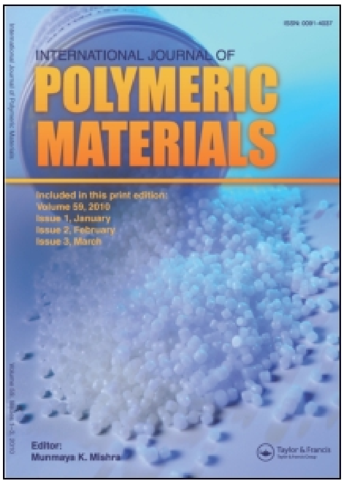

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Structural, Electrical and Optical Characterization of Pure and Doped Poly (Vinyl Alcohol) (PVA) Polymer Electrolyte Films

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Structural, Electrical and Optical Characterization of Pure and Doped Poly (Vinyl Alcohol) (PVA) Polymer Electrolyte Films

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A sodium ion conducting polymer electrolyte based on Poly (Vinyl Alcohol) (PVA) complexed with Sodium Iodide (NaI) was prepared using solution cast technique. The structural properties of composite PVA polymer electrolyte films were examined by XRD. The XRD results revealed that the amorphous domains of PVA polymer matrix increased in size with the increase of NaI salt concentration. The variation in film morphology was examined by scanning electron microscopy. FT-IR spectra studies for pure PVA and complexed films revealed the vibrational changes that occurred due to the effect of dopant salt in the polymer. DC conductivity was measured in the temperature range of 303–373° K and the conductivity was found to increase with the increase of dopant concentration as well as temperature. Optical absorption studies were made in the wavelength range 200–600 nm. The absorption edge, direct band gap, and indirect band gap values were evaluated.

Keywords: FTIR, ionic conductivity, optical band gaps, polymer electrolyte XRD, SEM

INTRODUCTION

Polymer electrolytes have a number of advantages over the conventional liquid electrolytes, such as longer shelf life, freedom from corrosive liquid leakage, easy fabrication in a wide variety of shapes, and so on [1]. Increasing attention has been focused on polymer electrolytes in the past three decades, especially on poly(ethylene oxide) (PEO)-based

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electrolytes in the development of polymer Li-ion batteries [2]. It has been realized that cations are solvated with polar groups on the polymer chains in polymer salt complexes whereas anions usually interact weakly with the aprotic host [3]. In polymer electrolytes, fast ion transport takes place in amorphous regions, where the ionic conductivity is two or three orders of magnitude higher than that of the crystalline domain [4].

Although PEO is one of the best "polymer solvents" for a variety of metal salts, there is a liquid–solid coexistence regime in the phase diagram of many PEO-metal salt systems above ambient temperatures [5]. Efforts have been made to improve the performance of the existing electrolytes and find new polymer electrolytes with better electrochemical and mechanical properties. Vargas et al. [6] investigated poly(Vinyl Alcohol) (PVA) for the phase behavior. Fritz and Breitsmer [7] developed ionically conducting polyelectrolytes based on PVA due to its bio-compatibility and wide spread use in biomedical fields [8]. Because of its superior mechanical properties and better ionic conduction, it has some technological advantages in electrochromic devices and fuel cells, etc. [9]. Hydrophilicity of PVA is an advantage for its applications, and also a limiting factor in its characterization because its molecules are prone to aggregate through hydrogen bonding due to its polyhydroxygroups [10].

A few attempts were made to develop electrolytes based on Sodium complexed films. Apart from the scientific interest, the use of Sodium has several advantages over their lithium counterparts; Sodium is available in abundance at a cheaper cost than lithium. It may be possible to obtain solid electrolytes of sufficiently high conductivity because sodium does not form any alloy with Aluminum, making it possible to use this metal as current collector instead of the costlier and heavier nickel. Furthermore, the softness of these materials makes it easier to achieve and maintain contact with other components in the battery. Investigations have also been made on sodium ion conducting polymer electrolytes based on PEO, PPO, and MEEP complexed with NaI, $NaClO_4$, NaSCN, and $NaCF_3SO_3$ [11–13]. In the present investigation, an attempt has been made to characterize the polymer electrolytes based on poly(Vinyl Alcohol) (PVA) complexed with Sodium Iodide (NaI) at different weight percentages to evaluate their potential in electro chemical cells.

EXPERIMENTAL

Films of pure PVA and various compositions of complexed films of PVA with NaI salt were prepared in weight percent ratios (90:10), (80:20), and (70:30) by solution cast technique using triple distilled water as solvent. The solutions were stirred for 10–12 h to get a homogenous mixture and then cast onto polypropylene dishes and allowed to evaporate slowly at room temperature. The final product was vacuum dried thoroughly.

The XRD patterns of the films were recorded with a HLG4/B-PC X-ray diffractometer with CuKα radiation and graphite monochromotor at room temperature. The surface morphology of the polymer films have been observed using JEOL JSM 840A Scanning Electron microscope. The samples were gold coated using the sputter coater Polaron SC 7610) at 10 mA current under 10^{-2} torr vacuum for 6 min prior to the imaging. FT-IR spectra of these films were recorded using EO-SXB IR spectrometer with a resolution of 4 cm^{-1}. The measurements were taken over a wave number range of 400–4000 cm^{-1}. DC conductivity measurements were measured using in-house built instrument, in the temperature range 303–373 K, with Keithley programmable electrometer (model 617). Optical absorption spectra were recorded at room temperature in the wavelength range 200–600 nm using Shimadzu UV-VIS-NIR (model-UV-3100) spectrophotometer.

RESULTS AND DISCUSSION

XRD Analysis

The X-ray diffraction pattern of pure PVA, Sodium Iodide salt, and PVA complexed with NaI salt are shown in Figure 1. It is clear from the figure that the pure PVA shows a characteristic peak for an orthorhombic lattice centered at 20° indicating its semi crystalline nature [14–15]. This peak becomes less intense as the NaI content is increased. This could be due to the disruption of the PVA crystalline structure by NaI. No peaks pertaining Sodium Iodide salt appeared in the complexes, which indicate the complete dissolution of salt in the polymer matrices.

The diffraction peaks are less intense in NaI complexed PVA films when compared to the pure PVA films. This shows a decrease in the degree of crystallinity of the polymer after the addition of NaI. No sharp peaks were observed for higher concentrations of NaI salt in the polymer, suggesting the dominant presence of amorphous phase [16]. This amorphous nature results in greater ionic diffusivity with high ionic conductivity, which can be obtained in amorphous polymers that have flexible backbone [17].

Morphological Studies

SEM is often used to study the compatibility between various components of the polymer electrolytes through the detection of phase

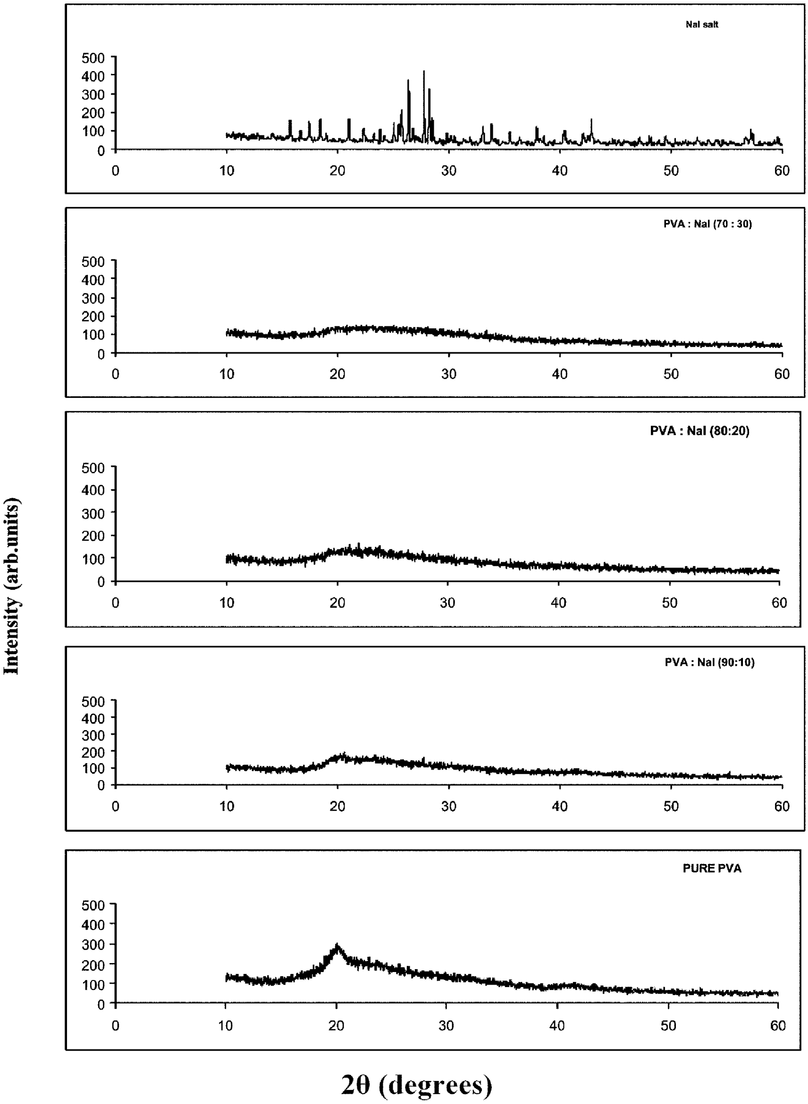

FIGURE 1 XRD patterns of pure PVA and complexes of different compositions weight percentage of NaI mentioned on the respective pattern.

separations and interfaces [18–19]. The compatibility between the polymer matrix and the inorganic fillers has great influence on the properties (mechanical, thermal, ionic conductivity) of the polymer electrolytes.

The morphology of the pure PVA and (PVA:NaI) (90:10), (80:20), and (70:30) polymer electrolytes, studied by SEM technique, is rather uniform but with different degrees of roughness (micrographs were submitted to the editor but not shown here). SEM of pure PVA films cast from aqueous solution exhibits no features attributable to any crystalline morphology. So the semicrystallinity of PVA discussed earlier is likely to be submicroscopic in nature. The increase in degree of roughness with increased NaI concentration indicates the segregation of the dopant in the host matrix. Therefore the morphological studies clearly show the phase segregation phenomenon in these complexed polymer electrolytes.

FTIR Analysis

The FTIR spectra for pure PVA, NaI complexed PVA of different compositions and NaI salt are shown in Figure 2. The following changes in the spectral features have been observed after comparing the spectrum of complexed PVA with that of pure PVA and NaI. The intermolecular hydrogen bonded O–H stretching frequency of PVA appearing in the range of $3528–3115\,\text{cm}^{-1}$ is shifted to $3587–3072\,\text{cm}^{-1}$, $3564–3125\,\text{cm}^{-1}$, and $3606–3129\,\text{cm}^{-1}$ in the 10%, 20%, and 30% salt complexed PVA films respectively. In addition to this, the C–H stretching of CH_2 exhibited at $2939\,\text{cm}^{-1}$ in pure PVA is shifted to 2942, 2947, and $2952\,\text{cm}^{-1}$, respectively. The C–H bending of CH_2 in pure PVA exhibited absorption at $1445\,\text{cm}^{-1}$, is shifted to $1462\,\text{cm}^{-1}$, $1457\,\text{cm}^{-1}$, and $1453\,\text{cm}^{-1}$ in the complexed films, respectively. Deformation is coupled to C–H wagging and gives raise to a peak at $1350\,\text{cm}^{-1}$ in pure PVA. It is shifted to $1331\,\text{cm}^{-1}$, $1334\,\text{cm}^{-1}$, and $1337\,\text{cm}^{-1}$ in the complexed films due to complexation of salt. C–C stretching occurring at $1235\,\text{cm}^{-1}$ in pure PVA is shifted to $1237\,\text{cm}^{-1}$, $1241\,\text{cm}^{-1}$, and $1245\,\text{cm}^{-1}$ in 10%, 20%, and 30% salt complexed films. The strong absorption peak at $1623\,\text{cm}^{-1}$ involving iodine group in NaI salt is shifted to $1648\,\text{cm}^{-1}$, $1644\,\text{cm}^{-1}$, and $1638\,\text{cm}^{-1}$, respectively, in the complexed films. All these changes in the FTIR spectra are clear indications for the complexation of PVA with NaI.

Electrical Properties

Conductivity of polymer electrolyte depends on the actual concentration of conducting species and their mobility. Figure 3 shows the variation of electrical conductivity as a function of temperature for pure PVA and for different compositions of NaI doped polymer electrolytes in the temperature range 303K–373K.

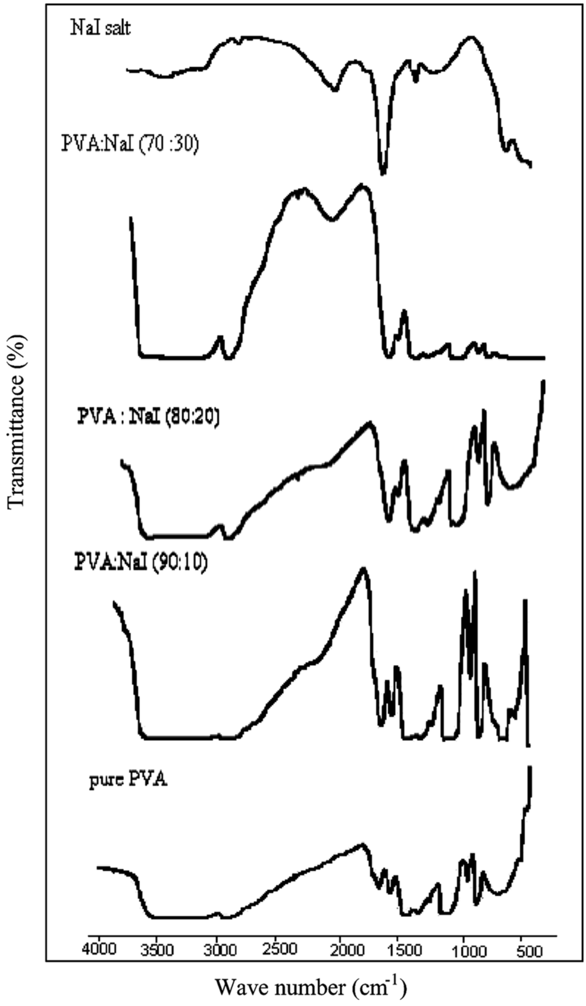

FIGURE 2 FTIR spectra of NaI complexed PVA polymer electrolyte films.

The conductivity (σ) varies with temperature (T) according to the equation

$$\sigma = \sigma_0 \exp(-E_a/kT)$$

where σ_0 is pre exponential factor, E_a is activation energy, k is Boltzman constant and T is absolute temperature.

The conductivity was found to increase with increasing temperature in pure PVA as well as all the compositions of polymer electrolytes. The

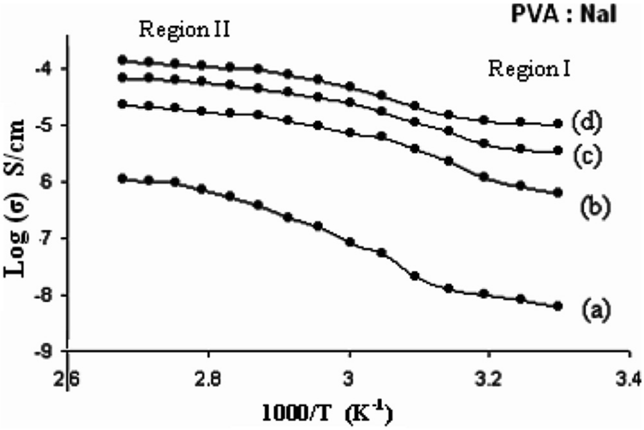

FIGURE 3 Temperature dependent conductivity of (a) pure PVA, (b) PVA:NaI (90:10), (c) PVA:NaI (80:20), and (d) PVA:NaI (70:30) polymer electrolyte films.

conductivity versus temperature follows Arrhenius behavior throughout, but with two regions having different activation energies. The conductivity values do not show any abrupt jump with temperature, which indicates that these electrolytes exhibit amorphous nature [20]. This type of behavior is observed in a number of PVA-based electrolyte systems [16,21].

The increase in conductivity with temperature can be linked to the decrease in viscosity and, thus, to an increased chain flexibility and mobility [22]. Because the conductivity–temperature data obey Arrhenius relationship, the nature of cation transport is quite similar to that occurring in ionic crystals, where ions jump into neighboring vacant sites and hence increase the ionic conductivity [23]. The existence of two regions in the conductivity–temperature plots and the increase in conductivity may be attributed to the transition from semi crystalline phase to amorphous phase. Due to this phase change the conductivity shows an increasing trend with temperature and this can be interpreted as hopping mechanism between coordinating sites, local structure relaxing and segmental motion of polymer [24]. As the amorphous region increases, however, the polymer chain acquires faster internal modes in which the bond rotations produce segmental motion. This in turn favors hopping inter-chain and intra-chain movements and the conductivity of the polymer thus becomes high. The activation energy (E_a) reflects a combination of defect formation and defect migration. This can be calculated from the log σ vs. 1000/T plots from Figure 3 and is given in Table 1. The low activation energy for

TABLE 1 Conductivity and Activation Energies (E_a) of PVA and (PVA:NaI) Polymer Electrolyte Films

Polymer electrolyte	Conductivity at 303 K (S/cm)	Activation energy (eV)	
		Region I	Region II
Pure PVA	9.73×10^{-9}	0.56	0.24
PVA:NaI (90:10)	9.46×10^{-7}	0.51	0.18
PVA:NaI (80:20)	5.95×10^{-6}	0.44	0.13
PVA:NaI (70:30)	1.02×10^{-5}	0.38	0.11

sodium ion transport is due to the completely amorphous nature of polymer electrolyte that facilitates the fast Na^+ ion motions in the polymer network. The amorphous nature also provides a bigger free volume in polymer electrolyte system with increase in temperature [20]. Figure 4 explains the variation of activation energy with NaI concentration. It is also observed that (PVA:NaI) (70:30) has the highest conductivity and lowest activation energy when compared to the other samples.

Optical Properties

The study of optical absorption gives information about the band structure. Insulators/semiconductors are generally classified into

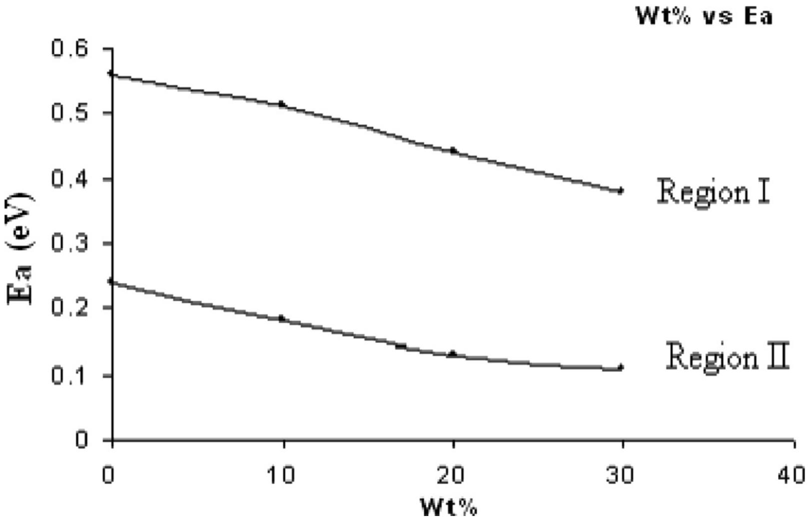

FIGURE 4 Activation energy with NaI weight percentage.

two types: (a) Direct band gap semiconductors and (b) Indirect band gap semiconductors. In direct band gap semiconductors, the top of the valence band and the bottom of the conduction band lie at the same zero crystal momentum (wave vector). If the bottom of conduction band does not correspond to zero crystal momentum, then it is called indirect band gap semiconductor. In indirect band gap semiconductor, the transition from valence band to conduction band should always be associated with a phonon of the right magnitude. Davis and Shalliday [25] reported that near fundamental band edge both direct and indirect transitions occur and can be observed by plotting $\alpha^{1/2}$ and α^2 as a function of energy $h\nu$.

The analysis of Thutupalli and Tomlin [26] is based on the following relationships

$$(h\nu\alpha n)^2 = C_1(h\nu - E_{gd})$$

$$(h\nu\alpha n)^{1/2} = C_2(h\nu - E_{gi})$$

for direct and indirect band semionductors/insulators respectively, where $h\nu$ is the photon energy, E_{gd} is the direct band gap, E_{gi} is the indirect band gap, n is the refractive index, α is the absorption coefficient, and C_1, C_2 are constants.

The absorption coefficient (α) was calculated from the absorbance (A). After correction for reflection, the absorption coefficient (α) was determined using the relation

$$\mathrm{I} = \mathrm{I_o}\exp(-\alpha \mathrm{x})$$

Hence

$$\alpha = \frac{2.303}{\mathrm{x}}\log\left(\frac{\mathrm{I}}{\mathrm{I_o}}\right) = \left(\frac{2.303}{\mathrm{x}}\right)A$$

where x is thickness of the sample.

To determine the nature and width of the bandgap α, $(\alpha h\nu)^2$ and $(\alpha \mathrm{h}\nu)^{1/2}$ were plotted as a function of photon energy (hν).

The position of the absorption edge was determined by extrapolating the linear portions of α vs. $h\nu$ curves (Figure 5) to zero absorption value. It is observed that the absorption edge for pure PVA lies at 5.8 eV whereas for 10, 20, and 30 wt%. NaI doped PVA films the absorption edge lies at 5.4 eV, 5.05 eV, and 4.95 eV, respectively.

When a direct band gap exists, the absorption coefficient has the following dependence on the energy of incident photon [25–26]

$$\alpha h\nu = C(h\nu - E_g)^{1/2}$$

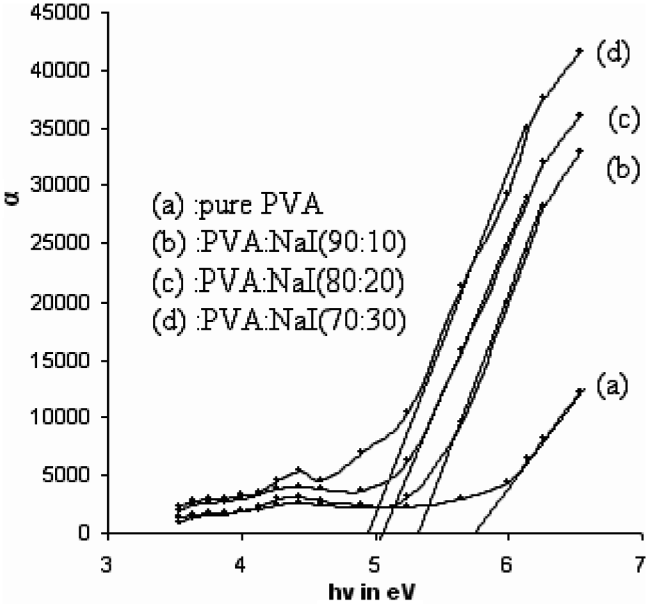

FIGURE 5 α vs. $h\nu$ (photon energy) plots of undoped PVA and NaI doped PVA films.

where E_g is the band gap, $C(= 4\pi\sigma_0/\mathrm{nc}\Delta\mathrm{E})$ is a constant dependent on the specimen structure, α is the absorption coefficient, ν is the frequency of incident light, and h is Planck's constant.

The direct band gap values were obtained by plotting $(\alpha h\nu)^2$ vs. $h\nu$ curves (Figure 6). For pure PVA, the optical band gap was observed to be 5.5 eV whereas for doped films the values were 5.2 eV, 5.0 eV, and 4.85 eV, respectively.

For indirect transitions, which require phonon assistance, the absorption coefficient has the following dependence on photon energy [25–26]

$$\alpha h\nu = A(h\nu - E_g + E_p)^2 + B(h\nu - E_g - E_p)^2$$

where E_p is the energy of the photon associated with the transition and A and B are constants depending on the band structure.

The indirect band gap values were obtained from the plots of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ as shown in Figure 7. For pure PVA, the indirect band lies at 4.9 eV whereas for the doped films its value lies at 4.75 eV, 4.60 eV, and 4.50 eV, respectively. All these values of absorption edge, Direct band gap and indirect band gap are tabulated in Table 2.

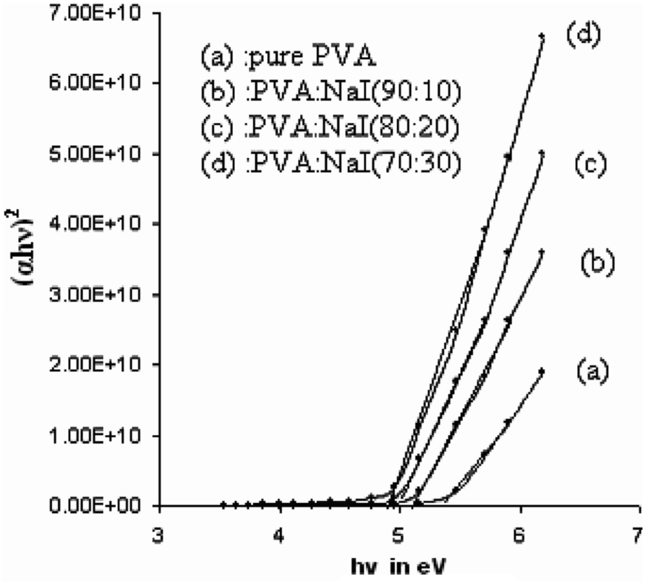

FIGURE 6 $(\alpha h\nu)^2$ vs. $h\nu$ (photon energy) plots of undoped PVA and NaI doped PVA films.

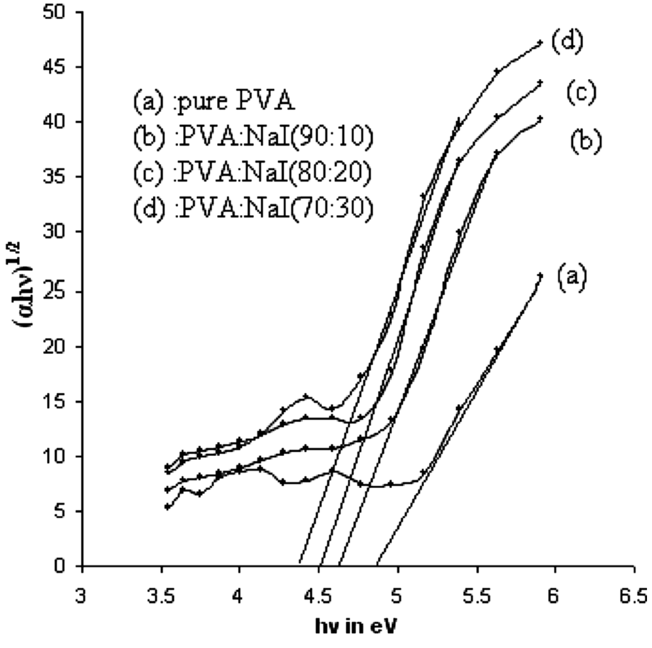

FIGURE 7 $(\alpha h\nu)^{1/2}$ vs. $h\nu$ (photon energy) plots of undoped PVA and NaI doped PVA films.

TABLE 2 Absorption Edge, Optical Band Gap (Both Direct and Indirect) of Undoped and NaI Doped PVA Polymer Electrolyte Films

Polymer electrolyte	Absorption edge (eV)	Band gap (eV)	
		Direct	Indirect
Pure PVA	5.80	5.40	4.90
PVA:NaI (90:10)	5.40	5.10	4.65
PVA:NaI (80:20)	5.05	5.00	4.50
PVA:NaI (70:30)	4.95	4.90	4.40

CONCLUSIONS

The complexation of the salt with the polymer is confirmed by X-ray diffraction (XRD) and FTIR studies. The surface morphology of Pure PVA and (PVA:NaI) polymer electrolyte films at different weight percentages is studied using Scanning Electron Microscopy. The increase in conductivity with increasing concentration of NaI is attributed to decrease in the degree of crysatllinity and increase in the amorphicity. The calculated activation energies in both regions show a decrease in the value with increase in the dopant concentration. Optical absorption edge and optical band gap (both direct and indirect) showed a decreasing trend with increased concentration of the dopant. The marked increase in electrical conductivity with increasing concentration of dopant salt makes it possible to consider this electrolyte system for electrochemical device applications.

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