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Optical and Electrical Properties of Thin Films of Polyaniline and Polypyrrole

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We prepared conducting thin films of polypyrrole and polyaniline doped with $(BF_4)^{-1}$ and studied some important electrical, optical and structural properties of them. Polypyrrole and Polyaniline thin films were prepared by electrochemical oxidation polymerization of pyrrole and aniline. The variation of electrical conductivity with temperature was investigated and indicated the semiconducting nature of these films with two activation energies in the experimental temperature range. The Density Functional Theory (DFT) based on Becke-3-Lee-Yang-Parr (B3LYP) level with 6-31+G* basis was used to compute the electronic spectrum frequencies for monomers and dimers of aniline and pyrrole and compared satisfactorily with our experimental results for optical absorption, especially in the case of polyaniline. The morphologies of polypyrrole and polyaniline were studied and showed that they comparable to those mentioned in literature.

Keywords: Polypyrrole, Polyaniline, conducting polymer, thin films, electrical conductivity, Optical band gap, XRD, UV-Vis absorption, Morphology.

1. INTRODUCTION

Conjugated Conducting polymers such as Polypyrrole (PPY), Polyaniline (PANI), Polythiophene (PT) and so forth are the most interesting conducting polymers due to their excellent chemical and electrochemical stability. They are easy to prepare in the form of large area thin films and are capable of storing charge throughout their entire volume [1, 2]. Conjugated polymers, most notably polypyrrole (PPY), polythiophene (PT), polyaniline (PANi), poly(3,4-ethylenedioxythiophene) (PEDOT), and poly(p-phenylene vinylene) (PPV) have been synthesized, in free-standing film and bulky powder forms, using electrochemical or chemical polymerization methods [3]. PPY and PANi can be formed chemically or electrochemically through oxidative polymerization of pyrrole and aniline monomers, the final form of PPY and PANi are those of a long conjugated backbone as seen in Figure

1.2. These polymers have resonance structures that resemble the aromatic or quinoid forms. In its neutral state the polymer is not conducting, the conductivity of both polymers (PPY and PANi) is $\approx 10^{-10}$ $(\Omega.\ \mathrm{cm})^{-1}$and they become conducting only in the oxidized state and have a conductivity of 10^{-3} -- 10^{2} and $10^{1}(\Omega.\ \mathrm{cm})^{-1}$ for PPY and PANi, respectively [4, 5]. The charge associated with the oxidized state is typically delocalized over several units of these polymer and can form a radical cation (polaron) or a dication (Bipolaron) [6, 7]. The introduction of charge to the chain can transform the aromatic structure in to the lower band gap quinoid structure.

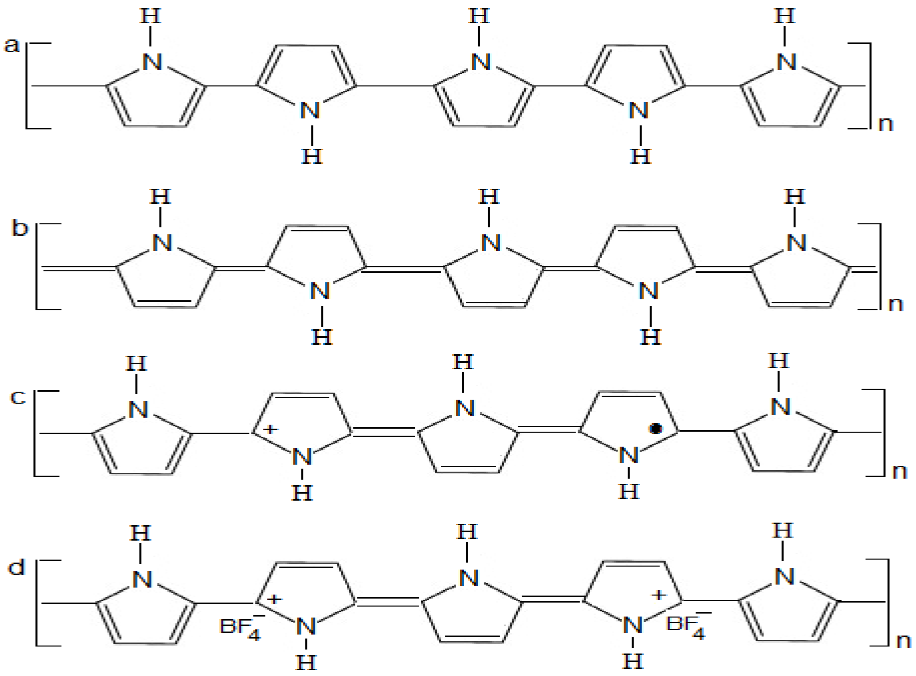


Figure 1. (a) Polypyrrole structure (b) with polarons state (c) with bipolaron state Chemical structures of polypyrrole In neutral (a) aromatic and (b) quinoid forms and in oxidized form with (c) polarons states (d) Bipolarons states

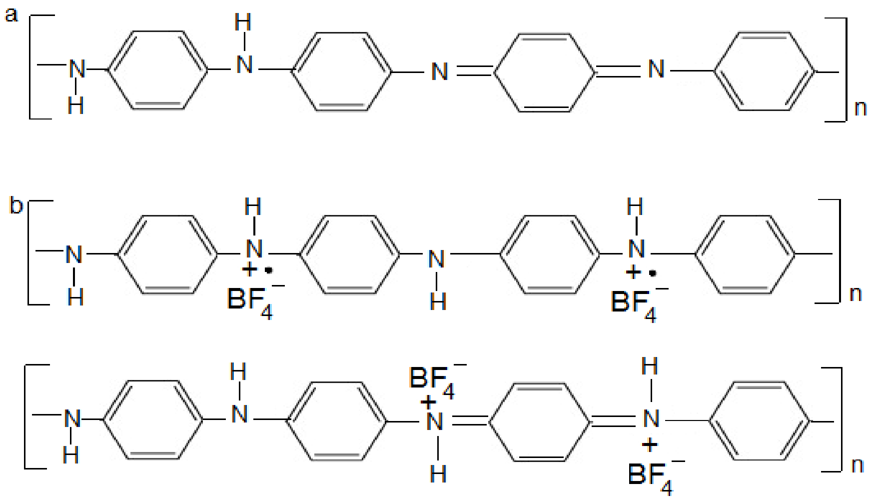


Figure 2. (a) Emeraldine form of PANi (b) with polarons states (c) with Bipolaron states

The properties of these polymers are very sensitive to fabrication conditions and to the type of preparation technique used. Therefore, the study of the properties of these conducting polymers with respect to different growing as well as ambient conditions is of high importance. These conjugating polymers thin films have been studied by many workers, because of their special electrical properties, their considerable thermal stability and oxidation resistance, these properties are favorable in applications such as optoelectronic, biosensors, electrochromic displays and chemical sensors [8-12], electrode materials in electro-catalysis in solar energy conversion [13, 14]. These conducting polymers have excellent mechanical and electrical properties and can be produced continuously as flexible film by electrochemical techniques. In Some applications of PANI has an electrical conductivity between 10^{-10} — 10^{-2} $(\Omega\ \mathrm{cm})^{-1}$ and they are used as hole injection layers for flexible light emitting diodes [15, 16]. These polymers are useful in the design of new structures, which are stable, and soluble in some cases, they have a delocalized conjugated structure. Materials with conjugated structures have been extensively studied for their rapid photoinduced charge separation and a relatively slow charge recombination of hole-electron pairs [17]. Liu and Coworkers [18] prepared PANI/Tio2 films and applied them to solar cells. Natural polyaniline has a forbidden band gap of 2.8 eV showing strong absorption for visible light; some researchers used it in photocatalysis [19, 20], doped polyaniline has an optical band gap 2.21 eV and room electrical conductivity ($\sigma_{25} = 3.12 \times 10^{-2} (\Omega.\mathrm{cm})^{-1}$) [21]. Films of PPY, PANI and PT are obtained directly through anodic polymerization of their monomers in aqueous or organic electrolytes. The preparation of PPY by oxidation of pyrrole dates back to 1888 [22] and by electrochemical polymerization to 1957. This organic polymer in fact attracted general interest and was found to be electrically conductive in 1963. Polyaniline was first synthesized in 1862 [23] and has been extensively studied as a conducting polymer since the 1980s [9, 24]. Depending on the synthesis conditions, it can be obtained in several forms and different structures. The physical form of each of polypyrrole and polyaniline is usually as an intractable powder resulting from chemical polymerization or an insoluble film resulting from electropolymerization [25-27]. Electrochemical method has the merit of easy control of morphology and electrical properties, but there stills the commercial mass production problem. The calculation of excitation energies density functional theory one of the most successful methods in the investigation of optical absorption spectrum, and is developing rapidly as a cost-effective general procedure for studying physical properties of molecules [28, 29]. We have present in this paper our investigation of electrical, structural and optical properties (UV-Visible.) of polyaniline and polypyrrole thin films.

2. EXPERIMENTAL DETAILS

2.1 Materials

Aniline, pyrrole, lithium tetrafluoroborate and acetonitrile (Sigma –Aldrich) were all used as received. Two Platinum electrodes having 6 cm^2 surface area were used as working and counter electrodes with inter-electrode distance of 2 cm.

2.2 Preparation of conducting polymer thin films

Thin films of polypyrrole were synthesized using electrochemical oxidative polymerization technique, polymerization was carried out in a cell by mixing 0.1M of pyrrole and 0.1M of $LiBF_4$, the solutions were degassed by argon bubbling for 10 min duration, the period of synthesis was 20 minutes, similar concentrations of aniline and salt were used for the polymerization of polyaniline films. The oxidation potential values between working and counter electrodes were 5 and 7V for pyrrole and aniline, respectively, the current increases sharply and stabilizes after some minutes at values of 13.8 mA/cm^2 and 27 mA/cm^2 for pyrrole and aniline respectively, the working electrode surface then becomes covered by black and dark blue for polypyrrole and polyaniline, respectively. This electrochemical polymerization gives us p-type films, it's an easy matter to dope or dedope the samples using chemical or electrochemical technique, for undoped samples, it's quite enough to be dope them by chemical methods "treated with the vapor of the dopant at room temperature for 1 hours". The dopants could be I_2, Br_2, AsF_5 etc. For example, I_2 is a good material for vapor phase doping (though it can also used in solution); a typical reaction might proceed as follows: polymer $+I_2 \rightarrow (\text{polymer}^+)\ (I_3^-)$. On the other hand, for n-doping, the dopant could be an alkaline metal, for example, Na^+. A more elegant and well controllable process is offered by electrochemical doping. This method is conducted in an electrochemical cell, by choosing a specific potential value; the doping level of the polymer can be precisely controlled and the polymer acting as the working electrode is either oxidized (electrons are taken out of the material) or reduced (electrons are put into the material), until an electrochemical equilibrium is reached. Finally, the thin films were chemically dedoped by washing successively by methanol. UV-Visible measurements were carried out on a spectrum shimadzu. Absorption Spectra were obtained by depositing the films of polypyrrole and polyaniline on clean quartz substrates. Electrical conductivity of thin films was measures using four-point probe method with 2400 Keithley source-meter. X-ray diffraction (XRD) studies were carried out using a Shimadzu-Japan (Model: XRD6000). The XRD patterns were recorded in 2Θ range of 5-60° with step width 0.05° and step time 0.6 sec using CuKα radiation (λ=1.54060 Å).

3. RESULTS AND DISCUSSION

3.1 Electrical properties

The primary means of characterizing all the polymers prepared was through conductivity measurements. The measurement of dc conductivities was accomplished through use of the 4-probe van der Pauw technique. In this method, four conductive metal probes are placed in line; current is injected and collected through the two outer probes, while the potential drop between the two inner probes is monitored. The I-V characteristics of thin films of doped polypyrrole and Polyaniline were recorded at room temperature and are found to be linear, the values of electrical conductivities at room temperature of doped thin films of PPY and PANi are 100 and 0.5 $(\Omega.\text{cm})^{-1}$, respectively. These values of electrical conductivity of the as-synthesized polymers (doping with $(BF_4)^{-1}$) were found greater than Iodine or bromine doping of dedoped polymer, which indicating a rather low doping level in these dedoped polymers. This difference in the values of conductivity is attributed to the effect of methanol treatment on the films, which shows that methanol has another effect other than dedoping, it is suggested that methanol plays an important role in the inhabitation of the reactive sites on the resin of polymer [30]. In addition, the chemical methods for doping the polymers by the gas molecules make these polymers relatively unstable in air, they lost the iodine through evaporation and the same results were found for polyaniline. Electrical conduction in these Polymers is dominant by polarons and bipolarons. At low doping levels, the chain is ionized and produce a radical cation (Polaron) which does not contribute significantly to the conductivity [31, 32], however at higher doping levels the polarons can combine or ionize to form spinless dications (Bipolarons) which extend over few rings. As the strength of applied field increases the number of such polarons and bipolarons increases which means an increase in current [33]. Doping results in the alternation of the aromatic configuration to the higher energy quinoid configuration and confines the charge localized along the Chain, which means increase in conductivity [34]. We observed that the temperature dependence for each polymer behaves in the usual activated manner indicating semiconducting property. This suggests that the conductivity increase with temperature is due to the increase of efficiency of charge transfer [35-37]. It is also proposed that the thermal curling affects the chain alignment of the polymer, which leads to the increase of conjugation length and which in turn brings about the increase in conductivity. Also, there will be molecular rearrangement on heating, which make the molecules favorable for electron delocalization [38]. We determined the electrical conductivity for few samples in temperature rang 300 to 400K; we found that these variations follow the Arrhenius model [39]. Plots of ln(σ) vs 1/T have been shown in Figure. 3.

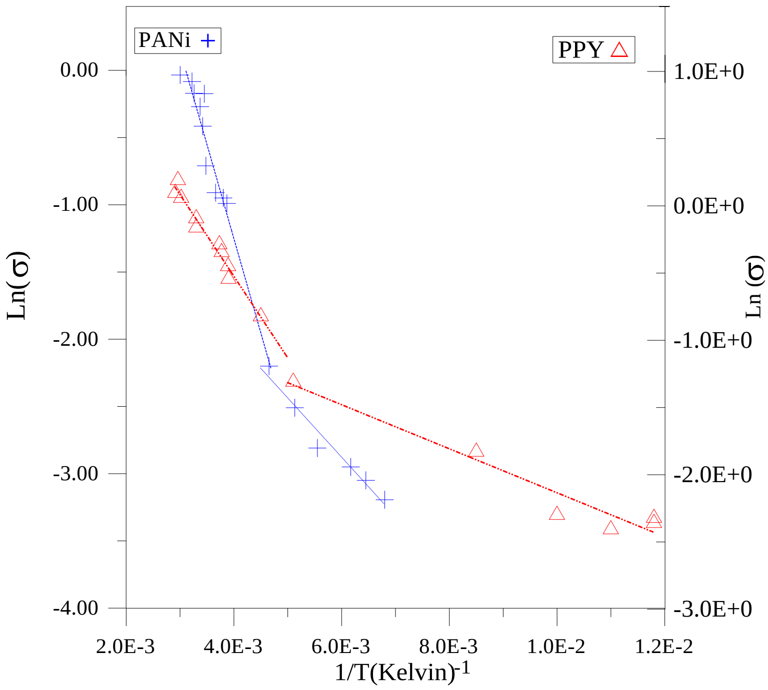


Figure 3. Plot of Ln *σ* versus 1 / T for polypyrrole and polyaniline thin films

The slope gives information about activation energies, we found that each of PPY and PANi thin films doped with $(BF_4)^{-1}$ has two activation energies, in the temperature ranges (300 to 360 K) and (80 to 360 K) for PPY; while for PANi from (300 to 360K) and (145 to 360 K), they are (0.053, 0.0124 eV) for PPY and (0.11, 0.037eV) for PANi. The activation energies of our samples do not differ significantly from the activation energies reported in literature data for PPY [40-43] and for PANi [44-47].

This variation of conductivity with temperature can be explained in terms of structural changes occurring in these thin films with temperature. In as Polymerize thin films of PPY and PANi there is some lattice defects, geometrical and physical imperfections randomly distributed on the surface and the volume of the film are responsible for the physical properties of thin films.

3.2 Optical properties

The absorption spectra of PPY and PANi thin films have been recorded over wavelength range 300 to 900 nm using a USB 2000 spectrophotometer at the room temperature.

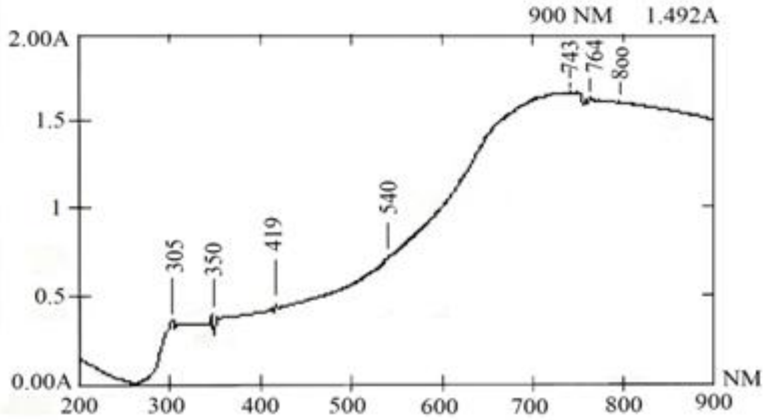


Figure 4. UV-Visible of doped Polypyrrole with $(BF_4)^{-1}$

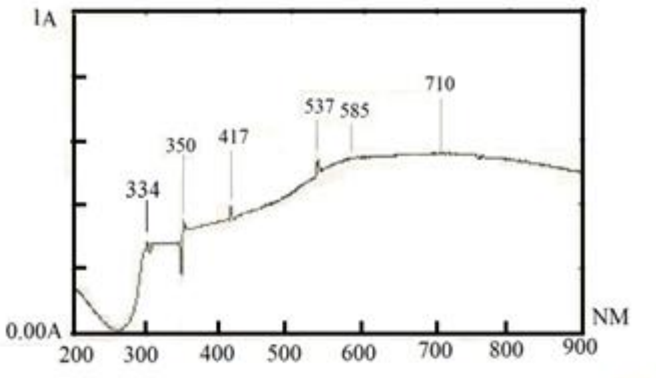


Figure 5. UV-Visible of doped Polyaniline with $(BF_4)^{-1}$

Figures 4 and 5 show the block diagrams of optical detection systems of thin films of polypyrrole and polyaniline, respectively.

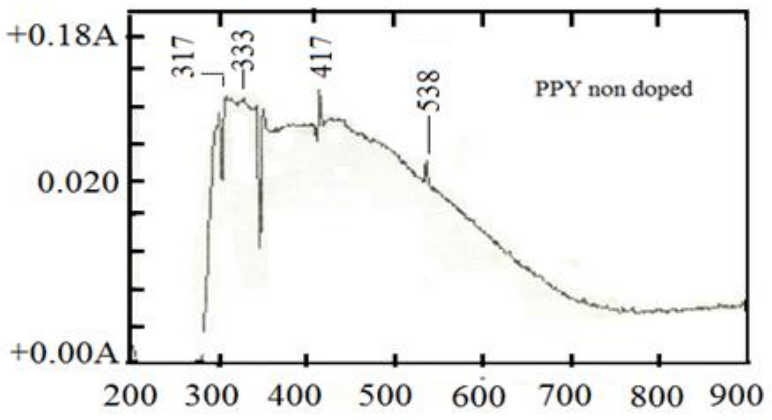


Figure 6. UV-Visible of non Polypyrrole

The absorption peak at 334 nm is attributed to the transition of electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) which is related to π→π* electronic transition. We also observed two absorption peaks at about 417 and 710 nm assigned to the polaron and bipolaron band transitions for polyaniline [48-51]. Polypyrrole also showed three bands, one at 305 nm corresponding to π→π* inter band transition and the other bands are at 419 and 750 nm which are also assigned to polaron and bipolaron band transitions for polypyrrole [52-55].

Table 1. Theoretical and Experimental of optical frequencies of monomer, dimer and polymer

Theoretical calculation of monomers and dimers frequencies(nm)				Experimental frequencies(nm)		Assignments
pyrrole	bipyrrole	aniline	Bianiline*	polypyrrole	polyaniline	
345	348	335	362	305	334	π→π*
450	474	420	427	419	417	polaron
877	680	735	754	750	710	bipolaron

*DFT based on Becke-3-Lee-Yang-Parr (B3LYP) level with STO-3G basis

The peak at 750 nm in polypyrrole spectrum has been assigned to –NH– species, which are generated during doping, a correlation between the intensity of this peak and the conductivity of the sample seems to exist as shown in Figure 6 of the spectrum of non-doping of polypyrrole, the same result was found for the non-doped film of polyaniline. We performed theoretical calculations to justify the interpretation of our results using hyperchem program for theoretical calculation of the electronic structures of pyrrole and aniline and there radical cations by using the Density Functional

Theory (DFT) based on Becke-3-Lee-Yang-Parr (B3LYP) level and standard 6-31+G* basis. From these calculations, the $\pi \rightarrow \pi^*$ transition was estimated theoretically to occur at around 335nm, comparable to the experimental of about 334nm for PANi. Thus, we got an excellent agreement between the experimental and computed frequencies of optical spectra for PANi. The computational results of PPY were less satisfying. This might be attributed to that our calculations did not extend beyond dimmer units. The calculated electronic transition frequencies for monomers and dimers are listed in table1.

The energy band gap of these polymers has been calculated with the help of absorption spectra. To calculate the optical band gap energy from absorption Spectra, the tauc relation is used [33]

$$\alpha\, h\nu = A\,[\, h\nu - Eg\,]^n \quad \text{---------------(1)}$$

where hν is the photon energy, h is Planck's constant, α is the absorption Coefficient, E_g is the optical energy gap, A is the constant, for direct transitions n=1/2. We plot a graph between $(\alpha\, h\nu)^2$ versus hν, the extrapolation of the straight line to $(\alpha h\nu)^2 = 0$ axis gives E_g. Figure 7 shows the plots of $(\alpha h\nu)^2$ versus hν for the polypyrrole and polyaniline doped with $(BF_4)^{-1}$, respectively. The values of E_g obtained for doped polypyrrole and polyaniline are 1.75 and 1.60 eV, respectively.

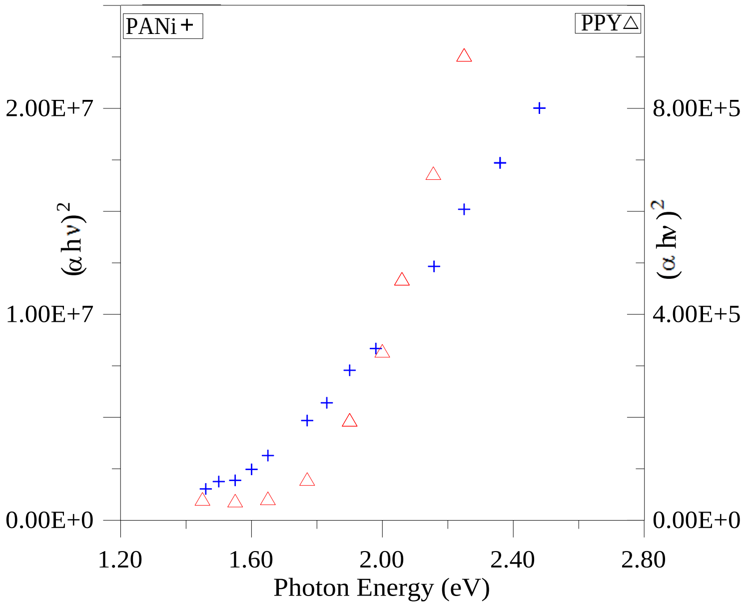


Figure 7. Plot of $(h\nu)^2$ vs. hν for for thin films of PPY and PANi

3.3 X-ray diffraction analysis

X-ray diffraction (XRD) was employed to characterize the structure of the electrochemically synthesized PANi and PPY Films, Figure 8 shows the X-ray diffraction pattern for as-deposited, PPY thin films which clearly indicated that they are amorphous. The diffraction patterns for PANi and PPY annealed at 260 C° for 30 min are shown in figures 9 and 10, respectively.

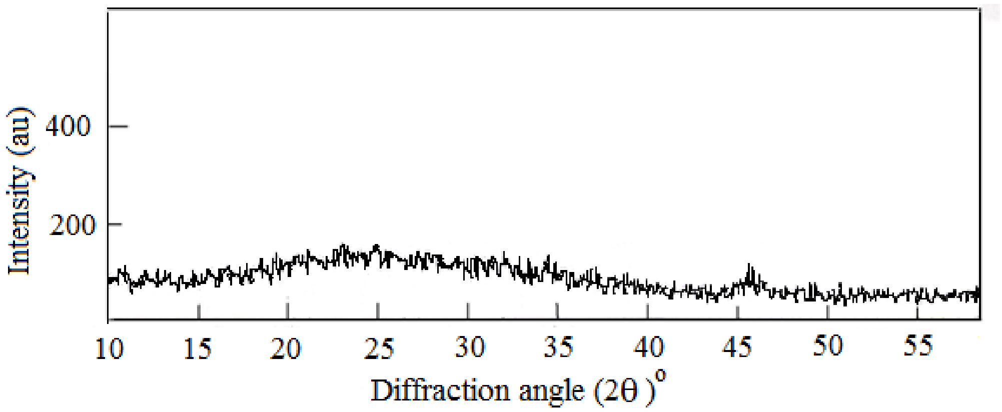


Figure 8. XRD Patterns of PPY thin films as-deposited

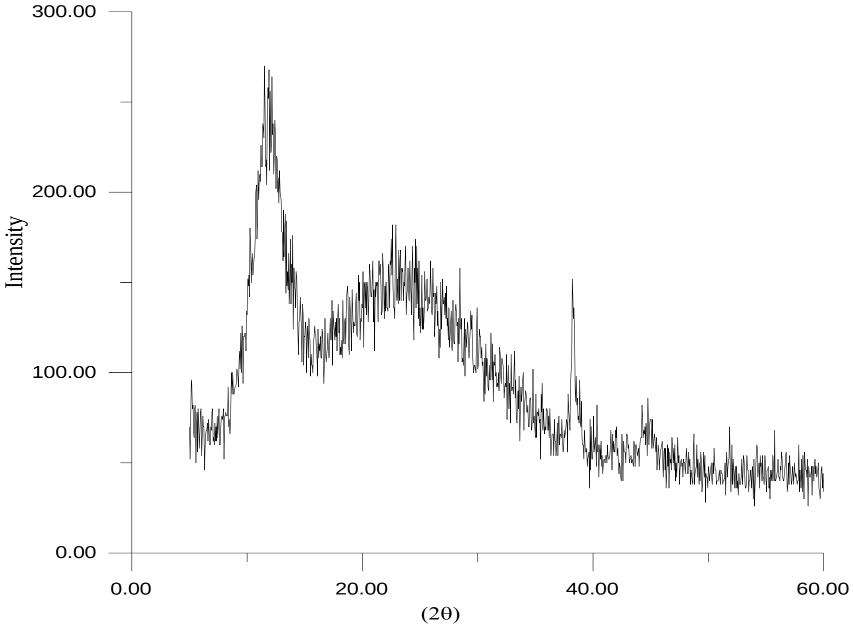


Figure 9. XRD Patterns of PANi thin Film (annealed at 260 Cº)

These figures indicates that the annealed films partially crystalline, the pattern of PANi film includes three prominent broad peaks and few smaller peaks riding over a broad hump, indicating that chain ordering is predominantly limited to short range.

The broad peaks observed at about 2θ =12º and 24.6º are similar to those observed by other workers [56, 57]. The other peaks located at 2θ =38º and 44.7º and the first 2 peaks are also similar to those mentioned in literature [58, 59]. The diffraction pattern of PPY thin film shows a peak at about 2θ = 12º [60], and a hump around at 2θ = 24º which is typical for conducting amorphous polymer polypyrrole [61, 62].

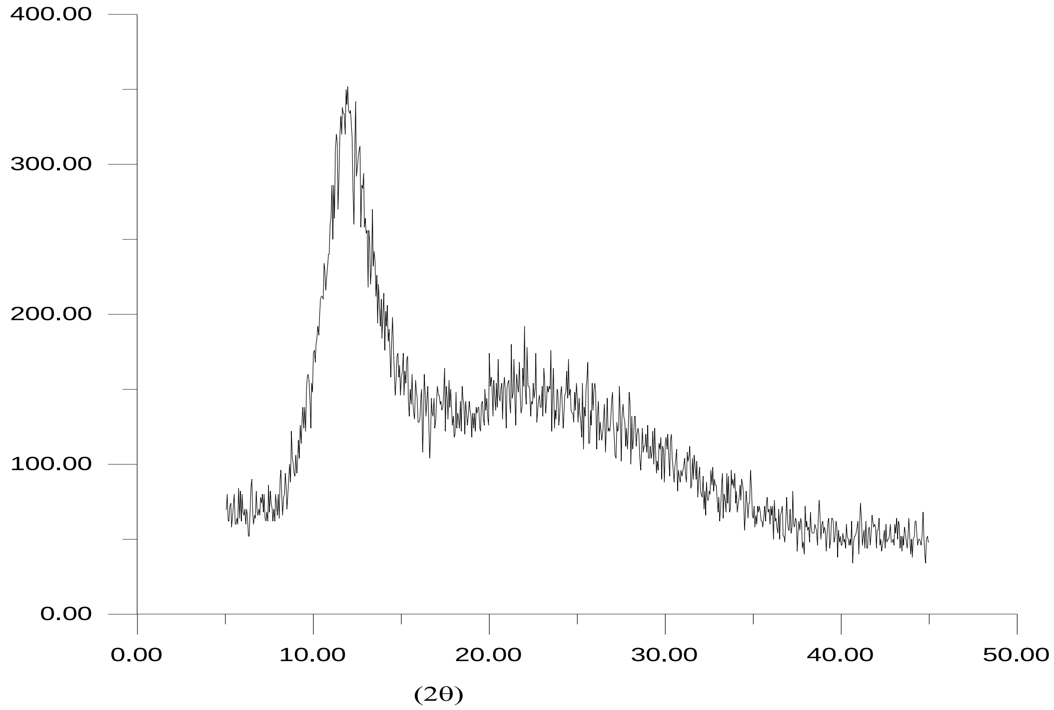
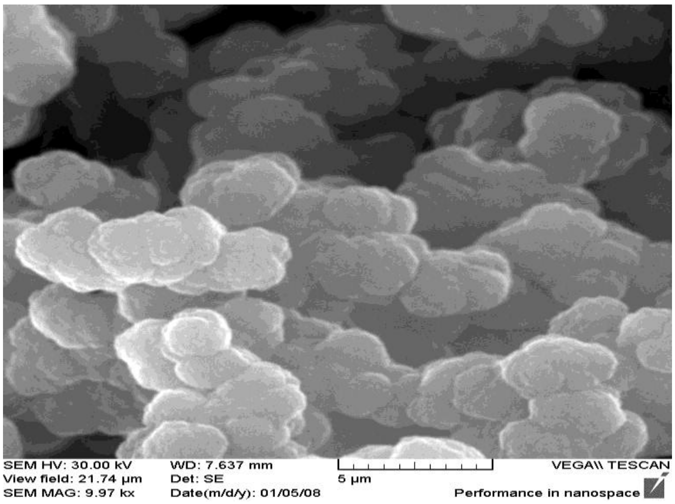


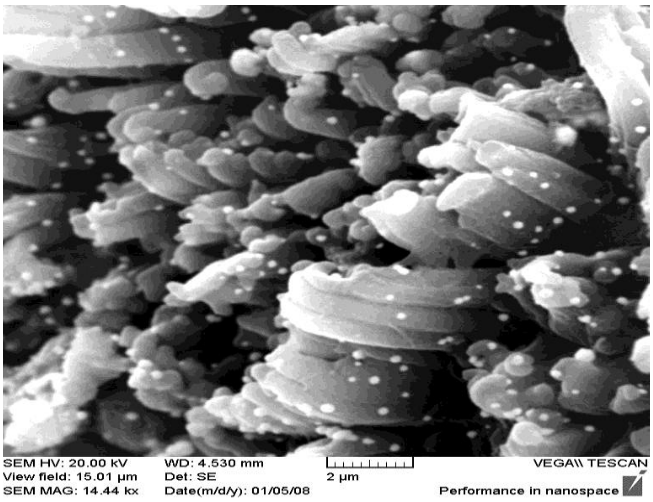
Figure 10. XRD Patterns of PPY thin Film (annealed at 260 Cº)

3.4 Surface morphology

SEM images of electrodeposited PPY and PANi Films are depicted in (Figure11 a and b) and clearly indicate the formation of PPY and PANi. Figure 11a shows that the surface of the films is not smooth and contains macro-granular structure formed by the aggregation of small globular structures with a diameter between 2000 and 3000 nm, which are typical 'cauliflower' structures. These structures refer definetly to an amorphous morphology. Figure 11b, which is of higher resolution, indicates that these structures seem to consist wire-like or rod-like structures.



(A)



(B)

Figure 11. Scanning electron micrographs images of patterned microstructures of (A) PPY and (B) PANi thin films

The diameters of the wires are about 500 and 600 nm. The aniline concentration was found to strongly affect the PANI morphology, when the concentration of monomer was higher than 0.5 M, no wires or rods were observed. When chemical synthesis was performed, PANi Morphology varies, as the concentration was decreased below 0.1 M and as low as 0.001 M, wire- or rod-like products were observed [63, 64].

4. CONCLUSION

In this work, we have reported electrical, optical and structural properties of electrochemically prepared flexible thin films of PPY and PANi Films. Dc electrical conductivity of these polymers has been investigated in the temperature range (80- 370*K)* the conductivity of PPY was $10^{-2}(\Omega.\text{cm})^{-1}$ and the conductivity of PANi ranged between 0.1 and 10 $(\Omega.\text{cm})^{-1}$. The variation of electrical conductivity with temperature of these films follows Arrhenius behaviour with two activation energies over the experimental temperature range. XRD characterization indicated the amorphous nature of the samples. Annealing of PPY and PANi Films partially crystalline them. Optical studies of PPY and PANi thin films showed absorption peak for $\pi\rightarrow\pi^*$ transition. Concerning the morphology of PPY and PANi thin films, a globular-shaped topographic structure were obtained for nearly all the PPY thin films and the formation of PANi micro-fibres has been observed.

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