International Journal of Scientific Research in Engineering and Management (IJSREM)
Volume: 07 Issue: 09 | September - 2023 SJIF Rating: 8.176 ISSN: 2582-3930

Studies on Optical Characterization of One Pot Chemically Synthesized polypyrrole/Poly (Vinyl Acetate) Composite Thin Films

Hameed R. Shaikh
Government Polytechnic, Amravati 444603, Maharashtra, India.

Abstract

In the present research work, the optical properties of one pot chemically synthesized polypyrrole/poly(vinyl acetate) composite films using $FeCl_3$ as an oxidant have been studied. The result of X-ray diffraction (XRD) analysis depicts the amorphous nature of the prepared composites. The surface morphology of prepared sample was analysed through FE-SEM, which shows granular morphology. The ultraviolet-visible (UV-VIS) spectroscopy was employed to study optical parameters. The composite films exhibited strong absorption below 250 nm with well-defined absorption peak at around 225 nm. The optical band gap values of all prepared samples ranges over 2.876 – 3.843 eV. These obtained values of optical parameters suggested that the prepared materials have the potential applications in optoelectronics devices.

Key words: optical properties; polypyrrole/poly(vinyl acetate), composite films.

1. Introduction

In recent few decades, electroactive polymers, mainly aromatic conducting polymers, have disbursing large interest among the researchers for use as advance polymeric materials because of their significant physical and optical properties [1–4]. Conducting polymers composites are significant materials enhancing the various prospective applications in different areas [5, 6]. Research in the field of such conducting polymers aims essentially at some appropriate modifications of existing materials therefore their applicability can be enhanced [7].

The synthesis of new efficient materials and for developing enhanced structural materials there is rising research concern towards composite materials derived from conducting polymers like polypyrrole, polythiophene, polyindole, polyacetylene and polyaniline linked with layered inorganic solids and also have been intensively studied due to theirgood environmental stability and high electrical conductivity [8-11].

Among these conducting polymers, polypyrrole (PPY) has drawn a lot of interest due to its excellent environmental stability, ease of synthesis and high electrical conductivity. It is especially promisingin commercial applications [12]. Polypyrrole has been actively used in many potential applications suchas electrochromic and electronic devices, membrane separation, light-weight batteries, sensors, rechargeable batteries,microwave shielding, supercapacitors, drug delivery, corrosion protection, and artificial muscle

[13-16]. However, the inherently poor solubility in common solvents, whichoriginates from the strong inter- and intrachain interactions, has limited some PPY's practical applications [17].

Abdirahman Yussuf et al. [18] successfully synthesized Ppy samples using different oxidants, andtheir performance in terms of electrical and thermal properties has been studied. It was found thatusing ferric chloride ($FeCl_3$) as an oxidant had a significantinfluence on electrical and thermal properties of the synthesized PPy samples as compared to the ammonium sulphate ($N_2H_8S_2O_8$). Dey et al. [19] successfully synthesized Ppy by varying M/O ratio using ferric chloride as oxidant and structural, absorbance as well as photoluminescence spectra of the polymer has been studied.

Inspiring from the above discussion and research gap identified from the literature reviews in the materials science, we plan to reports complex optical properties of polypyrrole/poly(vinyl acetate) composites films. In the present work, the one pot synthesismethod was adopted to prepare polypyrrole/poly(vinyl acetate) (Ppy/PVAc) composites films through chemical route by varying oxidant concentration. The optical parameters such as optical conductivity (σ), optical band gap (ε_g) are calculated through UV-VIS spectroscopy. Synthesized composite films were characterized by using field emission scanning electron microscope (FE-SEM) analysis, UV-VIS spectroscopy.

2. Experimental

2.1 Materials

All chemicals such as monomer pyrrole, oxidant $FeCl_3$, methanol used as organic media for the synthesis, were analytical grade and procured from SD Fine Chemicals, India. Poly(vinyl acetate) (PVAc) used as counter polymer procured from Hi media Chemicals, India.

2.2 Characterizations

The samples under investigation were characterized through XRD, FE-SEM and UV-Vis techniques to confirm the structural, thermal and optical properties. The XRD profile of powder samples were recorded on a Rigaku miniflex-II X-ray diffractometer using CuKα radiation (λ = 1.54 Å) in the 2θ range of 10 – 70°.As-synthesized films of composite materials were characterized by field emission scanning electron microscope (FE-SEM) (S-4800, Hitchi, Japan) to study surface morphology. UV-VIS spectroscopy done through Agilent Technologies cary 60 UV-VIS, for the estimation of various optical parameters under study.

2.3 Preparation of Ppy/PVAc composites films

Ppy/PVAc composite films were developed chemically at room temperature using $FeCl_3$as an oxidant. Mixed solutions of PVAc and methanol (10:90) were derived by taking the polyvinyl acetate (1 g) was

dissolved in methanol (9 ml) and stirred about 2 hand kept it for 24 h in order to make the homogenous solution. Then monomer Ppy (0.5 g) was added in to homogeneous solution of PVAc and continuously stirred about 2 h. Finally, the oxidant $FeCl_3$was varied in weight percentages (wt%) were added in to mixture solutions of Ppy-PVAc and continuously stirred about 6 h to complete polymerisation reaction**.**

In general,developed composites materials were kept to settle down for 2 h. Then these composite solutions were cast on the chemically cleaned and optically plane glass substrate to developed composites films.To dry the composite films of Ppy/PVAc through an isothermal evaporation of organic media, the whole assembly was placed for 24 hin a dust free chamber maintained at constant temperature. The composite films were washed with triply distilled water after the complete evaporation of organic media and remove from the glass plate then dried for 6 h at room temperature. In this way, Ppy/PVAc composite films were derived by varying oxidant concentration. By adopting same route, successful one pot syntheses of different Ppy/PVAc samples were carried out.

3. Results and discussion

3.1 XRD analysis

X-ray diffraction studies were carried out to examine the structural investigation of prepared Ppy/PVAc samples. The patterns were recorded on Rigaku miniflex-II X-ray diffraction using CuKα radiation (λ = 1.54 Å) in the 2θ range of 10-70°. Fig. 1 depicts the XRD profile of Ppy/PVAc composites films with 10 wt.%; 20 wt.%; 30 wt.%; 40 wt.%. The entire 2θ pattern does not show any sharp peak, which is the characteristic of crystalline nature. Besides that patterns contains the broad humps between 20 and 30°, which pointed out the amorphous nature of synthesized samples of composites [20].

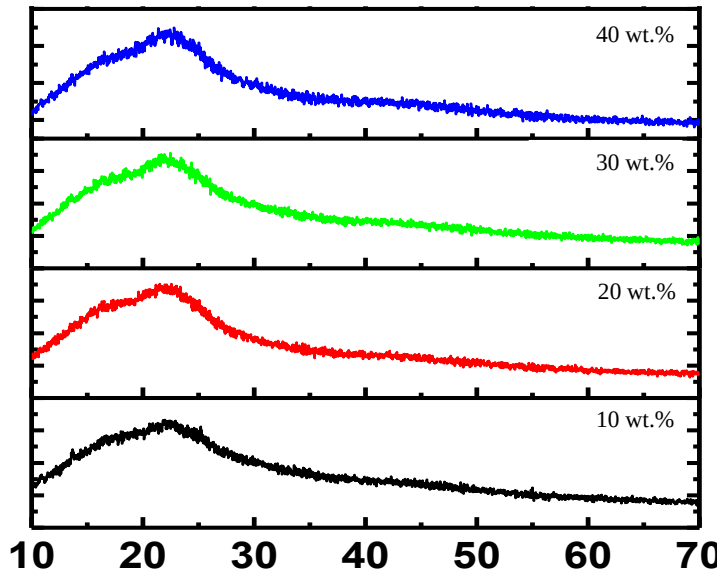

Fig. 1. XRD profile of Ppy/PVAc composite films.

3.2FE-SEM analysis

Surface morphology of optimized Ppy/PVAc composite film(30 wt. %) was analysed from FE-SEM micrograph displayed in figure 2. The nature of particles is irregular in structure also the surface has spongy amorphous nature. FE-SEM micrograph shows that grains are tremendously agglomerated, irregular in structure but they are well organized with one another [21].

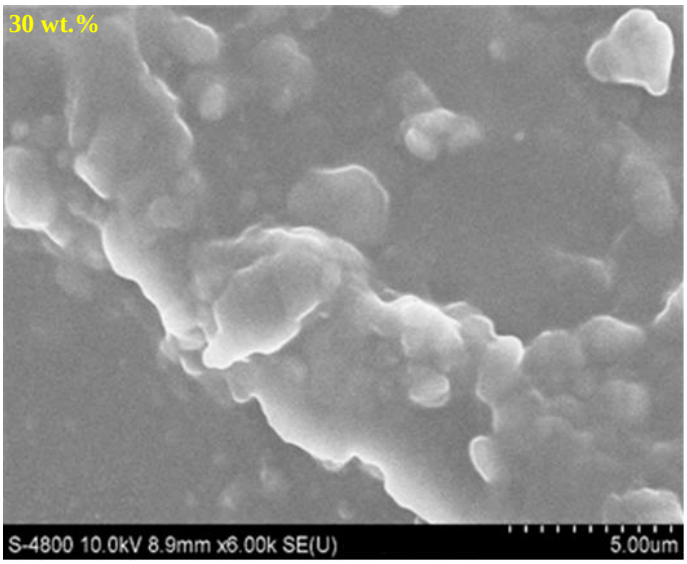

Fig. 2. FE-SEM micrograph of Ppy/PVAc composite film.

3.3 UV-VIS spectroscopy analysis

The figure 3 represents UV–VIS absorbance spectra of Ppy/PVAc composite films. The analysis of spectra wascarried out with a view to explore their optical parameters.The % absorption is higher on lower wavelengthside represents in figure. The absorbance spectra of each prepared samples show two majorpeak of absorption is centeredat wavelength 225 nm and 275 nm due to ꠸-꠸* transition [22]. The material has many applications depend upon its opticalband gap. The relation between absorptioncoefficient (α) and incident photon energy (hν) can be expressed as given relation [23],

$$\alpha = \frac{A(h\nu - Eg)^n}{h\nu} \qquad (1)$$

where, A is constant and Eg is band gap of material.

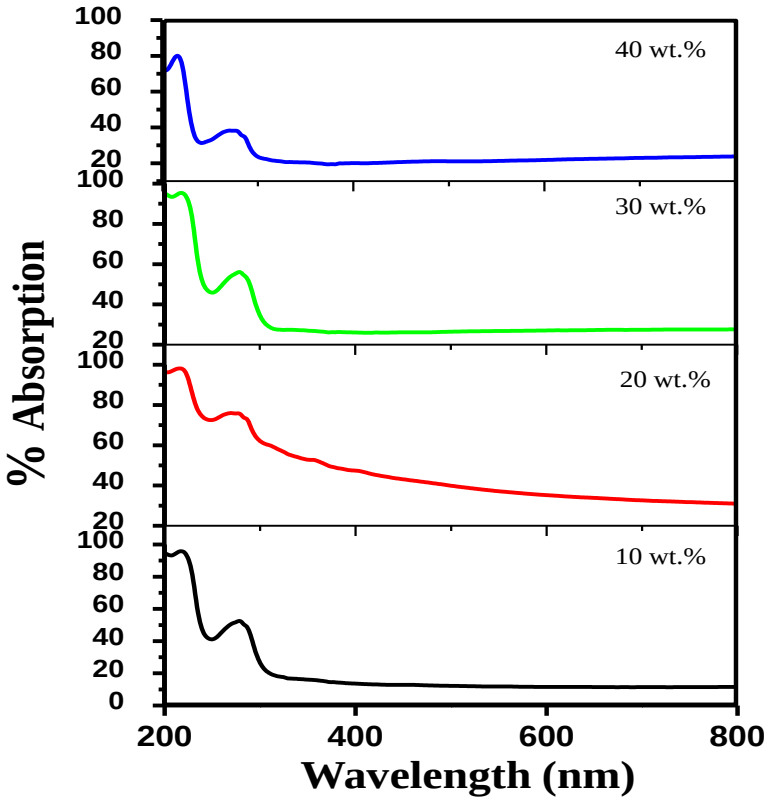

Fig. 3. Absorbance spectra of Ppy/PVAc composite films.

Fig. 4 shows the optical transmission spectra of Ppy/PVAc composite films plotted in the wavelength range 200 – 800 nm. The critical analysis of transmission curves was showed the peaks around 210 nm. Beyond 210 nm, transmission decreased sharply up to 230 nm and then raised gradually around 280 nm and thereafter remains almost constant. The onset of decrease of transmittance depicted the approximate values of the energy band gap [24].

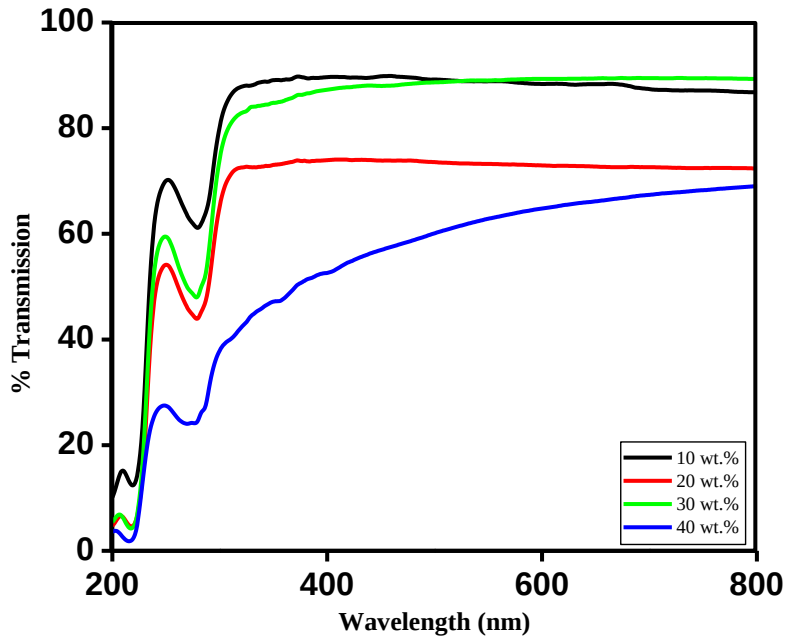

Fig. 4. Optical transmission spectra of Ppy/PVAc composite films.

3.4 Optical parameters

The optical band gaps of Ppy/PVAc composite films was calculated by plotting the $(\alpha h\nu)^2$ versus photon energy hν(eV) as display in figure 5. The value of optical band gaps of Ppy/PVAc composite filmsobviouslyrepresents that this material is applied in photocatalytic activities and optical devices.The figure directly shows that Ppy/PVAc composite films of 40 wt% oxidant has least optical band gap. Also, the Ppy/PVAc composite films of 25 wt% oxidant has largest optical band gap.

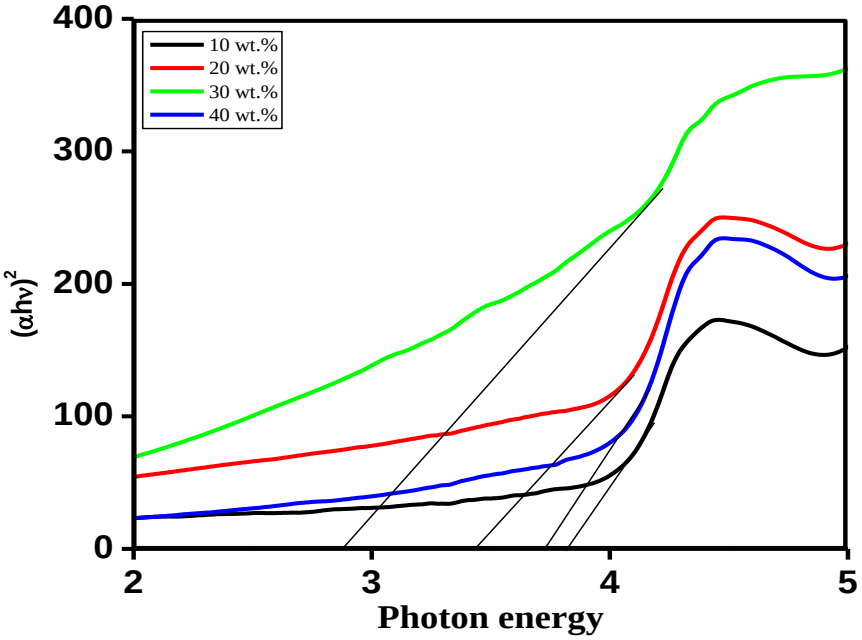

Fig. 5.Plot of $(\alpha h\nu)^2$ versus photon energy hν (eV) Ppy/PVAc composite films.

The optical response of material is generally calculated in terms of optical conductivity (σ) which is given by relation [25],

$$\sigma=\frac{\alpha nc}{4\pi} \qquad (6)$$

where, α is absorption coefficient, c is velocity of light and $n$is refractive index. From figure 6, it is observe that optical conductivity directly depend upon absorption coefficient and refractive index of Ppy/PVAc composite films. Figure 6 represents the variation of optical conductivity as a function of wavelength of Ppy/PVAc composite films of 25, 30, 35, 40, 45, 50 wt% of an oxidant. It can be noticed that optical conductivity increases rapidly over the range 225-350 nm. From figure 6, it is clearly observed that the optical conductivity of materials is increases with increase in wt% of oxidant up to 40 wt% of oxidant. Further, increase in wt% of oxidant results in decrease of the optical conductivity. The gradual increase in optical conductivity indicates the decrease in absorption coefficient [26]. From optical conductivity plot, it concludes that Ppy/PVAc composite film of 40 wt% oxidant has highest optical conductivity.

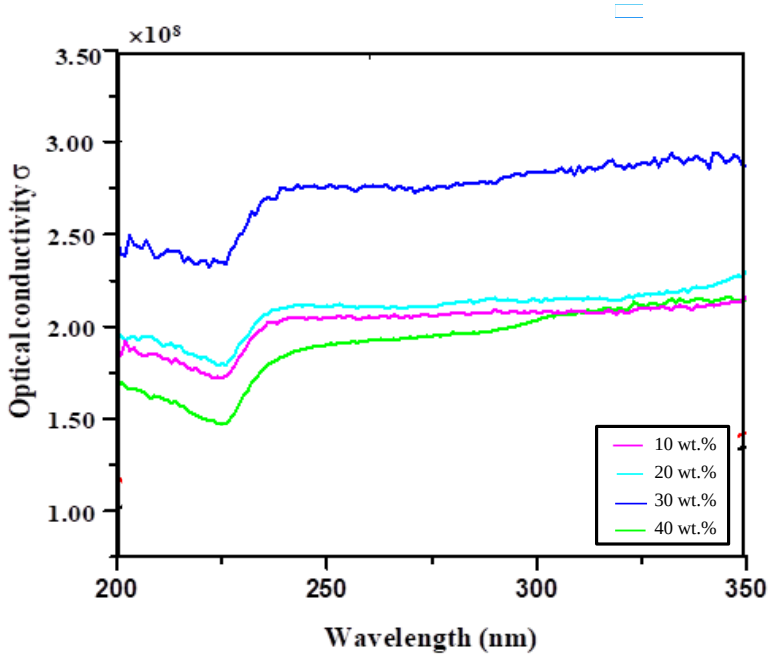

Fig. 6. Plot of optical conductivity (σ) versus wavelength (λ) of Ppy/PVAc composite films.

3.5 Photoluminescence analysis

Photoluminescence (PL) is the spontaneous emission of light from a material under optical excitation. The excitation energy and intensity are chosen to examine different regions and excitation concentrations in the sample [27]. Figure 7 shows PL emission spectra for Ppy/PVAc composite having different wt. % ratios. As seen in figure, all the emission peaks was centered at about 380 nm. The highest PL quenching was observed for the sample obtained with 30 wt. % ratios of Ppy/PVAc composite. This may be due to recombination of

initially generated electron-hole pairs, rather than their dissociation into separate charges, also the extent of polymerization may be more in case of the sample obtained with 30 wt.% ratios of Ppy/PVAc composite. The decrease in the PL emission intensity from wavelength 450 nm to 550 nm for Ppy/PVAc composite may be due to fast deactivation of the excited state by the electron transfer reaction, which attribute to more effective separation of electrons and holes [28]. The spectra of PL emission was obtained due to the π-π* transition of the benzenoid unit of polyaniline [29].

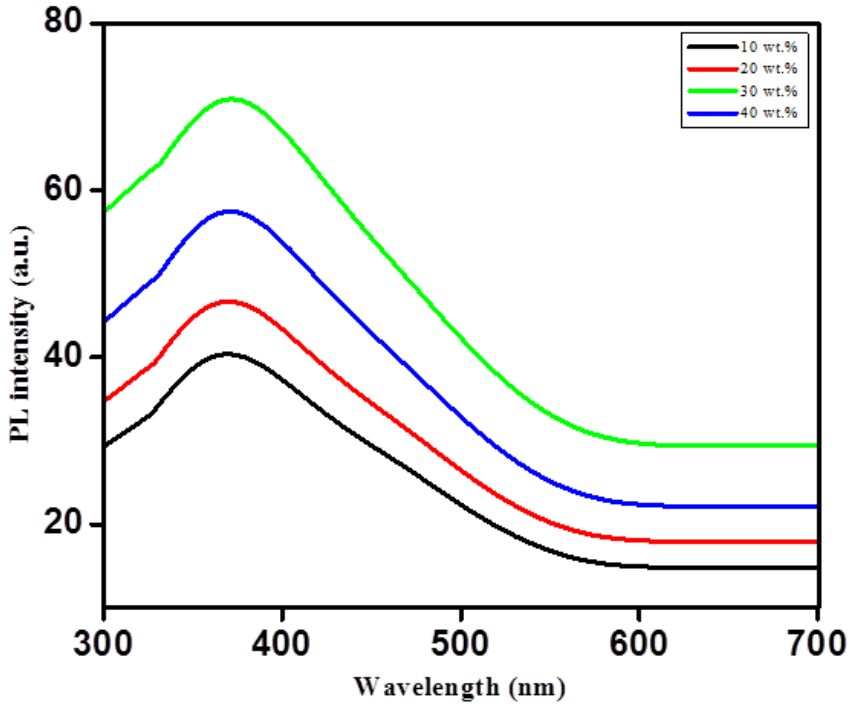

Fig. 7. PL emission spectra for Ppy/PVAc composite films.

4. Conclusion

In summary, Ppy/PVAc composite films synthesized chemically using oxidant $Ni(NO_3)_2$. The results indicate that for Ppy/PVAc composite films, loss factor decreases with increase in photon energy.The optical conductivity also increases with increase in wavelength and this can be attributed to increase in absorption. Ppy/PVAc composite film of 40 wt. % oxidant has highest optical conductivity. The optical band gap values of samples ranges over 2.876 - 3.843 eV. These optical band gaps indicate composite films have semiconducting properties and potential application in solar cells and optical devices.

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