μm) of PDH films obtained by different temperature from 10 to 40□

4. CONCLUSIONS

PDH nanofilm can be successfully obtained by two-step potentiostatic method. The optimal process for two-step electrochemical polymerization was polymerized at 1.6 V for 60 s in the first step, then at 10.0 V for 30 s in the second step. The optimal electrochemical polymerization temperature was 10 ^{o}C. More uniform and denser polymeric nanofilm of PDH can be obtained. It is expected that this technique will provide a novel method for preparation of triazinedithiol polymeric nanofilm on various metal surfaces.

ACKNOWLEDGEMENTS

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