



MICROSTRUCTURAL, ELECTRICAL AND THERMAL PROPERTIES OF LITHIUM ION CONDUCTING SOLID POLYMER ELECTROLYTE

Shreedatta Hegde¹, V Ravindrachary², S D Praveena³, B Guruswamy⁴, Rohan N Sagar⁵, C Shruthi⁶

Abstract-Lithium ion (Li⁺) conducting solid polymer electrolyte films have been prepared by solution casting method. The prepared films were characterized using different techniques. X-ray diffraction results reveal that the amorphous nature of PVA/LiCl composite increase with dopant concentration. SEM result gives the smooth surface morphology of the composites. DC conductivity results reflect the enhancement of ionic conductivity with dopant concentration. TGA result accounts for the increase of thermal stability of the polymer due to the incorporation of LiCl.

Keywords: Polymer composites, X-ray diffraction, SEM, Ionic conductivity, TGA.

INTRODUCTION

In recent years polymer electrolytes have attracted the researchers due to their tremendous applications in electrochemical devices. Particularly lithium ion conducting solid polymer electrolytes (SPE) have got wide range of applications such as in electrochromic devices, rechargeable batteries, sensors, supercapacitors, photo electrochemical cells, smart cards etc. The advantages of SPE over other electrolytes are their ability to form thin films, long life time, nontoxicity, light weight, their flexibility, proper contact with electrode materials in different electrochemical devices and elasticity. There are few limitations of SPE such as they are deficient in stability, low cation transfer, high crystallinity and low conductivity compared to liquid electrolytes. To enhance the conductivity in these SPEs various techniques have been employed such as polymer blending, copolymerization, addition of ceramic fillers, and plasticization. Since conductivity of the polymer composites lies mainly in the amorphous region, it is possible to increase the amorphous phase of the polymer from these techniques where the ions can dissociate and the glass transition temperature is lower in such electrolytes [1]. SPE can be prepared by appropriate preparation methods. One of the easiest methods to prepare SPE is the solution casting method. In this method an inorganic salt or dopant is dissolved in an appropriate polymer and draw the films. Here when the dopant is added to polymer the dopant interacts with the functional groups of the polymer and leads to the complex formation which contain cations and anions. In these polymer salt complexes cations are solvated with polar groups of the polymer and anions interact with the aprotic host. Usually the cation migration takes place in the amorphous phase of the system and helps to improve the ionic conductivity of the polymer electrolytes. Since these ions transport through the amorphous phase many researchers have aimed to increase the amorphous phase of the material so that one can enhance the conductivity of the polymer. Usually the change in conductivity of the polymer depends on microstructure and this change in microstructure depends on the type and nature of the dopant and the way in which the dopant interacts with the host polymer [2].

Poly (vinyl alcohol) (PVA) is a biocompatible, semicrystalline polymer containing both crystalline and amorphous phases and its advantages are high chemical stability, good film forming capacity, biocompatibility and high chemical resistance. The hydroxyl groups (O-H) that are attached to methane carbons in PVA are regarded as source of hydrogen bonding and is responsible for many physical properties of polymer. The physical properties of this polymer including charge-storage capacity can be increased by doping with suitable dopant. When PVA is doped with an inorganic or metal salt, the dopant interacts with the polymer either in the crystalline phase or amorphous phase. This interaction forms the charge transfer complex within the matrix and expected to change the optical, microstructural and electrical properties of polymer. Among the interactions the hydrogen bonding interaction

¹ Department of Physics, Mangalore University, Mangalagangothri-574199, India

² Department of Physics, Mangalore University, Mangalagangothri-574199, India,

³ Department of Physics, K V G College of Engineering ,kurunjibhag, Sullia -574327 ,India

⁴ Department of Physics, Mangalore University, Mangalagangothri-574199, India

⁵ Department of Physics, Mangalore University, Mangalagangothri-574199, India

⁶ Department of Physics, Mangalore University, Mangalagangothri-574199, India

between the hydroxyl groups of PVA and dopant is dominated one. Usually the conductivity of the polymer mainly lies in the amorphous phase because, the mobility of cations/anions in these PVA based polymer electrolytes reside in the amorphous phase. The motion of these charge carriers through segmental motion enhances the conductivity of the polymer composites. From the literature it is known that the lithium ion conducting solid polymer electrolytes possess high ionic conductivity, high stability, good mechanical stability and they make good contact with Li metal [3]. These advantages of lithium polymer electrolytes paved their use in high energy density lithium-polymer batteries. Compared to other metal salts, lithium salts are fast-ion conducting salts and their incorporation into crystalline or amorphous polymers improves the microstructural, electrical and thermal properties of polymers [4]. In view of the above in the present study the effect of LiCl doping on physical and chemical properties of PVA are investigated using various characterization techniques such as X-ray diffraction, SEM, electrical studies and TGA.

EXPERIMENTAL

Sample preparation and characterization

PVA obtained from CDH (P) Ltd. and LiCl obtained from LOBA Chemie, Mumbai. Pure PVA and different concentrations of LiCl salt doped PVA films were prepared by solution cast technique using double distilled water as solvent. Here a known quantity of PVA and LiCl are added to double distilled water and the solutions were stirred well for 24 hour to swell the granules. Then the viscous solution was casted on to glass petri dishes and allowed to evaporate the solvent slowly at room temperature. After drying the films were peeled from glass petri dishes and kept in vacuum desiccator for further study. Thickness of the films were in the range of 0.06-0.07 mm. PVA films with different fractions of LiCl were prepared 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.

X-ray diffraction spectra were recorded using RIGAKU MINIFLEX-600 benchtop X-ray diffractometer with Cu- K_α radiation of wavelength 1.5406 Å in the 2θ range $5^\circ - 60^\circ$ with a scanning speed and step size of 1° per min and 0.02° respectively. Surface Morphology of polymer films have been observed using CARLZEISS Scanning electron microscope (SEM). The samples were gold coated using a sputter coater for 6 min before the imaging to minimize sample charging effects due to electron beam. Electrical studies at room temperature were carried out using KEITHLEY-236 source measure unit. For the sake of good contact between electrodes and film, silver paste was deposited on both surfaces of the film during the electrical measurements. Wight loss behaviors of composites were studied using universal Thermogravimetric analysis TA (SDT-Q600) for pure PVA and LiCl doped PVA films in the temperature range of $25^\circ\text{C} - 600^\circ\text{C}$ at a scanning rate of 10°C per min.

RESULTS AND DISCUSSION

X – Ray diffraction

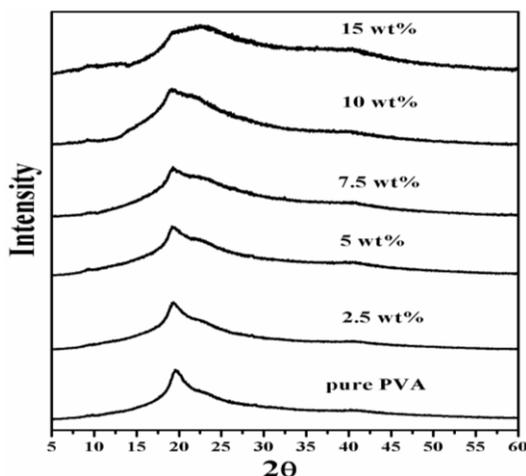


Figure 1. X-ray diffractogram of pure and LiCl doped PVA composites.

Figure 1 shows Wide Angle X-ray Diffractogram (WAXD) of pure and LiCl doped PVA. XRD spectra of pure PVA show a relatively sharp peak at $2\theta = 19.61^\circ$ reveal the semi-crystalline nature of PVA containing both crystalline

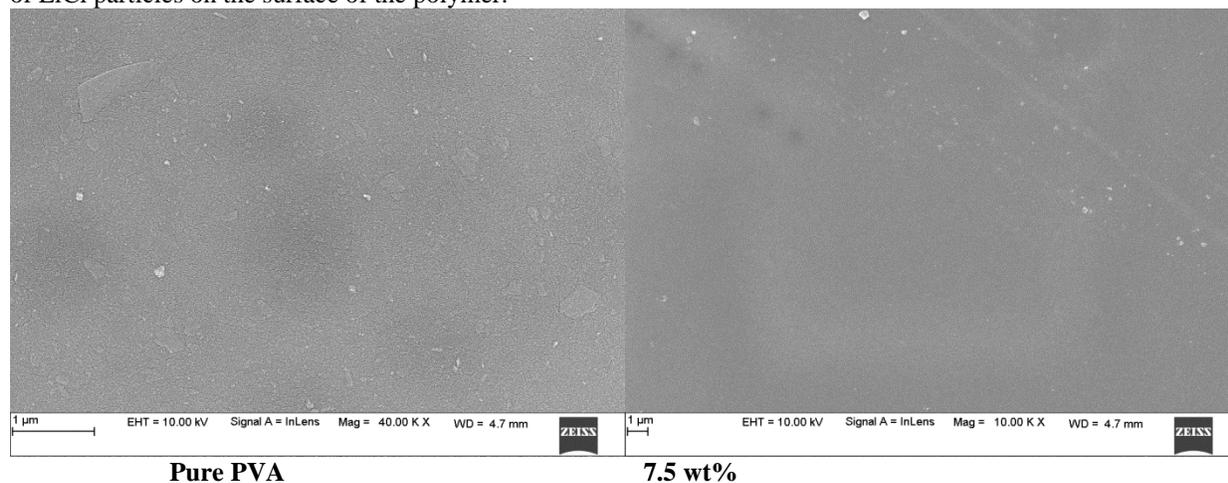
and amorphous phases. On incorporating LiCl into PVA matrix the intensity of the semicrystalline peak decreases and it gets broader with the increase of dopant concentration. Here in the composites peaks corresponding to LiCl are not observed indicates the complete dissolution of dopant into polymer matrix which allowed strong interaction between dopant and polymer. From the table 1 it is clear that crystallinity decreases with dopant concentration [5]. This indicates that upon doping the degree of crystallinity decrease and increase of amorphous nature of polymer composites with dopant concentration. Here the semicrystalline nature of PVA has been transformed into amorphous nature due to the addition of LiCl. This is mainly due to the fact that dopant interacts with the polymer via hydrogen bonding forms the complex and the complex formation is random throughout the matrix as a result reduction in crystallization of the polymer took place.

Table 1. Degree of crystallinity of pure PVA and LiCl doped PVA composites.

Sample	(%) of crystallinity
Pure PVA	56.83
2.5 wt% LiCl	51.02
5 wt% LiCl	43.78
7.5 wt% LiCl	39.24
10 wt% LiCl	37.46
15 wt% LiCl	36.05

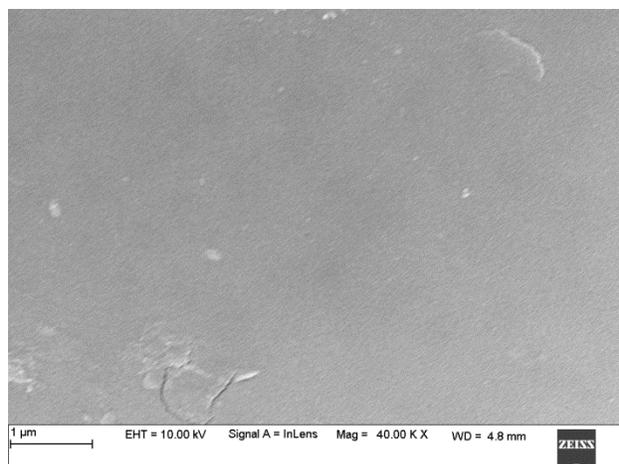
SCANNING ELECTRON MICROSCOPY (SEM)

Surface morphology of pure and LiCl doped PVA polymer composites are studied using SEM technique and the obtained images are shown in figure 2. The result shows that SEM images of pure PVA and the LiCl/PVA composites revealed the compact and homogeneous structures [6-7] but they differ in their degree of roughness. Pure PVA exhibits rough surface morphology with no pores and no interface layer, only rumples are deposited on the surface which indicates semi-crystalline nature of PVA. On incorporating LiCl into PVA the rough surface of PVA has been changed to smooth surface with reduction in the rumples. On increasing dopant concentration surface of the polymer composites gets smoothened and the rumples deposited on the surface gets reduced. This indicates that the dopant has diminished the semicrystalline nature of the polymer. The increase of smoothness indicates the increase of amorphous phase in the composites which is evident from X-ray diffraction results. The increase of amorphous phase indicates the homogeneous distribution of Li^+ ions into the polymer PVA without any aggregation of LiCl particles on the surface of the polymer.



Pure PVA

7.5 wt%



15 wt%

Figure 2. SEM images of pure and LiCl doped PVA composites.

DC – CONDUCTIVITY

Variation of ionic conductivity (at room temperature) of PVA with different concentration of LiCl polymer electrolyte as a function of LiCl concentration is shown in figure 3 and the values are tabulated in table 2. The conductivities are calculated using the relation,

$$\sigma = \frac{d}{RA}$$

Where d is thickness of the sample, R is Resistance obtained from I vs V plot and A is area of the electrode.

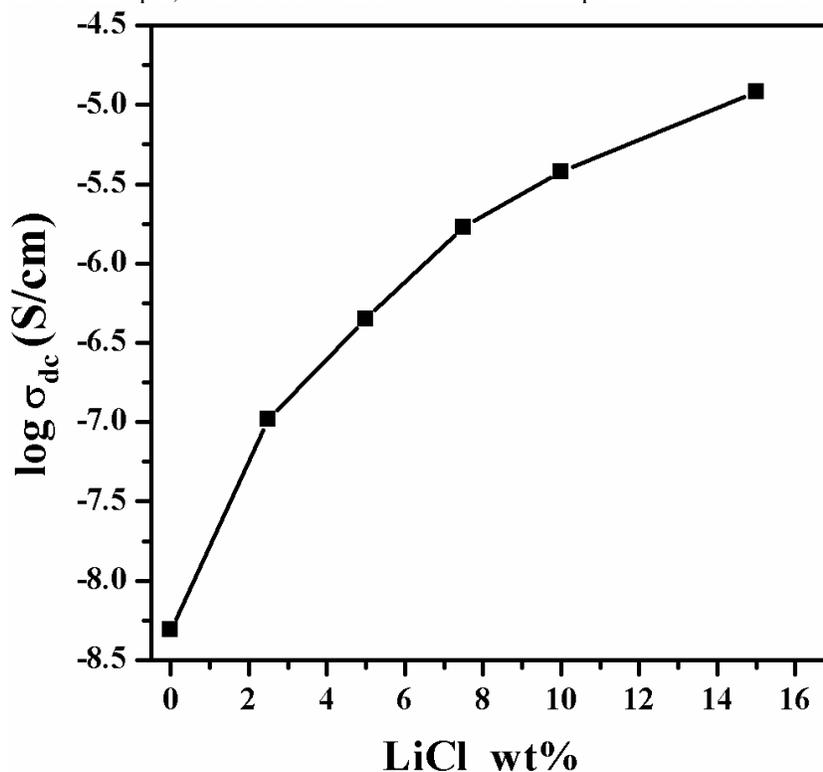


Figure 3. Logarithmic variation of DC conductivity of pure and LiCl/PVA composites with dopant concentration. The result showed that DC ionic (Li^+) conductivity of the composites increases with increase of dopant concentration. For pure PVA the conductivity is found to be of around $0.5 \times 10^{-8} \text{ Scm}^{-1}$ and it increases with the dopant concentration (see table 2). For the 15 wt% LiCl doped PVA composite the conductivity obtained is 1.20×10^{-7}

5 Scm^{-1} . This is because as dopant concentration increases number of charge carriers increases and the LiCl doped PVA composite system exhibited increased amorphous nature which is evident from XRD and SEM results. Since amorphous phase of the polymer contains flexible backbones and the polymer chain acquires faster internal vibration modes which increase segmental motion of the polymer chains and also the energy barrier between the sites reduces [8, 9, and 10]. This reduction in the barrier and internal vibration modes allows translational motion of the ions from one site to another which facilitate faster ionic mobility in the composite system. The increase of ionic mobility leads to the fast ion transport and hence the conductivity increases with dopant concentration.

Table 2. DC conductivity of pure and LiCl doped PVA composites.

PVA:LiCl polymer electrolyte	DC conductivity (S cm^{-1})
100:0	0.5×10^{-8}
97.5:2.5	4.05×10^{-7}
95:5	4.45×10^{-7}
92.5:7.5	1.69×10^{-6}
90:10	3.78×10^{-6}
85:15	1.20×10^{-5}

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis accounts for the thermal stability of polymer composites. For the present case the change in thermal stability of PVA due to the addition of LiCl has been studied using TGA measurements. Here the weight loss of the sample decreases slowly and after 300°C sample weight decreases rapidly over a narrow temperature range and finally levels off at the reactants used burnt out. Figure 4 shows TGA thermogram of pure PVA and LiCl doped PVA composites recorded in the temperature range from room temperature to 600°C at a scanning rate of 10° per min. From the thermogram two weight losses are observed for pure PVA. First weight loss of about 0-9% is observed in the temperature range of 50 - 150°C which is attributed to the moisture vaporization and desorption of physically or chemically absorbed water [11]. The sample lost 90% of its weight in the second stage of weight loss which is due to the decomposition of polymer chains of PVA hence this temperature is called degradation temperature. But in the composites three stages of weight losses are observed.

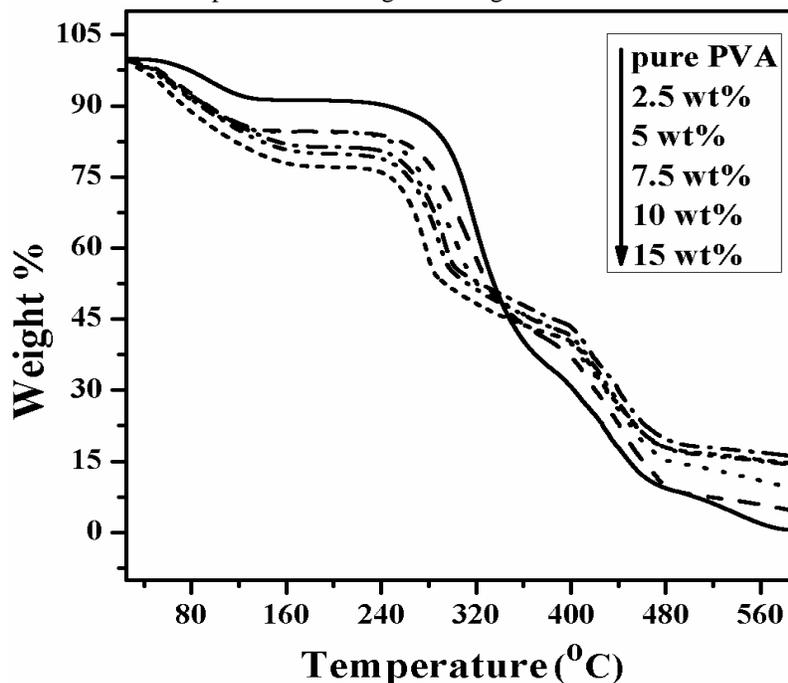


Figure 4. TGA thermographs of pure and LiCl doped PVA composites.

Table 3. Weight loss and onset temperature (T_0) of pure PVA and LiCl/PVA composites.

Doping level M (wt %)	Weight LOSS (%)					$T_0(^{\circ}\text{C})$
	100 ^o C	200 ^o C	300 ^o C	400 ^o C	500 ^o C	
0	2.66	9.05	20.98	69.56	92.14	258
2.5	11.02	15.21	31.4	62.94	91.91	252
5	11.73	15.75	36.85	60.67	85.67	243
7.5	11.22	18.64	44.03	56.92	81.92	237
10	12.21	79.59	45.41	59.08	83.3	239
15	15	22.82	48.99	59.92	82.97	227

First weight loss of about 15-25% is observed in the temperature range of 50-170^oC due to the evaporation of the solvent. The maximum weight loss of 35% took place in the second stage in the temperature range of 230-390^oC resembles the decomposition of polymer network of PVA chains. Third weight loss observed in the temperature range of 400-480^oC is about 30% which is due to the degradation of the salt. Above 500^oC TGA curves levels off completely. From the above results it is evident that the degradation temperature of the polymer composites increased with the increase of dopant concentration in PVA matrix because of the chemical interaction between LiCl and PVA and also due to volume effects. From this it is evident that the thermal stability of the polymer PVA has increased due to the incorporation of LiCl dopant.

CONCLUSION

In this work, the effect of LiCl doping on microstructural, morphological, electrical, and thermal properties of PVA have been investigated. X- ray diffraction study showed increase in the amorphous phase of the polymer composites due to complete dissolution of dopant into the polymer. In SEM study we observed that the surface morphology of the polymer electrolytes gets smoothed due to the addition of LiCl. DC ionic conductivity increases with increase of dopant concentration. TGA thermograms showed improved thermal stability of the polymer due to the incorporation of LiCl.

ACKNOWLEDGMENT

The authors are thankful to Dr. Ganesh Sanjeev, Microtron Center, Mangalore University for providing Electrical studies.

REFERENCES

- [1] M F Shukur, F M Ibrahim, N A Majid, R Ithnin and M F Z Kadir. PHYSICA SCRIPTA, 88, 025601 (2013).
- [2] Sunil G Rathod, RF Bhajantri, V Ravindrachary, Boja Poojary, PK Pujari, T Sheela and Jagadish Naik. Journal of Elastomers & Plastics 1-14. 2015.
- [3] J. Malathi, M. Kumaravadeivel, G.M. Brahmanandhan, M. Hema, R. Baskaran, S. Selvasekarapandian. Journal of Non-Crystalline Solids, 356, 2277-2281, 2010.
- [4] P. Chandrasekhar, P. Naveen kumar, U. Sasikala, V.V.R.N. RAO AND A. K. SHARMA. IRACST – Engineering Science and Technology: An International Journal (ESTIJ), Vol.2, ISSN: 2250-3498, No. 5, 2012.
- [5] Structural, optical, thermal and electrical studies on PVA/PVP blends filled with lithium Bromide. E.M. Abdelrazek, I.S. Elashmawi b, A. El-khodary, A. Yassin. Current Applied Physics, 10, 607-613, (2010).
- [6] Jinli Qiao, Jing Fu, Lingling Liu, Jing Zhang, Juan Xie, Guang Li. Solid State Ionics 214, 6-12, 2012.
- [7] Y. Pavani, M. Ravi, S. Bhavani, A.K. Sharma, V.V.R. Narasimha Rao. POLYM. ENG. SCI., 52:1685-1692, 2012.
- [8] C.S. Ramyaa, S. Selvasekarapandiana, T. Savithaa, G. Hirankumara, P.C. Angelo. Physica B, 393, 11-17, 2007.
- [9] N. Rajeswari, S. Selvasekarapandian, S. Karthikeyan, H. Nithya and C. Sanjeeviraja. International Journal of Polymeric Materials, 61:1164-1175, 2012.
- [10] M. Hema, S.Selvasekerapandian, G.Hirankumar, A.Sakunthala, D.Arunkumar, H.Nithya. Journal of Physics and Chemistry of Solids, 70, 1098-1103, 2009.
- [11] Structural, Dielectric, Thermal and Optical Properties of Ti³⁺ or Cr³⁺ PVA Polymer Films M. Obula Reddy and S. Buddhudu. Ferroelectrics, 413:123-141, 2011.