# Thin Film of Benzene Deposited on 304L Stainless Steel using Pulsed Microwave Plasma Enhanced Chemical Vapor Deposition

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## Abstract

*Thin films have been deposited by plasma polymerization onto 304L stainless steel and glass substrates using pulsed microwave Plasma Enhanced Chemical Vapor Deposition (PECVD) with pure benzene ($C_6H_6$) as precursor gas. The chemical structure and surface properties (wettability) of the deposited thin films were characterized by Fourier-Transform Infrared (FTIR) spectroscopy and the Water Contact Angle (WCA) measured using an optical tensiometer respectively. The effects of working pressure and deposition time on the chemical structure and surface wettability of the deposited thin films were studied. The results of the FTIR analysis showed that the structure of the film prepared from benzene changed inwhich the C≡C absorption bands became more prominent on decreasing the working pressure. The characteristic absorption peaks of benzene film were presented more prominently in the sample prepared with the longer deposition time. All the treated samples registered reduced WCA below 90°, their hydrophilic surfaces became more wettable. The deposition time had the greatest influence on the WCA measured. It was observed that wettability can be adjusted by the plasma parameters, enabling the production of coatings with properties suitable for specific practical applications.*

**Keywords:-** Plasma polymerization; Thin film; Pulsed Microwave; PECVD; FTIR; Chemical structure; Contact angle; Wettability.

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## 1. INTRODUCTION:-

Plasma polymerization is gaining importance for the last several years as a tool to modify material surfaces [1]. It has been defined as the formation of polymeric materials under the influence of plasma [2]. It refers to the deposition of polymer thin film through plasma dissociation due to the excitation of an organic monomer gas and subsequent deposition and polymerization of the excited species on the surface of a substrate [3]. Plasma polymerization can be used to fabricate polymer thin films (100Å-1μm) from a variety of organic and organometallic starting materials. 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 [4]. Polymeric thin films obtained by (PECVD) have several advantages over films produced by conventional polymerization [5]. The main advantage of plasma polymerization is that it can occur at moderate temperature compared to conventional chemical reaction [3]. Additionally, plasma polymerized surfaces have economical advantage of a green (environmentally benign) technology as compared to other processing methods [5]. In many cases, polymers formed by plasma polymerization have different chemical compositions as well as chemical and physical properties from those formed by conventional polymerization, even if the same monomers are used in plasma and conventional polymerization [6]. The resulting thin films that are highly coherent and adherent to a variety of substrates including conventional polymer, glass and metal surfaces may be prepared from monomers not polymerizable by conventional means. Plasma polymerized films which are pinhole-free and highly crosslinked and therefore are insoluble, can be tailored to exhibit properties such as chemically inert, mechanically tough and thermally stable [4,5]. Due to these excellent properties they have been undertaken very actively in the last few years for a variety of applications such as protective coatings, biomedical materials, electronic and optical devices [4]. Plasma polymerized coatings are increasingly being investigated in biomedical applications. These include surface modification of biomaterials to enhance implant integration and sterilization and to improve device multifunctionality, tribological and mechanical properties, as well as biocompatibility of artificial devices while obviating the needs for large expenses and long time to develop brand new materials [5, 6].

There are many sources used for plasma generation in PECVD processes, the common sources are direct current (DC), radio frequency (RF) and microwave (MW)

discharge [7]. Microwave discharges are widely used for generation of cold plasma at pressures from $10^{-5}$ Torr up to atmospheric pressure in the pulse and continuum wave regimes at incident powers ranged between several Watts and hundreds of kW for different applications [8]. Recently, pulsed power has been successfully employed in plasma polymerization of a variety of monomers. Greater retention of the monomer functional group is observed in the resulting polymeric film with pulsed plasma polymerization [9]. Magnetrons are the most common microwave generators because of their low cost and availability in the market for domestics used e.g. microwave ovens [10]. There are several classes of the microwave plasma generators including the waveguide microwave plasma generator [8] which was used in this study.

In this study pulsed microwave plasma system constructed for the deposition of polymer-like organic thin films of benzene on 304L stainless steel substrates used in medical applications and glass substrates (for FTIR analysis). Benzene and Argon were used as precursor and carrier gases respectively. The effects of working pressure and the deposition time on the chemical structure and surface wettability of the deposited thin films were investigated.

## 2. EXPERIMENTAL WORK

### *2.1. Deposition system:*

The deposition system used in this work is a home-made PECVD designed system which is illustrated in figure (1). It is a multi-purpose system for the treatment by plasma processes such as thin film deposition, surface cleaning, nitriding, and etc. The system consists of deposition chamber, vacuum system and microwave generator (plasma source). The deposition chamber composed of a stainless steel cylindrical chamber 25 cm long and 14.5 cm in diameter provided with four ports: the first port for vacuum system, the second for gas inlet (gas supply), the third for wave-guide and the last one with a glass window for observing the deposition process. The vacuum system consists of a turbo-molecular pump backed by mechanical pump (Varian model) and pressure gauges (Ionic and Pirani Gauges). The microwave is generated by the microwave furnace (commercial magnetron) at frequency of 2.45 GHz with maximum power of 900 W which was transmitted to the chamber via a waveguide.

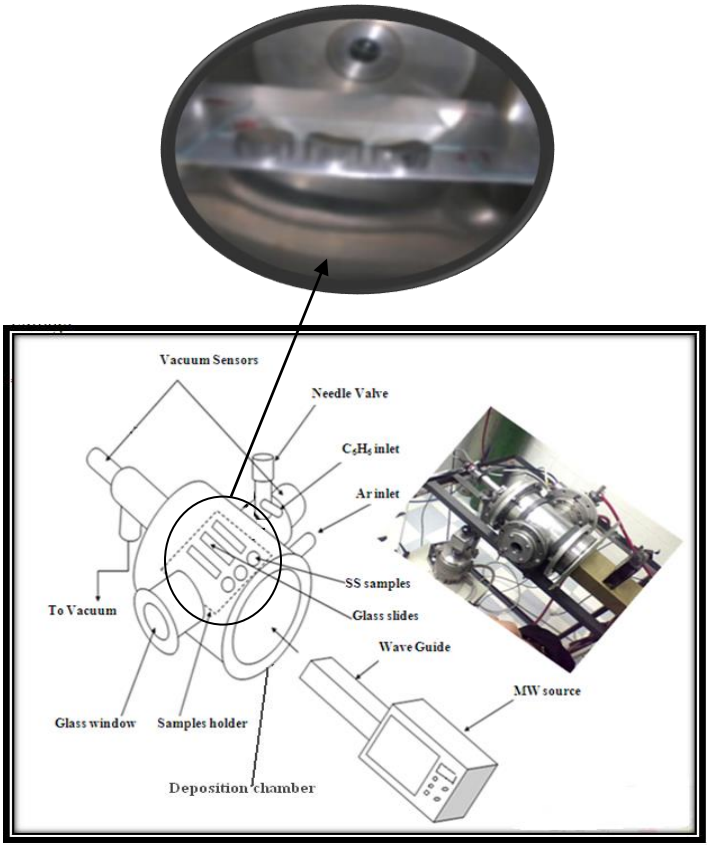


**Fig (1) Schematic diagram of the home-made pulsed microwave plasma system**

### *2.2. Sample preparation and deposition procedure*

Two types of materials were used in this experiment. The first type was disc shaped 304L Stainless Steel (SS) samples of 16 mm diameter and 8 mm thick which were cut by Electric Discharge Machining (EDM). The second type was glass slide of dimension 85x25x1 mm suitable for FTIR analysis. The surfaces of the 304L SS samples were mechanically wet ground on SiC papers down to 2000 grit and then polished with alumina paste and rinsed with distilled water. Both types of samples (SS and glass) and the deposition chamber were pre-cleaned by acetone before the deposition process.

The 304L SS is a biomedical grade austenitic type of stainless steel which is a common grade used in biomedical applications. This alloy contains mostly iron, about 17wt% chromium, 10wt% nickel and small amounts of other alloying species.

Before deposition, the microwave plasma of argon gas was applied to some samples at a power of 180 W for 15 min and working pressure of 3.7 mTorr (the pulsing time was 6 s), this process was carried out to remove any contaminations or organic oxides from the surface of samples and the chamber wall (i.e. pre-cleaning process for both chamber and samples). Thin film deposition processes were conducted at various parameters as indicated in table (1). Argon gas (Ar) used as a carrier. The mixture ($Ar/C_6H_6$) has a ratio of (30:70) respectively.

Table (1) Parameters of the deposition process

| Parameter | Value |
|---|---|
| **Power** | **540 W** |
| **Base pressure** | **0.088 – 0.13 mTorr** |
| **Working pressure** | **10, 30, and 50 mTorr** |
| **Deposition time** | **5, 15, and 30 min** |
| **$Ar/C_6H_6$ ratio** | **30:70** |

The working power $P$ was adjusted at 540 W, but the effective power for pulsed microwave discharge $P_{eff}$ was:

$P_{eff}$ = duty cycle x $P$

Duty cycle = $t_{on}/ (t_{on} + t_{off})$

where $t_{on}$ and $t_{off}$ are the time duration of plasma ON and OFF states respectively.

Duty cycle = 18/ (18+3) = 18/21 = 0.857 ~ 86%

$P_{eff}$ =540 x 0.857 = 463 W

### *2.3. Characterization of thin films:*

#### *2.3.1. Spectroscopic Characterization:*

#### *Fourier-Transform Infrared (FTIR) Spectroscopy:*

The FTIR absorbance spectrum of the sample provides information about the unique chemical bonds and molecular structure of the material. In this work, the chemical structure of the thin films formed by pulsed plasma polymerization from benzene at different deposition parameters was analyzed via the FTIR spectroscope (model Thermo Scientific™ Nicolet™ iS™10 FT-IR).

The spectrum (4000 – 400 $cm^{-1}$) can be approximately divided into four regions [11] as shown in figure (2) [12]. The O–H and C–H stretching region (4000 – 2500 $cm^{-1}$), the triple-bond C≡C region (2500 – 2000 $cm^{-1}$), the double-bond C=C and C=O region (2000 – 1500 $cm^{-1}$) and the fingerprint region (1500 – 600 $cm^{-1}$) [11]. The fingerprint region is different for each molecule. This is normally a complex area showing many bands, frequently overlapping each other. These overlapped regions make it difficult to make simple assignments [13], so the discussion will only focus on the other functional group regions (4000 – 1500 $cm^{-1}$).

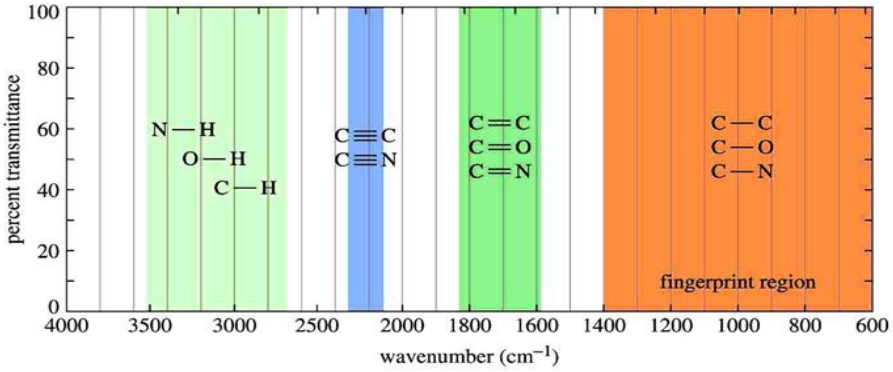


**Fig (2) IR Absorption Regions [12]**

### *2.3.2. Surface Analysis:*

#### *Wettability*

The surface wettability of the deposited thin films on 304L SS substrates was analyzed by measuring the WCA. The study of wettability is most easily accomplished when the solid phase is perfectly flat, smooth, chemically homogeneous and completely clean. When the contact angle of the water drop is high (>90°), the surface is referred to as hydrophobic surface which is exemplified by poor wetting, poor adhesiveness and low solid surface free energy. When the drop of water has low contact angle (<90°), the surface is referred to as hydrophilic surface which is exemplified by good wetting, good adhesiveness and high solid surface free energy [14,15] as shown in figure (3).

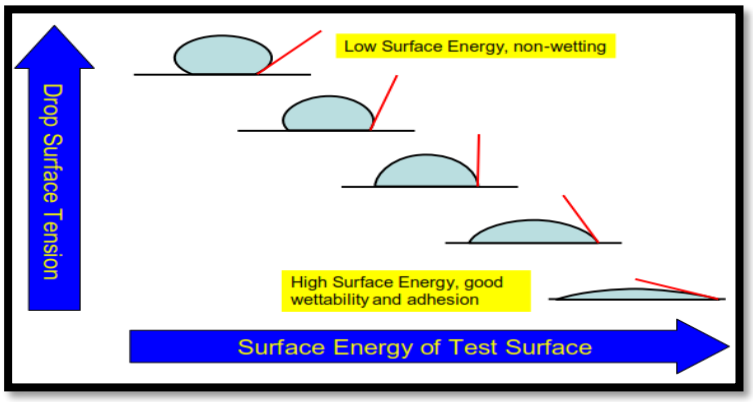


**Fig (3) Contact angles formed by sessile liquid drops on a smooth surface [15]**

## 3. EXPERIMENTAL RESULTS AND INTERPRETATION

During plasma deposition, the benzene decomposed into fragments and radicals [16] and thin film of amorphous hydrogenated carbon (a-C:H) was formed with different chemical structures. The mechanism of benzene decomposition involved the splitting of the ring and formation of radical and secondary products such as polymers as well as hydrogen abstraction from the ring as illustrated in figure (4).

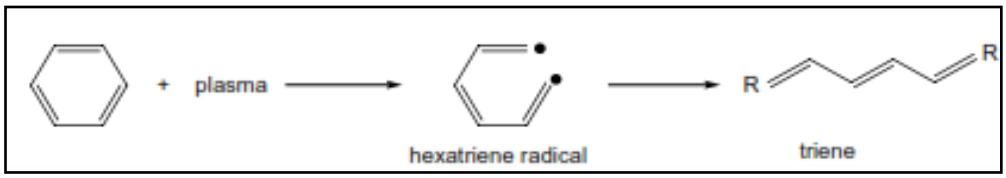


**Fig (4) Mechanism of benzene decomposition**

### *3.1. FTIR Spectrum*

The structure of IR spectrum for benzene, $C_6H_6$, is shown in figure (5). Every carbon has a single bond to hydrogen. Each carbon is bonded to two other carbons and the carbon-carbon bonds are alike for all six carbons. The molecule is planar. The aromatic CH stretch appears at 3100 - 3000 $cm^{-1}$. There are aromatic CC stretch bands (for the carbon-carbon bonds in the aromatic ring) at about 1500 $cm^{-1}$. Two bands caused by bending motions involving carbon-hydrogen bonds appear at approximately 1000 $cm^{-1}$ for the in-plane bend and at about 675 $cm^{-1}$ for the out-of-plane bend [17].

The spectrum of benzene was compared to the FTIR spectra of the deposited thin film shown in figures (6) and (7). The bands in the aromatic ring did not appear in the spectra of the deposited thin film. The bands related to the stretching modes of C–H were observed at ranges of 2939-2945cm$^{-1}$ and 1385-1457 cm$^{-1}$. The bands at 1670 – 1683 cm$^{-1}$ are related to the C=C bond. Some spectra show bands at 2177-2186 which are related to the C≡C bond. Table (2) illustrates the absorption bands detected in the spectra of the deposited thin film after comparing the peak numbers with the spectroscopic data in references [18] and [19].

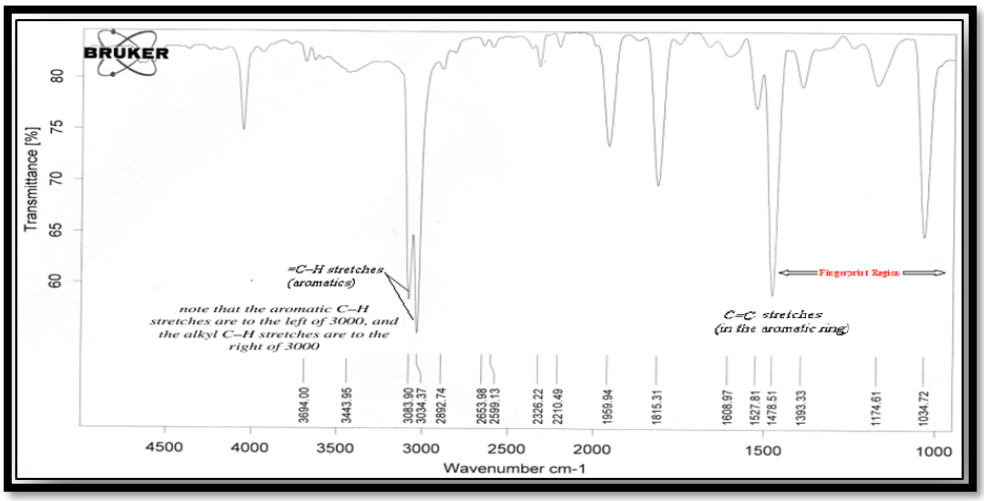


**Fig (5) IR spectrum of benzene**

**Table (2) Identification of bond frequency, absorption and functional groups of the thin films deposited on glass slides**

| Bond | Wave number (cm–1) | Intensity | Functional group |
|---|---|---|---|
| O – H str | 3428 - 3296 | S., br. | Polymeric-alcohol |
| C – H str | 2945 - 2939 | m | Alkanes |
| C ≡ C str | 2186 - 2177 | w | Alkynes |
| C = C str | 1683 - 1670 | v | Alkenes |
| C – H str | 1388 - 1385 | m-w | Alkanes |
| s=strong absorption v=variable intensity m=medium absorption w=weak absorption br=broad absorption | | | |

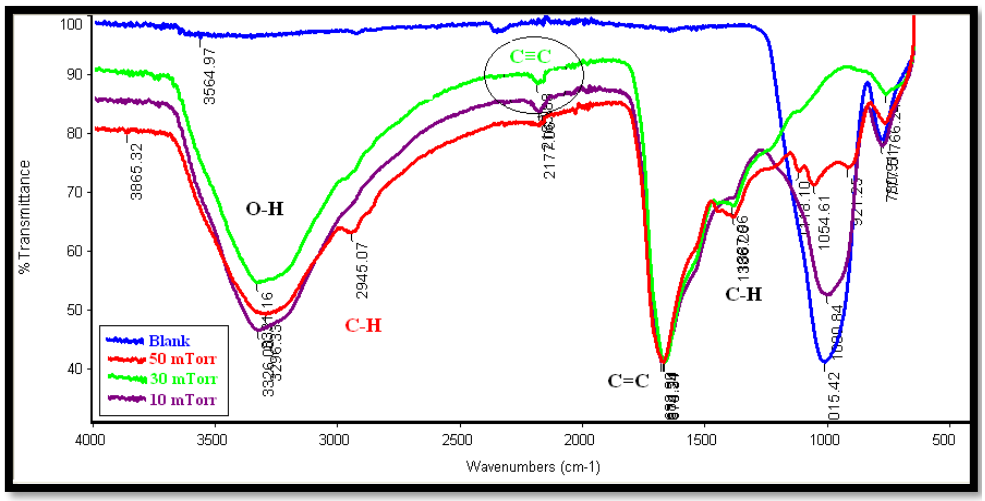


**Fig (6) IR spectra of thin films deposited from benzene at 50, 30 and 10 mTorr for 30 min**

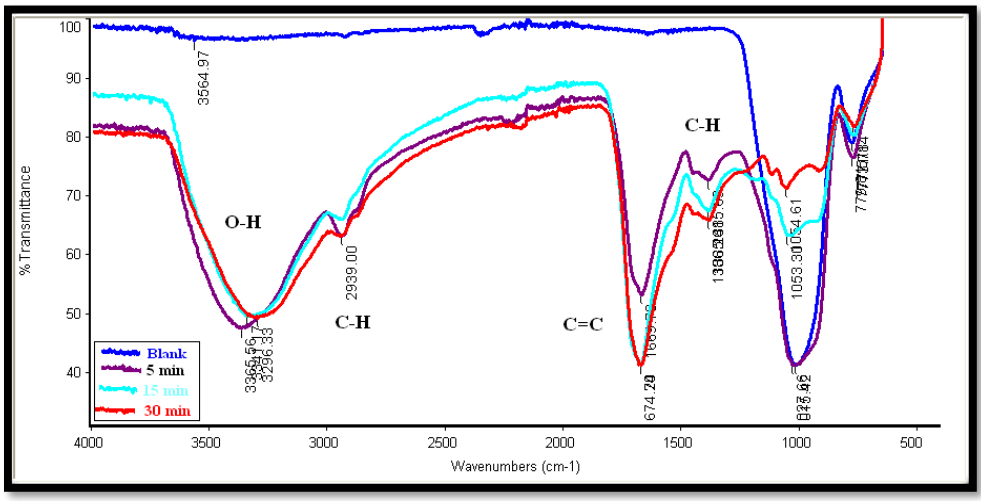


**Fig (7) IR spectra of thin films deposited from benzene at 50 mTorr for 5, 15 and 30 min**

The band related to the O-H bond appeared in all spectra in the range of 3296 - 3428 $cm^{-1}$ with different intensity, the peaks of this bond was broad and had strong absorption. Although, there was no oxygen compound used with benzene during the deposition process, the peaks of O-H bond appeared due to the remaining moisture inside the deposition chamber. This was conformed after using pre-cleaning with Argon plasma before deposition and using argon as a carrier gas with benzene by Ar:$C_6H_6$ ratio of 30:70 respectively as shown in figure (8). The figure shows the IR spectra of thin films deposited at 30 mTorr working pressure for 5 min from pure benzene with and without pre-cleaning and from mixture of Ar and $C_6H_6$ by ratio of 30:70.

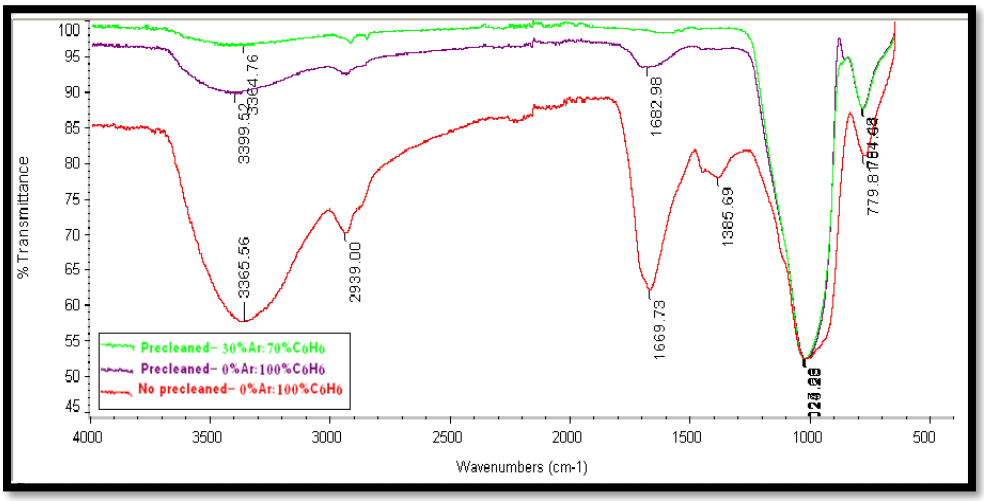


**Fig (8) IR spectra of thin film deposited from $C_6H_6$ with/without pre-cleaning and from mixture of Ar and $C_6H_6$ by ratio of (30:70) respectively**

### *3.1.1 Effect of working pressure on the film chemical structure*

Figure (6) shows the IR spectra of thin film deposited from benzene at different working pressures of 10, 30 and 50 mTorr for deposition time of 30 min. As the working pressure was increased, the chemical structure of the film changed. The band of C≡C was seen at 2177 and 2186 $cm^{-1}$ for deposition at 10 and 30 mTorr respectively. By further increase in working pressure to 50 mTorr the band of C≡C disappeared and the band of C-H was detected at 2945 $cm^{-1}$. The working pressure affected the chemical structure of the film deposited due to the amount of benzene introduced into the deposition chamber; as was clearly observed in figure (9).

### *3.1.2 Effect of deposition time on the film chemical structure*

Figure (7) shows the IR spectra of the benzene films deposited on glass substrates prepared with different deposition times of 5, 15 and 30 min at 50 mTorr. There are slight changes in the absorption intensity (% transmittance) of C=C vibration bands. The absorption intensity increased (i.e. transmittance decreased) by increasing the deposition time as shown in Figures (7) and (10), and the films formed become thicker though the film formed exhibited the same chemical structures (same functional groups). The FTIR analysis indicated that the deposition process in this work was more effective at 30 min deposition time.

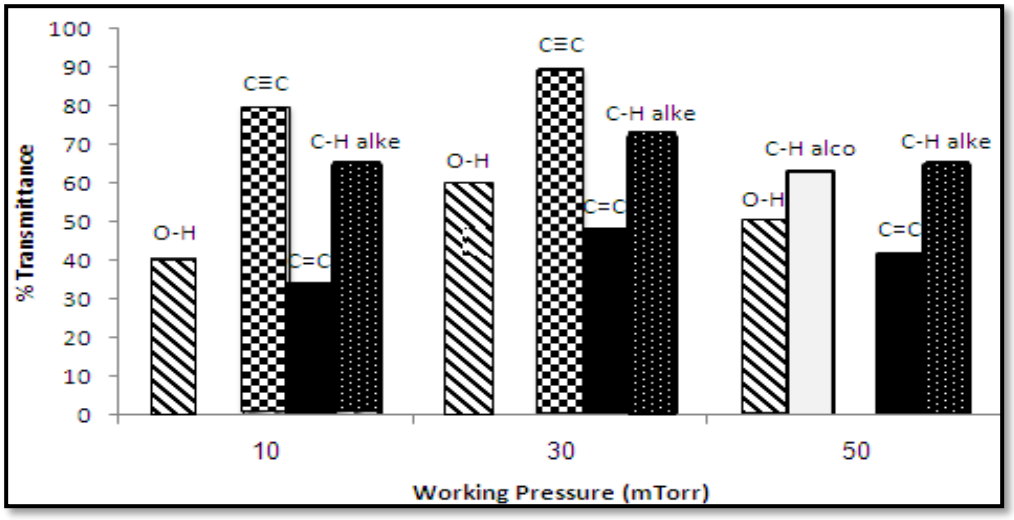


**Fig (9) Effect of working pressure on the absorption intensity (%Transmittance) of the bonds in the FTIR spectra of the thin films deposited from benzene for 30 min.**

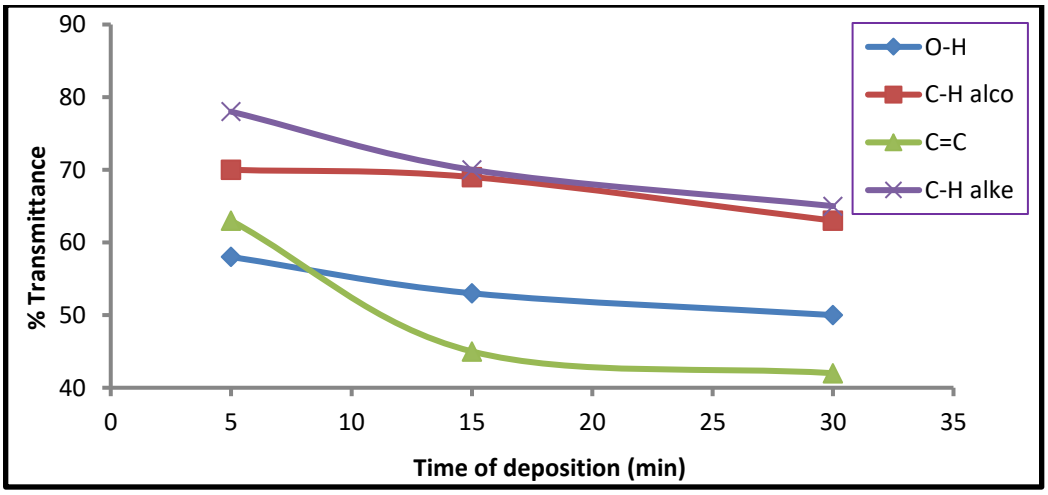


**Fig (10) Effect of deposition time on the absorption intensity (%Transmittance) of the bonds in the FTIR spectra of the thin films deposited from benzene at 50 mTorr.**

### 3.2. Wettability

The surface wettability of the deposited thin films on the 304L SS substrates was analyzed by measuring the water contact angle on the thin films deposited from benzene at different deposition parameters as shown in figure (11).

As can be seen in table (3), the contact angle (θ) is lower than 90° for all the samples and hence, are classified as hydrophilic surfaces (wettable).

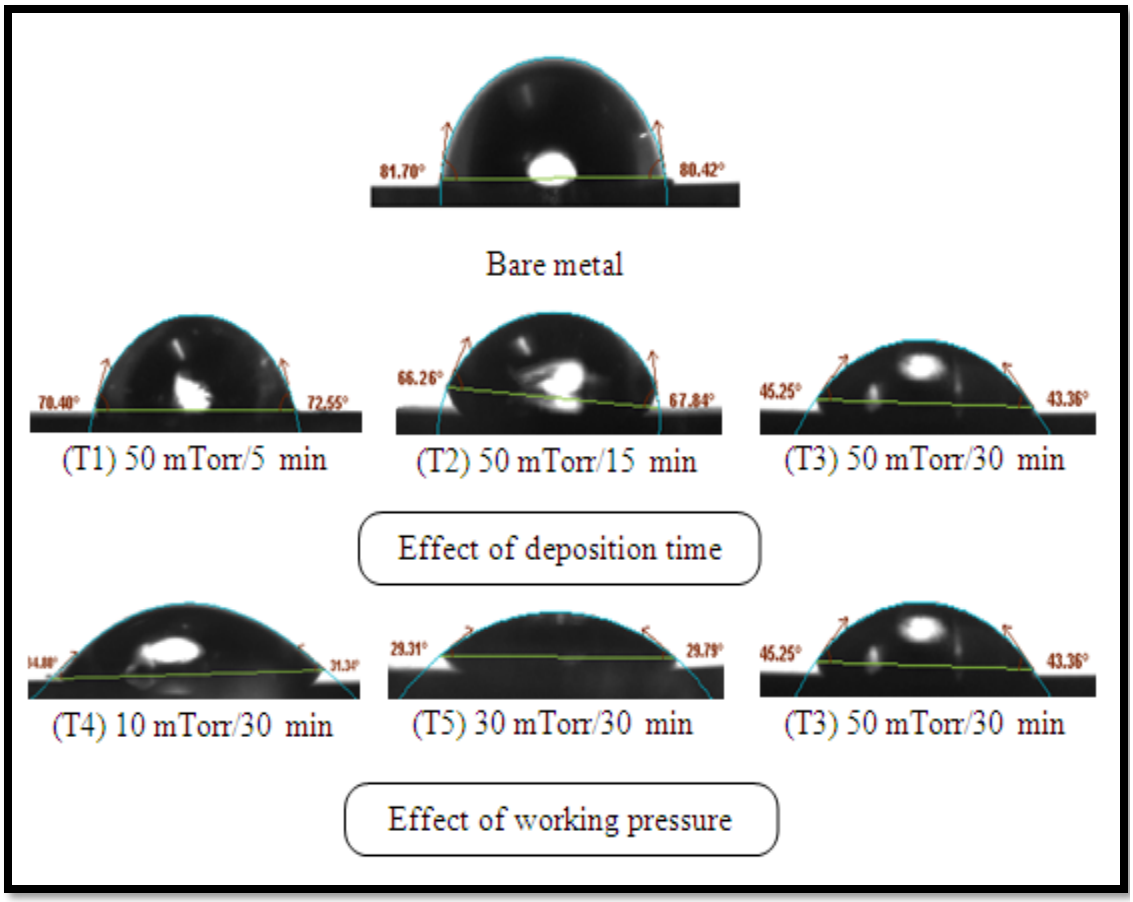


**Fig (11) Optical images of the water contact angle measurement of the thin films deposited from benzene at different deposition parameters**

**Table (3) The results of measured contact angle and surface free energy**

| Samples No | Working pressure (mTorr) | Deposition time (minutes) | Contact angle θ (degree) | Surface Free Energy SFE [mN/m] | Remarks |
|---|---|---|---|---|---|
| bare metal | | | 81 | 35 | |
| T1 | 50 | 5 | 71 | 46 | Effect of time |
| T2 | 50 | 15 | 67 | 49 | |
| T3 | 50 | 30 | 44 | 57 | |
| | | | | | |
| T4 | 10 | 30 | 33 | 63 | Effect of working pressure |
| T5 | 30 | 30 | 30 | 65 | |
| T3 | 50 | 30 | 44 | 57 | |

### *3.2.1 Effect of working pressure on the film wettability*

The water contact angle was decreased from 81° for untreated bare 304L SS surface to 33° and 30° for the thin film deposited at the working pressures of 10 and 30 mTorr respectively. But at 50 mTorr, the treated surface still registered a decrease in the water contact angle (to 44°), this decrease was smaller than the others as shown in figure (12). This is due to the change in the chemical structure of the deposited thin film as described in Section 3.1.1.

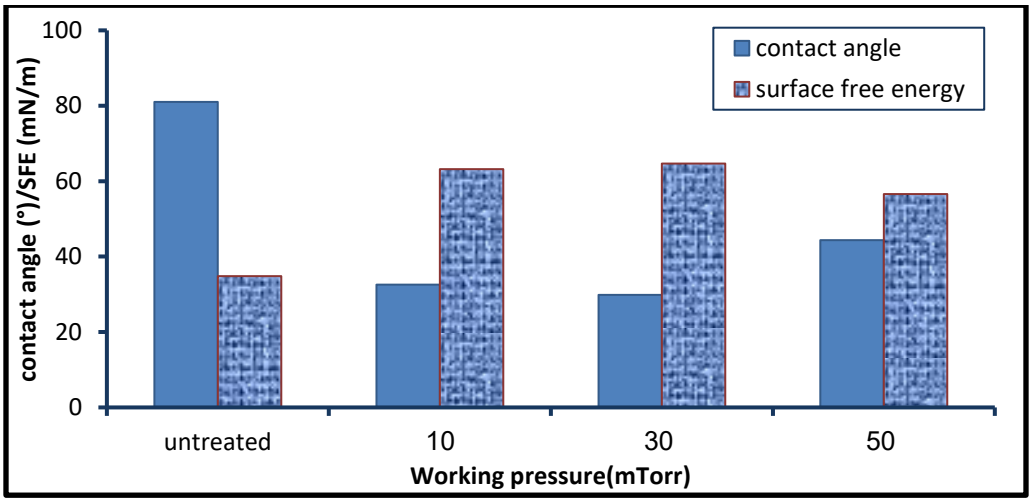


**Fig (12) The effect of working pressure on water contact angle and surface free energy of the thin films deposited from benzene for 30 min**

### *3.2.2 Effect of deposition time on the film wettability*

On the other hand, increase in the time of deposition led to decrease in the contact angle and increase in the surface free energy as shown in figure (13). So the surface was more wettable and had better adhesion with increase in the time of deposition.

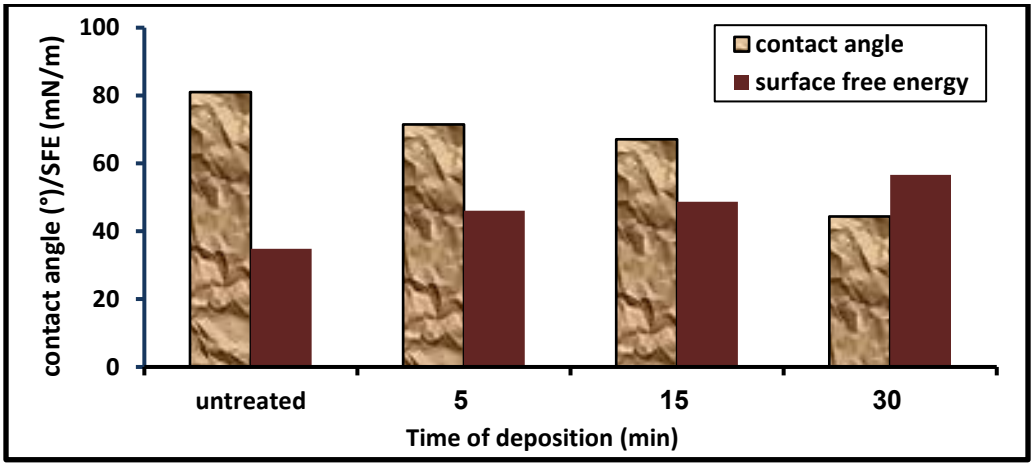


**Fig (13) The effect of deposition time on water contact angle and surface free energy of the thin films deposited from benzene at 50 mTorr**

## 4. Conclusion

Plasma polymerized thin films have been deposited on 304L Stainless Steel and glass substrates at room temperature using benzene as precursor gas by PECVD method. Pulsed microwave with frequency of 2.45 GHz and 540 W was applied for the ignition of the plasma. FTIR analysis indicated the decomposition of the benzene ring and formation of a-C:H films in aliphatic group. According to the effect of deposition parameters, the chemical structure of the thin films was affected by working pressure. The time of deposition was the most influential factor on the film surface wettability. So the deposition process is more effective at 30 minutes and 50mTorr. All the samples had contact angle ($\theta$) lower than 90° so they classified as hydrophilic (wettable surface).

## 5. Acknowledgements

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