SYNTHESIS AND CHARACTERIZATION OF POLYANILINE (PANI) DOPED WITH VANADIUM PENTOXIDE(V₂O₅)

S. S. ASHRAF^{a*}, S. ISLAM^b

^a School of Engineering Sciences and Technology, Jamia Hamdard, New Delhi-62,India

^b Department of Physics, Jamia Millia Islamia, New Delhi-25, India

Conducting polymers are organic macromolecules of electrical properties and lie between metallic and semiconductors. Polyaniline (PANI) / Vandiumpentaoxide (V₂O₅) composites are conducting polymers which have been synthesized by the technique of polymerization of aniline with vanadium pentaoxide (V_2O_5) using oxidant ammonium persulphate [(NH₄)₂ S_2O_8]. V_2O_5 has been added in PANI in three different weight percentages (wt %) i.e. 20, 30 and 40 wt %. Thus the synthesized polymer composites of PANI / V_2O_5 have been by X-ray diffraction (XRD), Fourier Transform Infrared characterized Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) techniques. The optical properties have been determined using Ultra Violet Visible (UV-Vis) absorption spectroscopy. DC conductivity of PANI / V_2O_5 has been carried out. It is found that electrical conductivity (σ_{dc}) and optical energy band gap (E_o) of polymer composites PANI $/V_2O_5$ both vary with the varying concentration of V_2O_5 in PANI. XRD patterns of PANI / V_2O_5 exhibits the increase in crystallinity with increasing weight percent of V_2O_5 in PANI which may be attributed to interaction of PANI with V₂O₅.SEM images of PANI / V₂O₅ show the change in surface morphology with varying concentration of V₂O₅ in PANI.

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1. Introduction

The conducting polymers are very prominent kind of materials having unique optical, electrical and chemical properties which make them potential candidates for various technological applications. These types of materials when doped, provide wider scope for accessing its electrical property from semiconducting to conducting[1, 2]. Owing to this unique property of these conducting polymers, new models have been developed to study the mechanism of charge transport [3, 4]. These unique properties have led to their emergence as new kind of materials.

Doping of these conducting polymers with oxides enables it to transform from semiconducting to conducting mode which results in transportation of charge. Amongst various kind of conducting polymers, polyanilines are studied widely due to its easier synthesisation in aqueous media and are environmentally stable. Polyaniline (PANI) and its derivatives have wide technological applications because of their high electrical conductivity and reversible proton doping. It is also easier to prepare it in bulk. In recent years PANI derivatives have engaged the increasing attention of many researchers due to its wide applications in making humidity sensors [7–10]. Its electrical conductivity is reported to be strongly dependent on the doping level, redox state and moisture content [11]. One of the PANI's derivatives has been Poly(o-toluidine) (POT) which is also a conducting polymer. It has wide applications in batteries, sensors and electronic devices [12].

POT possesses higher processibility and solubility compared to PANI. The efforts have been made to harmonize the mechanisms of process of aniline oxidation with the corresponding properties of POT like electrical conductivity, crystallinity and molecular weight. However their optical, dielectric and electrical properties get varied when taken in the composite form. Many researchers conducted studies on dielectric and electrical conductivity properties of composites

^{*}Corresponding author: shahabash@gmail.com

conducting polymers [8-10]. Recently heterogeneous conducting polymer composites such as organic-inorganic nanocomposites, have been studied extensively because these materials exhibit properties that could not be obtained by the homogeneous components. These composite polymers are potential candidates to be used in photo and electro catalytic systems and chemical current sources. By doping of these materials, quantum fields can be enhanced in these devices.

In our present research we have attempted to increase the properties of PANI doped with vanadium pentaoxide (V_2O_5). Amongst inorganic dopant, the vanadium pentaoxide (V_2O_5) is prominently used because of its many applications in electronic devices [19, 20]. V_2O_5 exhibits the photovoltaic and photoconductive actions both. In photovoltaic actions, the light energy is directly converted into electricity whereas in photoconductive actions, the electrical resistance decreases with increasing radiance. Doping of conducting polymers is processed by using Lewis acid. Further V_2O_5 is stable in nature and free of any hazardous effects and can be manipulated easily. V_2O_5 has been reported to be able to significantly improve the current efficiency of Organic Field-effect Transistor (OFET) and Organic Light Emitting Diode (OLED)[21]. It has many applications in electro chromic devices, sensors, catalysts and lithium batteries.

The present work attempts to synthesis of polyaniline (PANI) using oxidation polymerization process in aqueous medium and PANI/V₂O₅polymer composites at three different weight percentages (20, 30 and 40 wt %) of V₂O₅ in PANI. DC conductivity of PANI and PANI/V₂O₅havebeen determined. The PANI and PANI/V₂O₅ polymer composites have been characterized by X-ray diffraction (XRD) and UV-Visible (UV-Vis) spectrophotometry. Fourier Transform Infrared Spectroscopy (FTIR) analysis of PANI and PANI/V₂O₅ composites havebeen carried out to observe the structural changes with increasing weight percentage in polymeric chain. Surface morphology of undoped PANI and PANI/V₂O₅ polymer composites has been carried out using SEM.

2. Experimental

Analytical reagent (AR) chemicals have been used. Polyaniline (PANI) and Polyanilinevanadium pentoxide (PANI/V₂O₅) composites have been synthesized bypolymerization technique using oxidant ammonium persulphate[$(NH_4)_2 S_2O_8$] in aqueous medium. In this process 0.1 mole of aniline was dissolved in 1 mole of HCl acid. Further, 0.1 mole of ammonium persulphate $[(NH_4)_2 S_2O_8]$ was added in the obtained solution. It was stirred continuously for 5–6 hrs at 2–6 °C temperature. Once the aniline get dissolved in (NH₄) S₂O₈) solution, the colour of the solution becomes green. Thus polymerization reaction get started. The mixture of oxide and PANI were taken out and washed out in distilled water. Thus obtained precipitates were put in oven for 22 - 24 hours to get homogeneity. The homogenous precipitates were washed in tetra hydro furan to remove the last traces of unreacted PANI. The oxide in varying weight percentages (20, 30 and 40 wt %) was added in water and added on polyaniline (PANI) solution and stirred continuously so that vanadium pentaoxide (V_2O_5) can be dropped in the solution. Then $(PANI/V_2O_5)$ composites were filtered out. Now these composites were dried in oven for almost 24 hrs. After this these composites were undergone vacuum dried at 65-75°C temperature for 1-2 hrs. The characterization of obtained composites have been carried out using XRD,SEM,FTIR and UV-Vis.

The bulk samples of polymer composites PANI/V₂O₅ were grinned in order to get in powder form and then compressed at a pressure of about 6.5 to nn to make pellets. The dc conductivity of pellets composites have been measured using two-probe technique method at temperature lies between 250–500⁰K. Inside metallic sample holder, between the electrodes made up of steel, the pellets of PANI and PANI/V₂O₅ were mounted then dc voltage 1.5 V applied across electrodes. The corresponding current was determined using Keithley Electrometer Model 6157A and the corresponding temperature with a copper–constant thermo-couple[21, 22].

X-ray diffraction (XRD) analysis of PANI/V₂O₅ composites polymers was carried out through Panalytical (PW 3710) X-ray diffractometer instrument. The composites were analysed in diffraction angle range of $0-90^{\circ}$ with scan speed of 0.2° /sec. Ultra-violet Visible (UV–Vis) Spectroscopy of composites have been carried out using Camspec M550 UV–Vis

Spectrophotometer. The FTIR of composites polymers have been carried out by PerkinElmer FTIR spectrometer in frequency range300 - 5000 cm⁻¹. SEM was carried out to study the morphology of the polymer composites.

3. Results and discussion

3.1. DC conductivity

The dc conductivity derives from the charge carriers flowing into the π -electronic system by process of doping [23]. DC conductivity (σ_{dc}) of polymer composites PANI/V₂O₅ has been carried out at a constant 1.5 V dc voltage and at temperature lying between 250 -500⁰K. The temperature dependent conductivity is represented by the relation given below [24, 25]

$$\sigma_{dc} = \sigma_0 \exp\left(-\Delta Ea/kT\right) \tag{1}$$

or,

$$\ln\sigma_{\rm dc} = -\Delta Ea/kT + \ln\sigma_0 \tag{2}$$

Here ΔEa is called activation energy. Kand σ_0 are known as Boltzmann constant and preexponential factor and respectively. This is Arrhenius type equation. Temperature dependent electrical conductivity of composite polymers at three different weight percentages (20, 30 and 40 wt %) of V₂O₅ are shown in Fig. 1.



Fig.1 Graph between 1000/T (K^{-1}) versus $ln\sigma_{dc}(ohm^{-1}cm^{-1})$ of PANI/ V_2O_5 composites at three different weight percentages (20, 30 and 40 wt %) of V_2O_5 .

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The plots between 1000/T (K⁻¹) versus $\ln\sigma_{dc}(ohm^{-1}cm^{-1})$ give straight line and slopes of these graphs give activation energy (ΔEa) are. This exhibits that conduction mechanism have taken place in the doped PANI samples ie PANI/ V_2O_5 . Doping with V_2O_5 in PANI inserts charge carriers in electronic structure of PANI/ V_2O_5 . The interaction between electron with nuclei results in carrier delocalization in polymeric chain. Therefore, doping with V2O5 introduces charge transfer and counter ion. It also controls the Fermi energy. The carrier concentration increases and therefore charge carriers that lead to increase in conductivity of the composite polymers. As the slope of the straight line increases with increasing weight percentage of V_2O_5 upto 30 wt% and then increases at 40 wt %. Therefore, the corresponding conductivity (σ_{dc}) of the and the activation energy (ΔEa) of PANI/ V₂O₅ increases up to 30 wt % and then starts decreasing at 40 weight % of V₂O_{5.} The charge carriers are self-localized at lower doping levels and therefore they form nonlinear configurations. Due to higher value of inter-chain transfer integrals, charge transportation may be along the conjugated chains as a result of inter-chain hopping [25-27]. The wave functions are delocalized along the polymeric chain over several lattice constants if the polymer composites are heavily doped (40 weight %). Because of degenerate ground states, dominant charge carriers in ployaniline (PANI) are bipolarons and polarons. Once PANI was doped with vanadium pentaoxide (V_2O_5) , the charge carriers formed the nonlinear configurations, thus not bringing any substantial change in the conductivity. The nonlinear formation in PANI/ V₂O₅ occurs more in heavy doping (40 wt % V₂O₅)which can be considered a reason for it to exhibit lesser conductivity than 20 wt % and 30 wt % doped polymer. The variation of electrical conductivity (σ_{dc}) and corresponding activation energy (ΔEa) with increasing concentration of V_2O_5 are shown in Fig. 2.



Fig.2. Plot of electrical conductivity $ln \sigma_{dc}$ and activation energy (ΔEa) at different weight % of V_2O_5 .

The above figure exhibits that activation energy (ΔEa) initially increases with increasing dopant concentration. This may occur due of increment in carrier concentration and the possible change in Fermi energy. The increase in ΔEa may not be necessarily due to conductivity mechanism taking place in extended states far above mobility edge or by the process of hopping in localized states. This can be explained on the basis of Davis and Mott Model which suggests that pre- exponential factor (σ_0) in extended band must be greater by two or three orders to that of conduction in localized band [24]. In this case the value of σ_0 is of the order of 10^3 - 10^4 ohm⁻¹ cm⁻¹ which exhibits that conduction occurs due to excitation of charge carriers into extended state. Another reason for this conduction to take place is process of hopping because of presence of wider localized states near Fermi level. Thus the conduction through extended state does not occur. The observed values of activation energy(ΔEa), pre exponential factor (σ_0) and dc conductivity (σ_{dc}) are given in Table 1.

Sample	$\sigma_{\rm dc}(\Omega^{-1}~{\rm cm}^{-1})$	$\sigma_0 (\Omega^{-1} \mathrm{cm}^{-1})$	$\Delta Ea (eV)$
	1)		
Undoped	3.21×10 ⁻⁹	2.39×10 ⁻⁶	23.0×10 ⁻²
PANI			
PANI/V ₂ O ₅	6.37×10 ⁻⁸	2.01×10^{-1}	21.1×10 ⁻²
at 20 wt %			
PANI/V ₂ O ₅	2.13×10 ⁻⁶	1.12×10^{-4}	19.2×10 ⁻²
at 30 wt %			
PANI/V ₂ O ₅ at 40 wt %	8.27×10 ⁻⁷	4.16×10 ⁻⁴	43.2×10 ⁻²

Table 1.Values of dc conductivity (σ_{dc}) pre exponential factor (σ_o) and activation energy (ΔEa) with increasing concentration of V_2O_5 in PANI.

3.2. UV-Visible and dielectric studies

In UV-Vis absorption spectrum, the optical band gap (E_g) can be determined by using Tauc's relation [26,27] which is given as:

$$\alpha h \nu = A \left(h \nu - E_g \right)^n \tag{3}$$

where A is a constant, called band tailing parameter and E_g is called optical band gap. The index 'n' is associated with the type of transition which has values 1/2 and 2 for direct and indirect transitions respectively. In present study, the transition taking place is indirect.

The absorption coefficient (α) can be determined using the relation given below:

$$\alpha$$
 = optical density (O.D.) /thickness of the film (4)

and the value of extinction coefficient (k) can be written as

$$\mathbf{k} = \alpha \lambda / 4\pi, \tag{5}$$

where λ is incident photon's wavelength.

The optical band gap (E_g) of undoped (PANI) and doped (PANI/V₂O₅) can be measured from the graph between (α hv)^{1/2} versus incident energy (hv) shown in Fig. 3 [28,29].



Fig.3.Graph of $(\alpha hv)^{1/2}$ versus incident energy (hv) at varying weight % of V₂O₅.

The slopes of graph give the optical energy (band gap Eg). From the above observations it is found that E increases with increasing weight percentage of V_2O_5 . The observed values of Eg and k at different V_2O_5 weight percent are given in Table 2. The absorption spectrum depends on the atomic short range order and defects associated with them. The optical energy of composite polymers increases with incorporation of V_2O_5 in PANI which may occur due to increase of disorderness in the system and consequently density of defect states decreases. Therefore, it may be concluded that polyaniline doped with V_2O_5 has tremendous impact on the optical parameters of PANI. Since indirect transition takes place, therefore the values of activation energy (electronic band gap) and optical energy differ in optical study. This type of transition is a two-step process in which an electron absorbs photon (hu) and phonon as well. The photon supplies the minimum energy required to make transition and the phonon imparts momentum. Since the electronic band gap(activation energy) is the minimum energy required to excite the electrons from valence band to conduction band therefore the electronic band gap has values less than the optical energy (band gap) [27]. The UV-Vis absorption spectrum in wavelength 500-1100 nm is given in Fig. 4.



Fig. 4.Graph between wavelengthan reflectance at different weight % of V_2O_5 .

From the above UV-Vis absorption spectrum, the dielectric constant (ϵ '), dielectric loss (ϵ '')and refractive index (n) have been measured. The values of refractive index (n) has been determined by using the theory of reflectivity of light. According to this theory, the reflectance of light can be written in terms of Fresnel's coefficient. Further the reflectivity in terms of refractive index can be expressed as

$$\mathbf{R} = \left[(\mathbf{n} - 1)^2 + \mathbf{k}^2 \right] / \left[(\mathbf{n} + 1)^2 + \mathbf{k}^2 \right]$$
(6)

and $\alpha = 4\pi k/\lambda$, where λ is wavelength of the incident photon

The values of dielectric constant (ϵ ') and dielectric loss (ϵ '') can be measured using relation given below [26]

$$\varepsilon' = n^2 - k^2 \tag{7}$$

and

$$\varepsilon'' = 2nk$$
 (8)



Fig. 5. (a). Graph between Refractive index versus photon energy (hv) at different weight % of V_2O_5 ; (b). Graph between dielectric constant (ε ') versus photon energy (hv) at different weight % of V_2O_5 ; (c) Graph between dielectric loss (ε '') versus photon energy (hv) at different weight % of V_2O_5

The refractive index (n), dielectric constant (ϵ ') and dielectric loss (ϵ '') versus photon energy (hu) have been plotted and it is shown in Fig. 5a, b and c.

Sample	E _g (eV)	٤'	8"	n
PANI/V ₂ O ₅ at 0% V ₂ O ₅	3.19	2.28×10^4	7.57	8.34
PANI/V ₂ O ₅ at 20% V ₂ O ₅	3.41	1.40×10 ⁵	56.45	54.78
PANI/V ₂ O ₅ at 30% V ₂ O ₅	3.27	1.40×10 ⁵	56.54	30.99
PANI/V ₂ O ₅ at 40% V ₂ O ₅	3.29	1.39×10 ⁵	56.34	32.39

Table 2.Values of optical band gap (E_s), real and imaginary parts of dielectric constants (ε' , ε'') and refractive index (n) at varying weight % of V_2O_5 at temperature 450 ⁰K and wavelength 620 nm.

It is evident from the Figs. 5(a), 5(b) & 5 (c) that refractive index (n) and dielectric constant(ϵ ') of PANI/V₂O₅compositesboth exponentially increases with the increasing incident energy (hu). The higher values of dielectric constant (ϵ ') and dielectric loss(ϵ ") are accounted for large content of oxide present in V₂O₅. Because of this the crstallinity increases with increasing oxide. This can be seen in XRD pattern of PANI/V₂O₅ shown in Figure 7. This results in increasing interfacial interactions between polyaniline and vanadium pentaoxidethat may lead to

maximum polarization of space charge Because of static dielectric permittivity, the dielectric constant is produced which may be written as

$$\varepsilon_s = C_{gb} / C_0 \tag{9}$$

where, C_{eb} is called grain boundary capacitance. Dielectric constant depends on C_{eb} . The values of conductivity increases with the increasing concentration grain of vanadium pentaoxideinpolyaniline. The increase in charge carrier concentration results in increase grain boundary capacitance (C_{eb}) . The size of the grains also increases with increasing concentration of V₂O₅.Therefore the increment of grain size and grain boundary capacitance results in increase in dielectric constant. When concentration of V₂O₅ in PANI is below 40% then they exhibits decrease in dielectric constant and conductivity both due to poor interface between the polymers. Also they exhibits no change in value of dielectric constant in visible region. The change is only exhibited in Ultra-Violet region[30].

3.3. FTIR analysis

In FTIR spectrum, change in the functional groups are observed. There are two types of regions in this spectrum, one is called finger print region(0 to 1000 cm^{-1}) and another one is called functional group region (1000 cm^{-1} to 4500 cm^{-1}). Fig. 6shows FTIR spectrum of PANI/V₂O₅ at different weight % of V₂O₅ in PANI.



Fig. 6. FTIR patterns of PANI/ V₂O₅ at different weight % of V₂O₅.

From the above bands we can observe characteristics peaks of nitrogen quinoid ring (Q) in the range of 1572–1592 cm⁻¹ with decreasing broadening at increasing concentration of V_2O_5 [31]. On the basis of vibration theory of PANI and its derivatives we can say that the position of this band indicates the degree of oxidation in polymer PANI/ V_2O_5 . This band appears because of superposition of vibrations of C- C stretching in benzene ring (B). The observed characteristic peaks around 1455 cm⁻¹ and 1552 cm⁻¹ can be attributed to the stretching in the vibrations of N B Nand N Q N rings respectively. The band observed at 1486 cm⁻¹ is due to C - H stretching of secondary aromatic amine and the band found at 1091 cm⁻¹ may be attributed to the characteristic peak of bond B–NH–B or B– NH–Q bending in the plane modes.

The substituted benzene rings corresponding to deformations of C - H are allocated to band at 785 cm⁻¹. These are in good agreement with Bormashenko et al [31]. With the increasing

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weight % of V_2O_5 in PANI, the alkynes are formed corresponding to the 1678–1686 cm⁻¹ which results in C = C stretch. The re-orientation of molecular bonds are required to make alkyne formation. It requires huge amount of energy which is supplied during breaking of C – H and C – C bonds. To trigger alkyne formation, excitation energy should be greater than the threshold energy. Since in our study we get greater value of excitation energy than the threshold therefore, alkyne formation takes place and consequently π electrons are delocalized which results in making of triple bonds.

The comparison between doped PANI/ V_2O_5 and undoped PANI spectrum exhibits shift in Quinoid peaks from 1089 cm⁻¹ to 1071 cm⁻¹ and 1482 cm⁻¹ to 1474 cm⁻¹. This shift in peaks of doped PANI/ V_2O_5 in FTIR study indicates the formation of more ions during doping. The alkyne formation started taking place beyond doping of 20 % and above [32]. This shows that the triple bonds formations affect the semi-conducting properties of the doped PANI / V_2O_5 polymer. Hence the semi-conducting nature of the doped PANI / V_2O_5 polymers increases despite alkyne formation.

3.4. XRD analysis

XRD patterns of undoped PANI exhibits the amorphous nature as there is no sharp peak observed [34, 35] where as the XRD patterns of V_2O_5 doped PANI confirms the semi-crystalline nature of doped samples as shown in Fig.7.



Fig. 7. The XRD patterns of PANI $/V_2O_5$ at different weight % of V_2O_5 .

In undoped PANI (0% of V_2O_5) sample, the amorphous hump is found at 23^0 - 26^0 which gets shifted towards lower angle at $13-17^0$ in V_2O_5 doped PANI samples. In 20 weight % of V_2O_5 doped samples, three other small peaks appears near 15^0 (200), 20^0 (001) and at 26^0 (110), which confirm the presence of V_2O_5 in PANI. These three peaks are continuously appearing up to 40 weight % of V_2O_5 in PANI. Thus it is found that V_2O_5 dopant interacts well with PANI which results in continuously increasing conductivity and crystallinity of the composites PANI/ V_2O_5 . This increasing crystallinity of the composites PANI/ V_2O_5 may be attributed to polymer chain alignment or because of making of single or multiple helices [36, 37].

3.5. SEM analysis

The Scattering Electron Microscope (SEM) study of PANI/ V_2O_5 helps us to analyse the effect on morphology of PANI when it is doping with V_2O_5 . In the current analysis it is found that increase in weight percentage of dopant V_2O_5 in PANI exhibits the change in surface morphology of composite polymers PANI/ V_2O_5 shown in Fig.8 [38].

Further V_2O_5 appears to be dispersed in composite polymer PANI/ V_2O_5 as shown in Fig. 8 (b). With the higher concentration of dopant V_2O_5 in PANI, the clusters are formed as shown in Fig. 8(c)which results in higher value of conductivity. With the increasing weight % of V_2O_5 in PANI upto40%, the particle size appears to get reduced as shown in Fig.8 (d) which may be attributed to breaking up of clusters. Therefore it is concluded that higher concentration of V_2O_5 in PANI does not necessarily increase the size of the particles.



Fig. 8. SEM Images of PANI/V2O5 composite polymers at different weight % of V2O5.

4. Conclusions

In our study, polyaniline vanadium pentaoxide(PANI/ V_2O_5) composites at different weight percentage of V_2O_5 have been synthesized by oxidative polymerization technique using oxidant ammonium persulphate [(NH₄)₂ S₂O₈] in aqueous medium. It is observed that doping with V_2O_5 in PANI causes change in the structural, optical and electrical properties of PANI. From dc conductivity analysis it is found that conductivity of PANI/ V_2O_5 polymer composites increases with increasing dopant V_2O_5 concentration in PANI up to three orders of magnitude which indicates the semi-conducting nature of PANI/ V_2O_5 It may be suggested that conduction takes place because of present of large range of localized state in polymer composites PANI/ V_2O_5 .XRD analysis of PANI/ V_2O_5 at different weight percentage shows the increase in crystallinity with increasing concentration of V_2O_5 .

FTIR spectra confirm the presence of V_2O_5 in polymer chain and exhibits the structural changes in PANI with V_2O_5 doping. UV-Visible analysis shows the presence of indirect bandgap within the polymer composites which increases with increasing weight % of V_2O_5 . These PANI/ V_2O_5 polymer composites show the large values of real and imaginary parts of dielectric constant and dielectric loss with doping. SEM analysis polymer composites exhibits the change in surface morphology of PANI doped with V_2O_5 at different weight percent.

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