

## Optical and Dielectric Properties of Li<sup>+</sup> Ion Conducting Solid Polymer Electrolyte

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### ABSTRACT

Lithium ion (Li<sup>+</sup>) conducting solid polymer electrolytes have been prepared by solution casting method. The prepared films were characterized using different techniques. Fourier-transform infrared result revealed complexation of dopant with the polymer through interaction of Li<sup>+</sup> ion of LiCl with O-H and C=O group of polyvinyl alcohol (PVA). Ultraviolet-visible spectra show the change in optical properties such as optical energy band gap and activation energy with doping level. Dielectric studies revealed non-Debye nature of polymer electrolytes. Electrical properties revealed that the maximum dc conductivity of  $2.28 \times 10^{-4}$  S/cm has been obtained for 15 wt% LiCl doped PVA at room temperature.

**Key words:** Optical properties, Dielectric properties, Ion conductivity.

### 1. INTRODUCTION

In recent years, the solid polymer electrolytes (SPEs) have emerged as an excellent material for various electrochemical device applications. Among them, lithium ion (Li) conducting SPEs have received wide range of potential applications such as electrochemical cells, rechargeable batteries, and smart credit cards due to their advantages such as long lifetime, non-toxicity, lightweight, their flexibility and are capable to make better contact with electrode materials in different devices. SPE can be prepared by various methods and one of the easiest methods is the solution casting method. In this method, an inorganic salt (dopant) is dissolved in an appropriate polymer to obtain SPE; as a result, this SPE consists of cations and anions. Here, the interaction between functional groups of the polymer and dopant leads to the complex formation where the cations are solvated with polar groups of the polymer and anions are interact with the aprotic host. In these composite, the cations are migrated in the amorphous phase of the polymer and help in improving the ionic conductivity of polymer electrolytes. Since the ion transport in amorphous phase is more, many researchers have aimed to increase the amorphous phase of the host material [1-3]. Poly(vinyl alcohol) (PVA) is a semicrystalline polymer consist of crystalline and amorphous phases. When PVA is doped with an inorganic salt, the dopant interacts with O-H group of PVA either in the crystalline phase or amorphous phase and changes its properties. Usually change in the properties due to doping depends on chemical nature of the dopant and the kind of interaction between polymer and the dopant. Compared to other metal salts, lithium salts are fast-ion conducting salts due to their small ionic radius and their incorporation into crystalline or amorphous polymers, it changes the microstructural, electrical, and optical properties of polymers. In this paper, the modifications induced by LiCl in physical and chemical properties of PVA are investigated using various techniques.

### 2. EXPERIMENTAL

#### 2.1. Materials

PVA with molecular weight 1,25,000 and degree of saponification 86–89% obtained from CDH (P) Ltd, Mumbai, and LiCl was obtained from LOBA Chemie, Mumbai. Both these chemicals were used as received without any purification. Double-distilled water was used as solvent.

#### 2.2. Preparation of SPE

Pure and different concentrations of LiCl salt doped PVA films were prepared using solution casting method [2]. The concentrations of LiCl were varied from 0 wt% to 15 wt% using the relation,

$$M(\text{wt}\%) = \frac{m_d}{m_p + m_d} \times 100$$

Where,  $m_d$  and  $m_p$  are the mass of dopant and polymer, respectively. Thickness of the films was in the range of 100–120  $\mu\text{m}$ .

#### 2.3. Measurements

Fourier-transform infrared (FTIR) spectra were recorded using IR-Prestige 21 FTIR spectrophotometer SHIMADZU in the wavenumber range of 400–4000  $\text{cm}^{-1}$ . Ultraviolet (UV)-visible spectra of pure and LiCl doped PVA films were obtained using UV-visible 1800 spectrophotometer in the wavelength range of 190–900 nm. Electrical

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studies were carried out using Agilent 4294A precision impedance analyzer in the range of 40 Hz–5 MHz.

### 3. RESULTS AND DISCUSSION

#### 3.1. FTIR Analysis

Observed FTIR spectra of pure and LiCl doped PVA composite films are shown in Figure 1 and corresponding band assignments in Table 1. From Figure 1 and Table 1, it is clear that the O-H band of PVA ( $3425\text{ cm}^{-1}$ ) is shifted to lower wavenumber on doping indicates the interaction of dopant with polymer, particularly coordination interaction of  $\text{Li}^+$  with hydroxyl groups (O-H) of PVA through hydrogen bonding [2]. The C-H asymmetric and symmetric stretching bands at  $2928\text{ cm}^{-1}$  and  $2853\text{ cm}^{-1}$  of pure PVA are shifted along with decrease in intensity on doping. The C=O and C=C stretching bands of PVA are shifted in the composites with increase in their width. The corresponding bending and wagging of  $\text{CH}_2$  vibrations are also shifted. In 2.5 wt% LiCl doped PVA film, a new band is appeared around  $1262\text{ cm}^{-1}$  in the composites [3]. The band corresponding to C-H deformation at  $790\text{ cm}^{-1}$  is shifted to  $818\text{ cm}^{-1}$ . From the above results, it is clear that the appearance of new band and changes in the vibrational modes of the existing bands are due to the interaction of cation ( $\text{Li}^+$  ion) of salt LiCl with the hydroxyl group (O-H) of the polymer. Here, for composite films shift of IR bands to lower wavenumbers indicates increase of force constant which evidences for the specific interactions between dopant and polar groups of polymer. These interactions produced charge transfer complex (CTC) within the composite and altered the structure of the polymer.

#### 3.2. UV-visible Study

From the UV-visible spectra (Figure 2), it is clear that the absorption band appeared at 192 nm for pure PVA is assigned to  $\pi-\pi^*$  transitions and the band at 208 nm corresponds to the presence of unsaturated bonds (C=O and C=C) in the tail head of the polymer PVA [2]. For LiCl doped composite films, the absorbance increases along with shift in absorption bands as well as edges toward higher wavelength. These shifts indicate inter/intramolecular hydrogen bond formation between dopant and the polymer, leading to CTC formation. To understand, the other optical properties, such as optical energy band ( $E_g$ ), observed UV-visible spectra are translated into Tauc's plot (Figure 3a), and

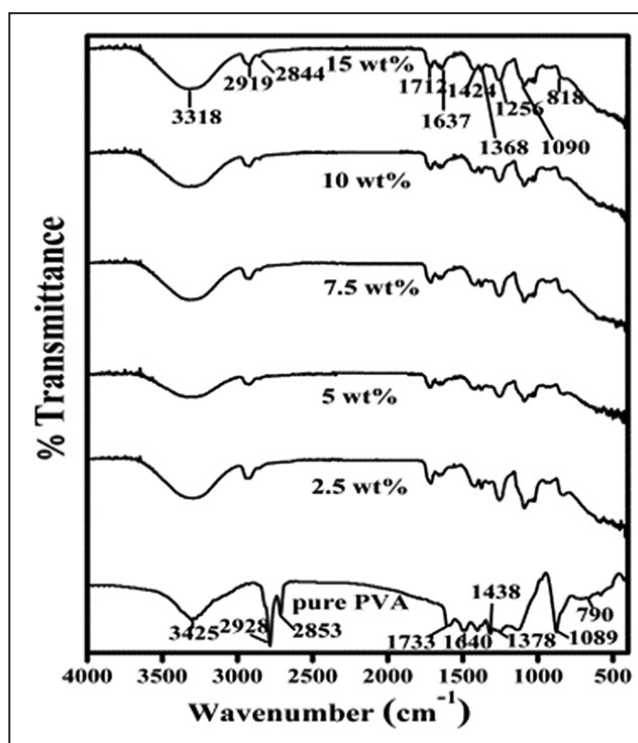
**Table 1:** FTIR peak assignments of pure PVA and 15 wt% LiCl doped PVA composite films.

Wavenumbers ( $\text{cm}^{-1}$ )		Peak assignments
Pure PVA	15 wt % LiCl doped PVA	
3425	3318	O-H stretching vibration
2928	2919	C-H asymmetric stretching vibration
2853	2844	C-H symmetric stretching vibration
1733	1712	C=O stretching vibration
1640	1637	C=C stretching vibration
1438	1424	Bending of $\text{CH}_2$ vibration
1378	1368	Wagging of $\text{CH}_2$ vibration
-	1256	C-H wagging
1089	1090	C-H stretching, O-H bending, C-O stretching
790	818	C-H deformation

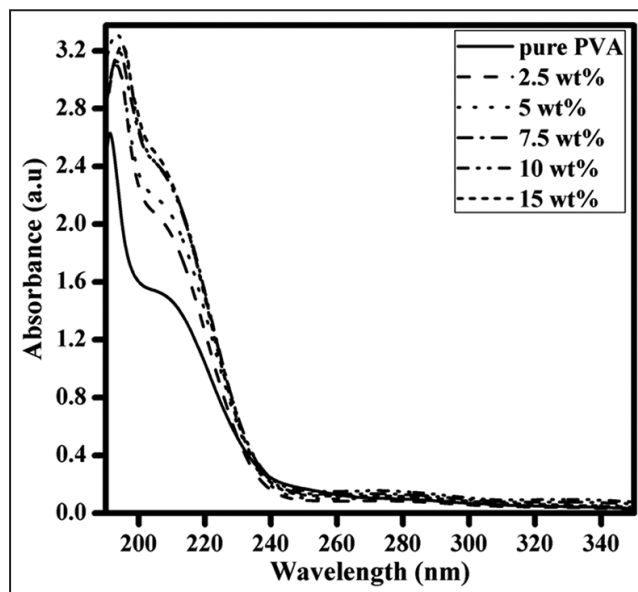
FTIR: Fourier-transform infrared, PVA: Poly (vinyl alcohol)

optical energy band gap is determined using the method explained in ref. 2. From Figure 3b and Table 2, it is clear that the optical energy band gap varies from 4.93 eV to 4.78 eV on doping.

This reduction of energy band gap with the increase of LiCl concentration can be understood using FTIR results. As seen in FTIR studies, when dopant interacts with the polymer, defects are formed within the polymer matrix in the form of polymer dopant complex. This complex helps in local cross-linking of chains within amorphous phase of the polymer. With increase of dopant concentration, these defects increase as a result energy band gap decreases.



**Figure 1:** Fourier-transform infrared spectra of pure and LiCl doped poly(vinyl alcohol) composites.



**Figure 2:** Ultraviolet-visible spectra of pure and LiCl doped poly(vinyl alcohol) composites.

To understand, this further another parameter called activation energy is estimated (Figure 3c) [2] and its variation is given in Figure 3d and Table 2. The result shows that the activation energy increases with doping level and supports the formation of defect states and complex within the polymer matrix.

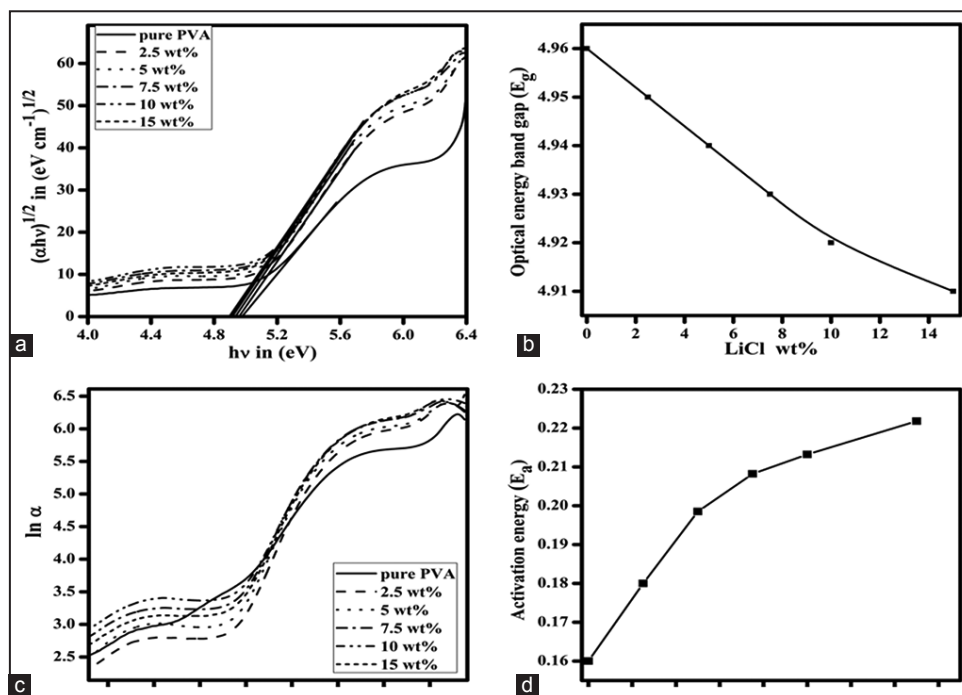
**3.3. Dielectric Studies**

To understand, polarization effect and conductivity behavior dielectric study were undertaken. Dielectric constant is calculated using the formula,

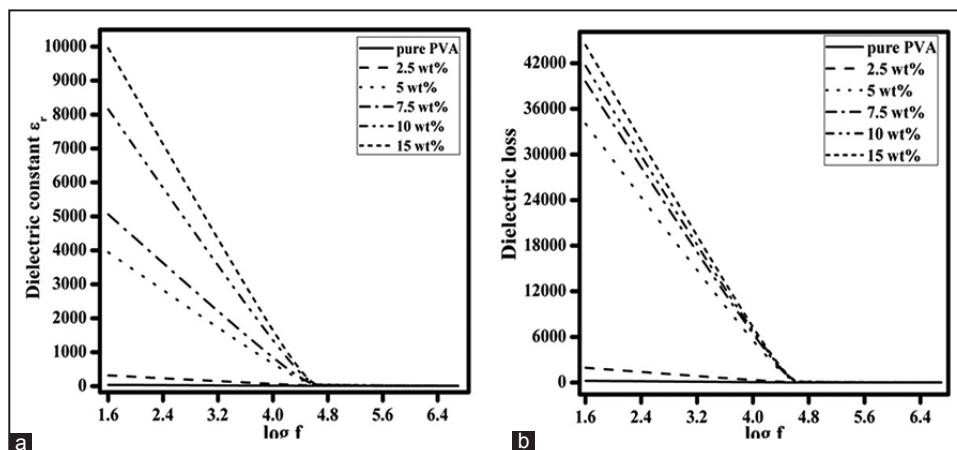
$$\epsilon_r = \frac{cd}{\epsilon_0 A}$$

Where, c is the capacitance, d is thickness of the sample,  $\epsilon_0$  represents permittivity in free space ( $8.85 \times 10^{-12} \text{ F m}^{-1}$ ), and A is area of the blocking electrodes. Figure 4a and b shows the observed variations of

dielectric parameters with frequency at room temperature. From the figure, it is clear that at lower frequencies the values of both dielectric constant and dielectric loss are high because of the fact that in this region the dipoles have sufficient time to orient themselves in the direction of the applied electric field [4]. In addition to this, due to the electronic polarization effect (space charge polarization), charge carriers are accumulated at the electrode and electrolyte interface. As frequency increases dielectric constant and loss decreases monotonically and attains a constant value. This change in dielectric property is due to the fact that as the frequency increases, space charge polarization drops and more number of ions cannot diffuse in the direction of the applied electric field as a result the charge carriers are less contributed to the dielectric property. This change confirms the non-Debye type behavior of polymer electrolytes [5]. Hence, due to insufficient time, the dipoles are unable to follow the field variation at higher frequencies.



**Figure 3:** Variation of (a)  $(\alpha h\nu)^{1/2}$  versus photon energy  $h\nu$ , (b) energy band gap with dopant concentration, (c)  $\ln \alpha$  versus  $h\nu$ , (d) activation energy with dopant concentration.

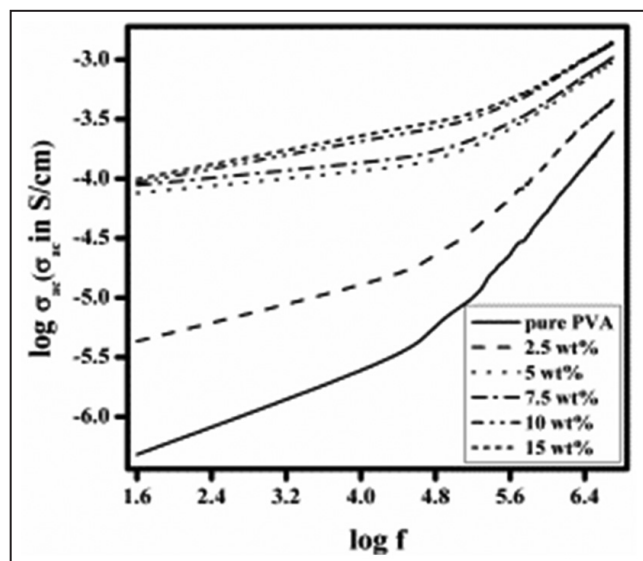


**Figure 4:** Variation of (a) dielectric constant with frequency for LiCl/poly(vinyl alcohol) (PVA) composites, (b) dielectric loss with frequency for LiCl/PVA composites.

**Table 2:** UV-visible absorbance, optical energy band gap, and optical activation energy values of pure and LiCl doped PVA composites.

Doping level M (wt%)	$\lambda_{\text{max}1}$ (nm)	$\lambda_{\text{max}2}$ (nm)	$\lambda_{\text{edge}1}$ (nm)	$\lambda_{\text{edge}2}$ (nm)	$E_g$ (eV)	$E_a$ (eV)
0	192	208	205	242	4.96	0.16
2.5	193	208	207	239	4.95	0.18
5	193	209	215	241	4.94	0.19
7.5	194	208	218	242	4.93	0.20
10	193	209	219	241	4.92	0.21
15	195	208	219	240	4.91	0.22

UV: Ultraviolet, PVA: Poly (vinyl alcohol)

**Figure 5:** Conductance plot of pure and LiCl/poly(vinyl alcohol) composites at room temperature.

### 3.4. Conductance Analysis

Using the measured dielectric parameters, the ionic conductivity ( $\sigma_{ac}$ ) within the polymer composites is calculated using the relation,

$$\sigma_{ac} = 2\pi f \epsilon_0 \epsilon_r \tan \delta$$

Where,  $\epsilon_0$  is permittivity in free space,  $\epsilon_r$  is dielectric constant,  $f$  is frequency applied, and  $\tan \delta$  is dielectric loss. Figure 5 shows the variation of conductivity with dopant concentration as well as frequency. As seen from FTIR results, the doping produce CTC which results into the increase of flexibility of polymer chains and change in the band structure and chemical composition of the polymer. As frequency increases bonds within the polymer PVA starts to rotate with frequency and the flexible polar groups that are present in the polar bonds cause dielectric relaxation. Hence, conductivity increases with increase of frequency. Variation of conductivity with frequency showed two regions such as frequency-independent plateau region at low frequencies which is attributed to the long-range conduction process within the composites and frequency-dependent dispersion region at higher frequencies which corresponds to strong interaction of charge carriers [5]. At lower frequency, due to the influence of space charge polarization, the charge carriers are accumulated at the electrode and electrolyte interface, due to this mobility of charge carriers is hindered. By extrapolating the low-frequency region to  $\log \sigma_{ac}$  axis, DC

conductivity of the bulk polymer composite material has been obtained. Hence, at room temperature, 15 wt% LiCl doped PVA composite exhibits maximum conductivity of about  $2.28 \times 10^{-4}$  S/cm. With rise of frequency space charge effect decreases and charge carriers get dissociated into the system. Hence, ionic mobility increases and this leads to increase of ionic conductivity.

### 4. CONCLUSION

In this work, the effect of LiCl doping on optical and electrical properties of PVA has been investigated. FTIR shows inter/intramolecular hydrogen bonding between  $\text{Li}^+$  ions of LiCl with O-H group of PVA results into the complex formation. UV-visible study revealed that the dopant affects microstructure of the polymer, hence, modifies the optical properties. Dielectric variation confirms the non-Debye type behavior of polymer electrolytes. Conductivity analysis shows an increase of conductivity with frequency as well as dopant concentration.

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**\*Bibliographical Sketch**

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