Thin Film of Benzene Deposited on304L Stainless Steel using Pulsed MicrowavePlasma Enhanced Chemical Vapor Deposition

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Abstract:

Thin films have been deposited by plasma polymerization onto 304L stainlesssteel and glass substrates using pulsed microwave Plasma Enhanced Chemical VaporDeposition (PECVD) with urebenzene (C6H6) as precursor gas. The chemicalstructure andsurface properties (wettability) of the deposited thin fims werecharacterized by FourierTransform Infrared (FTIR) spetroscopy and the Water Contact Angle (WCA) measured using an ptical tensiometer respectively. The effectsof working pressure addeposition time on the chemical structure and surfacewettability of the deposited thin films were studied. The results of the FTIR analysisshowed that the structure of the film prepared frombenzene changed inwhich theC≡C absorption bands became more prominent on decreasing the working pressure.

The characteristic absorption peaks of benzene film were presented more prominentlyin the sample prepared with the longer deposition time. All the treated samplesregistered reducedWCA below 90□, their hydrophilic surfaces became morewettable. The deposition time had the greatest influence on the CA 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:

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Plasma polymerization; Thin film; Pulsed Microwave; PECVD; FTIR;Chemical structure; Contact angle; Wettability.

Introduction:

Plasma polymerization is gaining importance for the last several years as a toolto modify material surfaces [1]. It has been defined as the formation of polymericmaterials under the influence of plasma [2]. It refers to the deposition of polymer thinfilm through plasma dissociation due to the excitation of an organic monomer gas andsubsequentdeposition and polymerization of the excited species on the surface of asubstrate [3]. Plasma polymerization can be used to fabricate polymer thin films(100Å1μm) from a variety of organic and organometallic starting materials. Amongmany chemical vapor deposition (CVD) methods, plasmaenhanced chemical vapordeposition (PECVD) process is very efficient method to produce homogeneous organic thin films on largearea substrates and offers good control over the filmproperties [4]. Polymeric thin filmsobtained by (PECVD) have several advantagesover films produced by conventional polymerization [5]. The main advantage ofplasmapolymerization is that it canoccur at moderate temperature compared toconventional chemical reaction [3]. Additionally, plasma polymerized surfaces haveeconomical advantage of a green (environmentally benign) technology as comparedto other processing methods [5]. In manycases, polymers formed by plasmapolymerization have different chemical compositions as well as chemical andphysical properties from those fomed by conventional polymerization, even if thesame monomersareused in plasma and conventional polymerization [6]. Theresulting thin films that are highly coherent and adherent to a variety of substratesincluding conventional polymer, glass and metal surfacesmay be prepared frommonomers not polymerizable by conventional means. Plasma polymerized filmswhich are pinholefree andhighly crosslinked and therefore are insoluble, ca n betailored toexhibit properties such as chemically inert, mechanically tough andthermally stable [4,5]. Due to these excellent properties they havebeen undertakenvery actively in the last few years for a variety ofapplications such as protectivecoatings, biomedical materials, electronic and optical devices [4]. Plasmapolymerized coatings are increasingly being investigated in biomedical applications.

These include surface modification of biomaterials to enhance implant integrationand sterilization and to improvedevice multifunctionality, tribological andmechanical properties, as well as biocompatibility of artificialdevices whileobviating the needs for large expenses and long time to develop brand new materials[5, 6].

There are many sources used for plasma generation in P
CVD processes, thecommon sources are direct current (DC), radio fequency (RF) and microwave (MW)discharge [7]. Microwave discharges are widely used for generation of cold plasma atpressures from 105 Torr up to atmospheric pressure in the pulse and continuum waveregimes at incident powers ranged between several Watts and hundreds of kW fordifferent applications [8]. Recently, pulsed power has been successfully employed inplasma polymerization of a variety of monomers. Greater retention of the monomerfunctional group is observed in the resulting polymeric film with ulsed plasmapolymerization [9]. Magnetrons are the most common microwave generators becauseof their low cost and availability in the market for domestics used e.g. microwaveovens [10]. There are several classes of the microwave plasma generators includingthe waveguide microwave plasma generator [8] which was used in this study.

In this study pulsed microwave plasma system constructed for the deposition ofpolymerlike organic thin films of benzene on 304L stainless steel substrates used inmedical applications and glass substrates (for FTIR analysis). Benzene and Argonwere used as precursor and carrier gases respectively. The effects of wo rking pressureand the deposition time on the chemical structure and surface wettability of thedeposited thin films were investigated.

Experimental Work:

Deposition system:

The deposition system used in this work is a home made PECVD designedsystem which is illustrated in figure (1) . It is a multipurpose system for the treatmentby 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 cylindricalchamber 25 cm long and 14.5 cm in diameter provided with four ports: the first portfor vacuum system, the second for gas inlet (gas supply), the third for waveguide andthe last one with a glass window for observing the deposition process. The vacuumsystem consists of a turbomolecular pump backedby mechanical pump (Varianmodel) and pressure gauges (Ionic and Pirani Gauges). The microwave is generatedby the microwave furnace (commercial magnetron) at frequency of 2.45 GHzwithmaximum power of 900 W which was transmitted to the chamber via a waveguide.

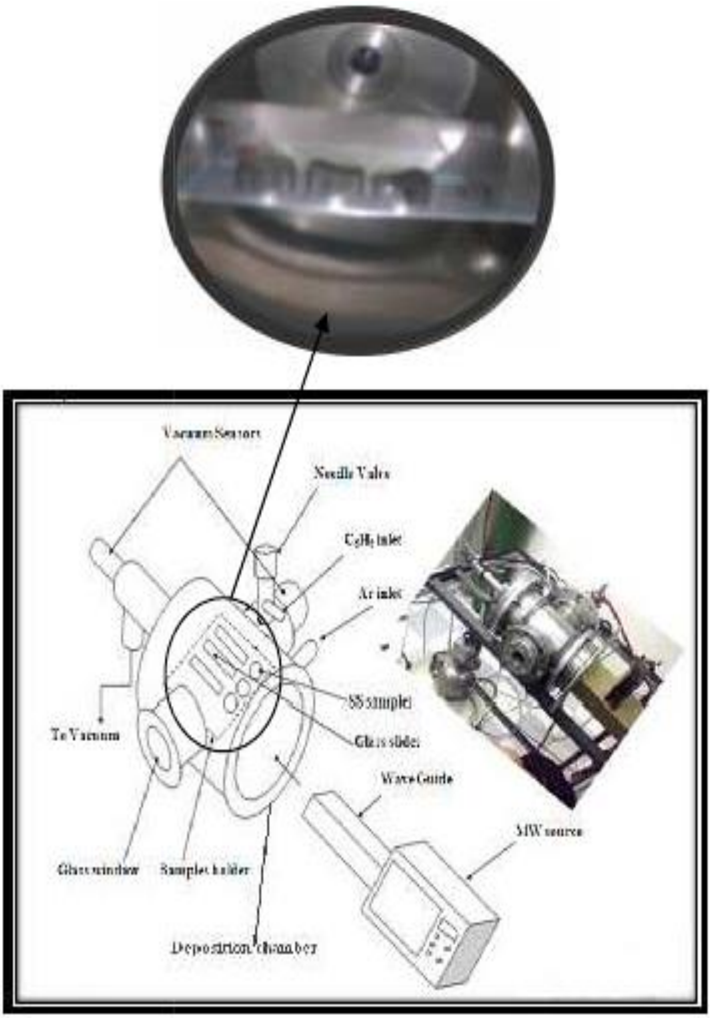


Fig (1) Schematic diagram of the homemade pulsed microwave plasma system

Sample preparation and deposition procedure:

Two types of materials were used in this experiment. The first type was discshaped 304L Stainless Steel (SS) samples of 16 mm diameter and 8 mm thick whichwere cut by Electric

Discharge Machining (EDM). The second type was glass slide ofdimension 85x25x1 mm suitable for FTIR analysis. The surfaces of the 304L SSsamples were mechanically wet ground on SiC papers down to 2000 grit and thenpolished with alumina paste and rinsed with distilled water. Both types of samples(SS and glass) and the deposition chamber were precleaned by acetone before thedeposition process.

The 304L SS is a biomedical grade austenitic type of stainless steel which is acommon 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 wasapplied to somesamples at a power of 180 W for 15 min and working pressure of 3.7 mTorr (thepulsing time was 6 s), this process was carried out to remove any contaminations ororganic oxides from the surface of samples and the chamber wall (i.e. precleaningprocess for both chamber and samples).

Thin filmdeposition processes wereconducted at various parameters as indicated in table (1). Argon gas (Ar) used as a carrier. The mixture (Ar/C6H6) 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/C6H6 ratio	**30:70**

The working power P was adjusted at 540 W, but the effective power for pulsedmicrowave discharge Peff was:

Peff = duty cycle x PDuty cycle = ton/ (ton + toff)where ton and toff are the time duration of plasma ON and OFF states respectively.

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

Peff =540 x 0.857 = 463 W

Characterization of thin films:

Spectroscopic Characterization:

Fourier-Transform Infrared (FTIR) Spectroscopy:

The FTIR absorbance spectrum of the sample provides information about theunique chemical bonds and molecular structure of the material. In this work, thechemical structure of the thin films formed by pulsed plasma polymerization frombenzene 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 fourregions [11] as shown in figure (2) [12]. The OH and CH stretching region (4000 2500 cm−1), the triplebond C≡C region (2500 – 2000 cm−1), the double-bond C=Cand 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 acomplex area showing many bands, frequently overlapping each other.Theseoverlapped regions make it difficult to make simple assignments [13], so thediscussion will only focus on the other functional group regions (4000 – 1500 cm−1).

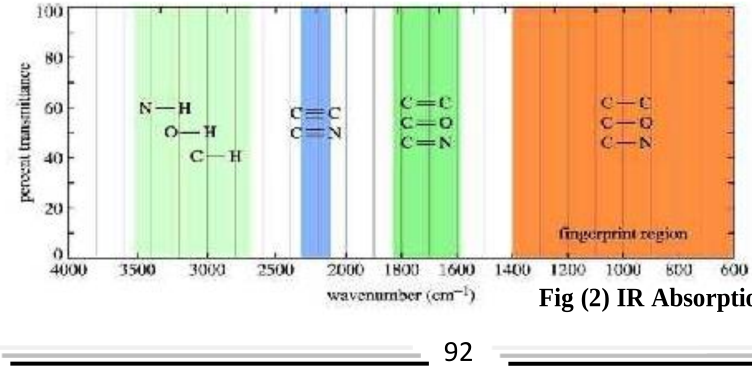


Fig (2) IR Absorption Regions [12]

Surface Analysis:

Wettability:

The surface wettability of the deposited thin films on 304L SS substrates wasanalyzed by measuring the WCA. The study of wettability is most easilyaccomplished when the solid phase is perfectly flat, smooth, chemicallyhomogeneous 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 poorwetting, poor adhesiveness and low solid surface free energy. When the drop of waterhas low contact angle (<90°), the surface is referred to as hydrophilic surface which isexemplified by good wetting, good adhesiveness and high solid surface free energy[14,15] as shown in figure (3).

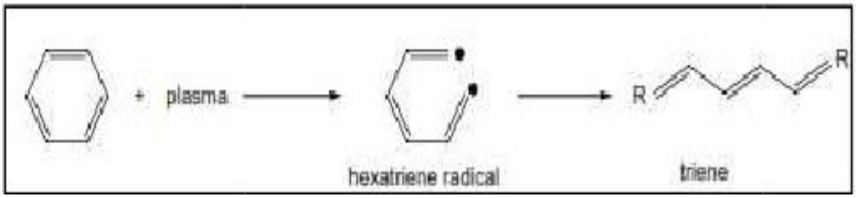


Fig (3) Contact angles formed by sessile liquid drops on a smooth surface [15]

Experimental Results and Interpretation:

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

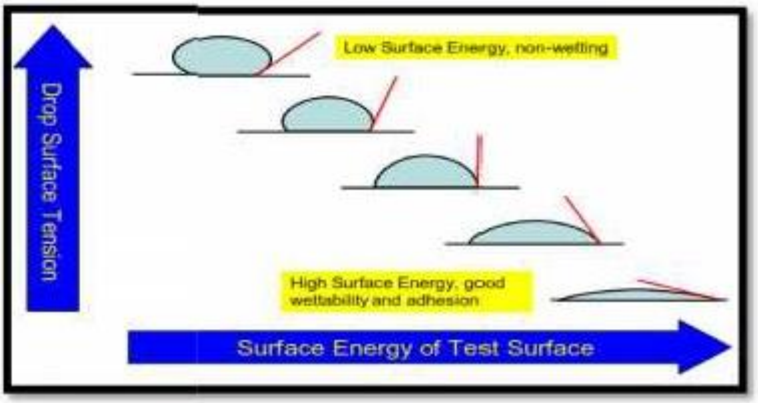


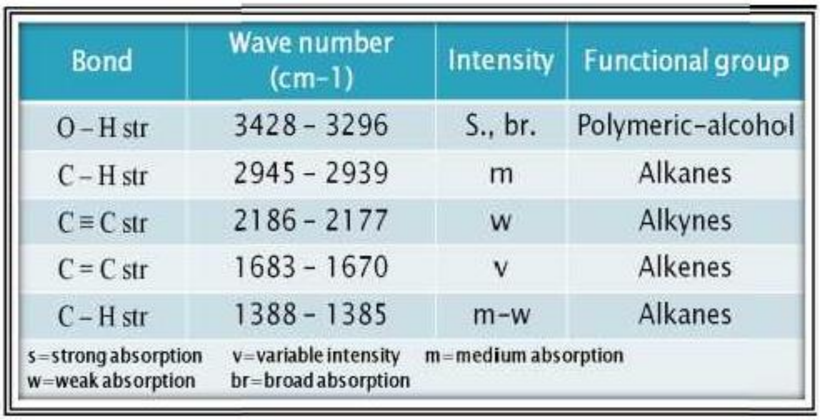
Fig (4) Mechanism of benzene decomposition

Ftir Spectrum:

The structure of IR spectrum for benzene, C_6H_6, is shown in figure (5). Everycarbon has a single bond to hydrogen. Each carbon is bonded to two other carbonsand the carbon-carbon bonds are alike for all six carbons. The molecule is planarThe aromatic CH stretch appears at 3100 3000 cm^{1}. There arearomatic CC stretchbands (for the carboncarbon bonds in the aromatic ring) at about 1500 cm^{1}. Twobands caused by bendingmotions involving carbonhydrogen bonds appear atapproximately 1000 cm^{1} for the inplane 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 depositedthin film shown in figures (6) and (7). The bands in the aromatic ring did not appearin the spectra of the deposited thin film. The bands related to the stretching modes ofCH were observed at ranges of 29392945cm^{1} and 13851457 cm^{1}. The bands at1670 1683 cm^{1} are related to the C=C bond. Some spectra show bands at 21772186 which are related to the C≡C bond. Table (2) illustrates the absorption bandsdetected in thespectra of the deposited thin film after comparing the peak numbers with the spectroscopic data in references [18] and [19].

Table (2) Identification of bond frequency, absorption and functional groups of thethin 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

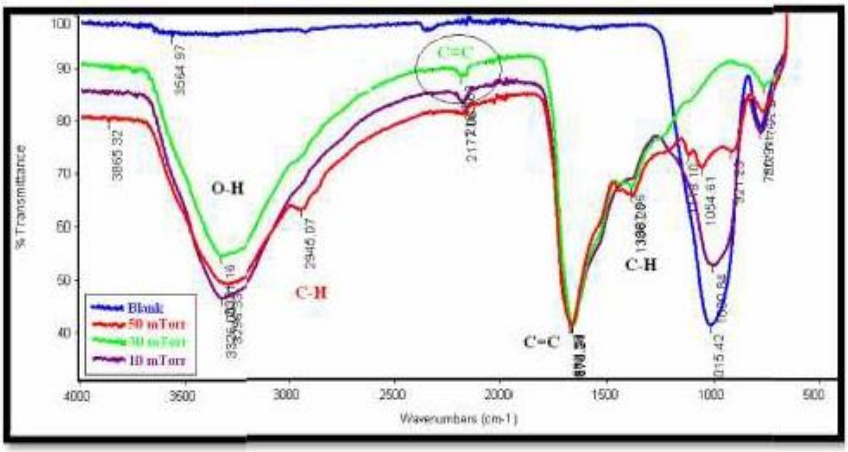


Fig (5) IR spectrum of benzene

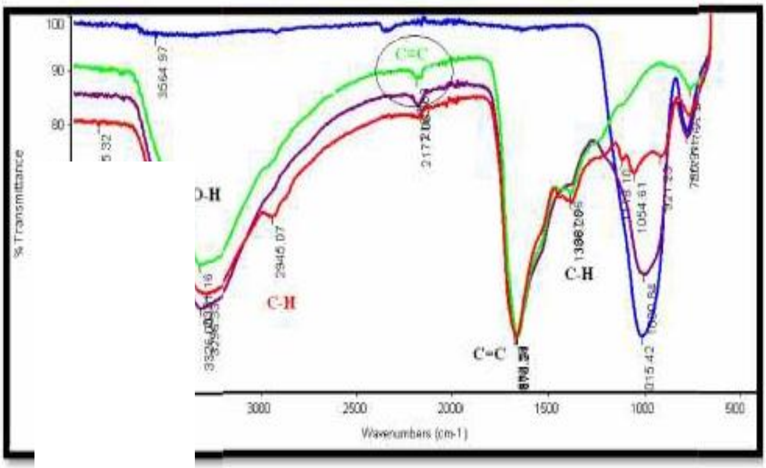


Fig (6) IR spectra of thin films deposited from benzene at 50, 30 and 10 mTorr for 30 min

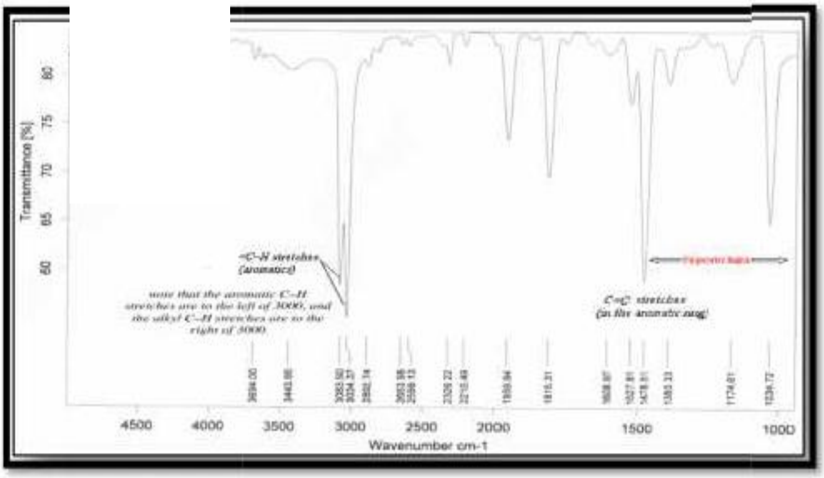


Fig (7) IR spectra of thin films deposited from benzene at 50 mTorr for 5, 15 and 30 min

The band related to the OH bond appeared in all spectra in the range of 3296 3428 cm^{1} with different intensity, the peak s of this bond was broad and had strongabsorption. Although, there was no oxygen compound used with benzene during thedeposition process, the peaks of OH bond appeared due to the remaining moistureinside the deposition chamber. This was conformed after using precleaning withArgon plasma before deposition and using argon as a carrier gas with benzene by Ar:C6H6 ratio of 30:70 respectively as shown in figure (8). The figure shows the IRspectra of thin films deposited at 30 mTorr working pressure for 5min from purebenzene with and without precleaning and from mixture of Ar and C6H6 by ratio of 30:70.

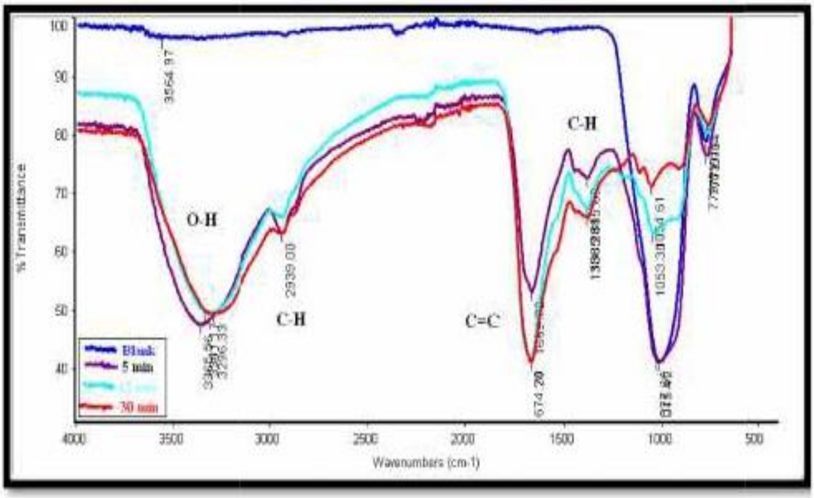


Fig (8) IR spectra of thin film deposited from C6H6 with/without pre-cleaning and frommixture of Ar and C6H6 by ratio of (30:70) respectively

Effect of working pressure on the film chemical structure:

Figure (6) shows the IR spectra of thin film deposited from benzene at differentworking pressures of 10, 30 and 50 mTorr for deposition time of 30 min. As theworking pressure was increased, the chemical structure of the film changed. The bandof C≡C was seen at 2177 and 2186 cm^{1} for deposition at 10 and 30mTorrrespectively. By further increase in working pressure to 50mTorr the band of C≡Cdisappeared and t he band of CH was deected at 2945 cm^{1}. The working pressureaffected the chemical structure of the film deposited due to the amount of benzeneintroduced into the deposition chamber; as was clearly observed in figure (9).

Effect of deposition time on the film chemical structure:

Figure (7) shows the IR spectra of the benzene filmsdeposited on glasssubstrates prepared with different deposition times of 5, 15 and 30 min at 50 mTorrThere are slight changesinthe absorption intensity (% transmittance) of C=Cvibration bands. The absorption intensity increased (i.e. transmittance decreased) byincreasing the deposition time as shown in Figures (7) and (10), and the films formedbecome thicker though the film formed exhibited the same chemical structures (samefunctional groups). The FTIR analysis indicated that the deposition process in thiswork was more effective at 30 min deposition time.

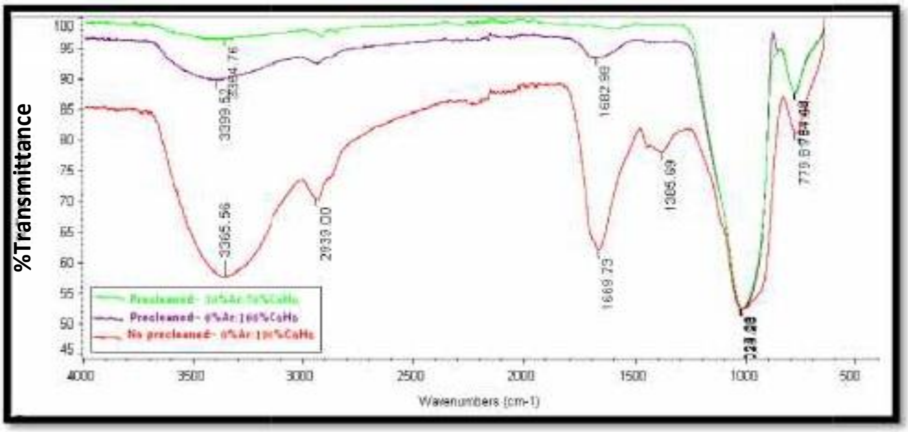


Fig (9) Effect of working pressure on the absorption intensity (%Transmittance) of thebonds in the FTIR spectra of the thin films deposited from benzene for 30 min.

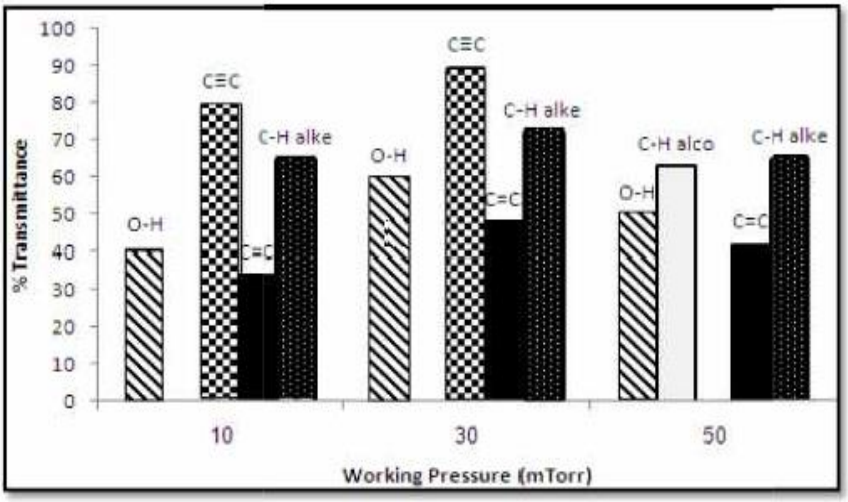


Fig (10) Effect of deposition time on the absorption intensity (%Transmittance) of the bonds inthe FTIR spectra of the thin films deposited from benzene at 50 mTorr.

Wettability:

The surface wettability of the deposited thin films on the304L SS substrateswas analyzed by measuring the water contact angle on the thin films deposited frombenzene at different deposition parameters as shown in figure (11).As can be seen in table (3), the contact angle (□) is lower than 90□ for all thesamples and hence, are classified as hydrophilic surfaces (wettable).

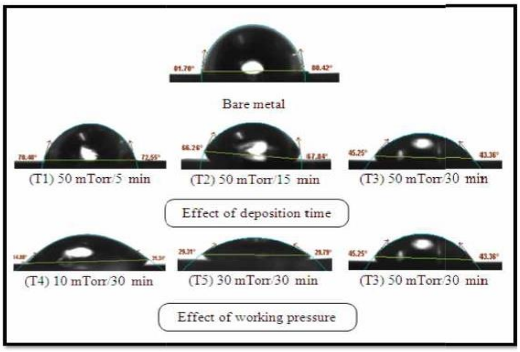


Fig (11) Optical images of the water contact angle measurement of the thin films deposited from benzene at different deposition parameters

Effect of working pressure on the film wettability:

The water contact angle was decreased from 81° for untreatedbare 304L SSsurface to 33° and 30° for the thin film deposited at the working pressures of 10 and30 mTorr respectively. Butat 50mTorr, the treated surface still registered a decreasein the water contact angle (to 44°), this decrease was smaller than the others as shownin figure (12). This is due to the change in the chemical structure of the deposited thinfilm as described in Section 3.1.1.

Samples No	Working pressure (mTorr)	Deposition time (minutes)	Contact angle □ (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	

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

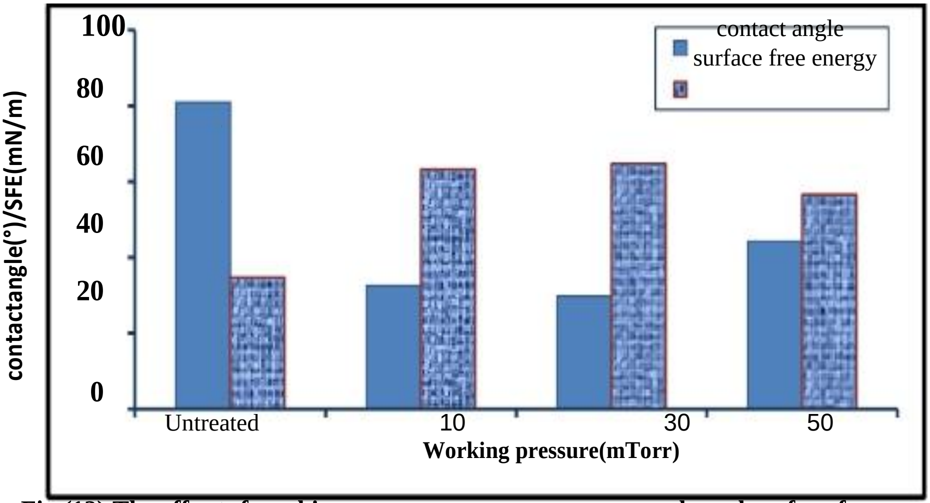


Fig (12) The effect of working pressure on water contact angle and surface freeenergy of the thin films deposited from benzene for 30 min

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 thecontact angle and increase in the surface free energy as shown in figure (13). So thesurface was more wettable andhad better adhesion with increase in the time of deposition.

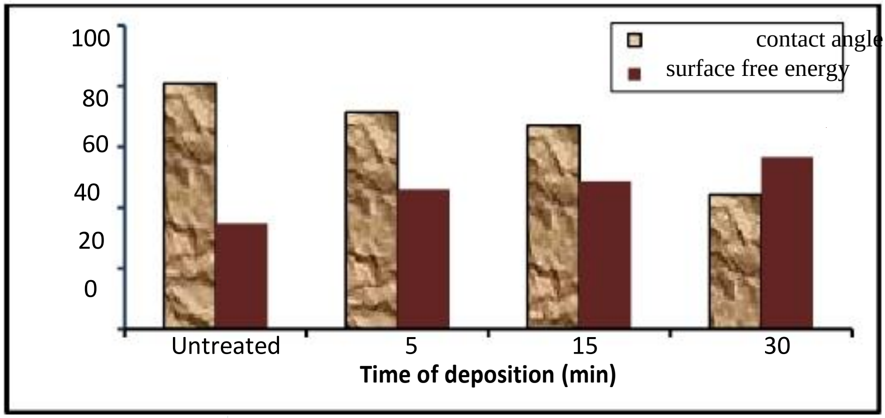


Fig (13) The effect of deposition time on water contact angle and surface free energy of the thin films deposited from benzene at 50 mTorr

Conclusion:

Plasma polymerized thin films have been deposited on 30L Stainless Steel andglass substrates at room temperature using benzene as precursor gas by PECVDmethod. 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 benzenering and formation of aC:H films in aliphatic group. According to the effect ofdeposition parameters, the chemical structure of the thin films was affected by working pressureThe time of deposition was the most influential factor on the filmsurface wettability. So the deposition process is more effective at 30 minutes and50mTorr. All the samples had contact angle (□) lower than 90□ so they classified as hydrophilic (wettable surface).

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ترسيب رقائق من البنزين على الصلب المقاوم للصدأ (304L) باستخدام تقنية الترسيب البخاري الكيميائي المدعم بالبلازما المتولدة بواسطة موجات الميكروويف النبضية

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المستخلص:

في إطار تطوير وتحسين الخواص السطحية للمواد المستخدمة في المجالات الطبية باستخدام تقنية ترسيب الرقائق تم في هذا البحث ترسيب رقائق لمادة البنزين (C_6H_6) بطريقة البلمرة بالبلازما على عينات من الصلب المقاوم للصدأ (304L) والشرائح الزجاجية باستخدام تقنية الترسيب البخاري الكيميائي المدعم بالبلازما المتولدة بواسطة موجات الميكروويف النبضية مع استخدام البنزين النقي كغاز لعملية الترسيب. وقد أجريت القياسات اللازمة للفيلم المترسب حيث استخدم مقياس تحويرات فورير بواسطة الأشعة تحت الحمراء Fourier Transform Infrared Spectroscopy "FTIR") لدراسة ومعرفة التركيب الكيميائي لهذا الفيلم، كما استخدم مقياس التوتر السطحي البصري (Optical Tensiometer) لقياس زاوية تماس الماء (Water Contact Angle "WCA") بين قطرة الماء والفيلم المترسب وحساب طاقة السطح الحرة (Surface Free Energy) وبالتالي معرفة مدى قابلية هذا الفيلم للبلل (wettability).

تضمن هذا البحث أيضا دراسة تأثير كل من ضغط الغاز العملي وزمن الترسيب على التركيب الكيميائي وزاوية تماس الماء للفيلم المترسب، وقد أظهرت النتائج أن بنية الفيلم المُعد من البنزين تغيرت حيث أصبح امتصاص رابطة ($C{\equiv}C$) أكثر وضوحاً بانخفاض الضغط العملي، كما أظهرت نتائج قياس زاوية تماس الماء (WCA) أنها أقل من 90° لكل العينات المعالجة وبالتالي أصبحت سطوحها (hydrophilic) أكثر قابلية للبلل. وقد كان لزمن الترسيب التأثير الأكبر على قياسات زاوية تماس الماء (WCA).

من خلال هذه الدراسة وُجد أن التركيب الكيميائي وخاصية البلل يمكن تعديلها وضبطها بواسطة بارامترات البلازما في عمليات الترسيب مما يتيح إنتاج طلاءات ذات خصائص مناسبة لتطبيقات محددة.

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