



Characterization of chemically synthesized polypyrrole and controlling on morphological properties of its thin films.

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Abstract

Polypyrrole has been prepared in this work by chemical oxidative polymerization technique using monomer pyrrole in the presence of the oxidant (FeCl_3) in two mediums; aquatic and alcoholic. The diagnostic tests and structural properties of polymerized pyrrole have been described, such as Fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and energy dispersive x-ray (EDX) tests. The energy band gap (E_g) was also calculated using ultraviolet-visible spectroscopy (UV-VIS) measurements. It has also employed the tests of atomic force microscopy (AFM) to study the effects of each of the formation duration of thin films and the concentration of reacted materials to control the thickness and other morphological properties of thin films prepared by dip coating.

Keywords: polypyrrole, conductive polymers, chemical polymerization, morphological properties, dip coating.

applications and gained significant attention due to their great specific advantages such as relatively simple synthesis and polymerization processing, good environmental and thermal stability, low cost, high conductivity, and good electrochemical properties, charge storage capability (Wolfart et al.).

Polypyrrole molecule consists of a 5-membered ring with nitrogen (N) as a heteroatom. PPy polymerization occurs upon monomer oxidation forming the polymer backbone chain. The chain of PPy has alternating single and double bonds, as shown in Figure (1) (Ayad).

1. Introduction

The unique properties of intrinsically conducting polymers have caught the attention of both academic and industrial communities, resulting in a growing interest in their potential applications such as field emission, supercapacitors and batteries, anti-corrosion coatings, sensors and biosensors, drug delivery, artificial muscles, and dye-sensitized solar cells (Wolfart et al.; Keothongkham et al.).

Among these conducting polymers, polypyrrole (PPy) and its derivatives were frequently studied polymers for many of these

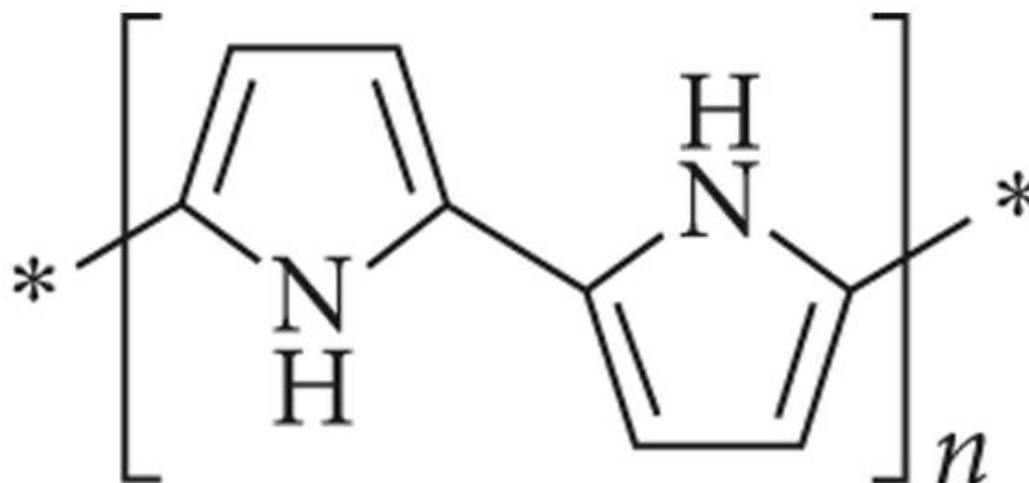


Figure 1: Structure of polypyrrole chain

was done slowly, then continued stirring for (3-4) h at room temperature. It has been observed that the color of the solution changed into black-green as an indication of the polymerization process, then it was left to rest for several hours. The precipitated polypyrrole was collected by filtration, then rinsed with distilled water several times to get rid of residues of (FeCl_3) and unpolymerized pyrrole, then dried in an oven at about 65°C for several hours (Ahmed et al.).

2.1.2. In alcoholic medium:

Chemical polymerization of polypyrrole has been carried out in FeCl_3 solution with methanol as a solvent with appropriate conditions. The solution of 14.8ml methanol and 4g FeCl_3 was first prepared in a beaker, and 1.8ml of the pyrrole (Py) monomer was added into the solution of FeCl_3 /methanol with constant stirring in the dark. (Yawale; Machida et al.)

In the polymerization process of pyrrole, the solution's color began changing to dark green/black when adding the Py monomer. (Yawale; Myers)

The processing was conducted at room temperature for four hours. The resulting precipitate was filtered using a traditional method by washing it multiple times with distilled water until getting a colorless filtrate.

Since polypyrrole was first synthesized in the 1970s, many articles have been published reporting various synthetic ways and applications (Wolfart et al.).

The conducting polymer polypyrrole can be synthesized in; chemical, electrochemical oxidation, and vapor phase routes (Yawale). In the current study, it has been synthesized by the chemical one in various solvents and investigated its properties.

2. Experimental

2.1. Polymerization of pyrrole

Some compounds of transition metals, such as those of Fe (III) and Cu (II), can act as initiators for polymerization and can also be used as dopants to replace pyrroles into black powder of polypyrrole that is electrically conducting (Myers).

Polypyrrole (PPy) as a polymer has been prepared from pyrrole (Py) as a monomer, provided by Sigma-Aldrich, in a chemical way in two mediums; aquatic and alcoholic.

2.1.1. In aquatic medium:

Pure polypyrrole was prepared by adding (1ml) of pyrrole into (150 ml) of distilled water in a beaker, which already contained (1.5 g) of FeCl_3 , and stirring for (10 minutes). The addition of Py into the solution



The samples of prepared polypyrrole were characterized using (FTIR), (XRD), (FESEM), (EDX), (UV-VIS), and (AFM). The tests were done on different instruments; Shimadzu (Model-8300) for FTIR, Shimadzu 6000 for XRD using Cu (K_{α}) radiation ($\lambda = 1.54\text{\AA}$), Tescan Mira3 for FESEM and EDX, Rayleigh UV-2601 for UV-VIS, and finally TT-2 AFM WORKSHOP for AFM.

3. Results and discussion

3.1 FTIR analysis

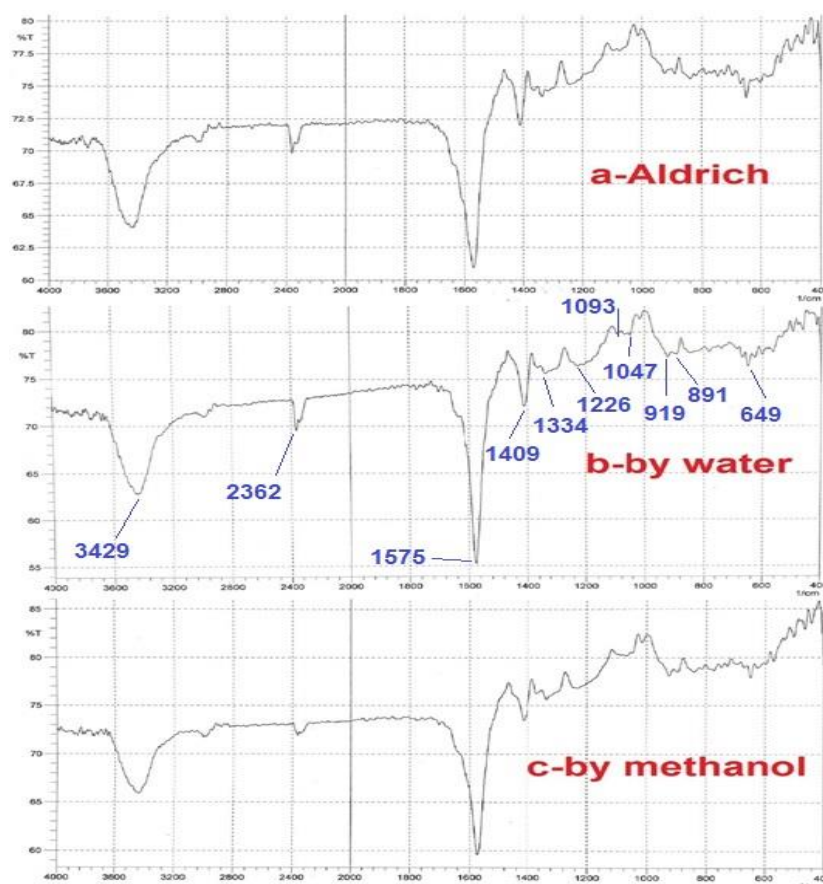
FTIR for powders prepared by the two mentioned polymerization mediums show a good similarity in the shape and peaks location with each other, and on the other hand, with the one taken for the powder provided by Sigma Aldrich, as shown in Figure (2), so it is enough to study only one of them (prepared in aquatic medium), and so for the rest of characteristics.

To eliminate any remaining traces of unreacted Py, Fe, and FeCl_3 formed during polymerization, the polymer was washed with methanol, then dried at room temperature for a few hours to obtain the powder, and finally dried in an oven set at approximately 65°C for (5-6) h (Yawale).

2.2. Preparation of thin films

The thin films of polypyrrole have been prepared by dip coating. The process was done by putting pre-cleaned glass substrates in a beaker ready for aquatic medium polymerization. The duration of films formation started at the moment of the begging of polymerization and ended at three selected times; (10, 17, and 24) minutes for a concentration of (1 ml pyrrole: 1.5 g FeCl_3 : 150 ml water), which represented group (A), then the process repeated with another concentration of (1.5 ml pyrrole: 2.25 g FeCl_3 : 150 ml water) which represented group (B).

2.3. Characterization of polypyrrole



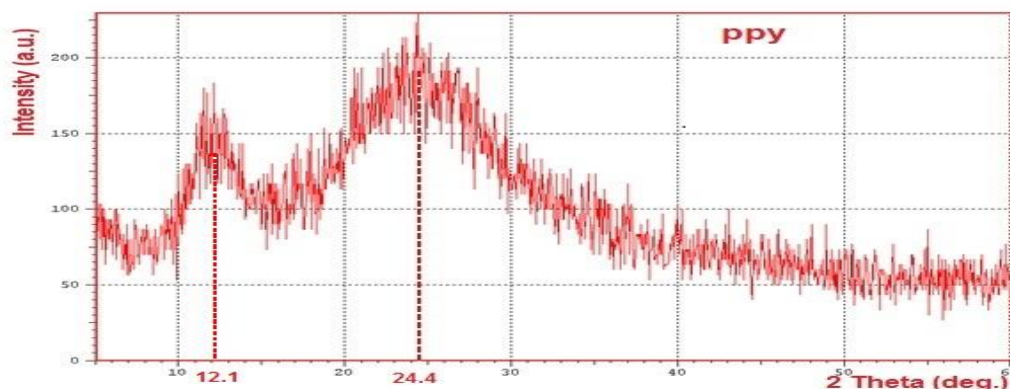


1047) cm^{-1} were due to C—N vibration bands (Ibrahim and Hashim).

The peaks at (919, 891, and 649) cm^{-1} represented the out-of-plane deformation of the C—H bond (Mahmud et al.; Hassan and others)

The well-matching peaks in the present work and those available in the literature confirm the formation of polypyrrole.

3.2 XRD analysis



broad peaks are noticed due to the scattering from polypyrrole chains at the interplanar spacing. The result agreed with the literature (Ayad; Sanches et al.; Chougule et al.; Hussein et al., *Designing Inorganic-Organic Nanofibers Nanocomposite for Supercapacitor Applications*).

Figure (2): FTIR spectra of pure PPy powders: a) provided by Sigma-Aldrich, b) prepared chemically in an aquatic medium, c) prepared chemically in an alcoholic medium.

The pyrrole ring's N—H stretching band was found at 3429 cm^{-1} . The stretching vibration band C—H occurred at 2362 cm^{-1} . (Ayad; Mahmud et al.; Saleh and Jawad; Ibrahim and Hashim; Hassan and others)

The band at 1334 was due to stretching vibration C=N. The peaks at (1226, 1093, and

Figure (3): XRD spectra of pure PPy powder prepared chemically in an aquatic medium

X-ray diffraction investigations show that the polypyrrole powder is semi-crystalline or partially amorphous, as shown in Figure (3) (Sanches et al.).

The Figure shows broad peaks were observed at $2\theta = 24.4^\circ$ and $2\theta = 12.1^\circ$. The

3.3 FESEM analyses

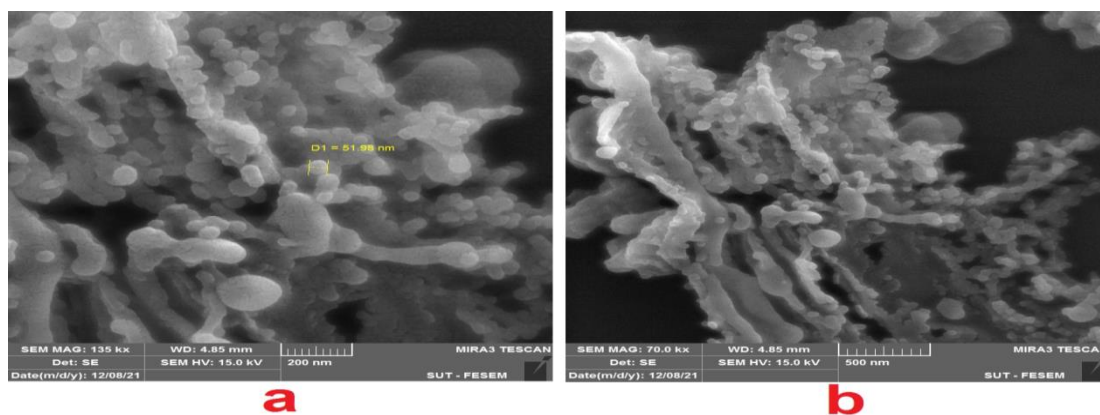


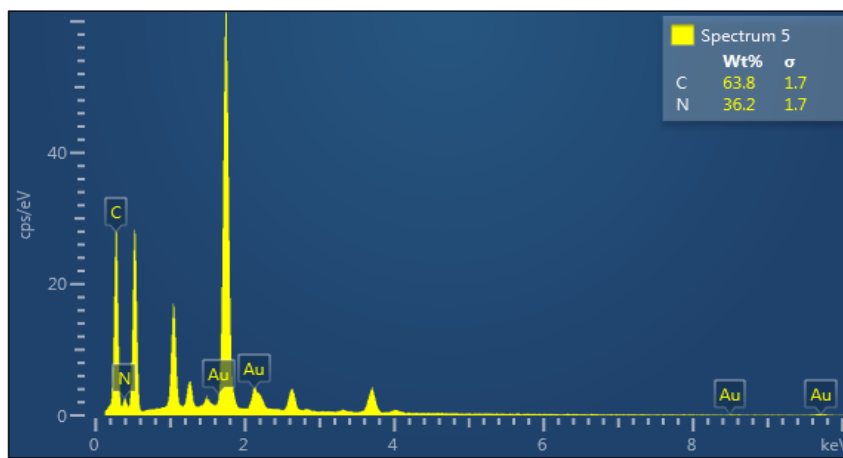
Figure (4): FESEM images of pure PPy film prepared chemically in an aquatic medium.



It is observed that the prepared PPy shows a uniform porous nature and various sizes of vacancies everywhere (Yawale). Larger particles exist in the graphs because of the density or overlapping of several smaller particles pending the preparation process (Razavi et al.).

The surface morphology of PPy analyzed by FESEM is shown in Figure (4). The Figure shows a cauliflower-like morphology arising from micro spherical grains with spongy and porous structures, and the partly amorphous nature seen supports the XRD spectra (Yawale; Sanches et al.; Razavi et al.). The average size of particles was about 52 nm.

3.4 EDX analyses



and nitrogen in high concentrations. It can be noticed that the intensity spikes indicate the high concentration of the matching elements in the sample (Razavi et al.).

Figure (5): EDX image of pure PPy film prepared chemically in aquatic medium

The results of the EDX analysis of polypyrrole thin film are shown in Figure (5). The image confirms the presence of carbon

3.5 The energy band gap

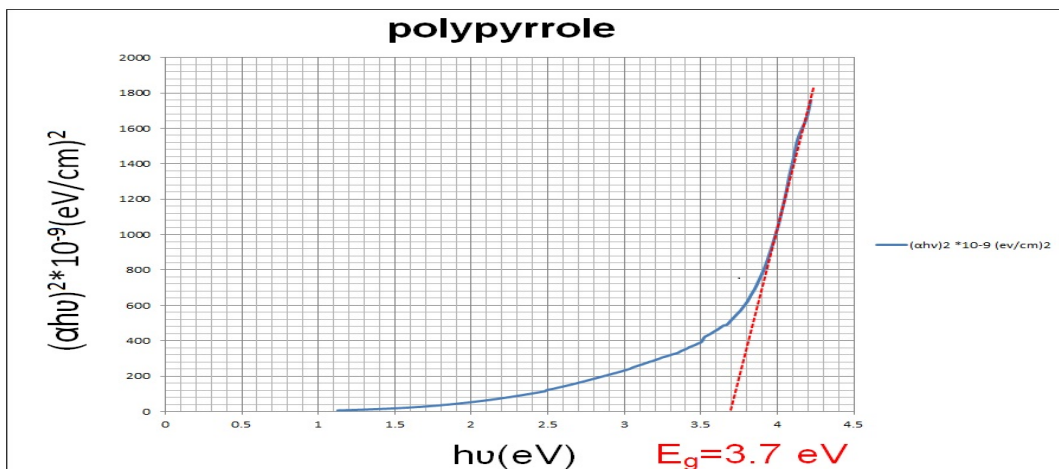


Fig. (6): Tauc plot for PPy films



value (3.7) eV represents the energy band gap (E_g).

This value is close to the study's (Hussein et al., *Enhancement the Photosensitivity of PPy- NFs / Nanoferrite for Photodetector*).

The polypyrrole's optical energy gap (E_g) has arisen from direct allowed transitions. UV-VIS tests determined it by using Tauc plots as shown in Figure (6) between $(\alpha h\nu)^2$ on the Y-coordinate and photon energy ($h\nu$) on the X-coordinate, and the cross of the tangent curve with $(h\nu)$ coordinate gives the

3.6 AFM analyses and controlling on morphological properties

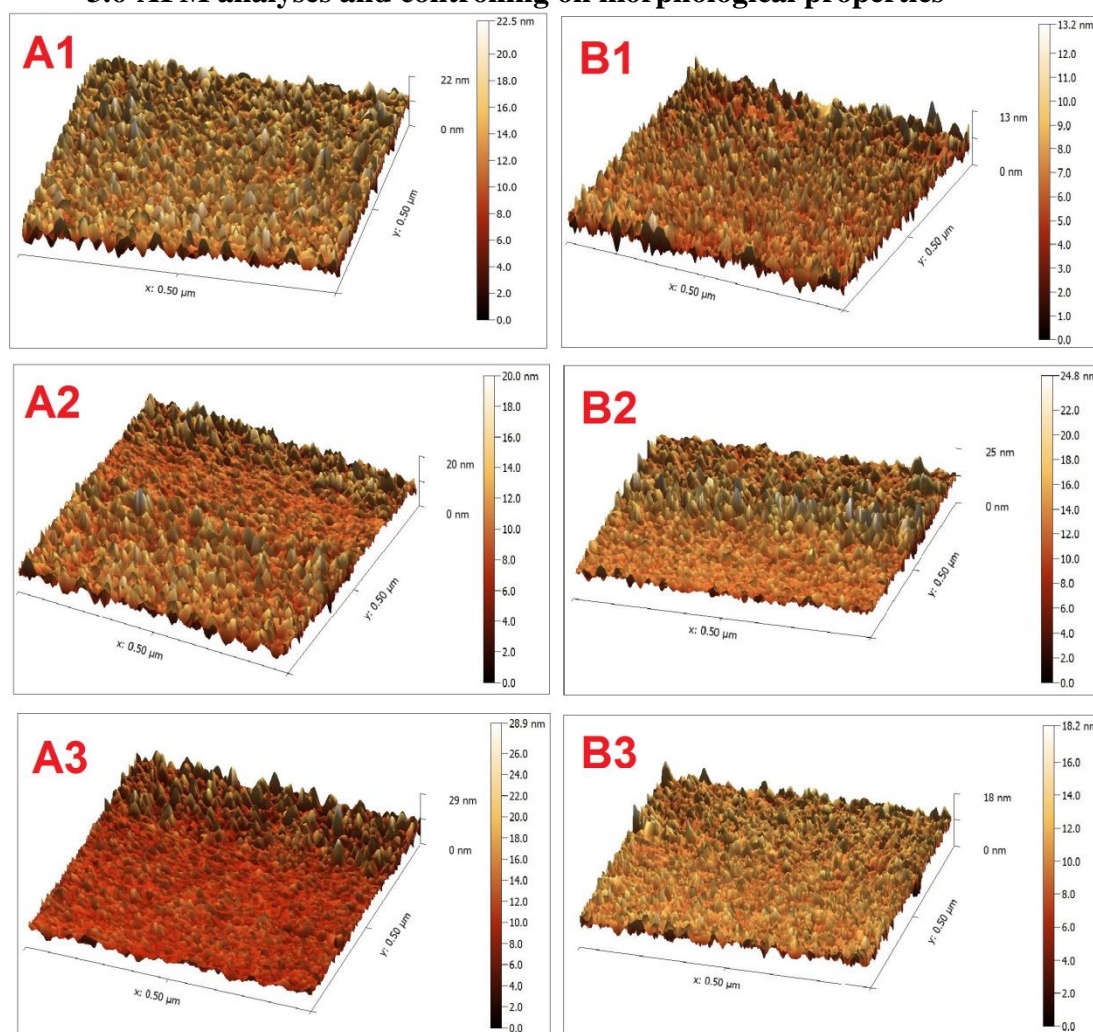


Figure (7): Three-dimensional AFM images of pure PPy films in two groups of concentration (A) and (B), and with three different durations (1), (2), and (3).

chemically in the aquatic medium by dip coating against the duration of formation of them during the polymerization process and for two groups of concentration; group (A) is for samples prepared with a concentration of 1 ml pyrrole: 1.5 g FeCl_3 : 150 ml water and group (B) is for samples prepared with a

The tests of AFM, as shown in 3D images of Figure (7) of polypyrrole thin films, reveal a sponge-like structure appearance for all samples.

It has been studied how to control the thickness and other parameters of the morphology of thin films prepared



10 min, (2) 17 min, and (3) 24 min.

concentration of 1.5 ml pyrrole: 2.25 g FeCl₃: 150 ml water. The durations were (1)

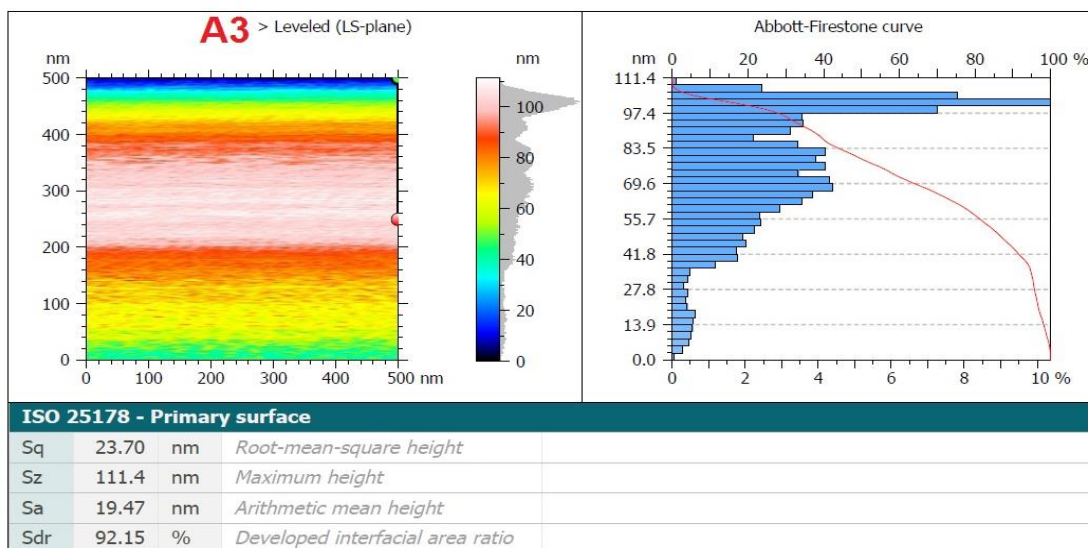
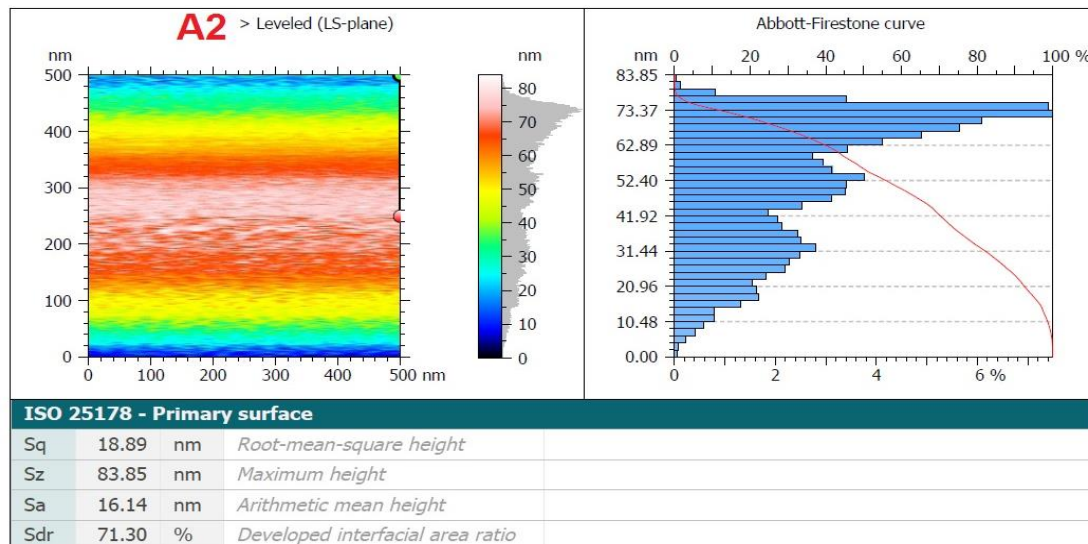
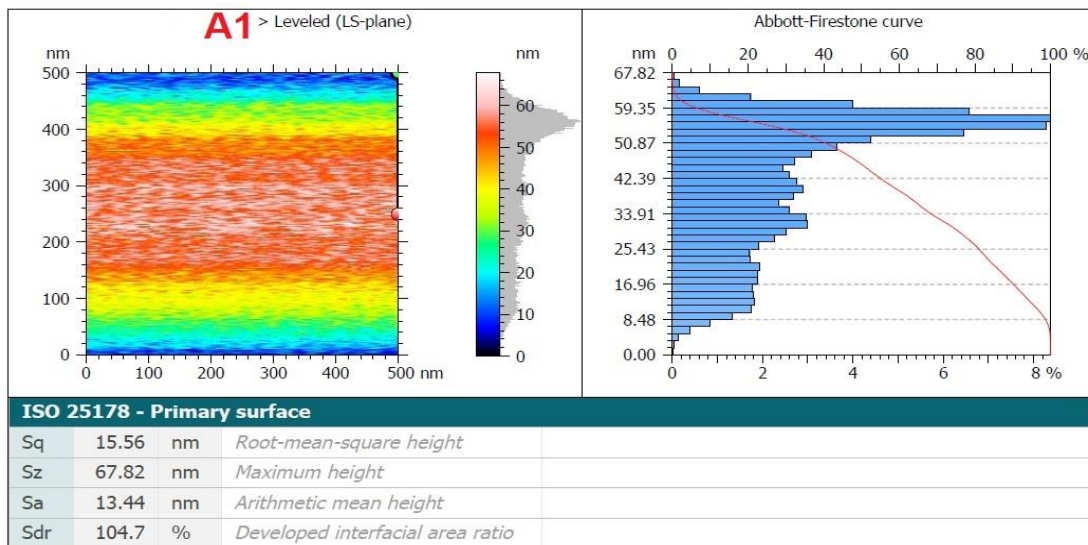




Figure (8): AFM images of pure PPy films for the group (A; with a concentration of 1 ml pyrrole: 1.5 g FeCl₃: 150 ml water) with three different durations; (1; 10 min), (2; 17 min) and (3; 24 min).

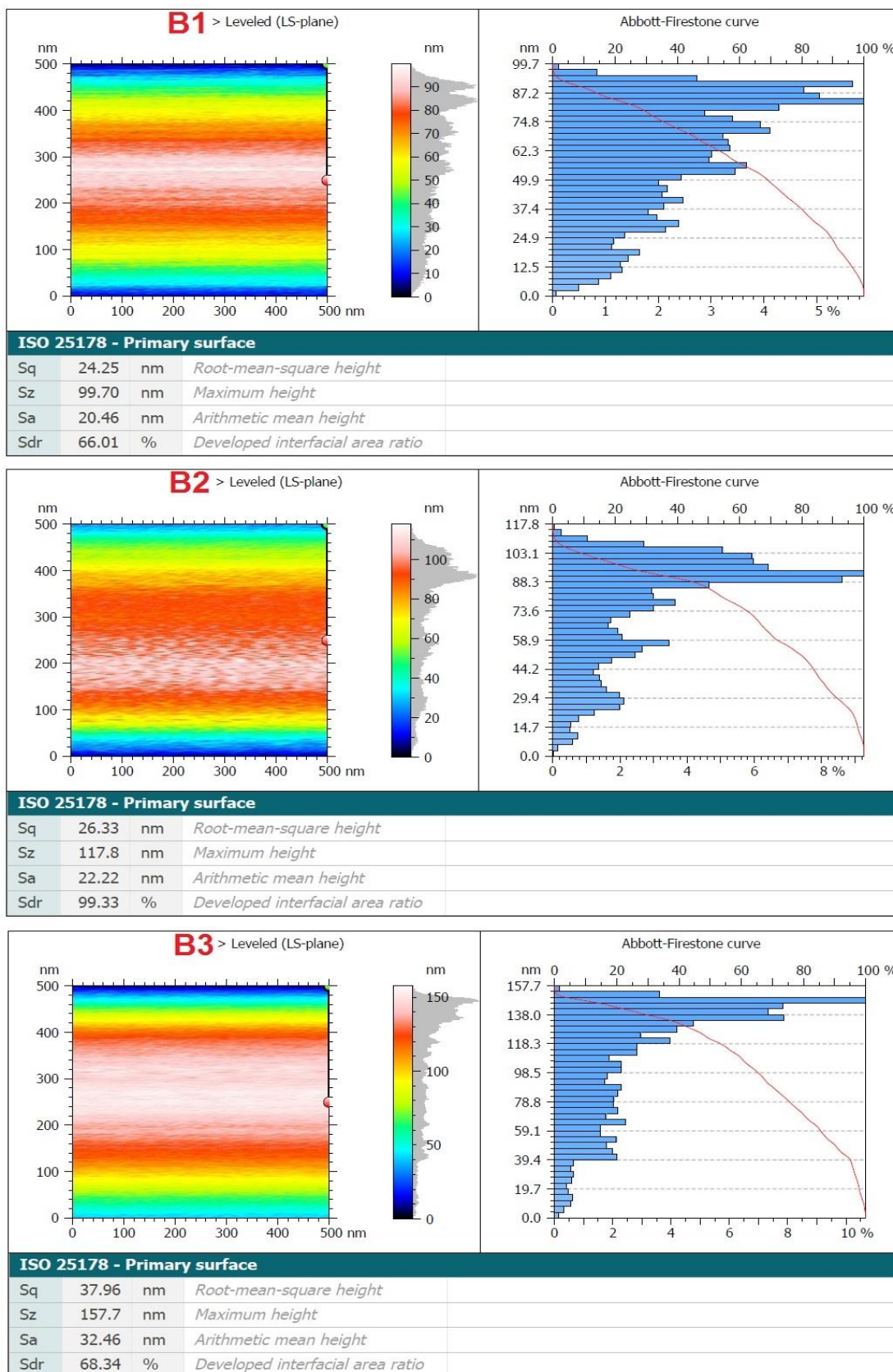




Figure (9): AFM images of pure PPy films for the group (B; with a concentration of 1.5 ml pyrrole: 2.25 g FeCl₃: 150 ml water) with three different durations; (1; 10 min), (2; 17 min) and (3; 24 min).

with a concentration of 1.5 ml pyrrole: 2.25 g FeCl₃: 150 ml water), and with three different durations (1; 10 min), (2; 17 min) and (3; 24 min).

Table (1): morphological parameters (thickness, rms, roughness, and particle size) of pure PPy films for two groups of concentration (A; with a concentration of 1 ml pyrrole: 1.5 g FeCl₃: 150 ml water) and (B;

	CONCENTRATION	THICKNESS (nm)		RMS (nm)		ROUGHNESS (nm)		PARTICLE SIZE (nm)	
		A	B	A	B	A	B	A	B
DURATION									
10 min		67.82	99.70	15.56	24.25	13.44	20.46	43.86	63.23
17 min		83.85	117.8	18.89	26.33	16.14	22.22	54.27	78.36
24 min		111.4	157.7	23.70	37.96	19.47	32.46	79.32	116.6

(PPy) provided by Sigma-Aldrich. XRD tests revealed broad peaks at $2\theta = 24.4^\circ$ and $2\theta = 12.1^\circ$ and a partially amorphous nature which is confirmed by FESEM analyses. FESEM analyses showed a cauliflower-like morphology with spongy and porous structures, and the average size of particles was about 52 nm. The results of EDX confirmed the presence of carbon and nitrogen in polypyrrole. The energy gap (E_g) determined by UV-VIS tests using Tauc plots was (3.7) eV. AFM tests showed that the given values of morphological parameters increased with each concentration and duration of polymerization.

Table (1) indicates that the given values of morphological parameters increase with each concentration and duration of polymerization.

4. Conclusions

Polypyrrole (PPy) was successfully synthesized by the oxidative chemical polymerization method. The polymerization was done using the monomer pyrrole (Py) with the oxidant ferric chloride (FeCl₃) in water and methanol. FTIR analyses confirmed the formation of polypyrrole in both mediums and showed a high agreement with the tests of

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