

Synthesis and Characterization of Polypyrrole (PPy) Thin Films

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ABSTRACT

Polypyrrole (PPy) was synthesized by chemical oxidative polymerization technique using monomer pyrrole and ammonium persulphate as an oxidant in a ratio of 1:1. Thin films of polypyrrole were prepared by dissolving polypyrrole in *m*-cresol and cast using spin coating technique on glass substrates. Thin films of polypyrrole were characterized by X ray diffraction (XRD), Scanning electron microscopy (SEM), Fourier transform infra red spectroscopy (FTIR), UV visible spectroscopy and electrical resistivity by four probe method. The XRD spectra showed that the polypyrrole is amorphous in nature. SEM studies revealed a uniform granular structure of PPy. The FTIR spectra shows that the presence of all characteristics absorption peaks of polypyrrole that is, 890 cm^{-1} (=C-H out-of-plane vibration), 1040 cm^{-1} (=C-H in-plane vibration), 1170 cm^{-1} (N-C stretch bending) and 1410 cm^{-1} (pyrrole ring vibration). UV visible study shows PPy films exhibit absorption peak at 446 nm (2.77 eV). Room temperature electrical resistivity of PPy is in the critical regime of the metal –to –insulator (M-I) transition.

Keywords: Polypyrrole, Chemical Polymerization, XRD, SEM, FTIR

1. Introduction

In recent years, intrinsic conducting polymers with conjugated double bonds have been attracted much attention as advanced materials. Among those conducting polymers, polypyrrole (PPy) is especially promising for commercial applications because of its good environmental stability, facile synthesis and higher conductivity than many other conducting polymers. PPy can often be used as biosensors [1,2], gas sensors [3,4], wires [5], microactuators [6], antielectrostatic coatings [7], solid electrolytic capacitor [8,9], electrochromic windows and displays, and packaging, polymeric batteries, electronic devices and functional membranes, etc. [10-12]. PPy coatings have an excellent thermal stability and are good candidate for use in carbon composites [13]. Furthermore, the electrochemical process parameters affecting the properties of the PPy coatings are also investigated [14]. PPy can be easily prepared by either an oxidatively chemical or electrochemical polymerization of pyrrole. However synthetically conductive PPy is insoluble and infusible which restricts its processing and applications in other fields. The problem has been extensively investi-

gated and new application fields have also been explored in the past several years. For example, PPy-based polymers can be used to load and release drugs and biomolecules [15]. PPy-based polymer blends can protect the corrosion of metals [16].

In the present investigations attempts were made to report on our observation of structure morphology, electrical and optical properties of polypyrrole thin films using the spin coating technique.

2. Experimental

Polypyrrole (PPy) was synthesized by chemical oxidative polymerization technique using monomer pyrrole. Analytical grade ammonium per-sulphate APS, (Sd fine) was used as oxidizing agent. The chemical polymerization was carried out in a beaker by mixing 0.1 M aqueous solution of pyrrole and 0.1 M of APS in 1:1 ratio by volume. The polymerization was carried out for a period of three hours. After termination of polymerization process, the precipitate obtained was filtered. The product was washed successively by methanol followed by distilled water. The films of polypyrrole were deposited

using spin coating method on pre cleaned glass substrate (size 10 mm × 10 mm). X-ray diffraction (XRD) studies were carried out using a Philips powder X-ray diffractometer (Model: PW1710). The XRD patterns were recorded in the 2θ range of 20-80° with step width 0.02° and step time 1.25 sec using CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). The morphology of the polypyrrole films was examined using Scanning Electron Microscope (SEM) (JEOL JSM 6360) using acceleration voltage of 25 kV. For this purpose thin layer of gold (50 \AA) was deposited on the film using physical vapour deposition. Chemical structure of thin film was examined by FTIR technique (Model: Perkin Elmer 100) using uncoated glass as reference. UV-Vis spectra of the samples, which were dispersed in de-ionized water under ultrasonic action, were recorded on a Simandzu-100 UV-Vis spectrophotometer. For resistance measurement, two gold electrodes, separated by 1 mm, were deposited on polypyrrole film and silver wires were attached using silver paint. The resistance was measured using four probe method.

3. Results and Discussion

3.1. FTIR Analysis

Figure 1 shows the FTIR spectra of PPy powder. The peaks at 811 cm^{-1} , 920 cm^{-1} are attributed to C–H wagging [17,18]. The characteristic peaks at 1558.4 cm^{-1} and 1487 cm^{-1} correspond to the C=C stretching, whereas peaks at 1685.7 cm^{-1} and 1315.4 cm^{-1} represent to respectively, C=N and C–N bonds [19]. The occurrence of small peaks at 3522 cm^{-1} is assigned to presence of N–H stretching vibrations. The peaks observed in the present work match well with the ones available in the literature [18,19] confirming the formation of Polypyrrole.

3.2. XRD Analysis

X-ray diffraction studies show that the PPy powder is

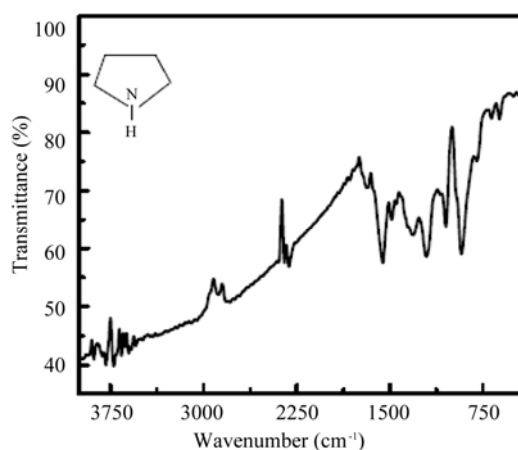


Figure 1. FTIR spectra of Polypyrrole film. Inset shows structure of pyrrole monomer.

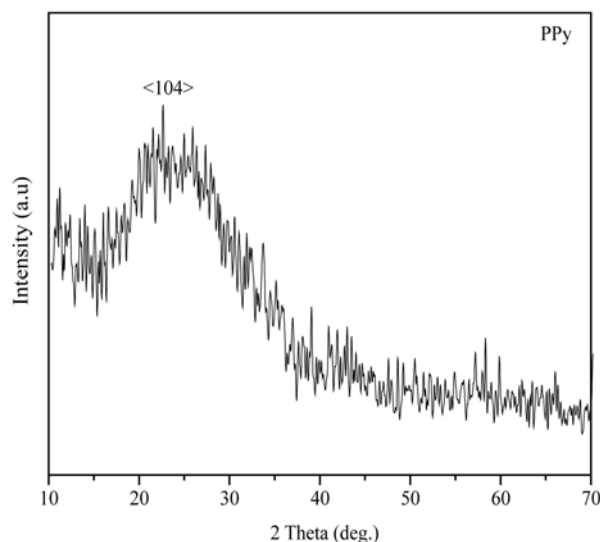


Figure 2. X-ray diffraction of PPy.

amorphous in nature, as shown in **Figure 2**. In **Figure 2**, broad peak was observed at about $2\theta = 24^\circ$. The broad peak is characteristic of amorphous PPy [20] and are due to the scattering from PPy chains at the interplanar spacing [21]. The average chain separation can be calculated from these maxima using the relation [22-25].

$$S = 5\lambda / 8\sin\theta \quad (1)$$

Where S is the polymer chain separation, λ is the X-ray wavelength and θ is the diffraction angle at the maximum intensity of the amorphous halo. The average chain separation (R) was found to be 4.38 \AA for PPy.

The average crystallite size from a sharp peak at 24° for PPy is estimated by using the Scherrer's formula [26].

$$D = K\lambda / \beta \cos\theta \quad (2)$$

Where D is the crystallite size, K is the shape factor, which can be assigned a value of 0.89 if the shape is unknown, θ is the diffraction angle at maximum peak intensity, and β is the full width at half maximum of diffraction angle in radians. When applied to the sharp peaks, Equation (2) leads to the average crystallite size of about 56 nm for PPy powder.

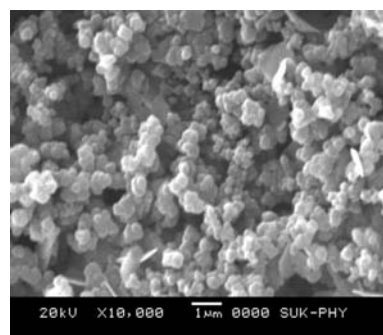


Figure 3. Microstructure of a polypyrrole thin film.

3.3. SEM Analysis

The microstructure of a polypyrrole thin film is shown in **Figure 3**. The film has a uniform granular morphology and the average grain size is $\sim 0.7 \mu\text{m}$.

3.4. UV-Vis Analysis

Figure 4 shows UV-Vis spectra of PPy film. PPy films exhibit absorption peak at 446 nm (2.77 eV) which are in agreement with literature values [27,28].

3.5. Electrical Studies

Figure 5 shows the variation of electrical resistance as a function of temperature of pure PPy. In this case it was observed that as temperature increases the electrical resistance decreases and hence conductivity increases. This suggests that the thermally activated behavior of conductivity has been confirmed. The decrease in resistance is due to the increase of efficiency of charge transfer in PPy

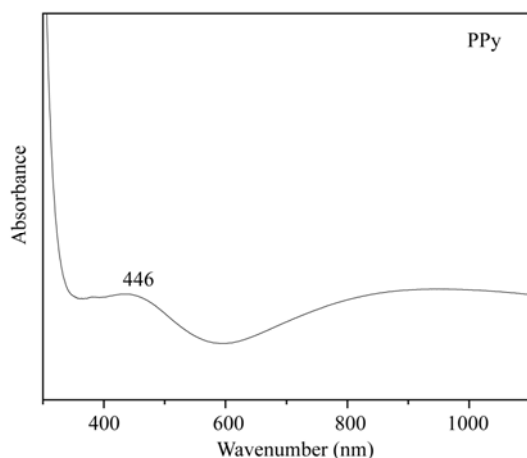


Figure 4. UV-Vis spectra of PPy film.

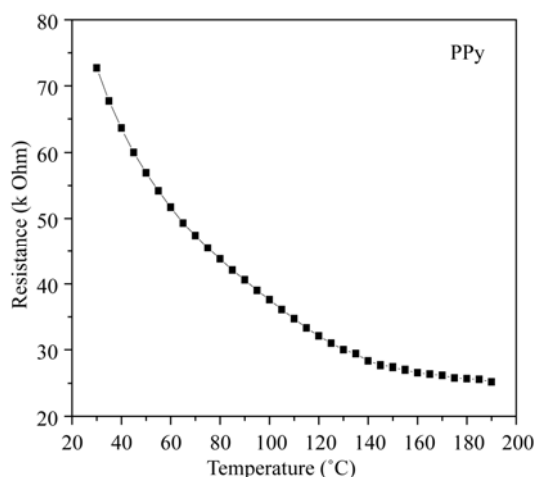


Figure 5. Variation of electrical resistance as a function of temperature of pure PPy.

with increase in temperature [29-30]. It is also suggested 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 decrease in resistance. Also, there will be molecular rearrangement on heating, which make the molecules favorable for electron delocalization [31]. The temperature dependence of the conductivity for conducting polymers is expressed by a variable range hopping (VRH) model proposed by Mott [32]. According to this model the behavior of electronic conduction in disordered and non-metallic materials is controlled by the thermally assisted hopping of electrons between localized states near randomly distributed traps and the resistance is given by,

$$R(T) \propto \exp\left[-T_0 / T^{1/(n-1)}\right] \quad (3)$$

$$kT_0 = d\alpha^3 / \rho_0 \quad (4)$$

where α is the coefficient of exponential decay of the localized states, ρ_0 is the density of states at the Fermi level, k is Boltzmann's constant, T_0 is absolute temperature, $R(T)$ is resistance at room temperature, n is number of electrons and d is a dimensional constant. However, many models have predicted as $R = T^{-1/2}$.

4. Conclusions

The polypyrrole synthesized using chemical polymerization process. The films had a uniform granular morphology. The structure of the films is confirmed by FTIR and XRD techniques. UV-Vis studies showed that the PPy films exhibit absorption peak at 446 nm (2.77 eV). The PPy shows a thermally activated behavior of conductivity.

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