

Characterization of Thin Films Deposited from Benzene Using Microwave Plasma Polymerization

Nuri Ayad Zreiba*, Lubna Emhemed Elzawi

Materials and Metallurgical Engineering Department, University of Tripoli, Tripoli, Libya

Email address:

nurizreiba@yahoo.com (N. A. Zreiba), ezawi@yahoo.com (L. E. Elzawi)

*Corresponding author

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Abstract: Microwave plasma enhanced chemical vapor deposition (MWPECVD) is a cheap and easy method for the modification of materials surfaces to enhance some required property. In this study, benzene as a monomer was deposited on both Aluminum alloy (2024-T3) and glass slide substrates at several pressures and deposition times using MWPECVD. The chemical structure and surface properties of as-grown thin films were analyzed on glass using FTIR and NMR. It is found that benzene rings are not fully preserved in the film structure. Some benzene rings were converted to saturated alcohol and/or ester functional groups in the crosslinked film structure. The corrosion resistance of aluminum alloy substrates both bare and covered with plasma polymerized thin films was carried out by potentiodynamic polarization measurements in standard 3.5% NaCl solution at room temperature. The benzene deposited film was found to be not fully suitable for protection of aluminum substrate against corrosion. The only film that stayed intact post the corrosion measurement is that for the deposition condition of 30 mtorr for 90 minutes. The change in the processing parameters seemed to have a strong influence on the film protective ability. SEM was used to study the surface morphology of deposited films on aluminum. It is found that the polymerized film roughness decreases with increasing monomer pressure and deposition time. Adhesion test done on films deposited on glass showed that the best adhesion occurs for deposition condition of 30 mtorr for 90 minutes and poor adhesion occurred at 7 and 9 mtorr for 90 minutes.

Keywords: Plasma Polymerization, Aluminum Alloy, Corrosion, Adhesion

1. Introduction

Plasma enhanced chemical vapor deposition (PECVD) can be used cheaply and effectively to deposit well-adherent thin films of 10 – 10000 Å thickness. Microwave enhanced CVD (MWPECVD) (which typically has an excitation frequency of 2.45 GHz) is one of PECVD methods [1]. It is generated by the application of direct or alternating electric fields to a low-pressure (10^{-1} to 10^3 Pa) gas. MPECVD has several advantages as compared to other plasma polymerization methods. This includes environmental factors plus the ability to deposit pure thin films or particles [2]. When a surface is exposed to the plasma, it is subjected to the action of those species that are, in a general way, very reactive. Structural, compositional and morphological changes can be induced in the solid surface substrate. The modification degree is

strongly dependent on the process parameters that include: plasma chemical composition, pressure, power & frequency, temperature, bias of the sample, and reactor geometry. Plasma polymerization results when organic or organometallic compounds and their mixtures with reactive and noble gases are employed. The resulting films have unique properties due to their dense cross linked bulk structure. These spatially uniform films exhibit good adhesion to a variety of substrates, excellent chemical inertness, high thermal resistance, and are formed from an inexpensive, solvent-free, room temperature process [3-6]. Angelini et al. [7] reported that PECVD appears to be a promising technique in enhancing the corrosion properties of Mg alloys. Also plasma pretreatment processes play an important role in determining the electrochemical behavior of deposited film [7]. Domingues et al. [8] and Abourayana et al. [9] have found that the plasma coatings obtained by

plasma deposition of hexamethyldisiloxane improved the corrosion resistance of the Alclad 2024-T3 alloy, and these coatings provide improved durability compared to the uncoated materials. Silva et al [10] have reported that higher quality diamond films with smaller grain size and better morphology were obtained by using microwave plasma enhanced chemical vapor deposition on ferrous substrates coated with Ti and Cr interlayers.

It should be mentioned that although extensive research has been done on plasma polymerization, a limited research exist on polymerization of pure benzene using microwave enhanced chemical vapor deposition [9, 11, 12]. Hence, the current work aims to investigate the effect of monomer pressure and deposition time on deposited polymeric thin films of benzene precursors on aluminum alloy type 2024-T3 and glass slide substrates at room temperature using MPECVD method.

2. Experimental Work

2.1. Materials and Deposition Process

Al alloy and glass wafers were used as substrates in the present investigation. Aluminum alloy type 2024-T3 of chemical composition given in Table 1 and microstructure as shown in Figure 1 is used to examine the adherence, surface

roughness and corrosion protection properties of deposited film. Glass slide substrates were used for deposited film structural analysis along with film thickness measurements and adhesion characteristics. The Al alloy substrates were cut to square shape with dimensions of ($1 \times 1 \text{ cm}^2$) and original thickness of 2 mm. Each sample was ground using 800 to 2000 SiC grit papers. The glass wafers have rectangular shape with dimensions of $2 \times 6 \text{ cm}^2$. The glass and Al alloy samples were cleaned using distilled water and acetone just before inserting into deposition chamber.

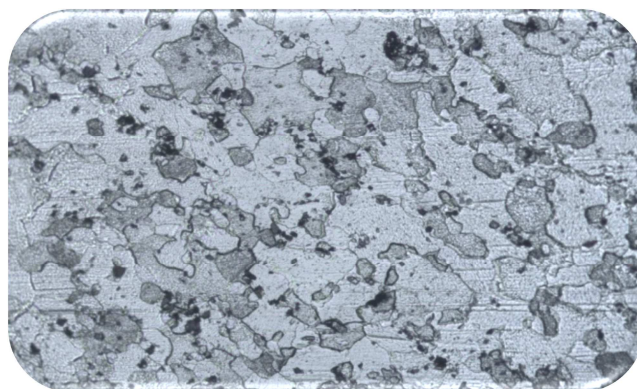


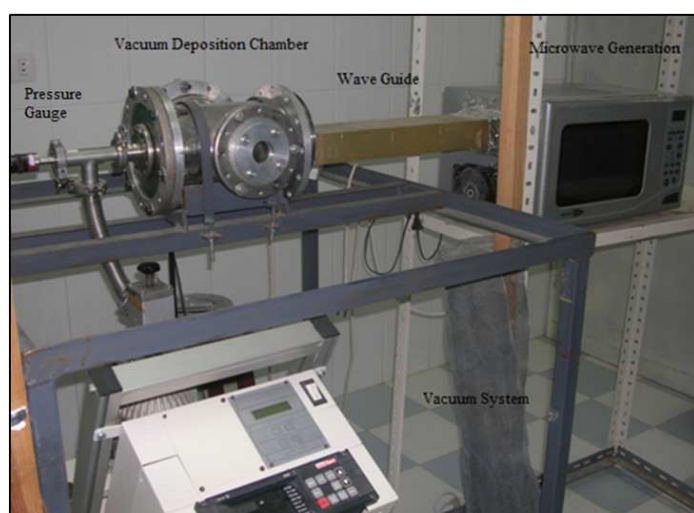
Figure 1. Microstructure of 2024-T3 containing CuMgAl_2 intermetallics, (Keller etchant at 200x).

Table 1. Chemical composition of Aluminum alloy 2024 substrate.

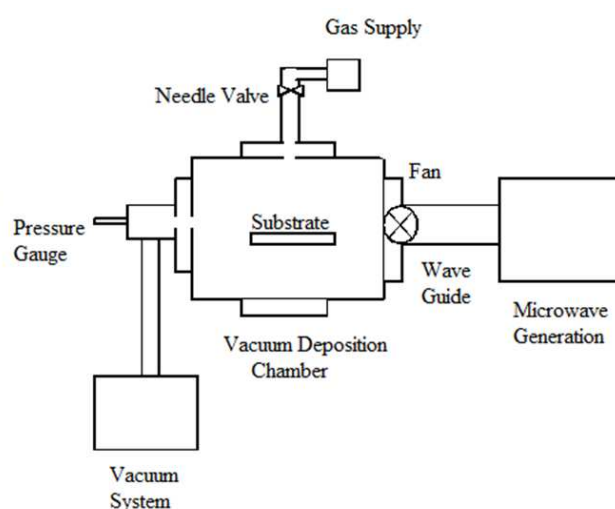
Element	Si	Fe	Cu	Mn	Mg	Zn	Ti	Cr	Ni	Pb	Sn	Al
Wt%	0.219	0.299	3.722	0.383	1.131	0.104	0.011	0.017	0.009	0.001	0.005	94.101

The plasma polymerization chamber used is a homemade stainless steel cylindrical vessel 25 cm long, and 12.5 cm in diameter. Microwaves are generated using a commercial magnitron Severin model microwave oven with frequency of 2.45 GHz and maximum power of 900 watt, connected to the chamber with a wave-guide. Before the deposition

process, the inside of chamber was ground using 1500 followed by 2000 SiC grit papers and then cleaned with acetone to remove any impurities present. Figure 2a and b show the components of plasma microwave deposition system, and a schematic sketch of whole set up, respectively.



(a)



(b)

Figure 2. a) Components, and b) Schematic diagrams of plasma microwave deposition system used.

Although different combinations of benzene (C_6H_6) monomer pressures and deposition times were tried, only

the conditions of 7, 9, and 30 mtorr with deposition times of 60 min and 90 min gave reliable results, see Table 2. It should be noted that deposition at pressures above 30 mtorr (less vacuum) produced particles instead of films, and vacuum better than 1 mtorr made deposition rates impractically low. Figures 3a and b show two of several attempts for deposition at different monomer pressures to reach the best ones indicated in Table 2. The sample in Figure 3a deposited at monomer pressure of 50 mtorr for 30 minutes shows over deposition. The deposited film stayed

intact for a period of time and then separated from the substrate. For deposition at pressure of 50 mtorr, and longer time of 45 minutes (not shown), the deposited film immediately separated from substrate. It is noted that the substrates gained golden color after deposition of benzene compared with base aluminum alloy, and color became darker (thicker film) with increase of both monomer pressure and deposition time. Using density of benzene, it is found that the film thickness range for trials is between 1 to 4 μm , see Table 2.

Table 2. Deposition parameters used in this work.

Monomer Pressure (P_g , mtorr)	Base Pressure (P_o , mtorr)	Power (Watt)	Time (Min)	Film Weight (mg)	Film Thickness (μm) $\pm 5\%$
7	1.7	540	60	1.1	1.0416
9	1.7	540	60	1.7	1.6098
30	1.7	540	60	3.7	3.5037
7	1.7	540	90	1.5	1.4204
9	1.7	540	90	1.9	1.7992
30	1.7	540	90	4.1	3.8825

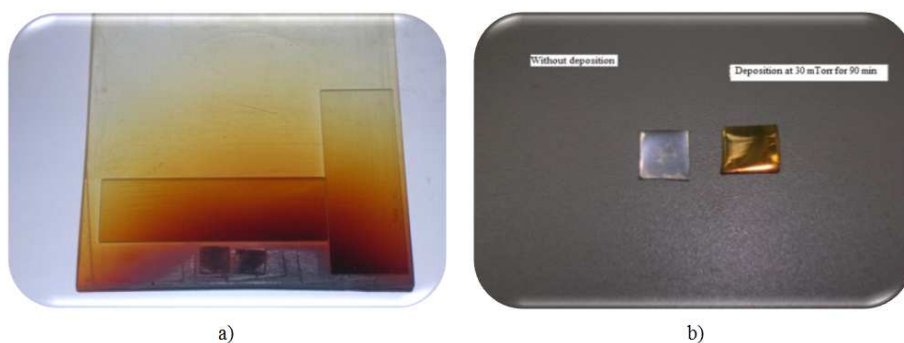


Figure 3. a) Samples showing over deposition (50 mtorr for 30 min.) b) Before and after deposition at 30 mtorr for 90 min.

2.2. Visual Inspection

This inspection is a test of samples in terms of color, adhesion and stability of deposited thin film with naked eye.

2.3. FTIR Analysis

Film deposition on glass wafers was subjected to Fourier Transformation Infrared Spectroscopy (FTIR Model # Vector 22 I) to identify functional groups of deposited films.

2.4. NMR Analysis

NMR measurements was carried out by BRUKER 300 MHz instrument. The specimen used in this inspection is scratched by razor blade to collect required sample.

2.5. Adhesion Scotch Tape Test

The ability to deposit highly adherent, highly cross linked and pinhole free films has led to the consideration of plasma polymers for the purpose of protecting metals and other substrates from the environment and from corrosive agents [13]. In the scotch tape test, the sample is placed in distilled water for a quarter of an hour dried well by a drier (cool air), then sealed with adhesive tape to remove the plaster. If the film stay on substrate not removed when detaching the

adhesive then the film is considered well adherent to substrate. This test carried out on films deposited on glass substrates. For the case of films deposited on Al alloy, the film is considered adherent if stays intact after corrosion test.

2.6. Surface Morphology

Scanning electron microscope (SEM) analysis was performed with a LEO1430VP microscope to obtain information regarding the morphology and surface roughness of plasma polymerized deposited thin films.

2.7. Corrosion Test

As regard to corrosion test, aluminum alloy (2024) both bare and covered with benzene film were subjected to accelerated corrosion test based on Tafel plot technique. Cu wire connectors were welded to the back of Al alloy using silver paint. After drying, all the surfaces of substrates were isolated using transparent nail polish except the treated surfaces. Polarization measurements were carried out potentiodynamically in 3.5% NaCl standard solution at room temperature. After immersion of the aluminum alloy in the solution, the potential of the aluminum was recorded at a scan rate of 1 mV /s within scan range from -2000 mV up to breakdown potential. A standard electrochemical test cell, equipped with a Potentiostat Model # PST05 instrument was used for measurements.

The protective efficiency, η (%) of the deposited films was determined from the polarization curves using, following formula [13].

$$\eta (\%) = \frac{i_{corr} - i_{corr}}{i_{corr}} \quad (1)$$

Where i_{corr}^0 and i_{corr} are the corrosion current density values without and with deposited film respectively, determined by extrapolation of cathodic Tafel lines of anodic and cathodic branches of potentiodynamic curve.

3. Results and Discussion

3.1. Visual Inspection

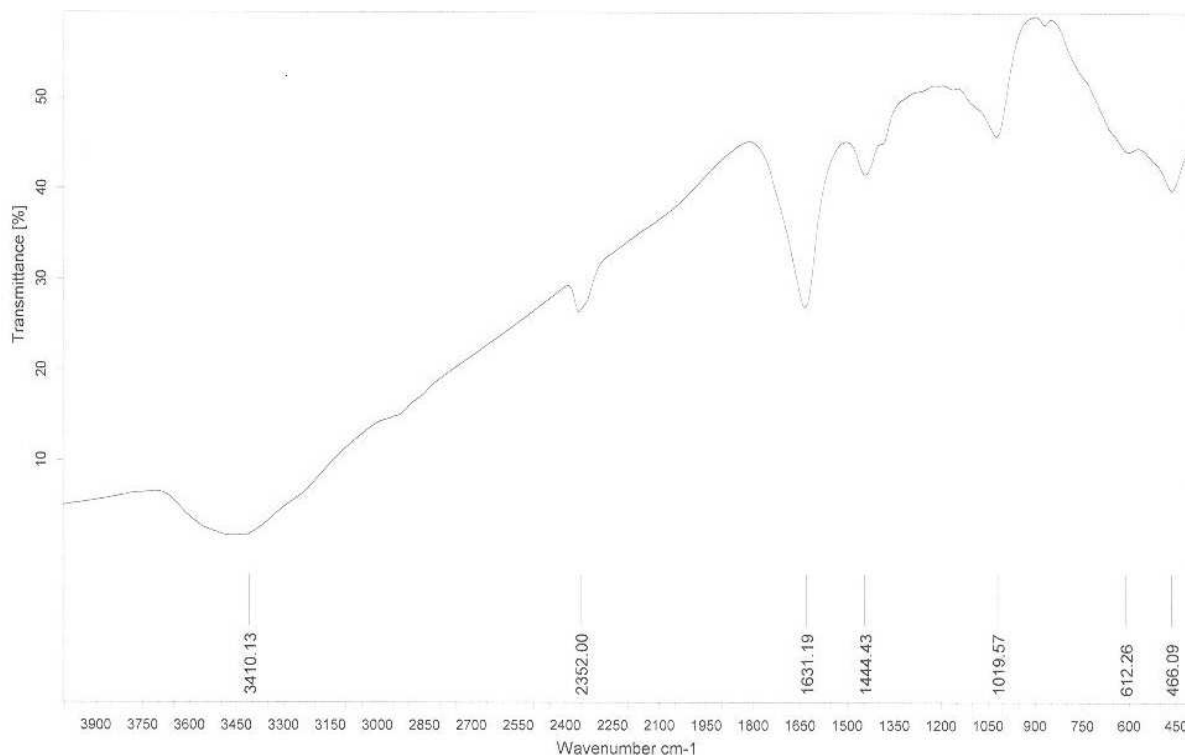
Changes of monomer pressure and deposition time had an effect on the color and adherence of deposited film on substrate. At monomer pressure of 50 mtorr for 45 minutes the deposited film was dark brown and it immediately detached from substrate and changes to black color when exposed to air. The color sequence occurs even at deposition time of 30 minutes where the film was stable for a period of time then detached from the substrate. As the monomer pressure is reduced to 5 mtorr for 45 minutes the substrate color did not change indicating very slow deposition. When monomer pressure was raised to 7 mtorr for 60 and 90 minutes, a light yellow color film resulted and film in such case was found to be stable. When monomer pressure was raised to 9 mtorr for 60 and 90 minutes, the deposition occurred with light golden color and deposited film was also stable. With raising monomer pressure to 30 mtorr for 60 minutes, the deposition changed to golden color. At 90

minutes, the substrates developed a dark golden color.

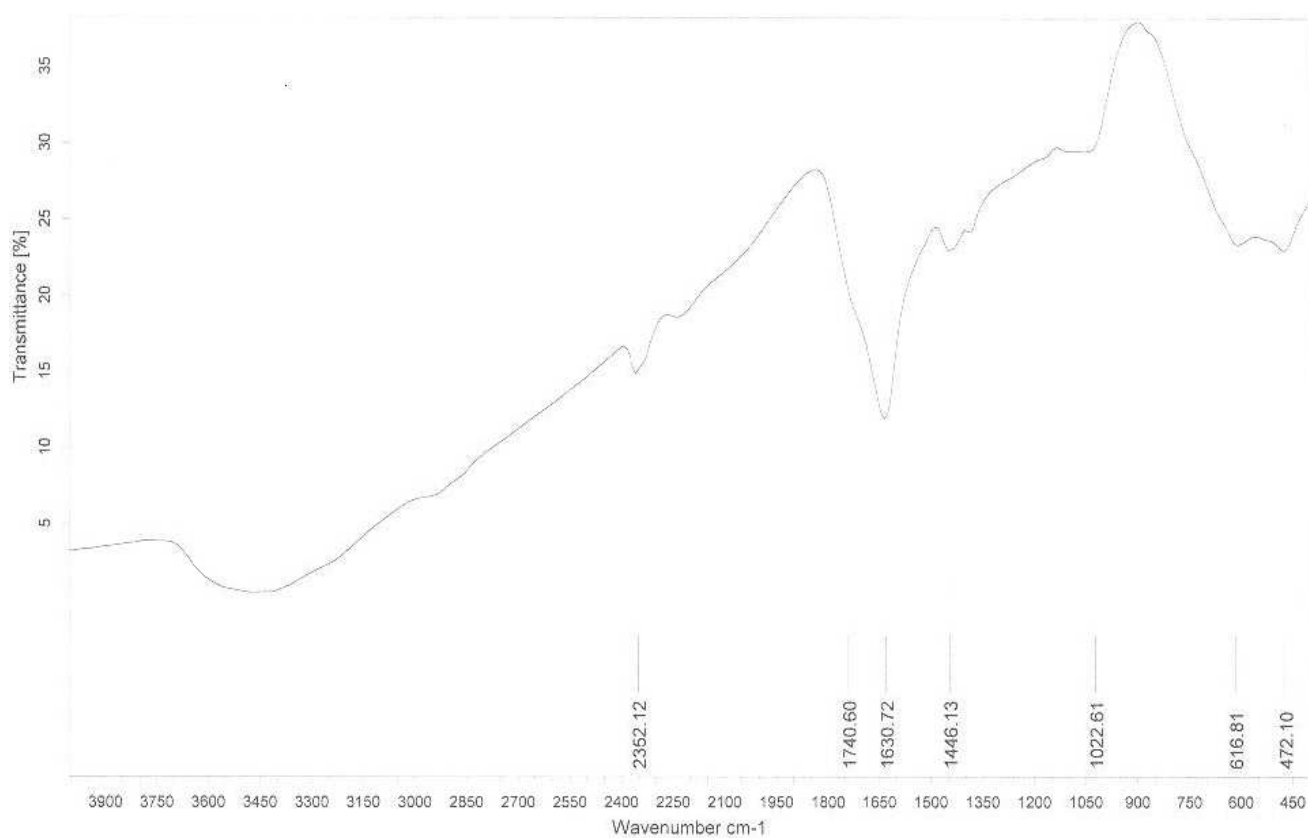
3.2. Chemical Structure Using FTIR and NMR

The infrared spectra of benzene deposited films on glass slides which were obtained for 9 mtorr and 30 mtorr monomer pressures for 60, and 90 minutes deposition times are shown in Figure 4 (a to d). According to literature [14], the absorption bands can be assigned as follows: 612-670 (weak, aromatic ring), 1000 – 1200 cm^{-1} (variable, C-O stretch, alcohol, or ester) where such peak intensity increases with deposition pressure, 1440 (variable C-C stretch, aromatic), where such peak increases with pressure, 2900 cm^{-1} (alkanes), 1630 cm^{-1} (C=O ester), 2357 cm^{-1} (Si-C stretching), 3200 – 3600 cm^{-1} (broad O-H hydrogen-bonded alcohols). From the findings, it can be stated that benzene rings are not fully preserved in the film structure, and that benzene rings were partially changed to alcohol and/or ester due to reaction of deposited structural units with oxygen of air. It is noted that infrared spectra of all substrates contain a constant intensity peak at $\sim 2357 \text{ cm}^{-1}$ which is assigned to Si-C stretching. To confirm such assignment, a portion of glass wafer without benzene film was crushed fine and FTIR tested. The infrared spectrum is found to contain a peak at 2357 cm^{-1} as shown in Figure 5.

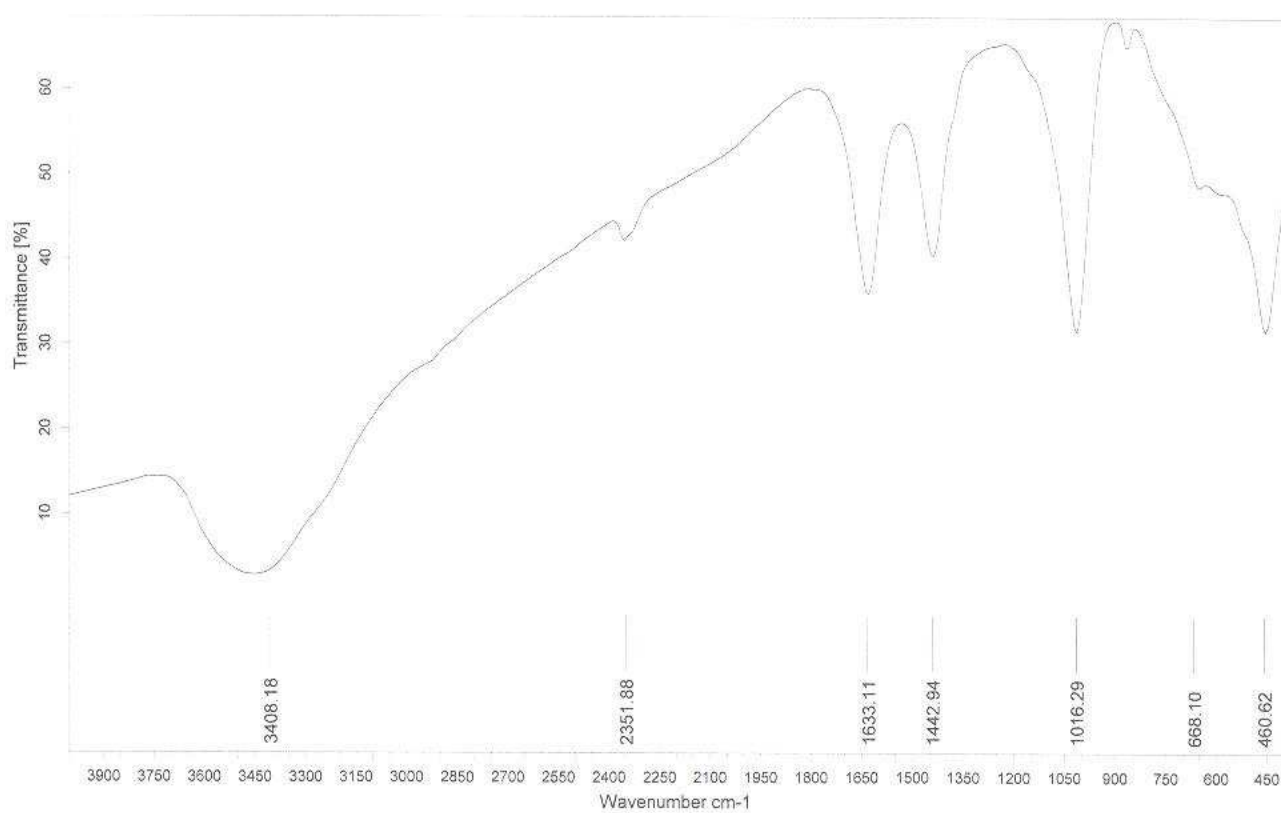
Comparing results of FTIR for glass slide with and without benzene film illustrates that benzene film when deposited adheres to glass substrate by bonding with Si from glass. It should be noted that FTIR samples were collected by scratching the deposited films using razor blade and in such method Si from glass bonded to film might have given the 2357 cm^{-1} peak for all given tested films.



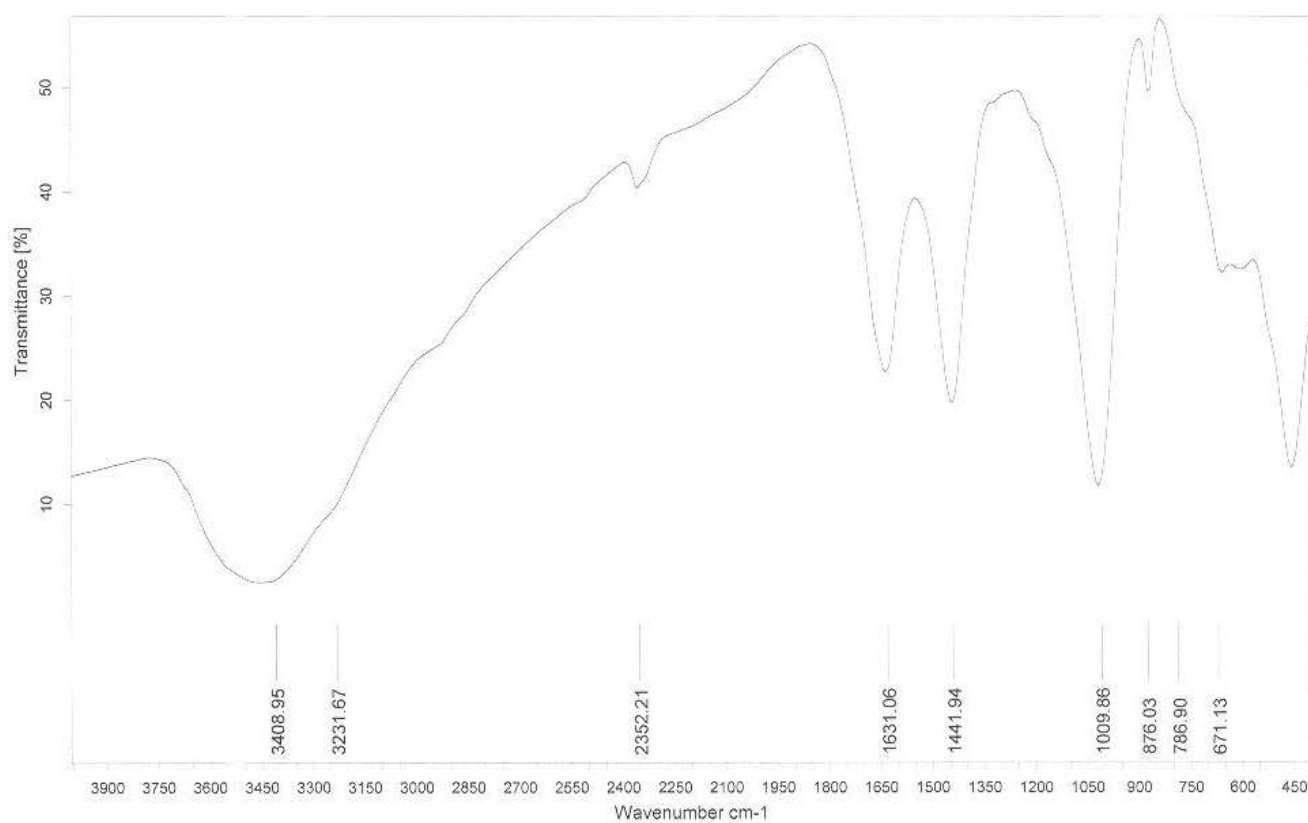
(a)



(b)



(c)



(d)

Figure 4. The infrared spectra of benzene deposited films obtained at: a) 9 mtorr for 60 min, b) 9 mtorr for 90 min, c) 30 mtorr for 60 min, and d) 30 mtorr for 90 min (Note the increase in intensity of low wave # peaks with momomer pressure and deposition time).

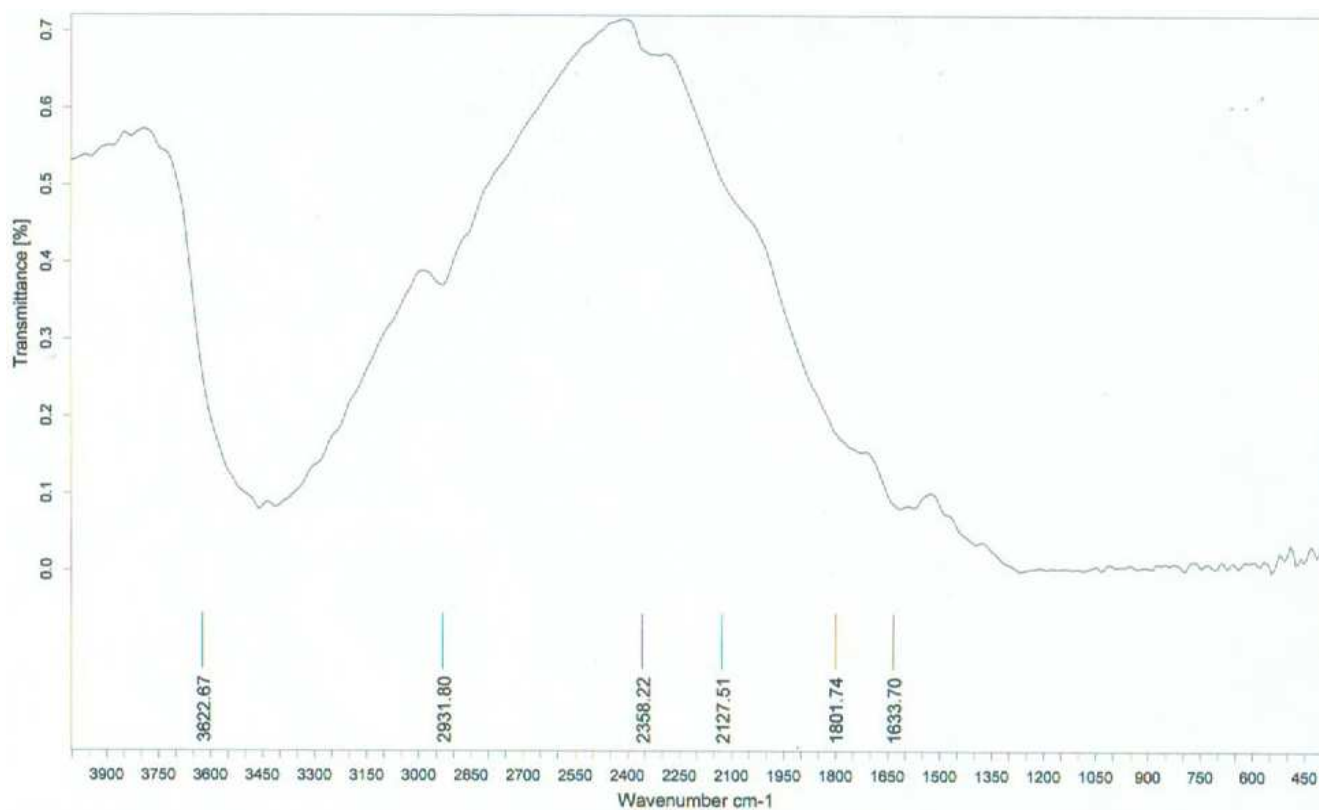


Figure 5. Infrared spectra of glass substrate without deposition.

NMR was also used to investigate plasma polymerized benzene film. NMR spectra measurement was done for the best quality deposited film, which was obtained at 30 mtorr monomer pressure for deposition time of 90 minutes. Figure 6 a and b show NMR result of ^1H NMR and ^{13}C NMR spectra, where ^1H provides information about number of protons present in molecules of deposited film, and ^{13}C provides information about the number of carbons in the

molecule [15]. NMR peaks were assigned as follows: ^{13}C NMR spectra: 170 – 185 ppm (C=O, ester), 150 – 200 ppm (C=O), 125 – 150 ppm (C in aromatic), 50 – 65 ppm (RCH_2OH), 25 – 35 PPM (R_3CH).

^1H NMR spectra: 1 – 5 ppm (OH, alcohol). Henceforth, NMR indicates that the benzene ring was partially decomposed to alcohol, alkane and ester derivatives supporting the FTIR results.

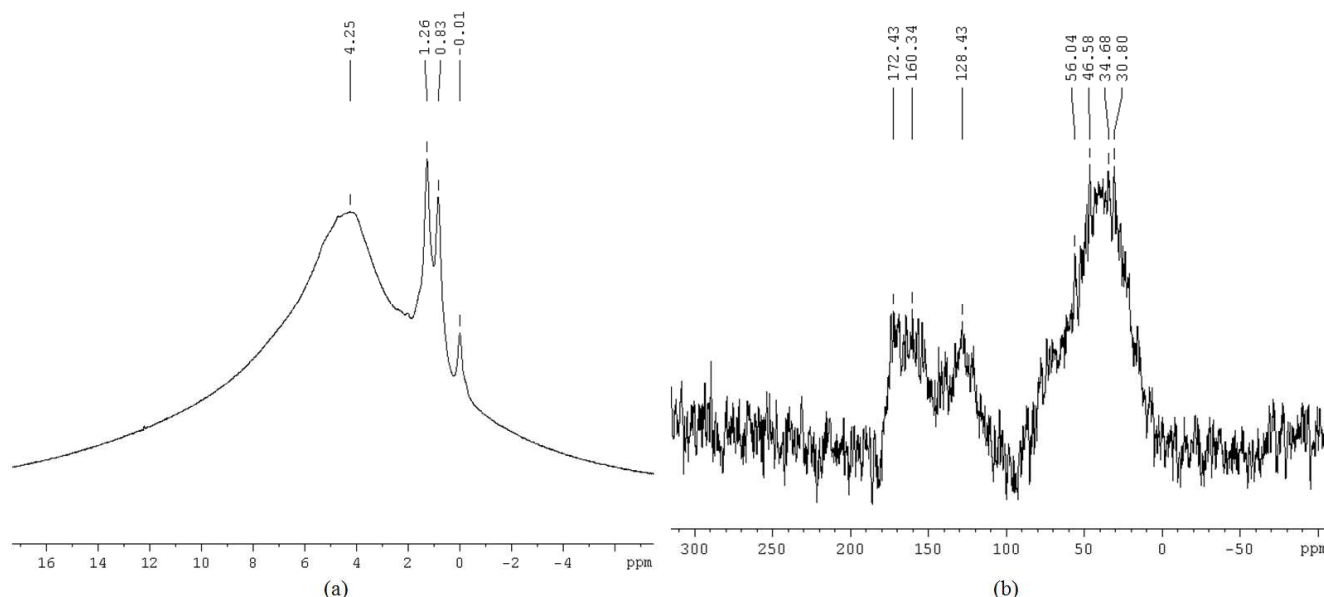


Figure 6. a) ^1H NMR spectra deposited thin film at 30 mtorr for 90 min, b) ^{13}C NMR spectra deposited thin film at 30 mtorr for 90 min.

3.3. Scotch Tape Test for Adhesion

The best result in this test which means good adhesion was for sample at monomer pressure of 30 mtorr and 90 minutes deposition time. The film in such sample was not removed after soaking the glass wafer containing film in distilled water for quarter of an hour. The films deposited at monomer pressures of 7 mtorr and 9 mtorr detached from glass substrate by soaking in distilled water for same time indicating bad adhesion to substrate.

3.4. Surface Morphology of Deposited Benzene Film on Al Alloy

Figures 7 (a-f) show the SEM images of the film deposited with different monomer pressures at 60 and 90 minutes. The images indicate that the surface roughness of benzene deposited films decrease with increasing plasma pressure and increasing deposition time. The image of Figure 7a, shows voids in film, while Figure 7b shows a compact film with no voids (bright spots in film indicate covered voids).

3.5. Potentiodynamic Measurements

Figures 8a and b show comparisons between potential-current curves for Al alloy substrates both bare and covered with benzene films, deposited at different monomer pressures for 60 and 90 minutes. Table 3 summarizes the corrosion

potential (E_{corr}), corrosion current density (i_{corr}), and protective efficiency (η) of Al alloy both bare and covered with benzene film. The table shows a shift of E_{corr} to less negative voltage with increasing monomer pressure for the deposition time of 60 and 90 minutes and the protective abilities of films increased with increasing monomer pressure. The highest protection efficiency was for 30 mtorr.

In general, Table 3 indicates that the deposited films on Al hardly improve corrosion resistance, and hardly decrease the corrosion rate of Al alloy substrate (only 165 mV improvement in E_{corr} , and about $0.06 \mu\text{A}/\text{cm}^2$ decrease in i_{corr} for highest η). The maximum η of 55.4% is for deposited film at 30 mtorr and 90 min. After corrosion test most benzene films detached from Al alloy substrate and the only film that partly remained on sample was of 30 mtorr for 90 minutes.

Table 3. Corrosion properties of aluminum alloy bare and covered with benzene.

	E_{corr} (mV)	i_{corr} (mA/cm ²)	η (%)
Bar Al	-726.5	0.0001	
7 mtorr, 60 min.	-612.5	0.0000794	20.6
9 mtorr, 60 min.	-578.7	0.0000630	36.91
30 mtorr, 60 min.	-571.0	0.0000501	49.88
7 mtorr, 90 min.	-595.0	0.0000616	38.35
9 mtorr, 90 min.	-574.5	0.0000562	43.77
30 mtorr, 90 min.	-561.5	0.0000446	55.4

Abourayana et al. [9] used rf discharge to deposit

benzene/argon protective thin films on Al 2024-T3 substrate. Their results indicate that using benzene alone gas gave a protective efficiency η of 53.94%. This value compares well with the current result of 55.4% for the 30 mtorr for 90 min case (Table 3). Purging argon with benzene tends to increase η and increase the adherence of deposited film to Al alloy substrate [9]. So, it is expected to get higher η using

microwave discharge by depositing benzene/argon mixture. Table 3 results indicate that highest η is obtained for deposition of 30 mtorr for 90 minutes. Increasing deposition time over 90 minutes resulted in the disintegration of film on both slide glass and Al alloy. In mean time, smaller deposition times gave very thin layers that could not be analyzed using the available facilities.

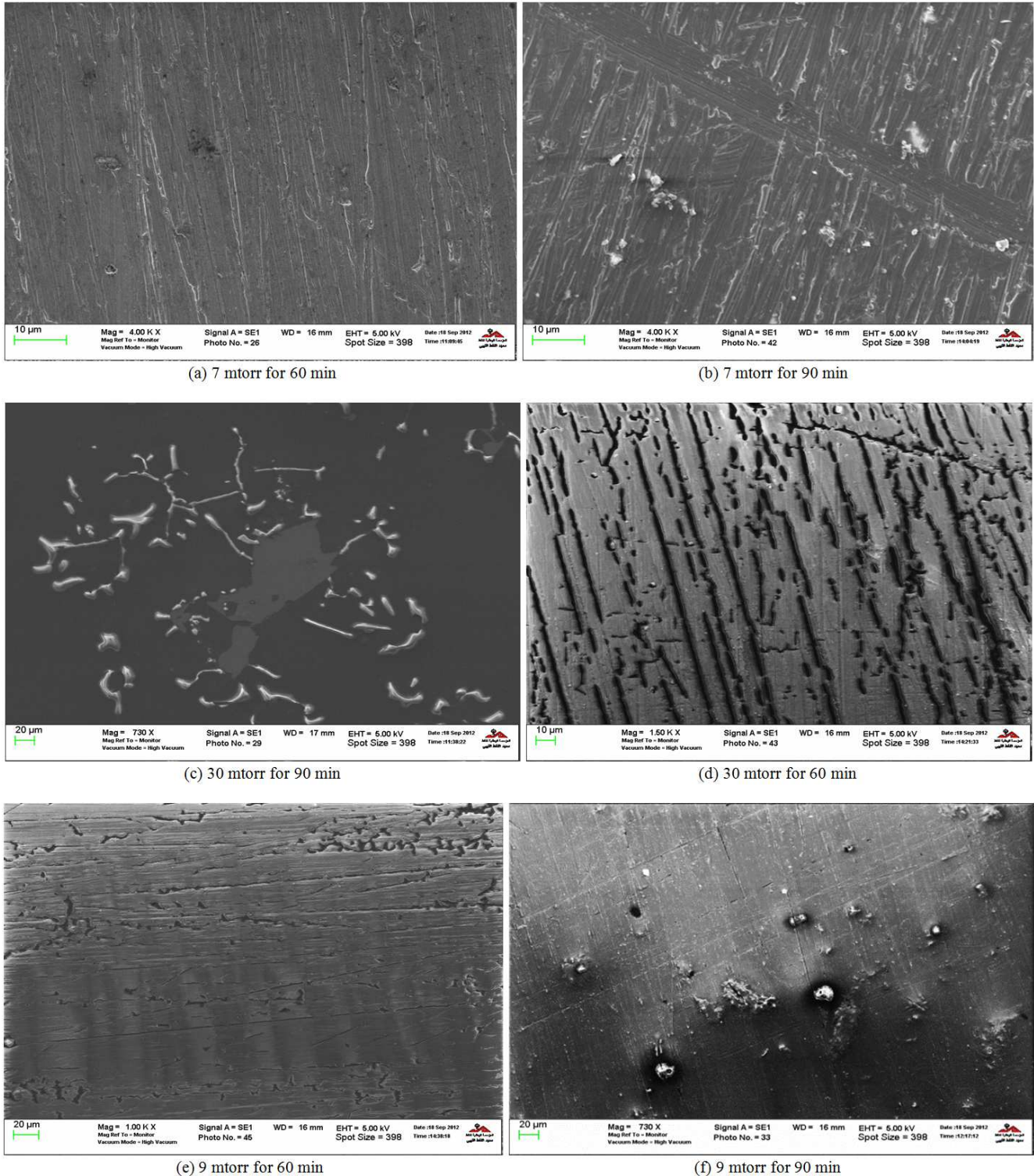


Figure 7. (a to f): SEM images of deposited benzene film on Al alloy substrate at different conditions.

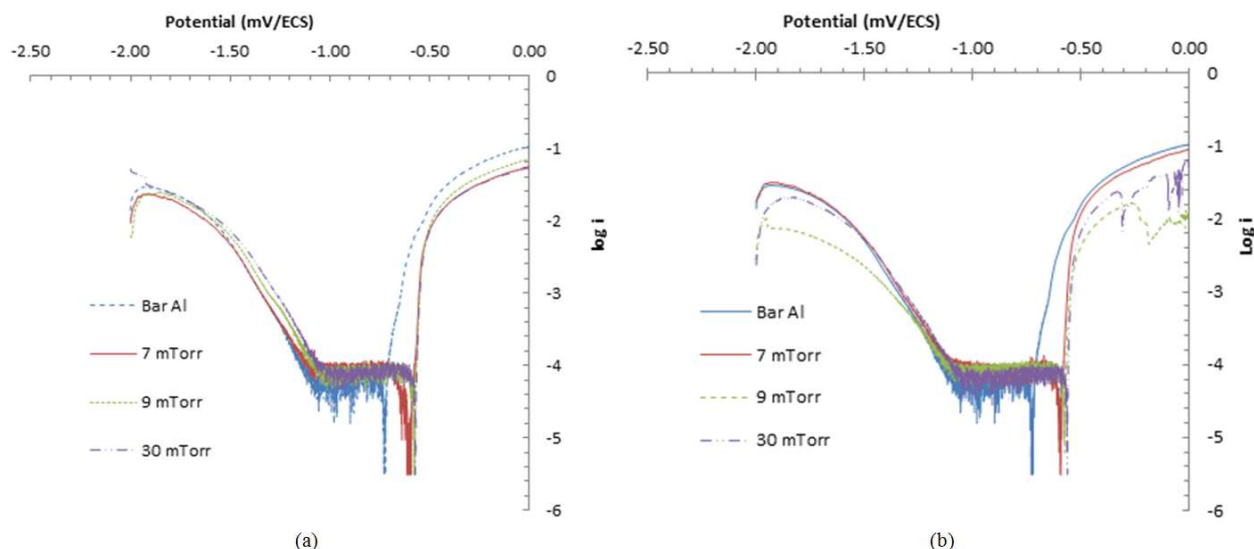


Figure 8. Potentiodynamic polarization curves of aluminum alloy bare and covered with benzene films for a) 60 min. and b) 90 min. at different monomer pressures.

4. Conclusions

Organic polymer thin films have been deposited on 2024-T3 Al alloy and glass substrates at room temperature using benzene as a monomer by using microwave plasma enhanced chemical vapor deposition.

FTIR and NMR spectra of benzene deposited films indicate that benzene rings are not fully preserved. It is partially converted to alcohol and ester functional groups.

Only a limited range of monomer pressures and deposition times produce an adherent, smooth, and corrosion protective film.

SEM images of deposited thin film from benzene at different monomer pressures and deposition times show that the roughness decreases with the increase of monomer pressure and deposition time, and the best deposited film obtained was at 30 mtorr for 90 minutes.

The corrosion measurement indicates that using benzene alone as a monomer limits the protection efficiency to as high as 55.4 % at 30 mtorr for 90 min.

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