

Fabrication and Comparison Thin Films from PFPy, PFFu, and PFTh by Anchoration

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Abstract: Three thin films were Fabricated of polymers poly formyl pyrrole, poly furfural and poly formyl thiophene and characterized by UV-Vis spectrophotometer and AFM. The films at 450 nm thickness required times 6, 20, 55 h for polymers PFPy, PFFu and PFTh respectively. In UV-Vis spectrum, the absorption coefficient of the maximum peak for polymers solutions and the films was determined. In the case of the film, the constant was smaller than it should be by a large difference due to light scattering in the solid state. In the atomic force microscope images, the PFPy thin film was the most roughness and particle size 154nm while the PFFu film had the average roughness and particle size 87nm while, the less rough one was PFTh film with particle size 36 nm.

Keywords: polymer thin films, anchoration, polymers poly formyl pyrrole, poly furfural, poly formyl thiophene, thin films.

1 Introduction

Conducting polymers were discovered in 1977, when poly(acetylene) was discovered by Hideki Shirikawa [1], more researchers have been interested in conducting polymers [2]. Discovered of conducting polymers was a turning point in the scientific world due to their wide range of applicability [3]. Recently conducting polymers are used in sensors [4][5], biosensors [5], enzyme immobilization matrices [6], solar cells [7], optical displays [8], light emitting diodes [7], and electro chromic devices [9]. This applications are commonly used they as thin films [10]. The polymer, thickness, surface morphology and conductive may select the applications [11]. hetero aromatic rings such as Pyrrole, furan thiophene and their derivatives was used to synthesis conductive polymers [13, 14]. Polypyrrole (PPy) and its derivatives are the most widely studied conductive polymers due to the easily oxidizable monomer in aqueous solution [15], the high electrical conductivity, good electrochemical properties, thermal stability [16]. Furfural was polymerized by Electropolymerization [17, 18]. and plasma methods [19], It was used for fabrication of film modified electrode [18, 19]. Thiophene derivatives have been used to synthesis polymers with wide applications such as solar cells and photoelectric cells [20]. Poly pyrrole, poly furan, poly thiophene and their derivatives are

common conducting polymers [13] can be synthesized by chemical, electrochemical, or plasma methods [21]. 2-formyl pyrrol was polymerization by acidic catalyst thionylchlorid [22] and Hydrochloric acid [23]. 2-formyl thiophene is polymerized by Hydrochloric acid [24] and its derivative by alkyl sulfonic acid (RSO₃H) [25].

In this research we fabricated PFPy, PFFu and PFTh thin films by anchoring it from reaction solution. Thickness, surface and morphology of the films were studied and compared with each other.

2 Experimental Sections

2.1 Materials

Pyrrole-2-carboxaldehyde 98% sigma, Hydrochloric acid 35.5% Sigma, hydrazine solution 35% Sigma.

2.2 Measurements

Poly(2-formylpyrrole) was characterized with UV spectrophotometer between 200 to 800 nm (Jenway) and FT/IR spectrophotometer between 4000 and 400 cm⁻¹ (JASCO FT/IR model M4100), Surface morphologies were examined by AFM (Nanosurf model:eseyscan2).

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2.3 Fabrication of Thin Films

The film was fabricated by anchorage in the reaction solution, monomer 0.5g was dissolved in the methanol 25ml, then 10ml of hydrochloric acid 35.5% was added. Substrates (glass slides 2 cm x 5 cm) was immersed in the reaction solution, and left in the solution for some time and removed and washed with deionized water, then with alcohol and left to dry without touching the film surface. The thickness of the film was determined by weight method.

3 Results and Discussion

3.1 Thin Films Fabrication

Thin films fabrication method is very easy and simple, and it depends on anchoring the polymer from the reaction solution. This method is insensitive to the type of substrate [26] Fig. 1 shows the film images which formed on glass slides. PFPy films are fabricated faster than others. A film with a thickness 450 nm of about 6 hours while, a PFFu film of an approximate thickness took about 20 hours. Thiophene films were the slowest, to get an approach thickness we needed about 55 hours. **Fig 1** shows the thin film images, PFPy film is a reddish brown color while PFFu film is dark black and PFTTh film is greenish black.

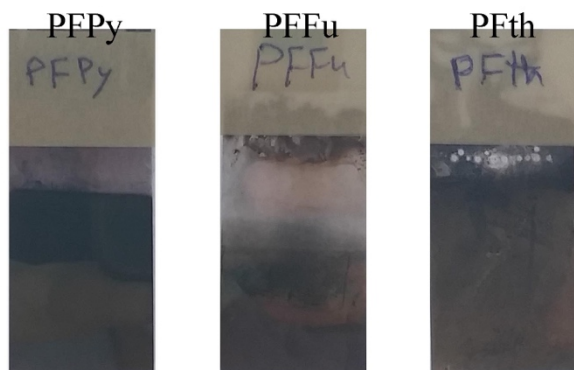


Fig. 1: film images on glass slid A) PFPy, B) PFFu and C) PFTTh.

3.2 UV-Vis Spectra

UV-Vis spectra were recorded for dry films on glass (fig 2). **Fig. 2-A,C** and **E** shows the absorption spectra of PFPy, PFFu and PFTTh films respectively for different thicknesses, films spectrum have a maximum absorption peak at 320, 490 nm for PFPy, 400 and 450nm for PFFu, 312, 450,650 and 760 nm for PFTTh. Absorption at this peaks can be used to determination films thickness. **Fig. 2-B,D** and **F** shows the absorption at 490, 400 and 450 nm for PFPy, PFFu and PFTTh films respectively vs their thicknesses. By Beer-lambert law, absorption is given by the equation:

$$Abs = \epsilon lc$$

For solids the concentration is constant:

$$Abs = \epsilon' l$$

Where $\epsilon' = \epsilon d$ linear absorption coefficient of the films is calculated from the equation:

$$\epsilon' = \frac{Abs}{l}$$

coefficient linear of the films was $\epsilon' = 0.0031, 0.005$ and 0.00032 nm^{-1} for PFPy, PFFu and PFTTh respectively.

Table 1: absorption coefficient (ϵ), linear absorption coefficient (ϵ') for polymers.

	ϵ (l/g.cm)	d (g/cm ⁻³)	ϵ'_{cal} $\times 10^3$ nm ⁻¹	ϵ'_{exp} $\times 10^3$ nm ⁻¹	$\frac{\epsilon'_{cal}}{\epsilon'_{exp}}$ %
PFPy	443	1.08	0.0478	3.10	1.54%
PFFu	4085	1.12	0.448	5.0	8.45%
PFTTh	43.5*	1.15	0.005	0.32	1.56%

* Refrance [24]

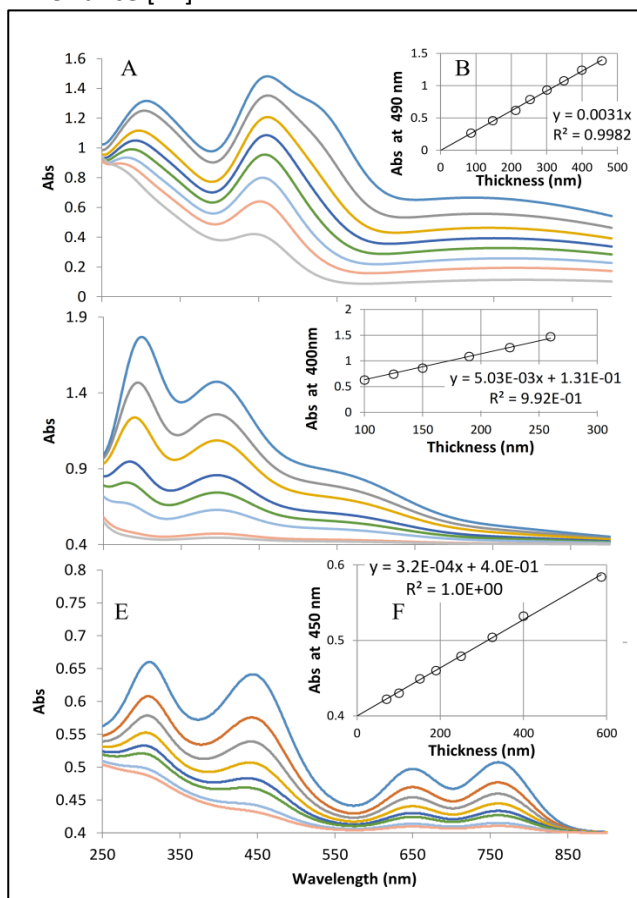


Fig. 2: A) absorption spectra of PFPy films, B) absorption vs thickness of PFPy Film, C) absorption spectra of PFFu films, D) absorption vs thickness of PFFu Film, E) absorption spectra of PFTTh films and B) absorption vs thickness of PFTTh Film.

Table 1: shows The molecular absorption coefficient (ϵ) of polymers in their solutions, the linear absorption

coefficients (ϵ') of their films and the percentage between them. The absorption accounts for only a small percentage of the light loss during measurement of the solid-state films while the remainder is lost as light scattered due to surface inhomogeneity.

3.3 Surface Morphology

To study surface morphology, atomic force microscopy is used [21], which is employed as a powerful technique to study the morphology of thin film surfaces and provides important information on the size of surface particles [22]. one film for each polymer were studied using atomic force microscopy (AFM). Fig. 3 shows 3D image, Topography, of films of polymers.

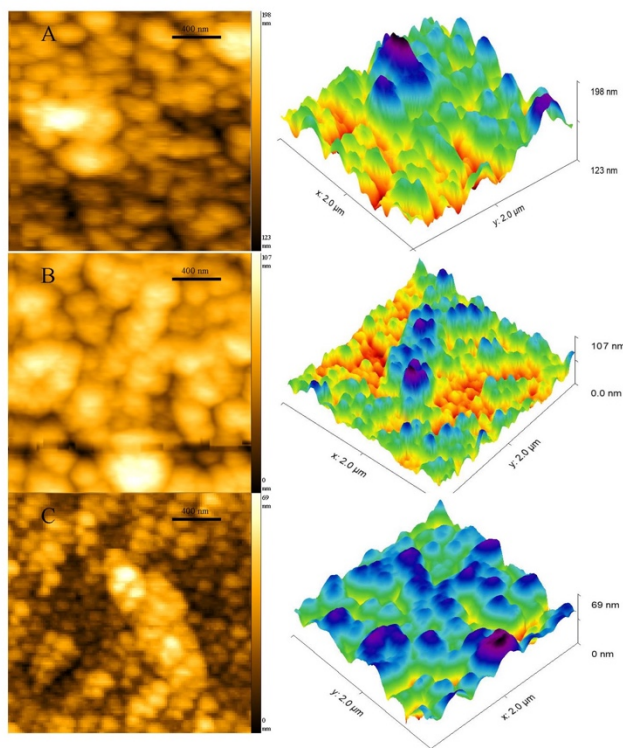


Fig. 3: AFM images (3D, topography) of films of polymers on glass as substrate. A) PFPy, B) PFFu, and C) PFTh.

The surface of the first film appears irregular consisting of a rough surface composed of particles of size (154 nm), the particles of the second film appear larger in size (87 nm) and the surface is less rough and less uniform, the surface of the third film is more homogeneous and its particle size is smaller (36 nm). The reason for this is the difference in the rate of the polymerization reaction for each polymer. The slower polymer (PFTh) is small particles and takes longer time, while the faster (PFPy) is large particles and takes longer time.

3.4 Roughness of Thin Films:

Atomic force microscopy (AFM) gives an important information on thin film surfaces. Many statistical parameters can be obtained such as root mean square (RMS) and roughness (R_a) [22]. Fig 4 shows roughness (R_a)

and root mean square (RMS) of thin films. The surface roughness is important in the study of surface and is a value that reflects the presence of segments (gaps and mountains) on the surface. Increase surface roughness means increasing the real surface of the film. The PFPy film seems the most rough, while the PFFu surface is less rough and PFTh is at least. The PFTh film composed of smaller particles size, was less rough.

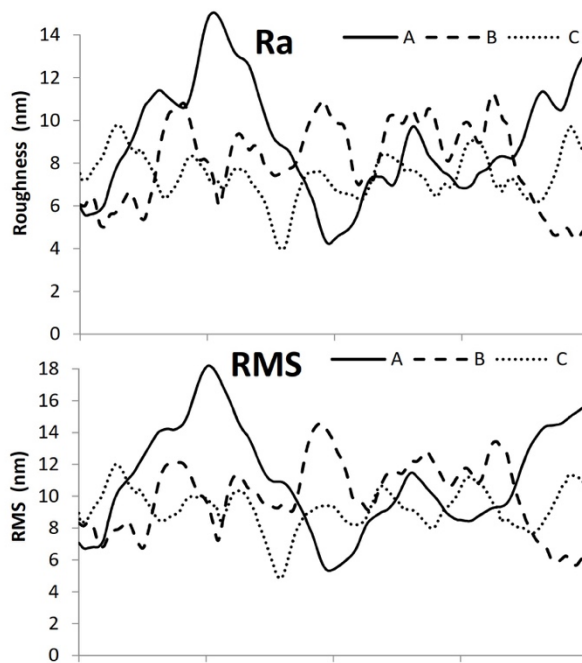


Fig. 4: Roughness (R_a) and root mean square (RMS) of thin films A) PFPy, B) PFFu, and C) PFTh.

4 Conclusions

Three polymer films were prepared by anchoring in the reaction mixture on glass substrates. The films required different times to obtain a thickness of about 450 nm. The films are composed of particles of different sizes (150, 87 and 36 nm) for films PFPy, PFFu and PFTh respectively. The polymer films formed were coarser with the increase in the size of the polymeric particles

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Conflict of interest: Authors declares that they have no conflict of interest.

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Conflict of Interest

All authors declare that there is no conflict of interest regarding the publication of this paper.

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