

# Structural and Optical Studies of Pure and TICI Doped Poly (Vinyl Alcohol) Polymer Electrolyte Films

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**Abstract—** Poly (vinyl alcohol) (PVA) is a water-soluble amorphous/crystalline polymer that is widely used in protective coating, biomedical and optical materials, orbents and membranes. In the present investigation, an attempt has been made to characterize the polymer electrolytes based on Poly(vinyl alcohol) (PVA) complexed with thallium chloride(TICI) at different weight percentage ratio. Solid polymer electrolyte films based on poly(vinyl alcohol) complexed with TICI were prepared using solution cast technique. The structural properties of these films were examined by XRD. The XRD results show that the amorphous domains of PVA matrix increased in the composite films. In FTIR spectra, changes are noticed in the C-H stretching vibrational mode at  $2900\text{ cm}^{-1}$  of PVA along with disappearance of few bands and the appearance of new bands. Morphological studies show that as the percentage of TICI concentration exceeds that of host concentration, the TICI gets aggregates on the surface of the film, increasing the surface roughness. The optical parameters including the energy band gaps (direct and indirect) and absorption edge are investigated. It is observed that direct and indirect band gaps (Direct band gap from 5.12-4.80 eV and indirect band gap from 4.82-4.67 eV) show a decreasing trend on complexing.

**Keywords—** Poly vinyl alcohol, thallium chloride, XRD, FTIR, SEM, Optical absorption, Absorption edge, Energy gap.

## I. INTRODUCTION

Polymers have gained much experimental attention due to their unique properties, such as low density, ability to form intricate shapes, versatile electric properties and low manufacturing cost [1]. The physical properties of these polymer materials can be enhanced by incorporating filler into its matrix, because dispersed filler will improve various physical properties of the host polymer [2]. Poly (vinyl alcohol) (PVA) is a water-soluble amorphous/crystalline polymer that is widely used in protective coatings, biomedical and optical materials, orbents and membranes [3]. In the present investigation, an attempt has been made to characterize the polymer electrolytes based on Poly (vinyl alcohol) (PVA) complexed with thallium chloride (TICI) at different weight percentage ratio.

## II. MATERIALS AND METHOD

Films of pure PVA and various compositions of complexed films of PVA with TICI salt were prepared in weight percent ratios (80:20), (60:40) and (40:60) by solution cast technique using double distilled water as solvent. The solution was stirred for 12hrs to get homogeneous mixture and then casted on polypropylene dishes and kept in hot air oven for 12hrs at a temperature of  $40^{\circ}\text{C}$ . The films thus formed were stored in desiccators. The XRD pattern of the films was recorded with a 'X' pert x-ray diffractometer at room temperature. The FITR spectra of these films were recorded using Bruker tensor-27 spectrometer with a resolution of  $4\text{ cm}^{-1}$ . The measurements were taken over a wave number range  $400\text{-}4000\text{ cm}^{-1}$ . The surface morphology of these polymer electrolyte films have been observed using JEOL JSM 840A scanning electron microscope. The optical absorption spectra of the present samples were recorded at room temperature using Shimadzu UV-VIS-NIR in the wavelength range  $300\text{-}900\text{nm}$  with a spectral width of  $3\text{nm}$ .

### III. RESULTS AND DISCUSSION

#### A. XRD Analysis

The X-ray diffraction pattern of pure PVA, TICI salt and PVA complexed with TICI are shown in Fig.1. The XRD pattern of pure PVA reveal that a broad peak is appearing at scattering angle  $19^\circ < 2\theta < 20^\circ$ , corresponding to a 'd' spacing of 0.457 nm. The pure PVA characteristic peak becomes less intense as the TICI content in the composite is increased. This could be due to disruption of PVA crystalline structure by TICI. The diffraction peaks associated with PVA has disappeared in 80:20 composite and reappeared again when TICI present is increased in PVA films. This shows a decrease in the degree of crystallinity of the polymer after the addition of higher concentrations of TICI. The increase in the composition of TICI in PVA, results in increase in the amorphous nature of the composite films. Higher and broader peaks are obtained in the case of 60:40 compositions indicating greater accumulation of atoms at lattice sites, creating greater lattice distortion.

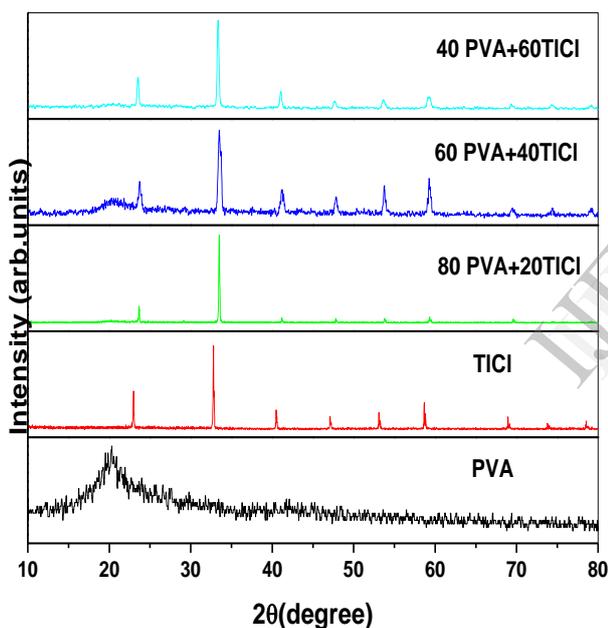


Fig. 1: XRD pattern of Pure PVA and PVA/TICI films.

#### B. FTIR

The FTIR spectra for pure PVA, TICI and PVA : TICI composites of different compositions are shown in the fig2. The following changes in the spectral features have been observed after comparing the spectrum of PVA : TICI composites. Changes are noticed in the C-H stretching vibrational mode at  $2900\text{ cm}^{-1}$  of PVA along with disappearance of few bands and the appearance of new bands. The inter molecular hydrogen bonded O-H stretching frequency of PVA appearing in the range of  $3590\text{ cm}^{-1}$  is shifted to  $3507\text{ cm}^{-1}$ . In PVA : TICI (60:40) composition and at higher compositions of PVA : TICI (40:60), this band

appears at  $3175\text{ cm}^{-1}$ . The C-H bonding of  $\text{CH}_2$  in pure PVA exhibits absorption at  $1474\text{ cm}^{-1}$  and is shifted to  $1418\text{ cm}^{-1}$  and  $1439\text{ cm}^{-1}$  in (80:20) and (40:60) compositions respectively.

#### C. SEM

Fig 3 (a,b,c) shows the SEM pictures of the surface of PVA : TICI(80:20); PVA : TICI (60:40)and PVA : TICI (40:60) films of different magnification respectively. These pictures show not many aggregates on the surface of the films. The increase in degree of roughness with increased TICI concentration, indicates, the presence of the dopant which is completely complexed with the polymer. As the percentage of TICI exceeds that of the host concentration the TICI gets aggregates on the surface of the film increasing the surface roughness.

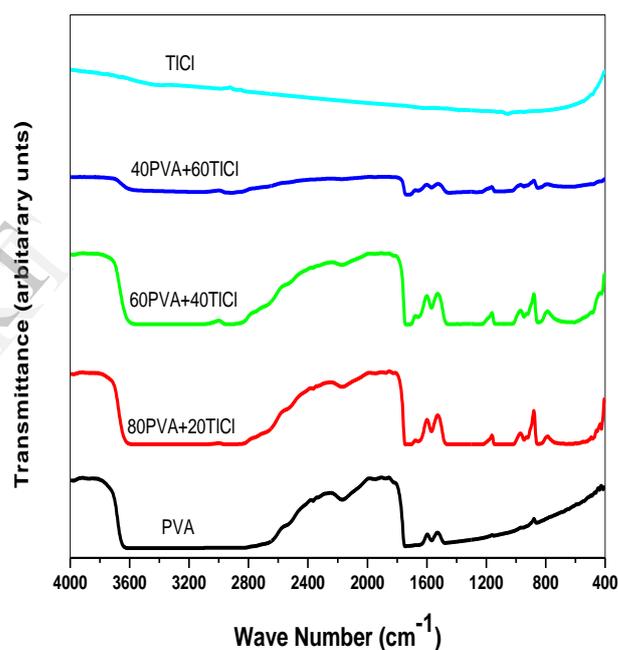


Fig. 2: FTIR spectra of Pure PVA, TICI salt and PVA/ TICI polymer films.

#### D. Optical Absorption Studies

The optical absorption (OA) studies are very interesting because it provides important information about the absorbance, transmittance and reflectance of the observed polymeric films [4]. The optical absorption and especially the absorption edge presents a useful method for the investigating optically induced transitions and for getting information about the band structure, the band tail and energy gap of the polymeric materials under consideration [5]. By studying the optical absorption spectrum, one can clearly identify its band structure [6-8]. The absorption coefficient  $\alpha(\nu)$  can be estimated from the optical absorption spectrum from the following equation [9].

$$\alpha(\nu) = 2.303 \times A/d \quad \dots\dots(1)$$

where 'd' is the film thickness in cm and 'A' is defined by  $\log(I/I_0)$  where  $I_0$  and  $I$  are the intensities of the incident and

transmitted beams respectively.

Regarding the optical transitions resulting from photons of energy  $h\nu > E_{opt}$ , the present optical data is studied according to the following relationship for near edge optical absorption [10].

$$\alpha(\nu)h\nu = B(h\nu - E_{opt})^r \quad \dots\dots\dots(2)$$

where ' $\alpha$ ' is the absorption coefficient,  $\nu$  is the frequency, B is the constant, h is the Planck's constant,  $E_{opt}$  is the optical energy band gap between the valence and conduction bands and r is the power that characterizes the transition process. Here 'r' takes the values of 1/2, 3/2, 2 and 3 for transitions designated as direct allowed, direct forbidden, indirect allowed and indirect forbidden respectively<sup>5</sup>. The determination of the

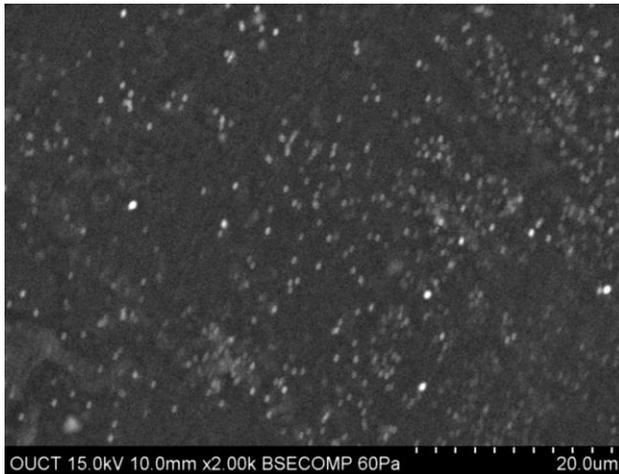


Fig 3 (a): SEM picture of PVA/TiCl (80:20)

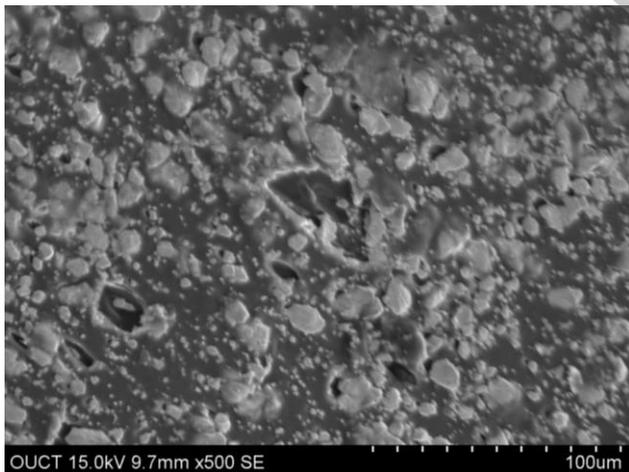


Fig 3 (b): SEM picture of PVA/TiCl (60:40)

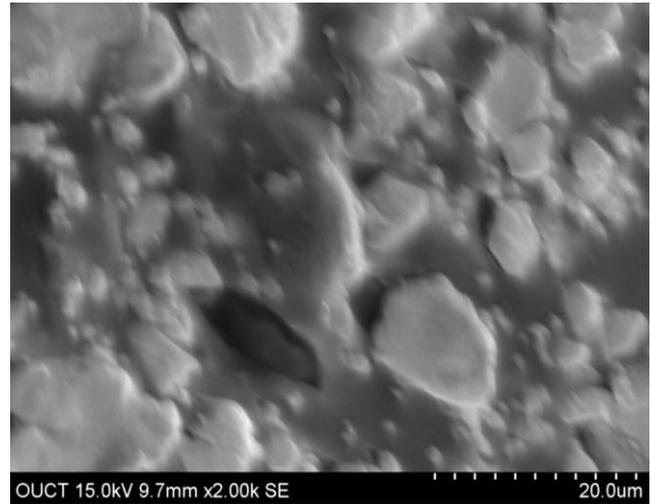


Fig 3(c): SEM picture of PVA/TiCl (40:60)

value of the optical energy band gap  $E_{opt}$  is done by plotting  $(\alpha h\nu)^{1/r}$  against  $h\nu$ .

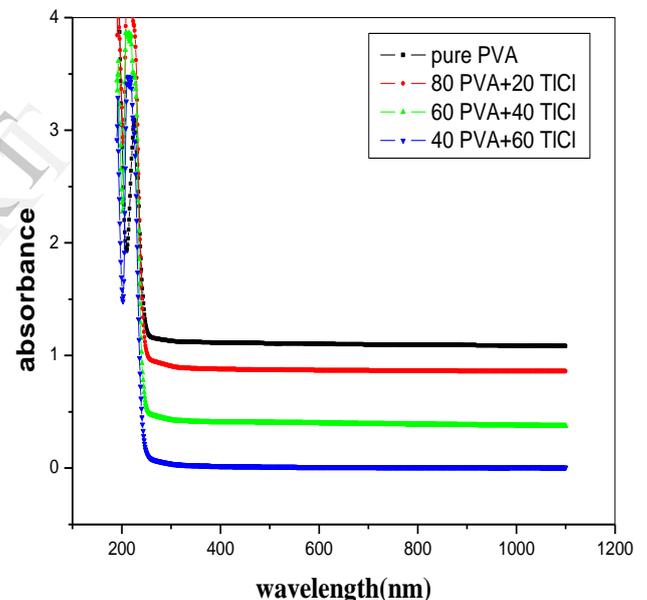
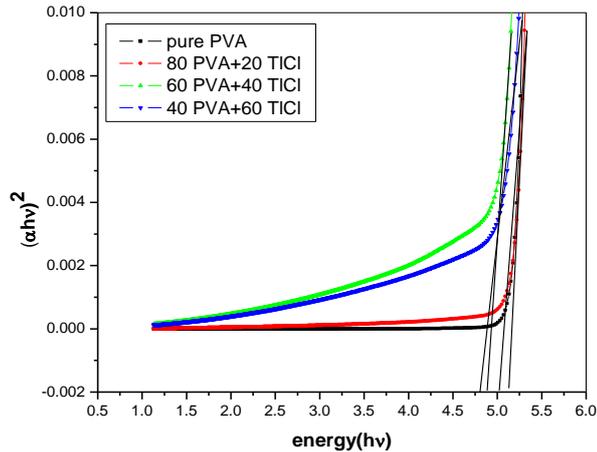
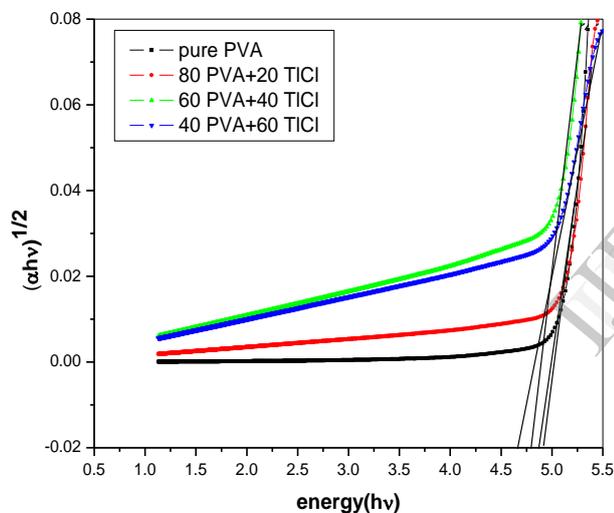


Fig. 4: OA spectra of Pure and TiCl complexed PVA films

The OA spectrum of pure PVA, PVA complexed with different concentrations of TiCl are shown in fig.4. The OA spectrum of pure PVA is characterized by an absorption peak at wavelength 283nm as well as unresolved shoulder at 330nm. No absorption peaks are noticed at higher wavelengths. The absorption peak at 283nm can be attributed to the absorption by simple carbonyl groups along the polymer chains. On the other hand shoulder can be assigned to the appearance of the  $-\text{CO}-(\text{CH}=\text{CH})_3$ -groups (5).

Fig. 5(a): Plot of  $(\alpha hv)^2$  versus photon energy (hv) for PVA:TICIFig. 5(b):  $(\alpha hv)^{1/2}$  versus photon energy (hv) for PVA:TICI

The addition of TICI to PVA matrix shows no substantial change in 283 nm peak but the shoulder which appeared in pure PVA has disappeared on addition of TICI. There is a decrease in UV absorption in the case of PVA/TICI films. The fundamental band edge, both direct and indirect transitions can be observed by plotting  $(\alpha hv)^2$  and  $(\alpha hv)^{1/2}$  versus photon energy hv. These plots are shown in fig 5. These plots present experimental data near the absorption edge and give a linear fit in the high energy range. The intercept on the energy axis on extrapolating the linear portion of the curves to zero absorption value may be interpreted as the value of band gap. The values of experimental band gaps of pure PVA and PVA complexed with TICI are listed in table 1.

TABLE 1: Absorption edge and Band Gap for PVA films complexed with TICI.

Polymer		Absorption edge (eV)	Band gap (eV)	
			Direct	Indirect
PVA	-	5.02 (247 nm)	5.12	4.82
PVA: TICI	90:10	4.94 (251 nm)	5.02	4.79
	80:20	4.77 (260 nm)	4.85	4.71
	70:30	4.65 (267 nm)	4.80	4.67

It is clearly evident from the table that both the direct and indirect band gap show decreasing trend on complexing. The decrease in optical band gap energies with increase in the TICI concentrations respectively explains the fact that the addition of TICI increases the disorder of these films. The increase in the degree of the disorder causes the band tail to increase. The decrease in band gap on increasing the TICI content in PVA matrix also indicates that there are charge transfer complexes which arise between the PVA and TICI molecule.

#### IV. CONCLUSIONS

The complexation of the salt with polymer is confirmed by XRD and FTIR studies. The morphological studies of pure PVA and (PVA:TICI) polymer electrolyte at different weight percentage is done using SEM. The optical band gap is evaluated and its dependence on filling was investigated. The decreasing trend of the optical band gap with increase in TICI concentration is attributed to the charge transfer complexes.

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