PREPARATION AND CHARACTERIZATION OF POLYPYRROLE CONJUGATED POLYMER IN THE PRESENCE OF IONIC SURFACTANT

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Conducting polymer Polypyrrole (Ppy) was synthesized through chemical polymerization method using pyrrole monomer with ferric sulfate Fe2 (SO4)3 as oxidant at various concentrations (0, 5, 10, 15 and 20%) ionic surfactant sodium dodecyl sulfate (SDS) as dopant. The structural properties were investigated using X-Ray diffraction (XRD) and Fourier Transform infrared (FTIR) spectroscopy. Examination by XRD showed the structure to be amorphous, while FTIR studies confirmed the formation of Ppy functional group. Examination of the conducting polymer using thermo gravimetric analyzer (TGA) and laser flash technique demonstrated that thermal diffusivity of Ppy improved as the concentration of SDS increased. The optical band gap energy (Eg) was obtained using UV-VIS-NIR diffuse reflectance spectroscopy. The Ppy band gap reduces as SDS increased, which was attributed to the formation of polarons and bipolarons state within electronic band gap. This improved and enhanced Ppy optical properties. The results demonstrate that a Ppy oxide with Fe2 (SO4)3 and doped with SDS gives excellent, attractive, easily synthesized and thermal stable conducting polymers.

1. Introduction

Conducting polymers have been studied extensively in the past few decades due to their exceptional conductive properties and fascinating applications in many fields [1-2]. High electrical conductivity, process ability and stability in air are some of the unique features of conducting polymers. Polypyrrole (Ppy) is one of the most prominent conducting polymers known for its high conductivity, stability and facile synthesis [3-5 These qualities have made Ppy relevant in the manufacture of various devices such as gas sensors, wires, micro actuators, biosensors, electro chromic windows and displays, batteries, electronic devices, packaging and functional membranes [6].

Different methods have been used to synthesize (Ppy) such as electrochemical, photo doping, charge injection and chemical polymerization. Chemical polymerization involves doping pyrrole monomer with various oxidants such as ferric chloride, ferric per chlorate, ammonium peroxydisulfate and others [7].

Recent findings have shown that the presence of ionic surfactants can strongly improve the morphology and thermal stability of Ppy conjugated polymer [8]. The optical band gap decreased from 2.32 to 1.3 eV due to $\pi-\pi^*$ transition polarons and bipolarons states [9-10]. Studies also have shown that Ppy doped with various acids produced more charge carriers which contributed to the formation of polarons and bipolarons. The band gaps have been found to be

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2.38, 2.39 and 2.33eV when Polypyrrole is doped with chloride ion (Cl-), Sulphate ion (SO_4 –) and dodecyl benzenesulphonate (DBS-) respectively [11].

Specifically, Ppy composite thin-film prepared with chitosan (CH) had band gap between 1.30 and 2.32 eV, depending on the concentration of dopant applied [12].

Thermal diffusivity value of Ppy thin-film doped with sodium m-nitrobenzenesulphonate $0.028cm^2/s$ was determined in a temperature range of 280 and 335 K. However, thermal conductivity of Ppy increased as temperature increases from 273 K to 333 K. This indicates an interaction between the phonons and conduction electrons.

The thermal diffusivity of Polypyrrole-polyethylene glycol conducting polymer (PPY-PEG) increased as PEG concentration increases which have been found in between (3.87and 7.88) $\times 10^{-7}$ m^2/s. This may be associated with electron migration due to thermal diffusion [13-14].

In this study, Ppy has been synthesized by chemical method using ionic surfactant sodium dodecyl sulfate (SDS) as dopant and ferric sulfate (Fe2 (SO4)3) as oxidant. XRD, FTIR, TGA, UV-VIS and thermal diffusivity studies have been done to investigate the structural, morphological, thermal and optical band gap properties with varied SDS concentrations.

2. Experimental

2.1 Materials

Pyrrole (99.8%) (Fluka), ferric sulfate (Fe2 (SO4)3) (Fluka) while sodium dodecyl Sulphate (SDS) (Sigma-Aldrich). Apart from pyrrole which was purified through vacuum distillation, all chemicals were used in their original form.

2.2 Sample preparation

Ppy powder was synthesized using chemical oxidation polymerization method [12-13]. 0.2M Fe2(SO4)3was dissolved in 80 ml distilled water and stirred for 10 minutes. Further, 20 ml of freshly prepared pyyrole solution (prepared by dissolving 0.2M pyrrole in 100 ml of distilled water with continuous stirring for 10 minutes) was added. The solution was stirred for 6hrs at room temperature. Precipitated powder was filtered, washed and dried at 50˚C for 36hrs. The dried powder was ground and compresses into pellets at 5 ton /cm3 pressures. The same procedure was repeated with variation of SDS concentrations which are marked as: S0 (0 % SDS) S5 (5% SDS) ,S_{10} (10% SDS) ,S_{15}(15% SDS) and S_{20} (20% SDS).

2.3 Characterization

Powder X-ray diffraction (PXRD) measurements have been carried out through X–ray diffract meters (X' pert Powder Analytical BV, Almelo, Netherlands) with 2θ range (4 -80)º using CuKα (λ = 1.54187 A˚) at 40 kV and 30 mA. FTIR spectra of the samples were recorded with Perkin–Elmer Fourier transform infrared spectrophotometry (model 1725 X) using KBr disc within a range of 280 and 4000 cm-1. The (TGA) analysis was conducted   using Metter Toledo Thermo gravimetric analyzer (TGA/ SBTA851e) at heating rate of 10˚C/min with airflow speed of 200cm3/min and a temperature range of 20 and 1000 ˚C. The optical properties were studied using a UV –VIS-NIR diffuse reflectance spectrophotometer (Shimadzu UV- 3600) in the range 220-800 nm. Thermal diffusivity was measured in respect of temperature using NETZSCH model LFA 457 Micro flash.

3. Results and discussions

3.1 Powder X-Ray Diffraction (PXRD) Study

The structural properties of the samples are described using (XRD) technique, in terms of reflection mode. As shown in Fig.1, Ppy S0 (pure) patterns exhibit a broad characteristic peak at around $2\theta = 24.7°$ corresponding to highly disordered region, which is a proof of amorphous nature of Ppy [15- 17]. This can be attributed to scattering of Ppy from all over chains. With the variation of SDS concentrations i.e., S_5 (5%), S_{10} (10%), S_{15} (15%) and $S2_0$ (20%), the Ppy spectra look almost similar but with peaks shifted toward lower diffraction angle with increase intensity. These were attributed to formation of quasi particle polarons and bipolarons which improved and enhanced Polypyrrole morphology. This is in total agreement with other studies [9-10] and [18].
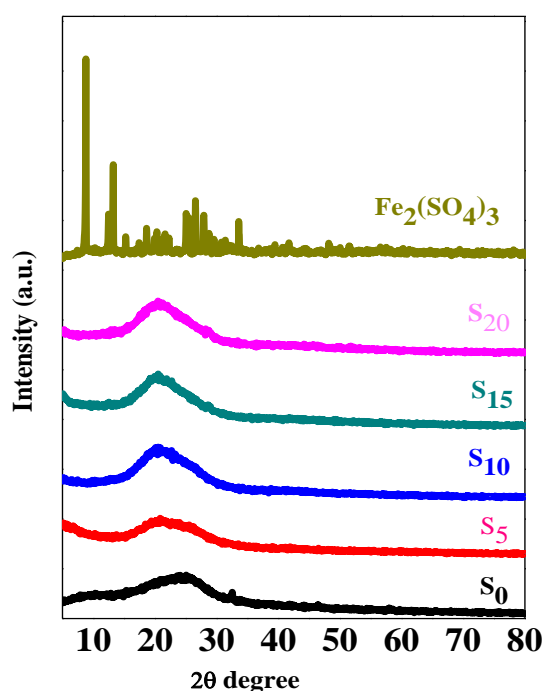

Fig. 1   X-ray pattern of Ppy powder at different SDS concentration.

3.2 Fourier Transform Infrared Spectroscopy (FT- IR)

Fig.2 shows the Polypyrrole (Ppy) FTIR spectra using different SDS concentration at room temperature. The peaks at 1539 cm-1 correspond to C–C stretching vibration of pyrrole ring. There was a redshift as a result of change of delocalized π electrons, according to alteration of structure and electron density that prompt the peaks shift as SDS increases [19].The absorption characteristic band was obtained between 1000-1600 cm-1 [20].The stretching mode of N-H and C-H is exhibited at 1030 cm-1 [21]. The peak in the range (1470-1440) cm-1 demonstrates C=C stretching bond [22, 15]. The peaks in the range of 1289 and 1400 cm-1 are attributed 1100 and 1250 cm-1 while the peak at 1023 cm-1 is assigned to C-H band [9] with the peak at 1141cm-11100. pyrrole [18, 13]
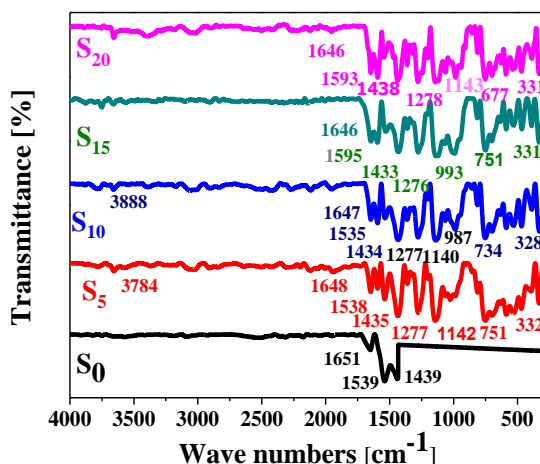
Fig.2. Ppy FTIR Pattern of SDS at various concentrations

3.3 The Thermal Stability (TGA)

Fig.3 shows Ppy thermo gravimetric analysis with different concentration of SDS using TGA/SFTA851thermogravimetric analyzer. The TGA curves for pure Ppy exhibits three degradation steps: the first one corresponds to the removal of water in the temperature range of 57.98 -133.62 ^{O}C while in the second step temperature increased from 133.62 to 502.14^{O} C due to Ppy degradation. The increment in the last step within the range 503 and 1013ºC can be attributed to the decomposition related to sulphonate functional group. The enhancement in thermal stability as SDS increased can be associated with increased alignment of Ppy chains this is supported byXRD.
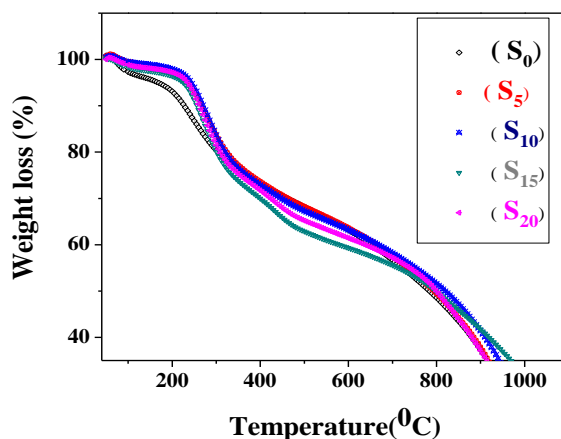

Fig. 3. Ppy thermo gravimetric (TGA) Curves at different SDS concentration.

3.4 UV-VIS Study

The optical energy gap of Ppy was calculated using Kubelka – Munk equation given in term of reflectance (R)

$$R_\infty = \frac{\alpha}{S} = \frac{(1-R_\infty)^2}{2R_\infty}$$

(1)

Where α is absorption coefficient, S represents the scattering coefficient per unit of sample thickness F(R∞) is Kubelka– Munk function, and R∞ IS diffuse reflectance:

$$R_{\infty} = \frac{R_{sample}}{R_{s\tan dard}}$$

(2)

We rewrite equation (1) to obtain

$$F(R_{\infty})(h\upsilon)^2 = A(F(h\upsilon - E_g))$$

(3)

The band gap was obtained from extrapolation of $(F.h\upsilon)^2$ versus $h\upsilon$ plot to the x-axis [11]. Fig.4 shows optical band gap (Eg) values were found to be 2.30, 1.94, 1.46 and 1.22 eV for S0, S_5, S_{10} and S_{20} respectively. The energy gap (Eg) decreases as SDS increases as a result of the formation of polarons and bipolarons in the band gap. The new electronic levels decrease the energy required for the electronic transition between the valance band (VB) and conduction band (CB), leading to a red shift in the UV–VIS spectrum i.e. the shift from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The (HOMO-LUMO) shift produce electronic localized state in energy gap according to $\pi - \pi*$ transition. These results in agreement with other studies [10-11, 13].
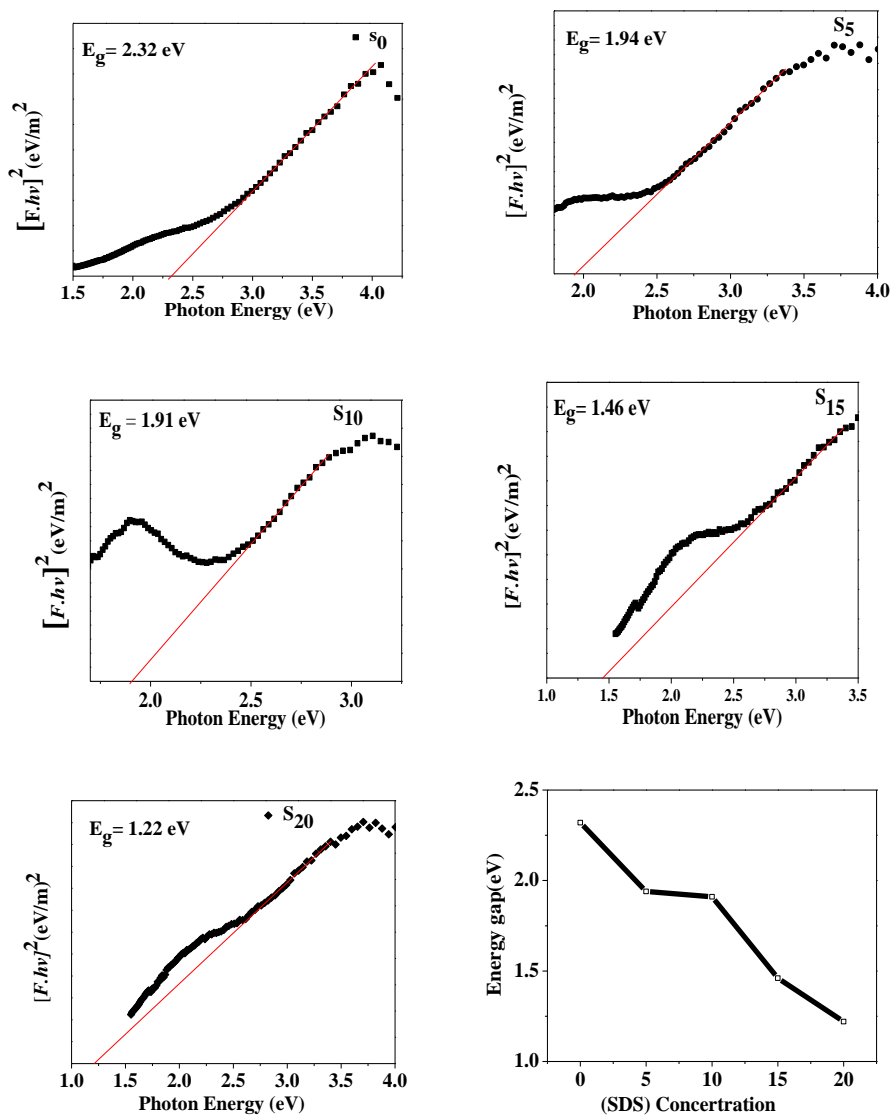

Fig. 4. Ppy optical energy gap at various SDS Concentrations

3.5. Thermal Diffusivity

Thermal diffusivity (α) measures the ability of a material to conduct energy. The relationship between thermal diffusivity (under transient conduction) and thermal conductivity (K) (under steady-state condition) described the heat transport in the material and is given by following equation [22].

$$\alpha = \frac{K}{\rho C_P}$$

(4)

Where αis the thermal diffusivity (m2/s), k the thermal conductivity (W/mK), ρ the bulk density (kg/m3) and Cp the specific heat at constant pressure (J/kgK).Mostly, the laser flash technique considered as a suitable method for measuring thermal properties of the materials and polymers. The set-up of the technique consists of a laser source which strikes the front of the cylindrical samples (10 mm long and a thickness between 1-2 mm).

Fig.5 exhibits the thermal diffusivity versus in situ temperature of Ppy at different SDS concentrations. The thermal diffusivity decreases as temperature increases as a result of increasing photon scattering and Ppy chains [18].The thermal diffusivity increases as SDS increases due to changes in thermal diffusion and photon carrier. These results concur with previous research findings [14].
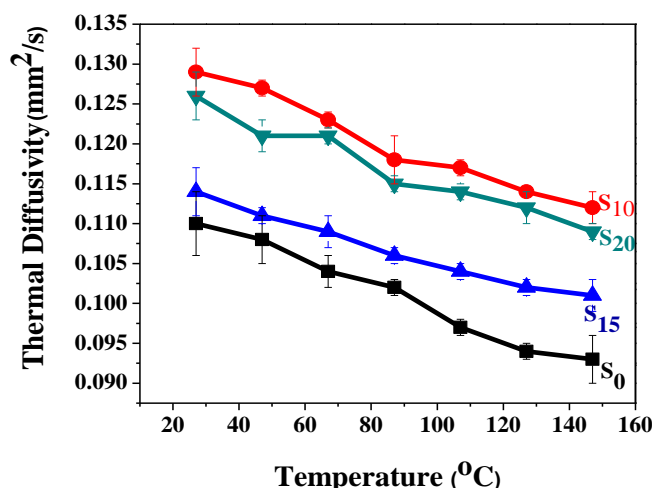

Fig. 5. Ppy Thermal Diffusivity pattern at different concentration (SDS)

4. Conclusions

Ppy conjugated polymers bulk form was synthesized by chemical polymerization method using various concentrations of ionic surfactant (SDS). The X-Ray results show similar wide peaks that are synonymous with amorphous nature of Ppy; the peaks shift to lower angle with an increase in SDS concentration. FTIR confirms that the SDS is incorporated to form Ppy. The thermal analysis shows enhanced and improved thermal diffusivity and thermal stability of Ppy at high levels of SDS. On the other hand, there was a reduction in optical band gap as the SDS increased. The present results demonstrate that Polypyrrole could be an excellent, attractive and thermally stable conducting polymer which can be easily synthesized.

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