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Atmospheric Pressure Plasma Deposition of Polyfuran

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The atmospheric pressure radiofrequency (RF) plasma polymerization of furan was carried out with the objective of synthesizing polyfuran thin film. The structure, compositions and morphology of the plasma deposited polyfuran film were investigated by Fourier transform infrared (FTIR), atomic force microscopy (AFM), ultraviolet-visible absorption spectroscopy (UV-vis) and thermogravimetric analysis (TGA). The formation of polyfuran was confirmed using FTIR and UV-visible analysis. The properties of plasma-deposited polyfuran were compared with those of chemically synthesized polyfuran. Although the plasma deposited thin film polyfuran shows lower thermal stability than that of chemically synthesized polyfuran. It has better solubility in CHCl₃, also. Thin uniform polyfuran films are obtained in plasma assisted polyfuran deposition, while particles are obtained in chemical polyfuran polymerization.

Keywords: polyfuran; atmospheric plasma deposition; thin films

1 Introduction

The discovery of electrical conductivity of organic conjugated polymers has opened a novel and very important field of modern functional material science. The heterocyclic polymers, such as polypyrrole and polythiophene, have also received a great deal of interest due to their high conductivity in doped state accompanied by a much higher stability in air (1, 2). However, the polyfuran has attracted relatively less attention and remained as an ill-defined conjugated polymer because the polyfuran with a regular structure and high conductivity was synthesized with difficulty (3). It is reported that polyfuran demonstrates some superior properties, such as electrochromic effect and good redox ability (4). Moreover, the resource of furan is much greater, and thus, furan is much less expensive than pyrrole and thiophene, because the furan comes from an agricultural and sideline product that is a reproducible resource. These characteristics of furan will attract the attention of more scientists in chemistry and materials science. Chemical and electrochemical synthesis of conjugated polymer coatings is well described in the literature (5, 6). However, both methods have their drawbacks. In general, the typical structure with alternate single and double bonds leads to rigid, insoluble polymers. Processing of the polymers resulting from chemical polymerization is therefore difficult. If the substrate is conductive, this

problem can be solved by using electropolymerization with deposition directly onto the substrate. Nevertheless, both chemical and electrochemical synthesis are usually performed in batch process. This is the reason why, until today, they have only been used for small-scale applications with high added values. High-speed, in-line processing, with low production costs, is not yet possible. Recently, synthesis of thin polymer films by the use of plasma polymerization has emerged as an interesting new approach. Plasma polymerization is a 'dry' technique that does not require the use of solvents. From an ecological and economical point of view, the absence of solvents and less solvent waste offers many advantages. At first, plasma polymerization was used for the formation of thin passive layers, but it has recently found its way into other applications. Some of those applications incorporate the deposition of conjugated polymers. Plasma polymerizations of thiophene and its derivatives under low pressure have already been reported; however, since this technique requires a high vacuum, it can only be carried out in a batch process (7, 8).

In the past decades, the electrochemical synthesis and properties of polyfuran (9), copoly(furan/pyrrole) (10), copoly(furan/2-methylfuran) (11) and polyfuran/polythiophene bipolymer films (12) have been studied. Nevertheless, it is observed that due to the high oxidation potential of furan, a significant cleavage of the furan ring generally occurred during the electropolymerization, hence, strongly breaking the expected π -conjugated structure. Therefore, a chemical oxidative polymerization of furan has been urgent. In fact, a few scientists have synthesized polyfuran (13), polyfuran/poly(2-chloroaniline) composites (14) and

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polyfuran/polyaniline (15) copolymers by chemical oxidative polymerization.

Plasma polymer films are studied in microelectronics, functional polymer films and biopolymer applications. Especially deposited thin films for optical applications and deposition on woven and nonwoven surfaces gain interest recently (16, 17). However, till the last decade, most of the plasma deposition and coating techniques were carried out in low pressure plasma. The technical difficulties and non uniformity in high pressure plasmas are partially resolved in atmospheric pressure plasma systems. Research on atmospheric pressure plasma systems gain momentum especially on surface coatings and surface modification. There are advantageous and disadvantageous of atmospheric pressure plasmas. Elimination of vacuum chambers decreases the cost of plasma system. The shape and size of the plasma systems can be modified in atmospheric pressure plasma systems.

In this paper, atmospheric pressure plasma deposition of furan is described. Until now, although the low pressure RF plasma polymerization of furan was studied by a few scientist (18, 19), atmospheric pressure deposition of polyfuran is new. The furan polymer deposition on glass is obtained using 13.56 MHz radiofrequency (RF) atmospheric pressure plasma. The atmospheric pressure glow discharge is obtained with a matching unit, helium flow and furan monomer.

The possibility of depositing conjugated polymer coating from furan, using plasma working under atmospheric pressure is also reported. Polyfuran deposition using plasma was compared with polyfuran chemically obtained. A detailed characterization is carried out with the help of conventional techniques such as FTIR and UV-Vis spectroscopy, TGA analysis and AFM.

2 Experimental

2.1 Materials

Furan, FeCl_3 , CHCl_3 and MeOH were purchased from Aldrich Chemical Company and were without any further purification. The highly purified helium is used in plasma system.

2.2 Atmospheric Pressure Plasma Depositon of Polyfuran

Dielectric barrier atmospheric pressure RF plasma system is built for furan thin film deposition. A 13.56 MHz RF source is used with a homemade matching unit. Helium is introduced to the system in order to obtain a glow discharge. During discharge, liquid furan is injected. Due to the low boiling point of furan, furan is evaporated suddenly and there was no need for heating the furan monomer. After 5 min process time, thin polyfuran film was obtained onto glass substrate.

2.3 Chemical Oxidative Polymerization of Furan

The polyfuran was prepared with FeCl_3 as an oxidant in CHCl_3 through chemically oxidative polymerization. A

representative procedure is as follows: Furan (0.01 mol) was dissolved 25 ml of CHCl_3 at 25°C in a water bath. FeCl_3 (0.02 mol) solution in 25 ml of CHCl_3 was then added dropwise to the furan solution with constant stirring for 0.5 h. The reactant solution was consistently stirred for 24 h in the water bath. The polyfuran precipitates formed thus isolated from the reaction mixture by filtration and washed with CHCl_3 and an excess of methanol until the filtrate was colorless and dried at 50°C under vacuum. The resultant polymer is insoluble material and in an undoped form.

2.4 Characterization

FTIR was used to analyze the chemical structure of the plasma deposited polyfuran and chemically synthesized polyfuran. The FTIR spectra of monomer liquid and polyfurans were measured on a Perkin-Elmer System FTIR spectrometer. Each spectrum were taken in the $4000\text{--}400\text{ cm}^{-1}$ range at a resolution of 4 cm^{-1} . UV-Vis absorption spectroscopy was used to determine the presence and extent of conjugated in the plasma deposited polyfuran and chemically synthesized polyfuran. UV-Vis absorption spectra of plasma deposited polyfuran was recorded into CHCl_3 using a Shimadzu spectrophotometer. Thermograms of the polymers were recorded by using a Perkin-Elmer thermogravimetric analyzer in the presence of N_2 atmosphere from 20 to 700°C with a heating rate of $10^\circ\text{C min}^{-1}$. The morphology of plasma deposited polyfuran film was characterized using an atomic force microscopy (AFM) in contact mode under a constant force (NanoSurf), the roughness was obtained from the $9.8 \times 9.8\ \mu\text{m}^2$ scan.

3 Results and Discussion

3.1 FTIR Spectroscopy

The FTIR spectra of chemically synthesized polyfuran, plasma deposited polyfuran and furan monomer are

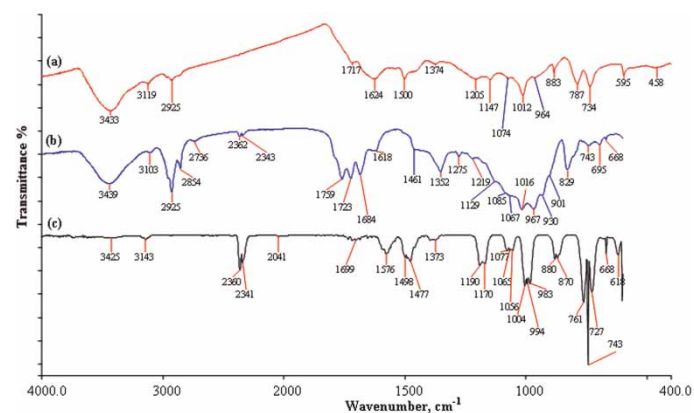


Fig. 1. FTIR spectrum of polyfuran chemically synthesized (a) plasma deposited polyfuran (b) and furan monomer (c).

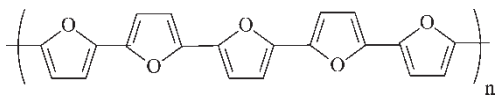


Fig. 2. Structure of linear polyfuran.

shown in Figure 1 (a–c), respectively. The furan monomer (Figure 1c) has characteristic peaks at 3143 cm^{-1} for the aromatic C-H stretch (20). Additionally, some bands are characteristics of the monomer (1576 , 1477 , 1190 , 994 , 870 , and 743 cm^{-1}). The peak at 1576 cm^{-1} represents the furan ring (21). There is a peak at 743 cm^{-1} that can be attributed to furan ring vibrations. The FTIR of a plasma deposited furan thin film shows four characteristic bands of 2,5-disubstituted furan units, that is, the C-H out-of-plane vibration at 743 and 829 cm^{-1} , C-O-C stretching vibration at 1014 cm^{-1} , C=C stretching vibration in the furan ring at 1618 and 1684 cm^{-1} , and the aromatic C-H stretching at 3103 cm^{-1} (18). The presence of these bands may indicate the formation of polyfuran (Figure 2). It should be noted that the peaks at 1759 – 1723 , 2925 , and 3439 cm^{-1} assigned to the stretching of carbonyl, aliphatic C-H structures, and hydroxyl groups were seen, respectively. The presence of the three bands implied the opening of a few furan rings with the consequent generation of nonconjugated structures (Figure 3). These bands are consistent with IR spectra reported the polyfuran

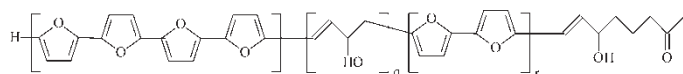


Fig. 3. Opening of furan ring during polymerization.

prepared by chemically and electrochemically means (17, 20). Polyfuran was also synthesized chemically using a FeCl_3 oxidant in this study (Figure 1a). FTIR spectrum of plasma deposited polyfuran have also similar bands to those of chemically obtained polyfuran. The intensities of bands in FTIR spectrum of plasma deposited polyfuran, corresponding to C-O-C stretching vibration at 1014 cm^{-1} and C=C stretching vibration in the furan ring at 1618 and 1684 cm^{-1} , are stronger also than those of chemically synthesized polyfuran. This result has also confirmed that there are more conjugated structures in atmospheric pressure plasma deposited polyfuran. Finally, the peak at 743 cm^{-1} present in the original monomer is reduced in intensity, indicating the cross-linking of the furan monomer and the formation of 2:5-substituted furan ring. By comparing the FTIR spectra of plasma deposited furan and FTIR spectra of polyfuran given in literature (12, 14, 18), it can be concluded that polyfuran by atmospheric pressure plasma deposition method was successfully obtained. Jobanputra et al. polymerized the furan by low pressure plasma polymerization method and carried out its FTIR analysis (18). They observed that the polyfuran exhibited stronger bands belonging to aliphatic C-H structures furan ring at 2959 cm^{-1} than that of the polyfuran plasma deposited in our work. Moreover, the bands attributed to the aromatic C-H stretch disappeared in FTIR spectra of low pressure plasma polymerized polyfuran (18). These results indicate that there are many opening of furan rings in the structure of plasma polymerized polyfuran by Jobanputra et al. In our plasma polymerized furan, it is observed that less intense aliphatic C-H stretching bands and the bands corresponding to aromatic C-H stretching in furan rings.

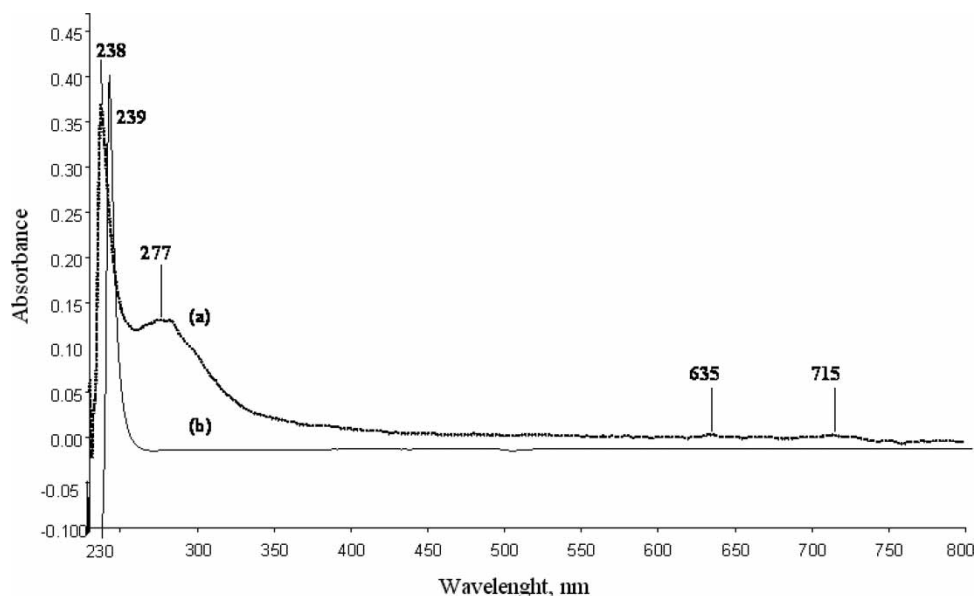


Fig. 4. UV vis spectra of plasma deposited polyfuran (a) and furan monomer (b).

3.2 UV-Vis Spectroscopy

The UV-Vis spectra of the furan and plasma deposited polyfuran were studied in CHCl_3 solvent (Figure 4). UV-Vis spectrum of chemically synthesized polyfuran can not be taken because chemically synthesized polyfuran was insoluble material in all common solvents. The furan monomer shows a maximum absorption (λ_{max}) at 245 nm, which can be attributed to the $\pi \rightarrow \pi^*$ transition of aromatic ring. In UV-Vis spectra of atmospheric pressure plasma deposited polyfuran, a new band has appeared at 277 nm however, the band intensity at 245 nm decreases. The absorption at longer wavelengths has confirmed increasing conjugation in the polymer structure (22). The new band observed at longer wavelength in the atmospheric pressure plasma deposited polyfuran exhibits an increasing degree of conjugation present in the resulting films, together with polymerization of furan. Moreover, weak adsorptions around 635 and 715 nm indicating $n \rightarrow \pi^*$ transition of the quinoid rings have also indicated that the polyfuran obtained should be a π -conjugated polymer (15).

3.3 AFM Image of Polyfuran and Conductivity

The surface morphology of the polyfuran film deposited on the glass substrate was measured using AFM. The AFM image in Figure 5 shows that quality polyfuran film could be obtained by deposited atmospheric plasma. The smooth morphology suggests that the plasma polymerization has occurred predominantly on the glass substrate surface. The plasma film grows through reaction with the monomer species that reaches the substrate surface.

The conductivity measurements with the four-point method showed that plasma deposition polyfurans have a high electrical resistivity, but this is a consequence of the polymer in a neutral state. The same effect was observed by plasma

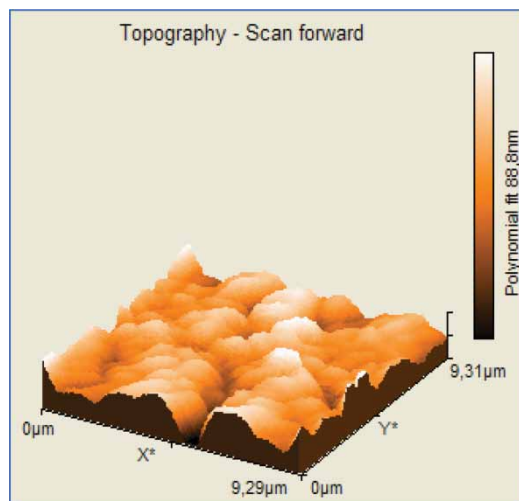


Fig. 5. AFM image of plasma deposited polyfuran.

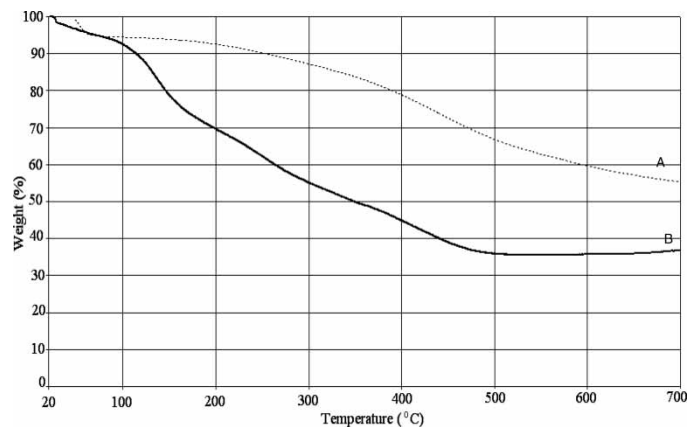


Fig. 6 TGA curve of chemically synthesized polyfuran (a) and plasma deposited polyfuran (b).

polymerized polypyrrole and its copolymer (23). Most of the films by the plasma method are generally insulating films.

3.4 TGA Analysis

The thermal properties of the polyfurans were analyzed in nitrogen atmosphere (Figure 6). In both the thermograms, a small weight loss of 3–5%, below 80°C, occurs, presumably due to the loss of residue monomer. TGA results were also tabulated in Table 1. As seen from Table 1, decomposition temperatures (T_i , T_m , T_f) of polyfurans are different from each other. The atmospheric pressure plasma deposited polyfuran decomposes with two steps, whereas chemically synthesized polyfuran with one step. The initial degradation temperature of plasma deposited polyfuran is lower than that of chemically synthesized polyfuran. This degradation temperature can show removal of units with low molecular weight from the structure. Atmospheric pressure plasma deposited polyfuran exhibited to similar thermal stability to polyfuran using SbCl_3 chemically (24). Moreover, the percentage of residue of plasma deposited polyfuran in here is higher than value given for polyfuran- SbCl_3 in literature.

Table 1. Thermal degradation temperatures of polyfurans

Sample	T_i (°C)	T_m (°C)	T_f (°C)	Residue %, at 700°C
Chemically synthesized polyfuran	190	434	542	56
Plasma deposited polyfuran	100	142	174	36
	233	244	464	

T_i : Initial degradation temperature, T_m : Maximum degradation temperature, T_f : Final degradation temperature.

4 Conclusions

Atmospheric pressure plasma deposition system was used to coat thin polymer film of furan onto a glass substrate with a solvent-free process at room temperature. The absence of solvents is advantage for plasma polyfuran synthesis, an ecological and economical point of view. It can be reasonably concluded that plasma polymerized polyfuran thin films were successfully formed. The atmospheric plasma polymerization with atomizing of the monomer direct to the reaction volume proved to be a useful tool to obtain polymers with a structure similar close to the chemical route. The deposition of the polyfuran in smooth continuous film is easily performed on glass substrate, which can be used as support in different applications, such as amperometric biosensors or in redox reaction.

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