

# Structural and Electrical Properties of Ammonium Thiocyanate Doped Poly Ethylene Oxide / Poly Vinyl Pyrrolidone Blend Polymer Electrolytes

M. Muthuvinayagam, K. Sundaramahalingam, D. Vanitha, M. Vahini

**Abstract:** Blend polymer electrolytes based on PEO:PVP with various wt% of  $NH_4SCN$  are prepared by simple solution casting method. The prepared polymer electrolytes are characterized using several techniques. The XRD studies confirm the amorphous and crystalline behavior of prepared BPEs. Functional groups present in the systems are confirmed by Fourier Transform Infrared spectroscopy (FTIR) studies. The electrical properties are analyzed by ac impedance technique. The maximum ionic conductivity is obtained for 20wt% of ammonium thiocyanate doped system and it is  $1.81 \times 10^{-3} S/cm^{-1}$ . The dielectric properties of polymer films are also studied and discussed.

**Keywords :** XRD, FTIR, AC Impedance, PEO:PVP, Dielectric analysis

## I. INTRODUCTION

In modern Life, polymer electrolytes are very important in batteries for the rapid development of portable electronic devices. Polymer electrolyte batteries have high energy density, high specific capacity [1-3]. Proton conducting polymer electrolytes are mostly considered because of their large applications in fuel cells and electro-chromic devices [4-7]. Several authors are working with proton conducting polymer electrolytes based on synthetic and Bio polymers [8-11].

At room temperature, PEO is semi crystalline nature. At high temperature, the conductivity of PEO is  $\sim 10^{-3} S/cm$ . PVP has more amorphous nature at room temperature. PVP is a conjugated polymer with excellent properties, thermal conductivity, environmental stability [12, 13]. Polymer blending is one of the techniques to improve the conductivity and electrochemical stability of BPEs. In 2011, K. Kiran kumar et al reported that PEO – PVP – NaF polymer

electrolyte has ionic conductivity of  $1.17 \times 10^{-7} S/cm$  [14]. In 2015, Sharanappa Chapi et.al reported that, PEO - PVP -  $CoCl_2$  Polymer electrolyte has conductivity of  $5 \times 10^{-6} S/cm$  [15]. In this work, PEO:PVP polymer blend electrolytes with various wt% of  $NH_4SCN$  are prepared and further analyzed.

## II. EXPERIMENTAL PROCEDURE

Polymer electrolytes are prepared with constant ratio of PEO:PVP (30:70) and x wt% of ammonium thiocyanate ( $x = 5 - 25$ ). The precursor materials analytical grade polyethylene oxide (PEO), poly vinyl pyrrolidone (PVP) are purchased from Sigma Aldrich., India. Ammonium thiocyanate with m.w=76.122 g/mol is purchased from Merck, India. The precursor PEO is dissolved in double distilled water. As well, PVP and ammonium thiocyanate solutions are also stirred separately. The above three solutions are mixed and stirred 36hours to become the viscous solution. The viscous solution was then poured in petridish. The flexible transparent films are obtained.

The blend polymer electrolytes are characterized by various approaches. XRD pattern of the BPEs are recorded by Bruker X-Ray diffractometer having ( $\lambda = 1.540 \text{ \AA}$ ) in the range of  $10^\circ - 60^\circ$ . FTIR spectrum of the electrolytes are recorded using “SHIMADZU IR Tracer 100” in  $400 - 4000 \text{ cm}^{-1}$  wave number. The AC impedance analysis are done by HIOKI 3532-50 Hi-tester in the frequency range of 42 Hz – 1 MHz.

## III. RESULTS AND DISCUSSION

### A. XRD Analysis

Fig. 1 shows the XRD spectra of various composition of ammonium thiocyanate doped PEO:PVP BPEs. In XRD Analysis, the parent polymer PEO has peaks at  $19^\circ$  and  $23^\circ$ . When copolymer PVP is added to PEO, the crystalline peaks are reduced and get only one hump at  $20^\circ$ . After ammonium thiocyanate is added to the polymer electrolyte, the hump at  $20^\circ$  is still reduced. And also hump at  $2\theta = 28^\circ$  is appeared due to addition of ammonium thiocyanate. The maximum hump and peaks are reduced for 20wt% of ammonium nitrate added system.

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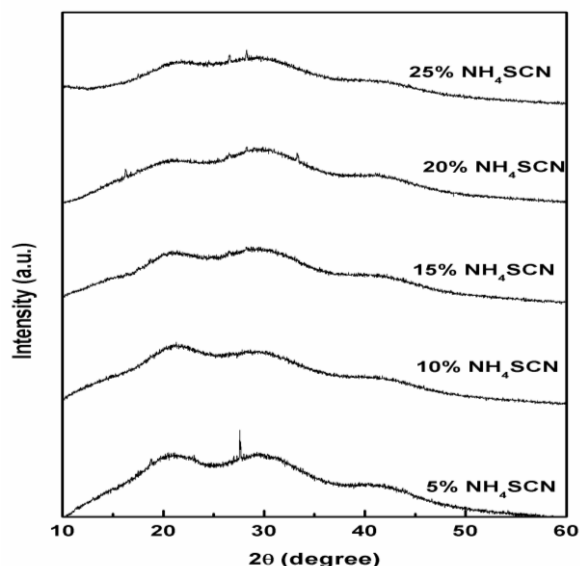


Fig. 1. XRD Pattern for PEO/PVP/ NH<sub>4</sub>SCN polymer electrolytes

**B. FTIR analysis**

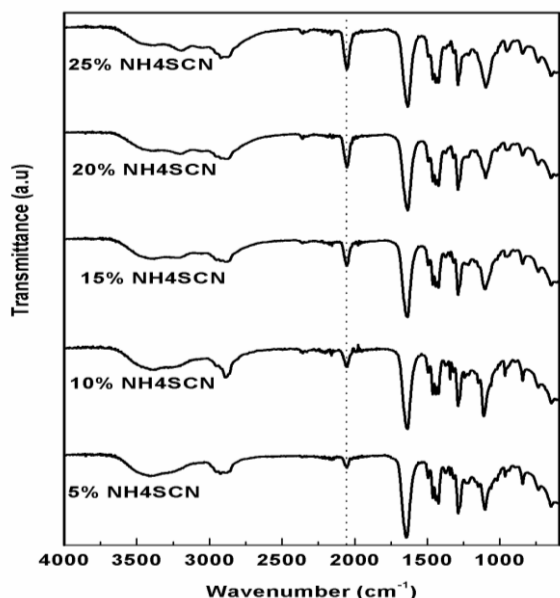


Fig. 2. FTIR Spectra of PEO/PVP/NH<sub>4</sub>SCN systems

In the blend polymer electrolytes, there are two possible interactions for the cation at electron rich ether group of PEO and C=O of PVP. By the addition of the salt, the corresponding ion will approach the suitable coordinating site. In the fig. 2, it is certainly observed that C=O displays minor shift and increase in intensity.

The sharp band is decreased in intensity by increasing the concentration of salt. The band noticed at 1461 cm<sup>-1</sup> is due to CH<sub>2</sub> scissoring mode of polymer PEO. Stretching vibration of C-O at 953 cm<sup>-1</sup> is due to PEO with CH<sub>2</sub> rocking asymmetric vibration. Vibration bands observed at 1282 cm<sup>-1</sup>, 1348 cm<sup>-1</sup>, 1461 cm<sup>-1</sup> are assigned to CH<sub>2</sub> asymmetric twisting, CH<sub>2</sub> bending of PEO and CH<sub>2</sub> wagging, respectively. Band at 834 cm<sup>-1</sup> is due to CH<sub>2</sub> rocking mode of PVP. Absorption band near to 1461 cm<sup>-1</sup> due to the CH<sub>2</sub> wagging. Likewise, Two strong bands at 1349 cm<sup>-1</sup> and 1687 cm<sup>-1</sup> which corresponds

to the C-N stretching and C=O stretching, and it confirms the presence of polymer PVP.. From this analysis, it is understood that there is strong complexation between polymers and salt. FTIR wave numbers and assignments are tabulated in table I.

**Table 1: FTIR Assignments and corresponding wavenumbers**

Wavenumber	Assignments	Ref.
956	CH <sub>2</sub> rocking asymmetric vibration	[16]
1283	CH <sub>2</sub> asymmetric twisting	[17,18]
1349	CH <sub>2</sub> bending of PEO	[19,18]
1461	CH <sub>2</sub> scissoring mode of PEO	[20]
1639	C=O stretching	[20]
2893	asymmetric CH stretching of CH <sub>2</sub>	[21]

**C. AC Impedance analysis  
Cole-Cole plot**

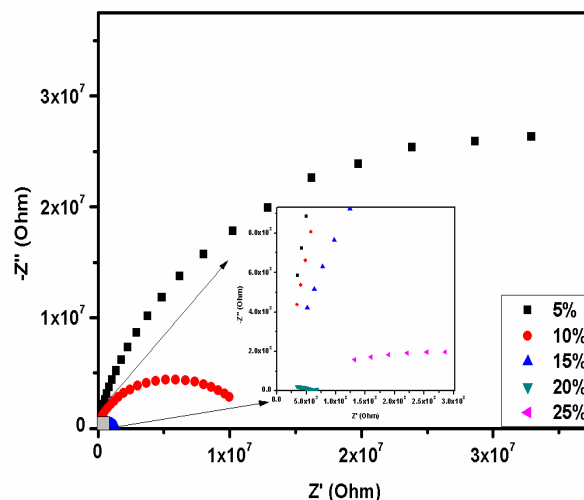


Fig. 3. Cole-Cole plot of PEO:PVP:NH<sub>4</sub>SCN BPEs.

The impedance plots for PEO/PVP/Xwt% ammonium thiocyanate (NH<sub>4</sub>SCN) polymer electrolytes at ambient temperature are shown in Fig. 3. There is one semi-circular portion in all the polymer systems. In the complex impedance representation, the bulk resistance of the films are decreased while increasing the concentration of NH<sub>4</sub>SCN, and the maximum bulk resistance reduction at 20wt% NH<sub>4</sub>SCN system. The ion migration and the polarization of immobile polymer chains produce the impedance effect from resistance and capacitance which represent the depressed semicircle [22]. Using the following formula to obtain the conductivity of BPEs,

$$\sigma = l/R_b A \quad (1)$$

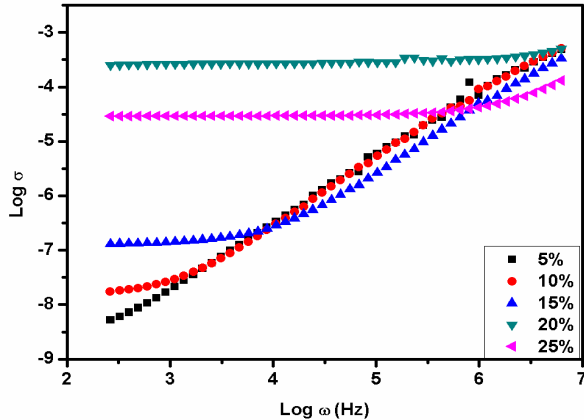
l-thickness of the film, A- area of the film area, B- R<sub>b</sub>-Film bulk resistance.

From the following formula, the conductivity is tabulated in table II.

**Table II: Conductivities of prepared PEO-PVP-xwt% of NH<sub>4</sub>SCN doped blend polymer electrolytes.**

Compositions	Conductivity (S/cm)
PEO/PVP/ 5wt% NH <sub>4</sub> SCN	$2.20 \times 10^{-10}$
PEO/PVP/ 10wt% NH <sub>4</sub> SCN	$1.03 \times 10^{-9}$
PEO/PVP/ 15wt% NH <sub>4</sub> SCN	$7.83 \times 10^{-9}$
PEO/PVP/ 20wt% NH <sub>4</sub> SCN	$1.81 \times 10^{-5}$
PEO/PVP/ 25wt% NH <sub>4</sub> SCN	$1.36 \times 10^{-6}$

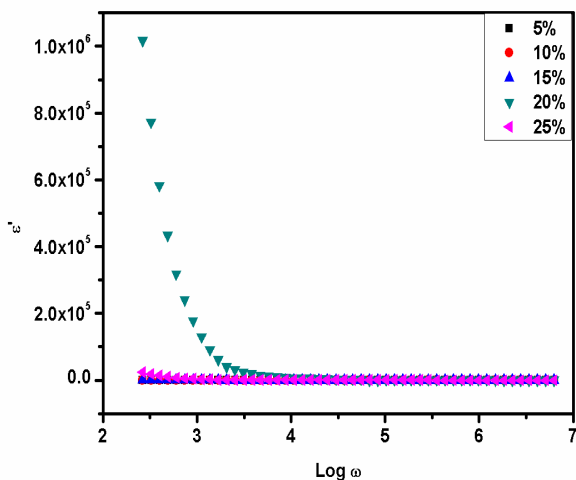
**Conductance spectra**



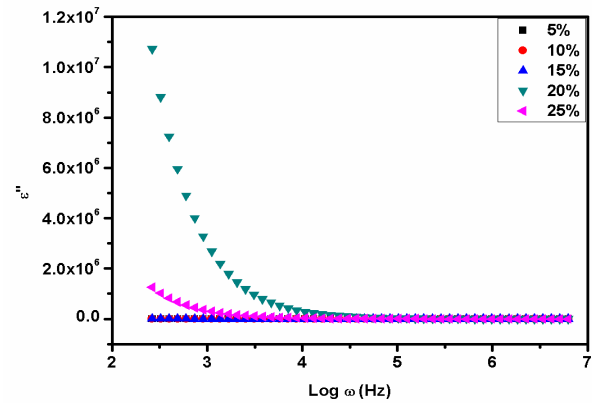
**Fig. 4. Conductance spectra for PEO:PVP:NH<sub>4</sub>SCN BPEs.**

Fig. 4. shows the conductance spectra of various wt% of NH<sub>4</sub>SCN doped PEO:PVP polymer blend. The conductance spectra of prepared polymers consist of two distinct regions. Due to the bulk relaxation phenomena the spike is obtained. By connecting the plateau region to the Y axis DC conductivity is calculated. 20 wt% of ammonium thiocyanate mixed system shows higher conductivity of  $1.81 \times 10^{-5}$  S/cm at 303K. For 25wt% of ammonium thiocyanate doped system, the ionic conductivity again decreases because of aggregation of salt at higher concentration.

**Dielectric constant and Dielectric loss**



**Fig. 5a. Dielectric constant for PEO/PVP/NH<sub>4</sub>SCN polymer blends.**



**Fig. 5b. Dielectric loss for PEO/PVP/NH<sub>4</sub>SCN polymer blends.**

In polymer electrolytes, dielectric constant, dielectric loss and ion conduction are very important. Reduces ion-ion interaction and also slow crystal formations are leads the high dielectric constant. Fig. 5a. Shows the dielectric constant for various wt% of NH<sub>4</sub>SCN doped to the PEO:PVP polymer matrix. From the figure, Initial the dielectric constant has high, when applied frequency increases, the dielectric constant has been decreased, at higher frequency it shows constant. Figure 5b shows the variation of dielectric loss with different frequencies with different compositions. The relation between dielectric loss and conductivity expressed as,

$$\epsilon'' = \sigma \omega \quad - (2)$$

The maximum dielectric loss is obtained for the higher conductivity sample.

**IV. CONCLUSION**

Different wt.% of ammonium thiocyanate (NH<sub>4</sub>SCN) doped PEO:PVP BPEs are prepared by simple solution casting. The structural confirmations are confirmed by XRD. In XRD, pure PEO peaks are reduced due to blending and adding ammonium thiocyanate salt. The maximum crystalline nature is reduced for 20wt% of NH<sub>4</sub>SCN doped PEO/PVP BPEs. Functional groups present in the polymer electrolytes are confirmed by FTIR. The conductivity is obtained at  $1.81 \times 10^{-5}$  S/cm for 20wt% of NH<sub>4</sub>SCN doped PEO/PVP polymer electrolyte.

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