

Study of Optical behaviour of Polypyrrole doped Polyvinylchloride films

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Abstract—The aim of the present work is concerned with the study of the optical behavior of Polypyrrole doped Polyvinylchloride films at different concentrations of Polypyrrole. The samples are casted as films. The films were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM). The optical properties of these films are evaluated using UV-VIS spectrophotometer. The XRD spectra showed the amorphous nature of the films. SEM studies revealed a uniform granular structure of PPy. From UV- VIS spectra optical band gap of the films has been calculated using the Tauc's relation and variations in the values of optical band gap with the variation of percentage concentration of PPy in PVC and have been found to vary from 2.3 to 4.1 eV. The band tail width of localized states has been calculated using Urbach's relation.

Keywords—Polypyrrole, Polyvinylchloride, Optical band gap, Urbach energy.

I. Introduction

In the recent years polymers have received much experimental attention due to their unique properties such as low manufacturing cost, low density, ability to form thick and thin samples, versatile electrical and optical properties [1]. It is well known that composites can be produced exhibiting enhanced properties that the constituent materials may not exhibit [2]. The dispersion of electrical conductive phase within an insulating polymer matrix affects the overall performance of the heterogeneous system. The interesting properties of such systems make them technologically important and competitive to other alternative materials due to their cost effectiveness. Current studies reveal that the measurement and understanding of optical properties of conductive polymer composites have attracted much attention due to their applications in sensors, LEDs, electro chromic display devices/smart windows and optical devices [3]. Optical characterization of thin films gives information about some important physical properties such as band gap energy and band structure and therefore may be of permanent interest for several different applications. The occurrence of electronic transitions in the structure of materials is directly related to the photon energy. The study of optical absorption and particularly the absorption edge is a useful method for investigating optically induced transitions and provide information about the band structure, band tail and band gap energy in polymeric materials under consideration [6]. The measurement of the optical absorption coefficient particularly near the fundamental absorption edge provide a standard method for investigation of optically induced electronic transitions and provide some ideas about the band structure and the energy gap in both crystalline and non crystalline materials [2]. The objective of the present paper is to

investigate the optical properties of Polypyrrole doped Polyvinylchloride films and to select the optimum conditions necessary for the required technical applications.

The doping of conducting polymers like Polypyrrole, Polyaniline, Polythiophene etc in insulating polymers like Polyvinylchloride, Polymethylmethacrylate, Polycarbonate and their blends has been an important area of research to produce conducting polymer composites which will have satisfactory electrical, optical, mechanical and thermal properties. Among all conducting polymers, Polypyrrole (PPy) has gained much interest due to some of its properties like environmental stability, low cost, relatively high conductivity and commercial availability. So Polypyrrole has been selected as conducting polymer in the present work. On the other hand Polyvinylchloride (PVC) which has good resistance to weathering and good mechanical strength has been selected as insulating polymeric matrix. In the present study free standing Polypyrrole (PPy) incorporated PVC films were prepared by a technique called mixing oxidative polymerization. Pure PVC and PPy doped PVC films with different proportions of PPy with varying thicknesses were prepared by solution cast method. The average thicknesses of these films lie in the range of 630 μm. The films were characterized by X-ray diffraction (XRD) and scanning electron microscopy. The optical absorption studies were made in the wavelength range 200-900 nm.

II. Experimental

A. Materials

Polyvinylchloride (PVC) (molecular weight 62,000 gm/mol) supplied by Sigma Aldrich was used as an insulating matrix. Pyrrole monomer supplied by Spectrochem, India, was used as received. Tetrahydrofuran purchased from HPLC was used as solvent and Anhydrous Ferric Chloride purchased from Otto Chemicals, was used as oxidant for polymerization of Pyrrole monomer.

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B. Sample Preparation

In present work, free standing films of pure PVC and Polypyrrole (PPy) incorporated PVC films with different concentrations of PPy have been prepared at room temperature by technique called mixing oxidative polymerization. The films were prepared by solution cast technique at room temperature (24°C). The concentration of PPy in PVC was kept as 6%, 11%, 14%, and 20%. The thickness of the films was determined using micrometer screw gauge. The average thicknesses of these films lie in the range of $630\mu\text{m}$.

C. Characterization Techniques

The X-ray diffraction studies were performed using X-ray diffractometer. The morphology of the samples were studied using scanning electron microscope (SEM). The optical absorption profiles of the samples were recorded at room temperature in the wavelength range 200-900 nm using Shimadzu-2600 Spectrophotometer

III. Results and discussions

A. XRD Analysis

For structural characterization the X-ray diffractogram of pure PVC and PPy (20% concentration) doped PVC films were obtained. Comparison of the XRD patterns (Figure 1 and Figure 2) reveals the following differences: The peaks observed for $2(\theta)$ values around $20-25^{\circ}$ for pure PVC film disappears in the PPy doped PVC film. The X-ray diffraction pattern in Figure 2 shows hump and broad peak was observed at 25° is characteristic of amorphous PPy and are due to the scattering from PPy chains at the interplanar spacing.

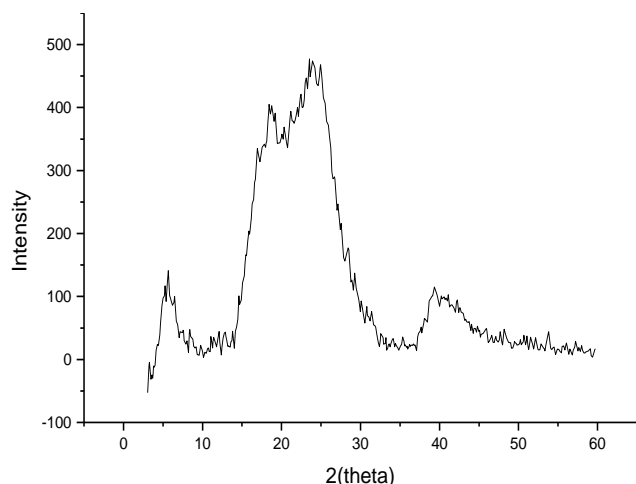


Figure 1. X-ray diffraction of Pure PVC film

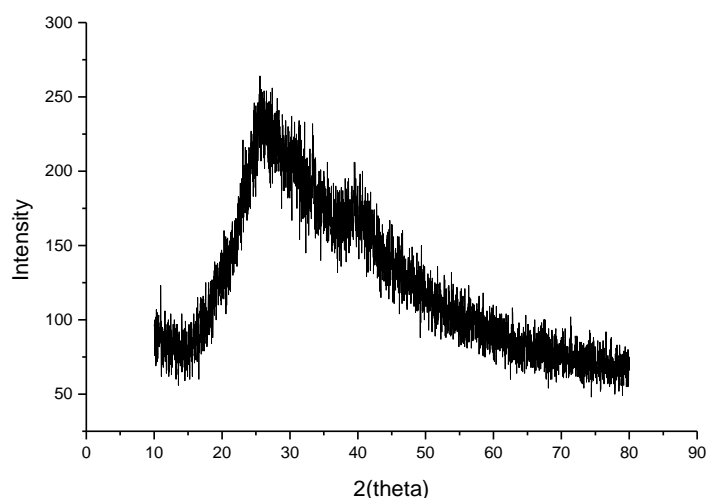


Figure 2. . X-ray diffraction of PPy (20 % concentration) doped PVC film

B. SEM Analysis

The morphology of PPy doped PVC films for two compositions were studied using SEM techniques. The film surfaces were of uniform type but with different degrees of roughness. Figures 3 and 4 show that the surface of the films contains macrogranular structure formed by aggregation of small globular structures which are typical cauliflower structures confirming the presence of PPy in PVC.

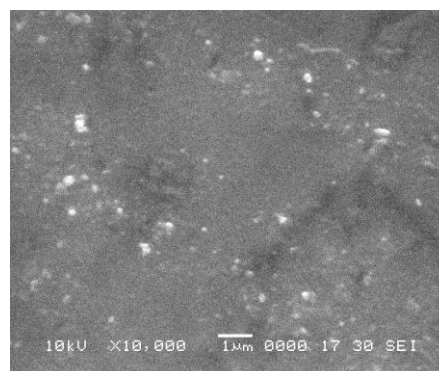


Figure 3. SEM Micrograph of PPy (11 % concentration) doped PVC film

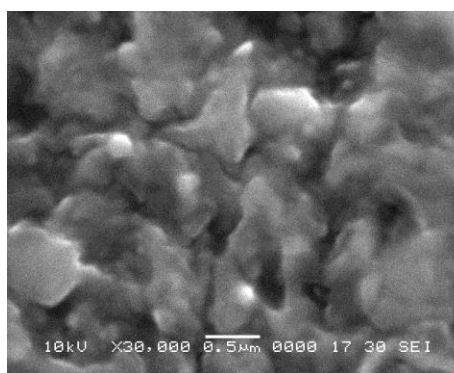


Figure 4. SEM Micrograph of PPy (20 % concentration) doped PVC film

C. Optical Characterization

The absorbance A of the samples were measured by means of UV-VIS spectrophotometer in the spectral range 200-900 nm at normal incidence. The spectral dependence of A on doping percentage of PPy in PVC films is shown in Figure 5. The absorption coefficient α is defined as the ability of a material to absorb light of given wavelength. Some valuable information such as electronic band structure and optical energy band gap can be obtained from absorption coefficient α . It is estimated from the optical absorption spectrum using the following equation:

$$\alpha(f) = \frac{2.303 A}{d} \quad (1)$$

Where d is the film thickness in cm, A is the absorbance and is defined as $\log(I/I_0)$ where I_0 and I are intensities of incident and transmitted beams respectively. The absorption edge for direct and indirect transitions for amorphous materials can be related to the incident photon energy hf in view of the models proposed by Tauc: for $(hf > E_{opt})$

$$\alpha hf = B (hf - E_{opt})^n \quad (2)$$

Where B is constant, E_{opt} is the optical energy band gap of the material. The value of n determines the type of electronic transitions causing optical absorption it can take values $1/2$, $3/2$, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions respectively. The determination of value of optical energy bandgap E_{opt} involves plotting of $(\alpha hf)^{1/n}$ versus hf and extrapolation of straight line to $(\alpha hf)^{1/n} = 0$ axis gives optical energy band gap. On other hand for optical transitions caused by photons of energy $(hf < E_{opt})$, the absorption of photons is related to the presence of localized states in the forbidden gap.

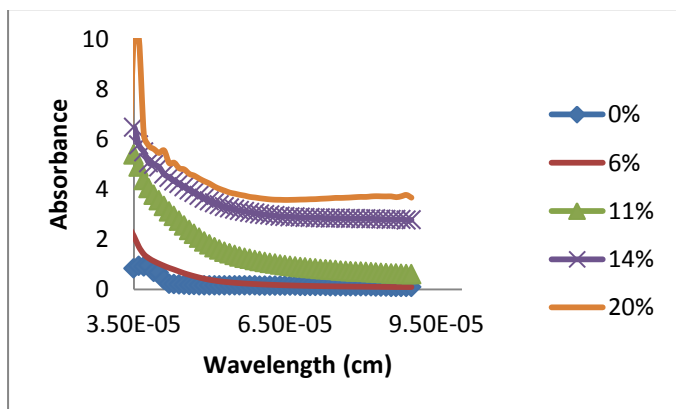


Figure 5. Optical Absorbance as a function of wavelength for Pure and PPy doped PVC films.

The width of the tail of these localized states called Urbach tail is an indicator of the defect levels in forbidden

gap. Following relation was used to calculate the width of Urbach tails:

$$\alpha(f) = \alpha_o \exp\left(\frac{hf}{E_u}\right) \quad (3)$$

Where f = frequency of radiation, α_o is a constant and E_u is the Urbach energy interpreted as the width of the tails of localized states in the forbidden gap and is associated with the amorphous state of material. The magnitudes of the Urbach energy E_u were estimated by taking the reciprocal of the slopes of the linear portion of the curves from the plot of $\ln\alpha$ versus (hf) .

Optical Absorption:

Figure 6 shows variation of absorption coefficient α versus wavelength for pure PVC and PPy doped PVC with varying concentrations of PPy. The absorption edge shifts towards the larger wavelength side and becomes broader. Also it can be seen that absorption coefficient values increase in these polymer systems, attributing to the decrease in the energy gap. It is clearly observable from the curves that there is less absorption in visible region as compared to the UV region for all samples.

The observed shift in the fundamental absorption edge of UV-Vis spectra can be correlated with the optical band gap energy E_{opt} given by Tauc's relation (Equation 2).

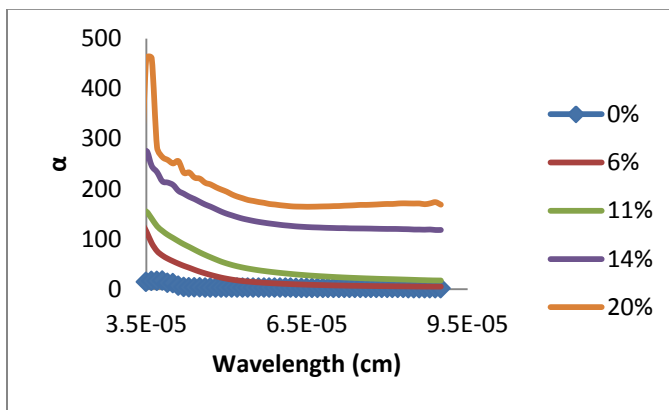


Figure 6. Absorption coefficient as a function of wavelength for Pure and PPy doped PVC films.

Figures 7 and 8 show plots of $(\alpha hf)^2$ versus hf for pure PVC and PPy doped PVC films. The linear portion was best fitted with $n = 1/2$ which indicates the transition of direct type. Intercept of linear portion of the plots on hf axis gives the value of direct optical band gap energy E_{opt} of the films. The values of E_{opt} for pure PVC is 4.1 eV where as the optical energy gap is found to decrease with concentration of PPy except for 20% concentration of PPy in PVC film. The change in the optical band gap of the PVC films on doping with PPy can be explained in terms of charge transfer complex formation between PVC and PPy and is characterized by shifting of absorption band in addition to the broadening in absorption in UV-Vis spectrum [5]. The lower values of E_{opt}

on addition of PPy in PVC may be attributed to the creation of localized states in the band gap as a result of compositional disorder. Also the increase in the number of unsaturated defects increase the density of localized states in the band structure and consequently leads to the decrease in optical band gap on addition of PPy in PVC.

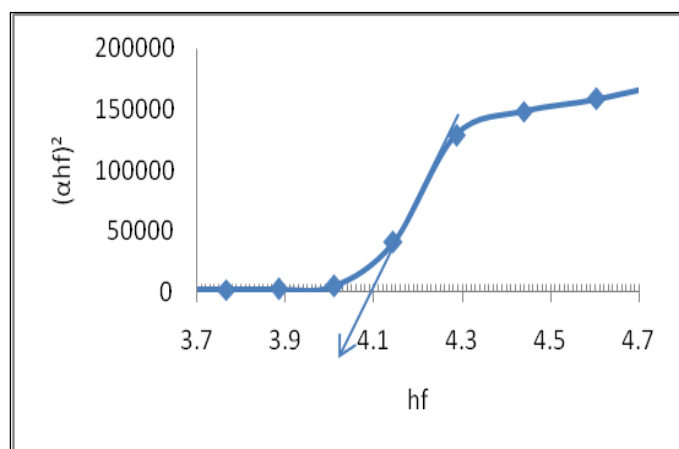


Figure 7. Plot of $(\alpha hf)^2$ versus hf for Pure PVC film

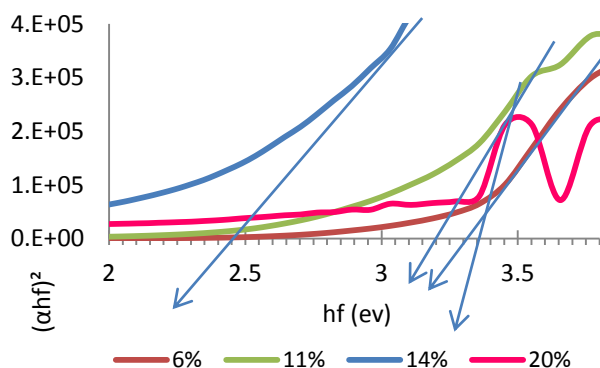


Figure 8. Plot of $(\alpha hf)^2$ versus hf for PPy doped PVC films

According to Mott and Davis the width of the mobility edge depends on the degree of disorder and defects present in the amorphous structure. Such defects produce localized states in the forbidden gap [8]. The width of the band tails of the localized states have been obtained by analyzing the optical absorption spectra in the frame work based on Urbach's empirical formula (Equation 3). In order to illustrate this the natural log of α was plotted as a function of photon energy hf for the studied films (Figure 9). The magnitudes of the Urbach energy E_u were estimated by taking the reciprocal of the slopes of the linear portions of these curves. The variation of Urbach energy with the variation of % concentration of PPy in PVC films is shown in Figure 10. The larger the values of Urbach energy the greater are the compositional, topological or structural disorder.

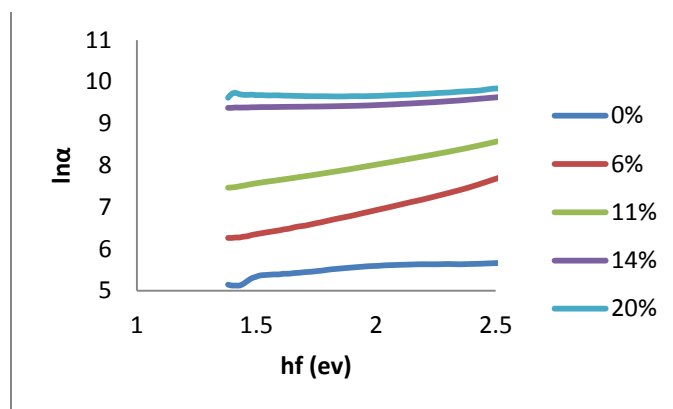


Figure 9. Plot of $\ln \alpha$ versus hf for Pure and PPy doped PVC films

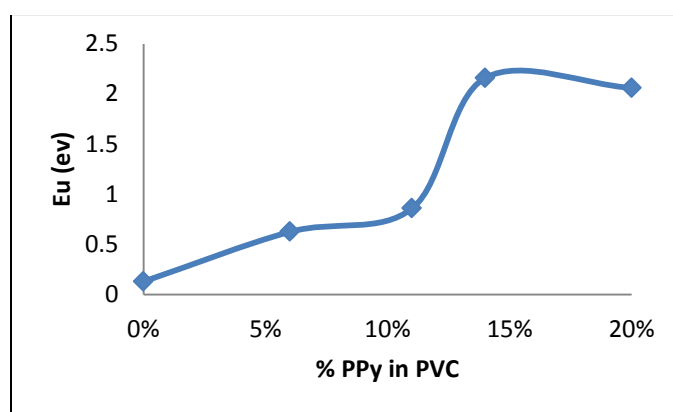


Figure 10. Plot of Urbach energy E_u versus % PPy concentration in PVC

iv. Conclusion

Following conclusions can be drawn on the basis of experimental data. The amorphous nature of the films was confirmed from the XRD spectra. The observed variation in the optical parameters such as optical band gap and Urbach energy of PPy doped PVC films may lead to tailor the optical properties of these films as per specific requirements. The optical absorption spectra showed that the absorption mechanism is direct allowed transition. The decreasing trend of the optical band gap with % concentration of PPy in PVC may be attributed to the formation of charge transfer complexes and suggests the presence of deep localized state in the band gaps. The increase in values of Urbach energy with increase in % concentration of PPy in PVC suggests increase in the compositional, topological or structural disorder.

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