Synthesis and Characterization of Plasma Polymerized Thin Films Deposited from Benzene and Hexamethyldisiloxane using (PECVD) Method

Hisham M. Abourayana, Nuri A. Zreiba, Abdulkader M. Elamin

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Abstract**—**Polymer-like organic thin films were deposited on both aluminum alloy type 6061 and glass substrates at room temperature by Plasma Enhanced Chemical Vapor Deposition (PECVD) methodusing benzene and hexamethyldisiloxane (HMDSO) as precursor materials. The surface and physical properties of plasma-polymerized organic thin films were investigated at different r.f. powers. The effects of benzene/argon ratio on the properties of plasma polymerized benzene films were also investigated. It is found that using benzene alone results in a non-coherent and non-adherent powdery deposited material. The chemical structure and surface properties of the as-grown plasma polymerized thin films were analyzed on glass substrates with FTIR and contact angle measurements. FTIR spectra of benzene deposited film indicated that the benzene rings are preserved when increasing benzene ratio and/or decreasing r.f. powers. FTIR spectra of HMDSO deposited films indicated an increase of the hydrogen concentration and a decrease of the oxygen concentration with the increase of r.f. power. The contact angle (θ) of the films prepared from benzene was found to increase by about 43% as benzene ratio increases from 10% to 20%. θ was then found to decrease to the original value (51°) when the benzene ratio increases to 100%. The contact angle, θ, for both benzene and HMDSO deposited films were found to increase with r.f. power. This signifies that the plasma polymerized organic films have substantially low surface energy as the r.f power increases. The corrosion resistance of aluminum alloy substrate both bare and covered with plasma polymerized thin films was carried out by potentiodynamic polarization measurements in standard 3.5 wt. % NaCl solution at room temperature. The results indicate that the benzene and HMDSO deposited films are suitable for protection of the aluminum substrate against corrosion. The changes in the processing parameters seem to have a strong influence on the film protective ability. Surface roughness of films deposited on aluminum alloy substrate was investigated using scanning electron microscopy (SEM). The SEM images indicate that the surface roughness of benzene deposited films increase with decreasing the benzene ratio. SEM images of benzene and HMDSO deposited films indicate that the surface roughness decreases with increasing r.f. power**.** Studying the above parameters indicate that the films produced are suitable for specific practical applications.

Keywords**—**Plasma polymerization, potentiodynamic test, Contact angle.

I. INTRODUCTION

PLASMA polymerization is a versatile technique for the deposition of films with functional properties suitable for a wide range of modern applications. This is due to the high degree of control of their properties, which may be varied widely by plasma parameters [1].

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Plasma polymerization can be used to fabricate thin polymer films (100 Å - 1 µm) from a variety of organic and organometallic starting materials. Plasma polymerized films are pinhole-free and highly crosslinked and therefore are insoluble, thermally stable, chemically inert and mechanically tough. Furthermore such films are often highly coherent and adherent to a variety of substrates including conventional polymer, glass and metal surfaces. Due to these excellent properties they have been undertaken very actively in the last few years for a variety of applications such as permselective membranes, protective coatings, biomedical materials electronic and optical devices and adhesion promoters [2]. Plasma polymers are also used as dielectric and optical coating to inhibit corrosion. Among many chemical vapor deposition (CVD) methods, plasma-enhanced chemical vapor deposition (PECVD) process is very efficient method to produce homogeneous organic thin films on large area substrates and offers good control over the film properties [3]. The use of plasmas for thin film coating deposition has been widely researched. The deposition of coatings for the purpose of corrosion protection has received some attention, which until recently principally focused on steel surfaces [5], although the protection of nonferrous metals has also been studied for copper [1,6] and aluminum substrates [7]. The research described in this study involves the growth of plasma-polymerized organic thin films were deposited at room temperature on aluminum alloy type 6061, and glass substrates using the benzene and hexamethyldisiloxane (HMDSO) as a precursor materials by PECVD method. Effect of argon and r.f. power on the physical properties of benzene films and the effect of r.f. power on the physical properties of HMDSO films were investigated in this study.

II. EXPERIMENTAL WORK

The experimental setup employed in this work, schematically depicted in Figure 1, is a multi-purpose system which enables thin film deposition, surface cleaning and treatment by plasma processes. Essentially, it is composed of a stainless steel cylindrical vessel, fitted with two circular parallel plate electrodes. A radiofrequency (13.56 MHz, 0-300 W) supply is connected to the upper electrode via an impedance matching circuit. The system is evacuated by a rotary pump from atmospheric pressure down to 10^{-3} torr and then by a turbo molecular pump. Base pressure reaches 10^{-5} torr which is low enough to provide good quality depositions. The admission of gases to the chamber is controlled by needle valves. HMDSO and benzene as a liquid compounds is placed in stainless steel evaporation cells. These are coupled to the plasma reactor flanges using needle valves. The chamber

pressure is monitored by a wide-range manometer, composed of Pirani and Penning gauges. For the plasma polymerization process, substrates are mounted in the lower grounded electrode. Glow discharge is generated by the application of radiofrequency power to the upper electrode while the chamber walls are earthened.

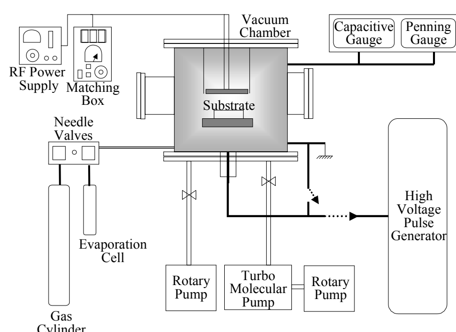

Fig.1 Experimental apparatus employed for film deposition.

After cleaning the samples ultrasonically using acetone, isopropyl alcohol and distilled water under atmospheric condition, the pre-cleaned substrates are then immediately introduced into vacuum chamber. After evacuating the chamber, the substrates are in situ treated with Ar plasma to obtain an oxygen free surface and a buffer layer for enhancing film adhesion. This process is carried out at 50 watt r.f. power, with time duration of 15 min and working pressure of 50 mtorr.The samples used in this study were divided into three groups depending on the plasma parameters. The films in group one were deposited from benzene with different benzene/argon ratios which are 100:0, 20:80, 15:85, and 10:90. The typical conditions of the PECVD process applied are 150 min deposition time, 100 watt r.f. power and 60 mtorr working pressure. In group two the films were deposited from benzene with different r.f. power which are 50, 100, and 150 watt. The typical conditions of the PECVD process applied are 150 min deposition time, 15% benzene/argon ratio, and 60 mtorr working pressure. In group three the films were deposited from hexamethyldisiloxane with different r.f power. The typical conditions of the PECVD process applied were 90 min deposition time and 60 mtorr working pressure.

The chemical structure and surface properties of the as-grown plasma polymerized thin films were analyzed on glass substrates with FTIR and contact angle measurements. Surface roughness of films deposited on aluminum alloy substrate was investigated using scanning electron microscopy (SEM). The corrosion resistance of aluminum alloy substrate both bare and covered with benzene films was carried out by potentiodynamic polarization measurements in standard 3.5 wt. % NaCl solution at room temperature.

III. Results and Discussion

A. Chemical Structure

Figures 2 (a-d) show the infrared spectra of the benzene deposited films prepared with different benzene/argon ratios. As can be seen, there are bands around 3024 – 3055 cm^{-1} and 698 cm^{-1}. These are related respectively to stretching and bending modes of C–H vibration in the aromatic ring. Two other stretching absorption bands can also be detected in the range 2870 – 2920 cm^{-1}, corresponding to C–H vibration in the aliphatic structures [8, 9, and 10]. From these bands, it can be stated that even though benzene rings are preserved in the film structure, the great majority is fragmented during the deposition process. The wavelength of the absorption bands with their respective assignments are listed in Table 1.

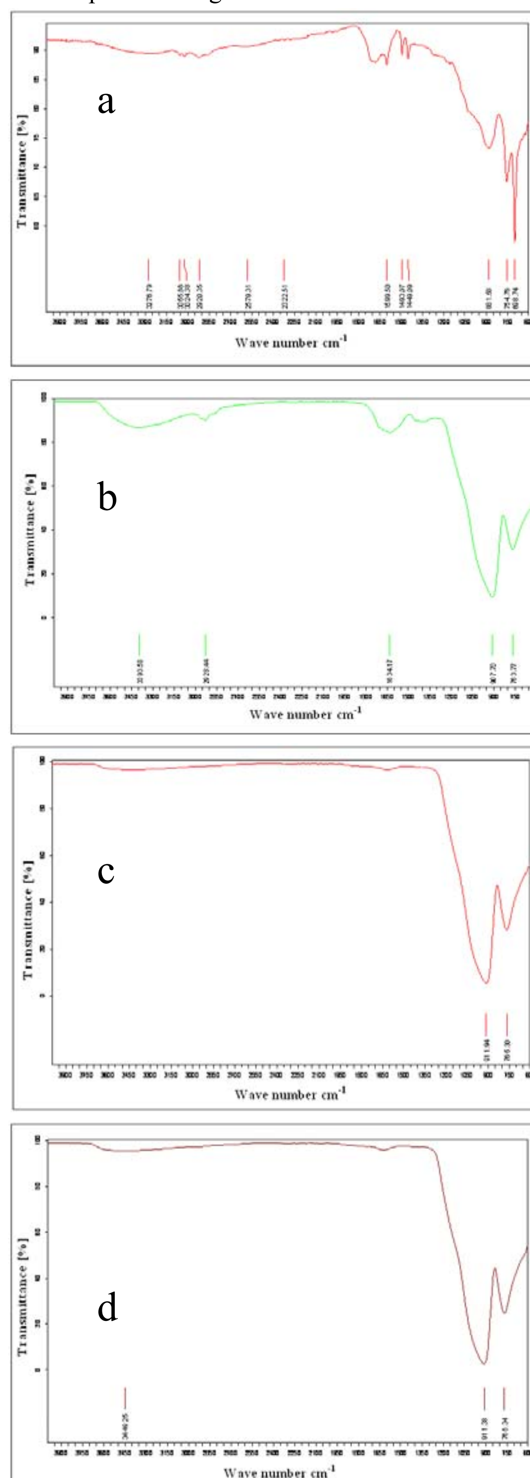

Fig. 2 (a - d) Infrared spectra of benzene films prepared with (a) 100:0, (b) 20:80, (c) 15:85 and (d) 10:90 benzene/argon ratio

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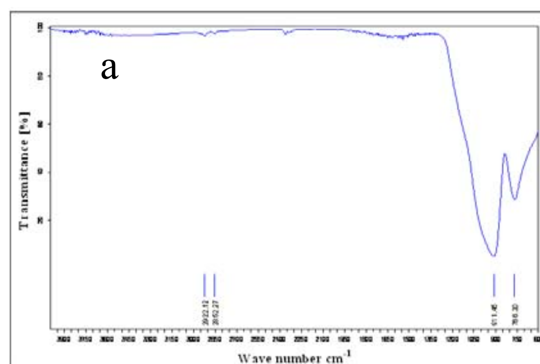
As shown in figure 2 (a-d), the bands related to C–H bending in aromatic ring (675 – 1000 cm^{-1}) were increased when the benzene ratio decreases, and the bands related to C=C stretching vibration (1400 – 1600 cm^{-1}) were decreased with decreasing benzene ratio.

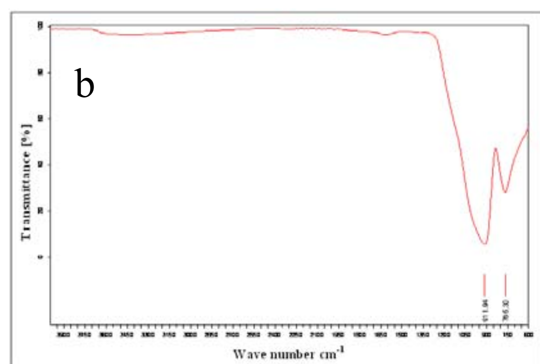
TABLE I
ABSORPTION BANDS OF BENZENE FILMS DETECTED IN THE SPECTRA OF FIGURE 2 (A-D)

Wavelength (cm^{-1})	Vibrational Groups
675 - 1000	C-H bending in aromatic ring
1400 - 1600	C=C stretching vibration in the ring
2820 -2960	C-H stretching in aliphatic groups
3000 - 3100	C-H stretching in aromatic ring

Figures 3 (a-c) show the infrared spectra of the benzene deposited films prepared with different r.f. powers. The bands at 765 – 911 cm^{-1}, are related to bending modes of C–H vibration in the aromatic ring appear at all samples. However the concentration of the bands detected in the range 2852 – 2922 cm^{-1} corresponding to C–H vibration in the aliphatic structures was decreased with r.f. power and appears only at 50 watt r.f. power.

The band lying around 3400 cm^{-1}, is attributed to O–H vibration. Although oxygen was not deliberately incorporated in the plasma, the band at 3400 cm^{-1} indicates the presence of this element in the film. The existence of radicals or dangling bonds in the structure of materials prepared by plasma processes enables the incorporation of O-containing groups through reactions with atmospheric O_2 and H_2O. Another possible source of contamination is the residual atmosphere in the reactor during the film preparation.





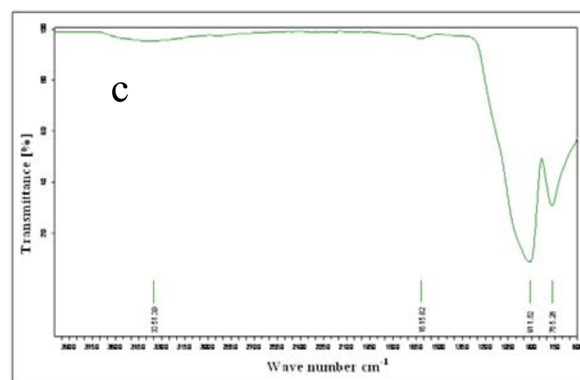
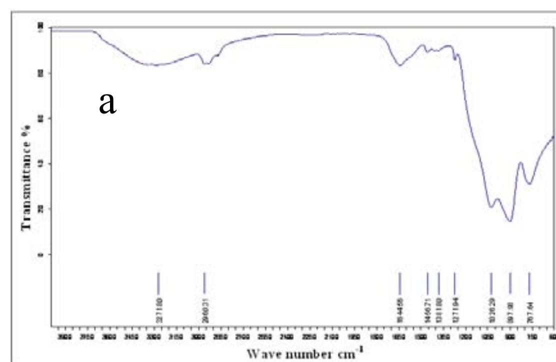
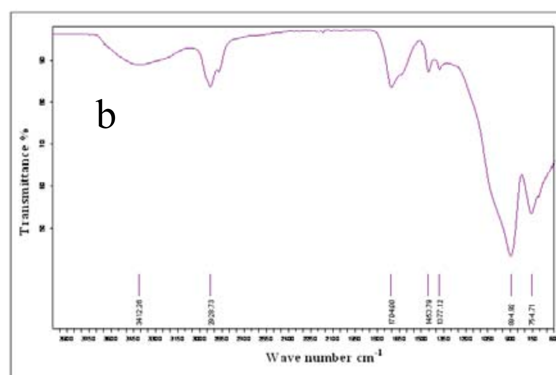


Fig. 3 (a - c) Infrared spectra of benzene films prepared with (a) 50 watt, (b) 100 watt and (c) 150 watt r.f. power

Figure 4 (a-c) shows the infrared spectra of the films deposited from hexamethyldisiloxane plasmas with 50, 100 and 150 watt r.f powers. Absorption bands related to the HMDSO film detected in the spectra of Figure 4 (a-c) are listed in Table 2 [8- 10].

The FTIR spectra show a growth of the bands due to Si–CH_3 and CH_3 groups and a decrease of the bands due to Si–O–Si and SiOH groups when the applied power increases. The presence of Si–H groups is revealed by the weak absorption at 2127 cm^{-1}. This band is present only in the spectrum of the higher power (150 watt) prepared film. They indicate that the concentration of H is increased with r.f. power and the concentration of oxygen was decreased when increasing r.f. power.





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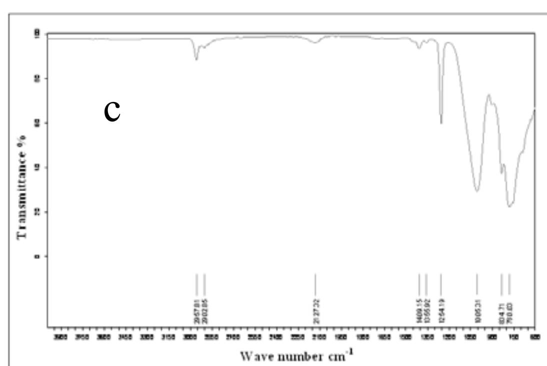

Fig. 4 (a - c) Infrared spectra of hexamethyldisiloxane films prepared with (a) 50 watt, (b) 100 watt (c) 150 watt r.f. power

TABLE II
ABSORPTION BANDS OF HMDSO FILMS DETECTED IN THE SPECTRA OF FIGURES 3 (A-C)

Wavelength (cm^{-1})	Vibrational Groups
750 - 780	Bending (Si–O) in Si–O–Si
800 - 900	Rocking (CH_3) in $(Si–CH_3)_x$
1000 - 1050	Stretching asymmetric (Si–O) in Si–O–Si
1250 - 1280	Bending symmetric (CH_3) in $Si–(CH_3)_x$
1350 - 1410	Bending asymmetric (CH_3) in $Si–(CH_3)_x$
2100 - 2150	Stretching Si–H in $Si–H_x$
2900 - 2960	Stretching asymmetric CH in CH_3
3250 - 3415	Stretching O–H in SiOH

B. Contact Angle

Table 3 shows the contact angle (θ) of the films prepared from benzene glow discharges with different benzene/argon ratio. As a general trend, θ is lower than 90° for all the samples and hence classified as hydrophilic. It is also interesting to note that θ increase about 43% as benzene ratio increases from 10% to 20%. A θ' decreases to the original value (51°) when the benzene ratio is increased to 100%. It means that film surface becomes more receptive to water or polar liquids in a general way.

TABLE III
CONTACT ANGLE OF BENZENE FILMS AS A FUNCTION OF THE BENZENE/ARGON RATIO

% Benzene	Contact angle (°)	Surface energy (dyne / cm)		
		Polar	Dispersive	Total
10 %	51.0 ± 2.5	21.20	44.87	66.07
15 %	61.1 ± 2.9	16.14	45.35	61.49
20 %	73.6 ± 0.8	10.63	43.65	54.28
100 %	51.4 ± 2.1	19.58	45.31	64.89

The behavior of θ as a function of the r.f. power in benzene glow discharges is depicted in Table 4. Here again all the samples are hydrophilic, since their contact angle are less than 90º. Wettability is higher for the 50 and 100 watt r.f. power, and changes just around 25% for the films prepared with the highest r.f. power (150 watt).

TABLE IV
CONTACT ANGLE OF BENZENE FILMS AS A FUNCTION OF THE R.F. POWER

r.f. power (watt)	Contact angle (°)	Surface energy (dyne / cm)		
		Polar	Dispersive	Total
50	60.4 ± 2.1	15.58	45.32	60.90
100	61.1 ± 2.9	16.14	45.35	61.49
150	75.9 ± 0.8	9.37	45.31	54.90

Table 5 depicts the contact angles (θ) of the films prepared from hexamethyldisiloxane plasmas at 50, 100, and 150 watt r.f. power. The results indicated that the samples deposited at the power 50 and 100 watt are hydrophilic while the one prepared at 150 watt is slightly hydrophobic (θ > 90º).

TABLE V
CONTACT ANGLE OF HEXAMETHYLDISILOXANE FILMS AS A FUNCTION OF THE R.F. POWER

r.f. power (watt)	Contact angle (°)	Surface energy (dyne / cm)		
		Polar	Dispersive	Total
50	51.0 ± 2.5	21.20	44.87	66.07
100	75.1 ± 1.6	11.75	34.21	45.96
150	97.6 ± 2.0	5.01	23.09	28.10

C. Potentiodynamic Measurements

Fig 5 shows the corrosion behavior of the aluminum alloy substrate both bare and covered with benzene films deposited at different benzene/argon ratios. In general the corrosion potential shift to more positive values with benzene/argon ratios. Table 6 represents corrosion potential (E_{corr}), corrosion current density (i_{corr}) and protective efficiency (P_i) of aluminum alloy both bare and covered with benzene films at different benzene/argon ratios obtained from potentiodynamic curve. As shown in Table 4.6 the protective abilities of films increased with increasing benzene % up to 20%. The highest protective efficiency was 75 % at 20% benzene ratio. These results indicate that the deposited film is suitable for protection of the aluminum substrate against corrosion, and changes in the processing parameters seen have a strong influence on the film protective ability.

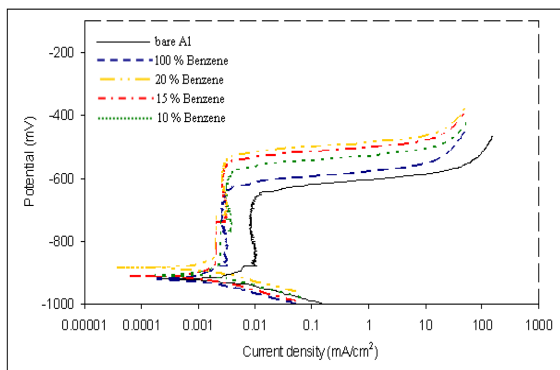

Fig. 5 Polarization curves of aluminum alloy both bare and covered with benzene film as a function of benzene/argon ratios

TABLE VI
CORROSION PROPERTIES OF ALUMINUM ALLOY COVERED WITH BENZENE FILMS WITH DIFFERENT BENZENE/ARGON RATIOS OBTAINED FROM POTENTIODYNAMIC CURVE

	E_{corr} (mV)	i_{corr} (mA/cm^2)	P_i %
Bare Al	- 921.6	0.00113	
10 % benzene	- 909.4	0.00093	17.69
15 % benzene	- 912.4	0.00039	59.30
20 % benzene	- 885.0	0.00028	75.06
100 % benzene	- 920.7	0.00052	53.94

Fig 6 shows the behavior of the aluminum alloy substrate both bare and covered with benzene films at different r.f. powers. In general the corrosion potential is shifted to more positive values with r.f. power. Table 7 represents corrosion potential (E_{corr}), corrosion current density (i_{corr}) and protective efficiency (P_i) of aluminum alloy both bare and covered with benzene films at different r.f. powers obtained from potentiodynamic curve. As shown in Table 7 the protective abilities of films increased with increasing r.f. power. The highest protective efficiency was 60.22 % at 150 watt r.f. power. These results indicate that the deposited film is suitable for protection of the aluminum substrate against corrosion. However changes in the processing parameters seen not to have a strong influence on the film protective ability.

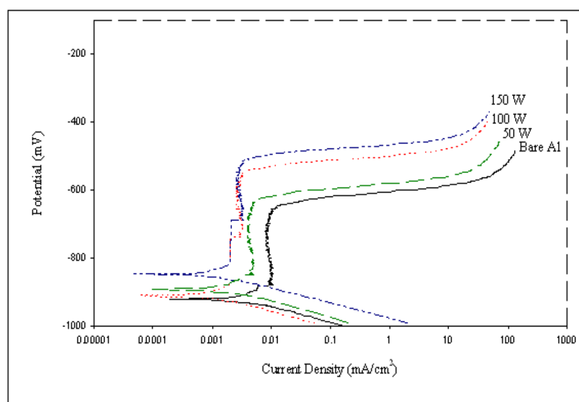

Fig. 6. Polarization curves of aluminum alloy both bare and covered with benzene film as a function of r.f. power

TABLE VII
CORROSION PROPERTIES OF ALUMINUM ALLOY COVERED WITH BENZENE FILMS OBTAINED FROM POTENTIODYNAMIC CURVE

	E_{corr} (mV)	i_{corr} (mA/cm^2)	P_i %
Bare Al	- 921.6	0.00113	
50 watt	- 892.1	0.00080	18.61
100 watt	- 912.4	0.00039	59.30
150 watt	- 847.9	0.00040	60.22

Fig. 7 shows the behavior of the aluminum alloy substrate both bare and covered with hexamethyldisiloxane film. The corrosion potential shift to more positive value as the r.f. power increases. Moreover, the cathodic branch of the polarization curves is markedly suppressed by coverage of the electrode with the film, indicating inhibition of oxygen reduction because the densely packed and tightly interconnected HMDSO film acted as an efficient barrier layer to the diffusion of molecular oxygen. The anodic process was also inhibited in the presence of the film, suggesting that the tightly interconnected film suppressed diffusion of an electrolyte, like chloride ions, to the surface. Table 8 represents corrosion potential (E_{corr}), corrosion current density (i_{corr}) and protective efficiency (P_i) of aluminum alloy both bare and covered with HMDSO films at different r.f. powers obtained from potentiodynamic curve. As shown in Table 4.8, the protective abilities of films increased with increasing r.f. power. The highest protective efficiency was 50 % at 150 Watt r.f. power.

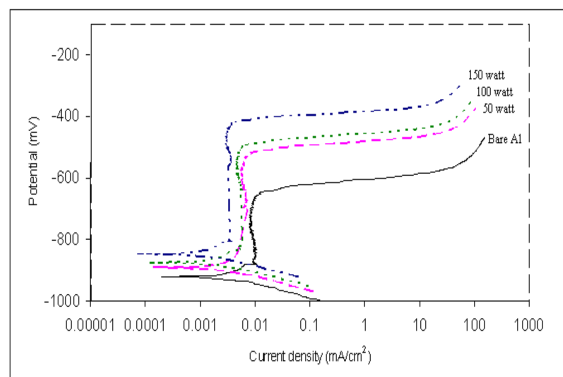

Fig. 7 Polarization curves of a bare aluminum electrode and covered with HMDSO film as a function of r.f. power

TABLE VIII
CORROSION PROPERTIES OF ALUMINUM ALLOY COVERED WITH HMDSO FILMS OBTAINED FROM POTENTIODYNAMIC CURVE

	E_{corr} (mV)	i_{corr} (mA/cm^2)	P_i %
Bare Al	- 921.6	0.0012	
50 watt	- 897.5	0.0009	25.0
100 watt	- 866.8	0.0008	33.3
150 watt	- 830.9	0.0006	50.0

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D. Surface Morphology

Figure 8 (a-d) show the SEM image of the film surface with different benzene ratio. It is clear that the surface roughness increases with decreasing the benzene ratio. Figure 8(a) appears the size of powder particle formed when deposited the benzene films without argon (100% benzene).

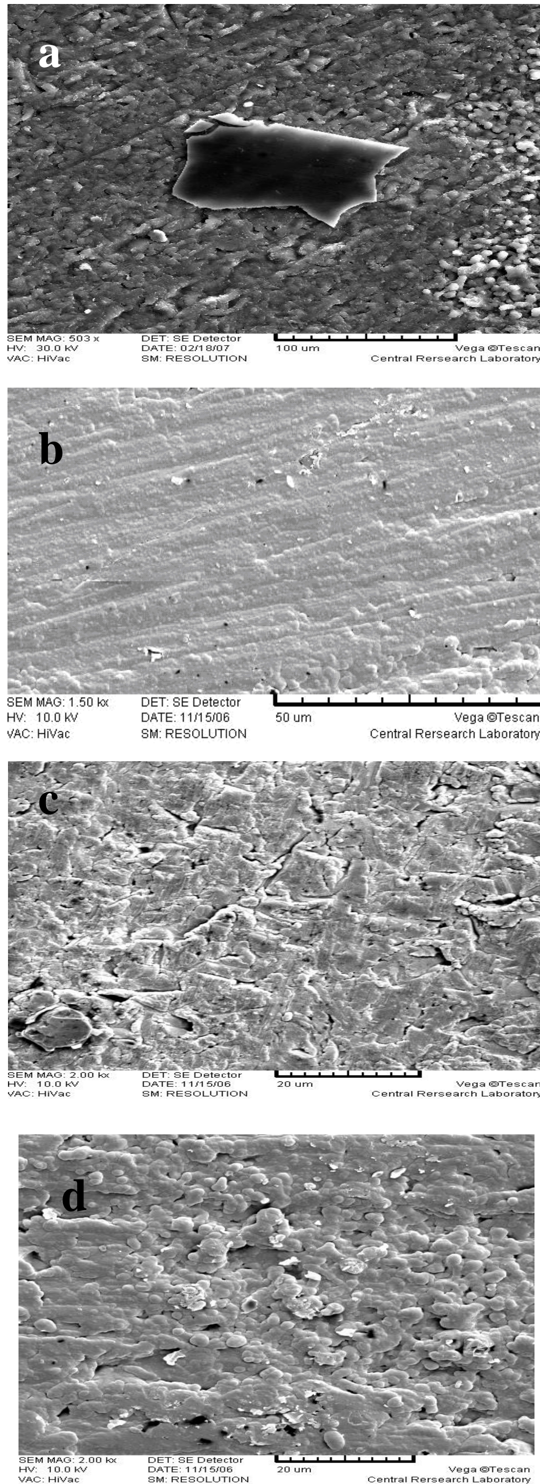

Fig. 8 (a-d) SEM images of polymer like thin film as a function of benzene/argon ratios (a) 100% benzene, (b) 20% benzene, (c) 15% benzene and (d) 10 % benzene

Figures 9 (a-c) shows the SEM image of polymer-like thin films deposited from benzene at different r.f. powers. The images show that the surface roughness decreases with increasing r.f. power and that the best film homogeneity is obtained at r.f. power of 150 watt.

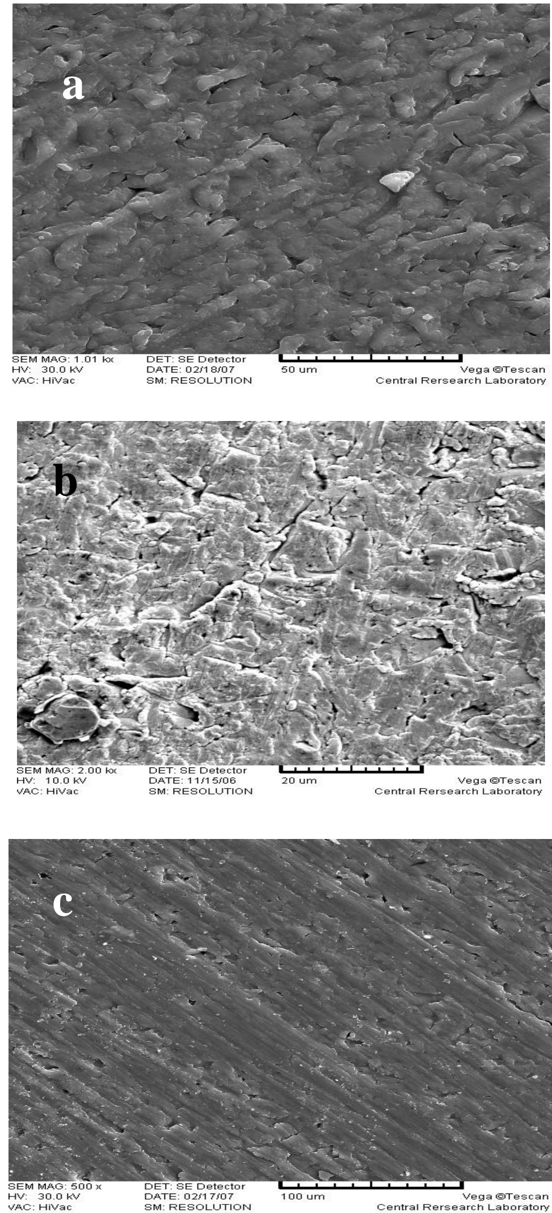

Fig. 9 (a-c) SEM images of polymer like thin film deposited from benzene at (a) 50 watt, (b) 100 watt and (c) 150 watt r.f. power

Figures 10 (a-c) show the SEM images of polymer-like thin films deposited from hexamethyldisiloxane at different r.f. powers. The images appear that the surface roughness decreases with increasing r.f. power.

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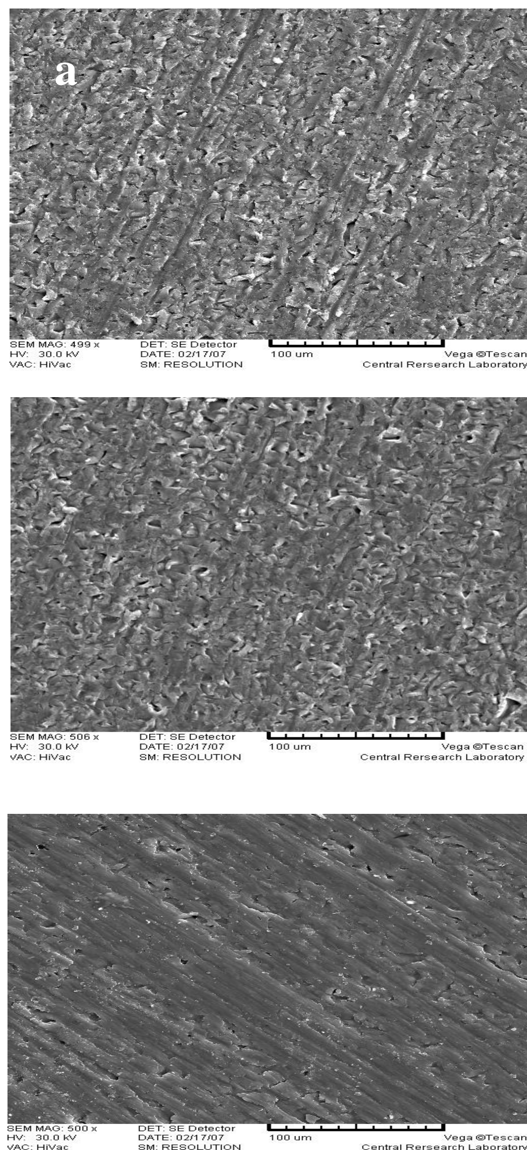

Fig. 10 (a-c) SEM images of polymer like thin film deposited from HMDSO at (a) 50 watt, (b) 100 watt and (c) 150 watt r.f. power

ACKNOWLEDGMENT

Under the agreement between Guaratingueta University, in Brazil and Plasma Research Laboratory, in Libya, the experimental work was carried out at plasma laboratory in Guaratingueta University. The authors acknowledge the invaluable contribution of Dr. Milton Kayama and Dr. Honda from Guaratingueta University (Sao Paulo-Brazil) for concerning the deposition equipment and Dr. Ellidiane Rangel from Sorocaba University (Sao Paulo-Brazil) for her technical assistance. This work is financially supported by the National Bureau for research and development and the plasma research laboratory.

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