Research Paper Medical Science

Study of Proton Conducting Blend Polymer Electrolyte Based on PVA-PVP

M.Premalatha	Department of Physics, S.F.R. College for Women, Sivakasi
***N.Vijaya**	Department of Physics, S.F.R. College for Women, Sivakasi.* Corresponding author
S.Selvalakshmi	Department of Physics, S.F.R. College for Women, Sivakasi
S.Monisha	Materials Research Centre, Coimbatore

ABSTRACT

Proton conducting polymer blend electrolytes based on poly (vinyl alcohol) (PVA) and poly (vinyl pyrrolidone) (PVP) doped with ammonium thiocyanate in different compositions have been prepared by solution casting method using distilled water as solvent. The complex formation between the blend polymer and the salt has been confirmed by Fourier transform infrared spectroscopy. The amorphous nature of the polymer blend electrolyte has been confirmed by X-ray diffraction analysis (XRD). The band gap energy for polymer blend electrolyte is found to be 4.89 eV. This band gap decreases with the addition of NH4SCN salt. The highest conductivity at 303 K has been found to be 6.942x10-4 S cm-1 for 40 mol% NH4SCN-doped system. The increase in conductivity of the doped blend polymer electrolyte with increasing temperature suggests the Arrhenius type thermally activated conduction process. The activation energy is 0.2467 eV for the highest conductivity sample.

KEYWORDS FTIR, XRD, UV-Vis Spectroscopy, AC impedance Spectroscopy, Ionic conductivity

1. Introduction

Solid polymer electrolytes play a vital role in the development of electrochemical devices such as batteries, fuel cells, supercapacitors and sensors [1-3]. The main objectives in the polymer research are to develop polymer systems with high conductivity, long life time which are environmentally friendly and have low cost [2,4]. Various approaches have been adopted to improve the electrical, mechanical and electrochemical properties of polymer electrolytes. Polymer blending is one of the most promising ways by which these properties could be changed. Polymer blends are physical mixtures of structurally different polymers that interact through secondary forces and that are miscible to the molecular level. The significant advantages of polymer blends are that the properties of the final product can be tailored to the requirement of applications, which cannot be achieved by one polymer. Generally, blending of two polymers not only results in the improvement of mechanical strength but also helps increasing the conductivity by suppressing the crystallization of polymer chain [5].

Poly (vinyl alcohol) (PVA) is a semicrystalline and biodegradable polymer containing a hydroxyl group attached to methane carbons which can be a source of hydrogen bonding. Poly (vinyl pyrrolidone) (PVP) is a synthetic biodegradable polymer and it deserves a unique attention among the conjugated polymers due to its easy processability, moderate electrical conductivity and rich in charge transport mechanism. Both these polymers are environmentally friendly and having high polar side groups.

The aim of present work is to develop a proton conducting blend polymer electrolyte based on PVA-PVP doped with different concentrations of Ammonium thiocyanate. Ammonium salts have already been reported as good proton donors to the polymer matrix [6,7].

2. Experimental Technique

In this work, PVA (Mw: 125,000, S d fine chem-Ltd, India), PVP (Mw: 44,000, S d fine chem-Ltd, India) and NH_4SCN (Reachem) were used as raw materials. Blend polymer electrolytes were prepared with 50 mol% PVA:50 mol% PVP and ammonium thiocyanate of various concentrations in mol% using distilled water as solvent by solution casting technique. PVA was stirred in distilled water for 3 hours and after its complete dissolution, PVP was added and stirred for 2 hours after which different concentration of (10%, 20%, 30%, 40%, 50%) ammonium salt was added. The mixture was stirred till it became homogeneous. Then the homogeneous viscous solution was poured in the polypropylene petri dishes and kept in vacuum oven at 60°C for two days to obtain free standing flexible thin films.

A SHIMADZU-IR Affinity-1 spectrophotometer was used to carry out Fourier transform infrared spectroscopy (FTIR) studies in the wave number range of 500-4000 cm^{-1}. The optical properties of the films were characterized by UV-VIS spectroscopy. The electrical properties of the blend polymer electrolytes were investigated by using a computer controlled HIOKI 3532 LCR analyzer in the frequency range of 42 Hz-1 MHz over the temperature range of 303 K-343 K.

3. Results and discussion

3.1. FTIR Characterization

The complex formation between the polymer blend and salt was analyzed by FTIR spectroscopy. The FTIR spectra of pure blend polymer (50% PVA:50% PVP) and the blend polymer doped with 40% of NH_4SCN is shown in figure 1. The absorption peaks observed in the pure blend 50% PVA:50% PVP are 3379 cm^{-1}, 2948 cm^{-1}, 1743 cm^{-1}, 1650 cm^{-1}, 1288 cm^{-1}, 842 cm^{-1}. These peaks are attributed to O-H stretching, CH_2 asymmetric stretching, C=O stretching, C=C stretching, C-O-C stretching, CH_2 bending respectively. These peaks are found to be shifted in 40% NH_4SCN doped sample. The characteristic peaks at 3379 cm^{-1} and 2948 cm^{-1} are shifted to 3179 cm^{-1} and 2958 cm^{-1} respectively in the salt doped blend polymer sample. The absorption peaks at 1743 cm^{-1} and 1650 cm^{-1} are displaced to 1752 cm^{-1} and 1639 cm^{-1} respectively in the blend polymer with 40% NH_4SCN. The peak at 1288 cm^{-1} gets shifted to higher wavenumber at 1292 cm^{-1} in the doped blend film. There is a new peak appearing at 2098 cm^{-1} in the

blend polymer film with 40% NH_4SCN. This peak is attributed to aromatic S-C=N stretching of NH_4SCN [8]. This reveals the interaction of NH_4SCN with blend polymer matrix. The shifting of peaks, change in intensity and appearance of new peak indicate the complex formation between 50 % PVA:50% PVP blend polymer and ammonium thiocyanate.

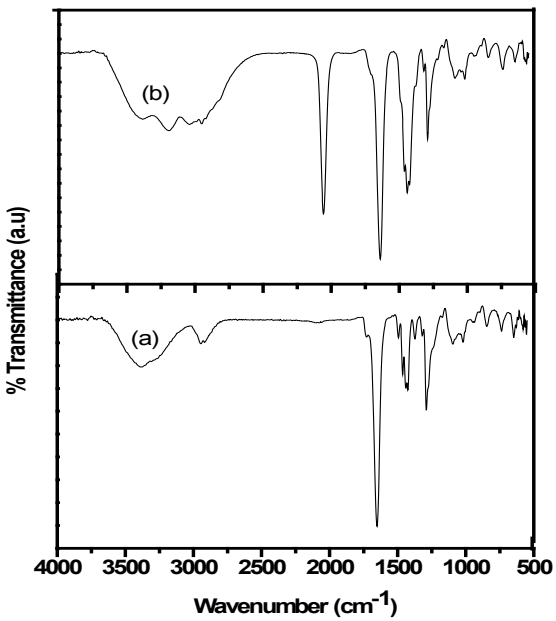


Figure 1 FTIR spectra of (a) 50% PVA:50% PVP (b) 50% PVA:50% PVP:40% NH_4SCN

3.2. XRD Characterization

The XRD patterns of pure 50% PVA:50% PVP blend and the blend doped with 40% NH_4SCN are shown in Figure 2.The two diffraction peaks at 15.29° and 23.16° observed from figure 2(a) can be associated with the semicrystalline nature of pure 50% PVA:50% PVP blend. These peaks are found to be combined to form a single broad peak in the 50% PVA:50% PVP: 40% NH_4SCN film (figure 2(b)). This may be due to the amorphous nature of 50% PVA: 50 % PVP blend with the addition of NH_4SCN. Peaks corresponding to pure NH_4SCN have been found to be absent in the salt doped blend polymer-salt complex, indicating the complete dissociation of salt in the blend polymer matrix.

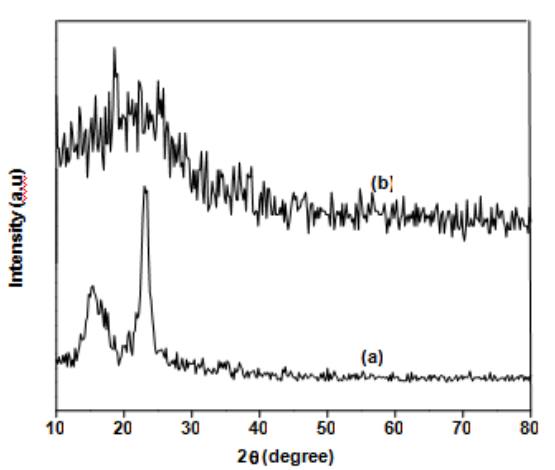


Figure 2 XRD patterns of (a) 50% PVA:50% PVP (b) 50% PVA:50% PVP: 40% NH_4SCN

3.3. UV-VIS Characterization

The study of optical absorption gives information about the band structure of solids. The optical band gap energy and the absorption coefficient have been determined from the UV-Vis spectra using the formula

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

where α is the absorption coefficient, hν is the photon energy, A is the characteristic parameter and E_g is the band gap. To determine the width of the band gap, $(\alpha h\nu)^2$ has been plotted against the photon energy (hν) which is shown in figure 3. The value of optical band gap is calculated by extrapolating the linear portion of the (hν) versus $(\alpha h\nu)^2$ plot to x-axis. The direct optical energy gap for 50% PVA:50% PVP blend polymer is found to be 4.89 eV and that for 40% NH_4SCN doped blend polymer film is 2.81 eV. This shows that the optical band gap of pure 50% PVA: 50% PVP polymer blend decreases with the addition of salt [9-11].

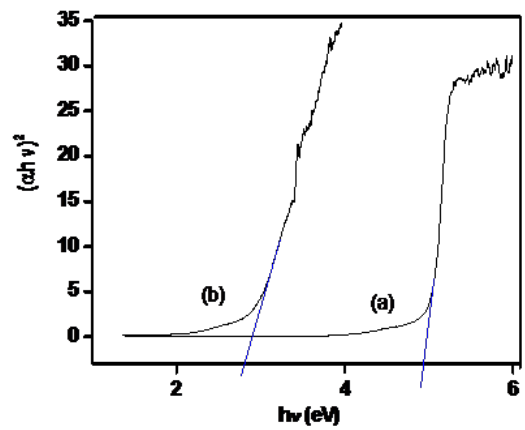


Figure 3 Plots for determining direct band gap energy for (a) 50% PVA:50% PVP (b) 50% PVA: 50% PVP:40% NH_4SCN

3.4. Conductance spectra Analysis:

The variation of ac conductivity with respect to frequency for different concentrations of NH_4SCN with 50 % PVA:50% PVP blend polymer electrolyte system is shown in figure 4. The plot consists of a low-frequency dispersion region due to space charge polarization at the blocking electrodes followed by a frequency independent plateau region corresponding to dc conductivity of the blend polymer electrolyte and a dispersive region at higher frequencies due to bulk relaxation phenomenon [12]. The extrapolation of the plateau region to the y axis gives the value of dc conductivity (σ_{dc}) [13]. The conductivity values of all blend polymer electrolytes at different temperatures are given in Table 1. The maximum conductivity is found to be 6.94×10^{-4} S cm^{-1} at ambient temperature for 50% PVA:50% PVP:40% NH_4SCN blend polymer electrolyte. At higher concentration of the salt (50% NH4SCN), the conductivity value decreases. This may be due to the formation of ion multiplies [14].

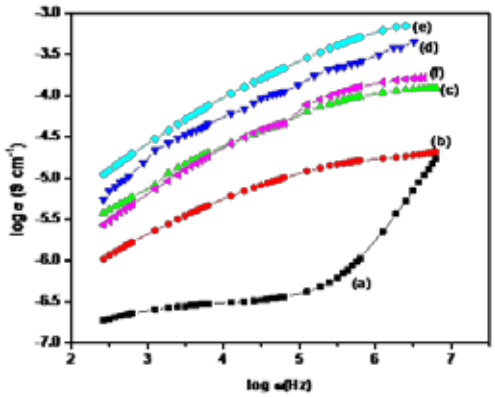


Figure 4 Conductance spectra for the blend polymer electrolyte for all compositions at 303 K (a) 50% PVA:50% PVP (b) 50% PVA:50% PVP:10% NH_4SCN (c) 50% PVA:50% PVP:20% NH_4SCN (d) 50% PVA:50 % PVP:30% NH_4SCN (e) 50% PVA:50% PVP:40% NH_4SCN (f) 50% PVA:50% PVP:50% NH_4SCN

Table 1 Conductivity values of all blend polymer electrolytes at different temperatures

Compositions	DC Conductivity (σ_{dc}) (S cm^{-1})					E_a(eV)
	303K	313K	323K	333K	343K	
50% PVA:50% PVP	3.397×10^{-7}	4.247×10^{-7}	9.379×10^{-7}	2.565×10^{-6}	5.043×10^{-6}	0.6690
50% PVA:50% PVP:10% NH_4SCN	1.882×10^{-5}	6.823×10^{-5}	8.894×10^{-5}	1.505×10^{-4}	2.296×10^{-4}	0.5581
50% PVA:50% PVP:20% NH_4SCN	1.167×10^{-4}	3.042×10^{-4}	4.563×10^{-4}	6.084×10^{-4}	6.688×10^{-4}	0.4078
50 %PVA:50% PVP:30% NH_4SCN	4.617×10^{-4}	9.18×10^{-4}	1.074×10^{-3}	1.628×10^{-3}	1.939×10^{-3}	0.3584
50 %PVA:50% PVP:40% NH_4SCN	$\mathbf{6.942\times10^{-4}}$	$\mathbf{9.689\times10^{-4}}$	$\mathbf{1.275\times10^{-3}}$	$\mathbf{1.551\times10^{-3}}$	$\mathbf{1.851\times10^{-3}}$	**0.2467**
50% PVA:50% PVP:50% NH_4SCN	1.664×10^{-4}	1.405×10^{-4}	2.099×10^{-4}	3.635×10^{-4}	5.206×10^{-4}	0.3139

Figure 5 shows the conductance spectrum for 50% PVA:50% PVP:40% NH_4SCN at different temperatures. The high ionic conductivity obtained for this blend polymer electrolyte may be due to its amorphous nature which is evidenced from XRD analysis. It is observed from the Table 1 that the conductivity (σ_{dc}) increases with increasing temperature for all compositions of doped blend polymer films.

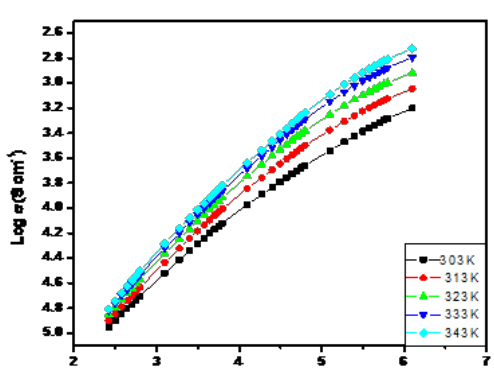


Figure 5 Conductance spectrum for 50%PVA:50%PVP:40%NH_4SCN at various temperatures

3.5 Temperature – dependent conductivity analysis

The variation of dc conductivity of the blend polymer electrolyte for various compositions with respect to temperature from 303 K to 343 K is shown in figure 6.

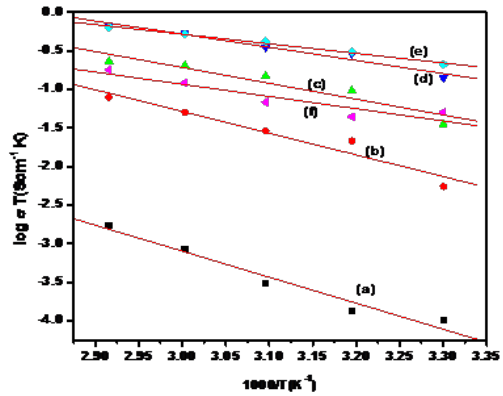


Figure 6 Variation of dc conductivity as a function of temperature for (a) 50% PVA:50% PVP (b) 50% PVA:50% PVP:10% NH_4SCN (c) 50% PVA: 50% PVP:20% NH_4SCN (d) 50% PVA:50% PVP: 30% NH_4SCN (e)50% PVA:50% PVP:40% NH_4SCN (f) 50% PVA: 50% PVP:50% NH_4SCN

From this figure, it has been observed that, as the temperature increases, the ionic conductivity also increases. The conductivity values obey the Arrhenius type thermally activated conduction process given by the relation:

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

where σ_0 is the pre-exponential factor, E_a is the activation energy for conduction and k is the Boltzmann constant. The increase in conductivity with temperature can be interpreted as a hopping mechanism between coordinating sites, local structural relaxation and segmental motion of the polymer electrolyte complexes [15]. The polymer chain acquires faster internal modes in which bond vibrations produce segmental motion, when the temperature increases. This, in turn, favours hopping interchain and intrachain ion movements and accordingly the conductivity of the polymer electrolyte becomes high [16]. The activation energy is found to be low of 0.2467 eV for the highest conductivity sample (50% PVA:50% PVP:40% NH_4SCN).

4. Conclusion

The polymer blend electrolyte films composed of 50% PVA:50% PVP and 50% PVA:50% PVP doped with different concentrations of NH_4SCN prepared by solution casting technique have been characterized. FTIR analysis reveals the complexation behavior of the blend electrolyte films. XRD study confirms the amorphous nature of the blend polymer-salt complexes. The direct band gap energy for 50% PVA:50% PVP blend electrolyte is found to decrease from 4.89 eV to 2.81 eV with the addition of 40% NH_4SCN. The maximum dc conductivity obtained from the impedance studies is 6.942×10^{-4} S cm^{-1} for 50% PVA:50% PVP:40% NH_4SCN blend electrolyte system. From the Arrhenius plots, the activation energy is found to be low (0.2467 eV) for the highest conductivity sample.

REFERENCES

[1] Gray F.M, Ed., Solid Polymer Electrolytes-Fundamentals and Technological Applications, VCH Publishers Inc.: New York, 1991. | [2] Baskaran, R., Selvasekarapandian, S., Kuwata, N., Kawamura, J., and Hattori, T. (2006), 'AC impedance, DSC and FT-IR investigations on (x) PVAc–(1– x) PVdF blends with LiClO4', Mater. Chem. Phys., 98, 55-61. | [3] Armand, M. (1994), 'The history of polymer electrolytes', Solid State Ionics, 69, 309-319. | [4] Scrosati, B. (2000), 'Recent advances in lithium ion battery materials', Electrochim. Acta., 45, 2461-2466. | [5] Rajendran, S., Sivakumar, M., Subadevi, R., and Nirmala, M. (2004), 'Characterization of PVA-. PVdF based solid polymer blend electrolytes', Physica B, 348, 73-78. | [6] Naranappa Vijaya, Subramaniyan Selvasekarapandian, Shunmugavel Karthikeyan, Moni Prabu, Natarajan Rajeswari, and Chinnapa Sanjeeviraja (2013), 'Synthesis and Characterization of Proton conducting Polymer Electrolyte based on Poly (N-vinyl pyrrolidone) (PVP)', Journal of Applied Polymer Science, DO:10.1002: app 37765. | [7] Vijaya, N., Selvasekarapandian, S., Hirankumar, G., Karthikeyan, S., Nithya, H., Ramya, C.S., and Prabu, M. (2012), 'Structural, vibrational, thermal, and conductivity studies on proton-conducting polymer electrolyte based on poly (N-vinylpyrrolidone)', Ionics, 18, 91-99. | [8] Henrique de Santana, Leidimara Pelisson, Diogo R. Janiaski, Cássia Thaïs B. V. Zaia And Dimas A. M. Zaia J. (2010), 'UV Radiation And The reaction between ammonium and thiocyanate under prebiotic ,chemistry conditions', Serb. Chem. Soc., 75 (10), 1381-1389. | [9] Subba Reddy, Ch.V., Sharma, A.K., and Narasimha Rao, V.V.R. (2006), 'Electrical and optical properties of a polyblend electrolyte', Polymer, 47, 1318-1323. | [10] Omed Gh. Abdullah, Bakhtyar K. Aziz and Sarkawt A. Hussen (2013), 'Optical Characterization of Polyvinyl alcohol - Ammonium Nitrate Polymer Electrolytes Films', Chemistry and Materials Research, 3(9), 84-90. | [11] Omed Gh. Abdullah, Bakhtyar K. Aziz, Dler Mohammed Salh (2013), 'Structural and optical properties of PVA: Na2S2O3 polymer electrolytes films', Indian Journal of Applied Research, 3(11), 477-480. | [12] Ramesh, S., and Arof, A.K. (2001), 'Ionic conductivity studies of plasticized poly(vinyl chloride) polymer electrolytes', Mater. Sci. Eng. B, 85, 11-15. | [13] Bhuvaneswari, R., Karthikeyan, S., Selvasekarapandian, S., Vinoth Pandi, D., Vijaya, N., Arun Araichimani, and Sanjeeviraja, C. (2014) 'Preparation and characterization of PVA complexed with amino acid, proline', Ionics DOI 10.1007/s11581-014-1206-0. | [14] Baskaran, R., Selvasekarapandian, S., Kuwata, N., Kawamwa, J., and Hattori, T. (2006), 'Conductivity and thermal studies of blend polymer electrolytes based on PVAc–PMMA', Solid State Ionics, 177, 2679-2682. | [15] Jaipal Reddy, M., Sreekanth, T., and Subba Rao, U.V. (1999), "Study of the plasticizer effect on a (PEO+NaYF4) polymer electrolyte and its use in an | electrochemical cell", Solid State Ionics, 126, 55-63. | [16] Reddy, C.V.S., Sharma, A.K., and Rao, V.V.R.N. (2003), "Conductivity and discharge characteristics of polyblend (PVP + PVA + KIO3) electrolyte", J. Power Sources, 114, 338–345. |