

**AN INVESTIGATION ON DIELECTRIC BEHAVIOR OF TERNARY  
POLYMER ELECTROLYTE FOR LI ION BATTERY****A.Neelaveni<sup>1</sup>, K.Anbzhakan<sup>2</sup>, N.Sivakumar<sup>1</sup>**<sup>1</sup>PG and Research Department of Physics, Chikkaiah Naicker College, Erode– 638004, Tamil Nadu, India.<sup>2</sup>Department of Physics, Gobi Arts and Science College, Gobichettipalayam-638453, Tamil Nadu, India.*Corresponding author mail id: nskdnp@ gmail.com***ABSTRACT**

Though the initiatives by the researchers have led to improvements in bio polymer electrolytes, the poor mechanical strength is continued to exist at high temperature. But through this combination (PMMA:PVC:PVAc: LiClO<sub>4</sub>) or ternary polymer blend electrolyte, the electrolyte has spent more time with electrodes to perform a better Li ion battery at high temperature . Significantly it exhibits good mechanical strength which is highest among PMMA-PVC combination. Decrease in T<sub>g</sub> values describes the good miscibility of the polymers. The polymer chains have hosted the more lithium ions, was shown by XRD analysis. The spectral region at 1242.16cm<sup>-1</sup>, 1257.59 cm<sup>-1</sup>, 1427.32 cm<sup>-1</sup>, 1442.75 cm<sup>-1</sup> from FTIR confirms the complex formation between polymers and the salt. Hence the AC impedance analysis reveals the highest conductivity at room temperature which is about 3x10<sup>-5</sup> S/cm and also the values seems to be increasing on increasing temperature.

**KEYWORDS**

Ternary polymer blend electrolyte, ac impedance, XRD, FTIR, DSC.



## INTRODUCTION

Polymer electrolytes are gaining much technological importance as they are used in **Lithium** ion batteries, fuel cells, electrochromic display devices etc., which are finding novel application in electrochemical field as power sources for various household, defence, medical instruments etc.,[1] . So far, about one and half of the decade blend polymer electrolytes are flourishing in enormous rate, as they are known for good conductivity, mechanical strength and thermal stability. Initially the blend polymer electrolytes were prepared using PAN(poly acrylonitrile),PEO(poly ethylene oxide), PVC(poly vinyl chloride) etc.,[2]. After few years co-polymers gained much interest and played as host polymers while blending with crystalline polymers, because co-polymers has high degree of elasticity and thus have a tendency to change the crystalline nature of the corresponding partner into amorphous one and seems to be readily miscible[3-5]. Again when plasticizer enters inside the matrix the performance seems to be much better. Miscibility and thermal stability also seems to be supportive when blend is made with a co-polymer[6]. But there are certain issues are arising when dealing with the co-polymers with low

weight percentage like when doped with lithium salts it readily allows the air to get react with lithium as they are hygroscopic which in turn creates a question mark regarding its thermal stability and standardizing the weight percentage for higher conduction seems to be crucial. So, by keeping these points in mind a try has been given to work with polymer material with crystalline nature and blending it with amorphous material. Since PVC blended with PMMA has undergone a deep investigation and shows good conductivity, thermal stability, but the weight percentage is limited at (5:5) ratio[6]. Therefore an idea is made to make this binary blend into ternary blend with the support of a new polymer. PVAc(poly viny acetate) is chosen as a third polymer which acts as supportive one to the binary matrix, as PVAc seems to be miscible with PMMA which makes the idea of making this ternary blend desirable[7]. Another question arises during this process i.e instead of going for third polymer there is a possibility for replacing any one of the two crystalline polymers with a co-polymer, but this again creates issues in mechanical strength and thermal stability as PMMA content goes very low when reaching the

higher conductivity and co-polymers which seems to be miscible with PMMA are costly. Thus polymer blends comprising PVC/PMMA/PVAc doped with  $\text{LiClO}_4$  are prepared with different ratios by solution casting technique and their dielectric properties, thermal properties, miscibility, amorphous nature are investigated. To the best of our knowledge this work is never reported by others.

## 2. Experimental

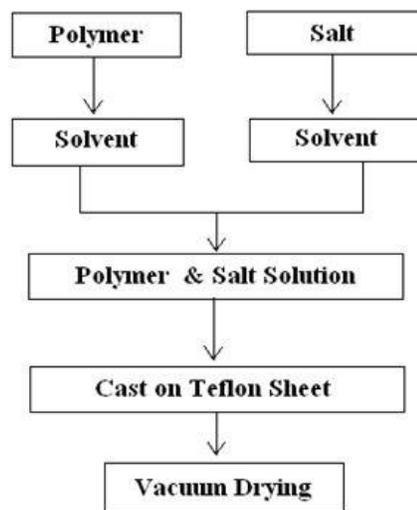
### 2.1 Materials

PVC(poly vinyl chloride;  $M_w = 62.50$  g/mole), PMMA(poly methyl methacrylate;  $M_w = 100.12$  g/mole), PVAc(Polyvinyl acetate;  $M_w = 86.09$  g/mole),  $\text{LiClO}_4$ (Lithium perchlorate;  $M_w = 106.41$  g/mole )used as dopant are purchased from Sigma Aldrich, THF(Tetra hydra furon) used as solvent and as plasticizer was purchased from Merch are used in the preparation of polymer blends[8].

### 2.2 Preparation of ternary blend electrolyte

The total weight of the polymer blend is fixed to be 1g. Different weight percentages of PVC:PMMA:PVAc are made and they are

separately dissolved in 10ml of THF and stirred continuously for 24 hrs. After that, the dissolved solutions are mixed together and known ratio of  $\text{LiClO}_4$  is dissolved in the mixed solution and stirred continuously for 48 hours. The stirred solution is now casted in the clean glass petri dish and allowed to evaporate in hot air oven at  $40^\circ\text{C}$ . After few hours a uniform film with good mechanical strength is obtained and it is again evaporated in vaccum oven to remove further traces of THF. Having completed all this procedures the prepared polymer electrolyte is subjected to various characterizations.



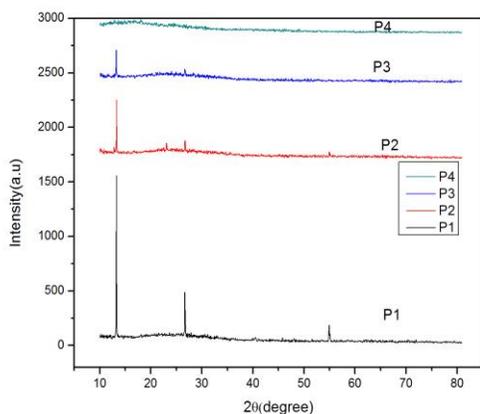
*Preparation of Polymer Salt Complex*

**Figure 1. Flow chart of polymer electrolyte synthesis by solution casting technique**

### 3. Result and Discussion

#### 3.1 XRD Analysis

X-ray diffraction analysis was taken to examine the crystallinity of the prepared polymer blends. Here Cu-K $\alpha$  line was used in normal  $\theta - 2\theta$  scan. The readings are recorded using XPERT-PRO diffractogram at the scan range of. From the X-ray diffractograms it is seen that for 100m%(PMMA:PVC:PVAc) i.e P1 seems to be having crystalline nature as PVC is a dominant crystalline polymer, while increasing the incorporation of LiClO<sub>4</sub>, the crystalline peaks of the samples seems to be decreasing and finally for the sample P4 the peaks are fully disappeared. This reveals the increase in amorphous nature and decrease in crystalline nature which in turn confirms the complete miscibility of the lithium salt in the polymer matrix [8].



**Figure 3.1. XRD diffractogram of polymer electrolytes P1,P2,P3 and P4.**

#### 3.2 FTIR studies

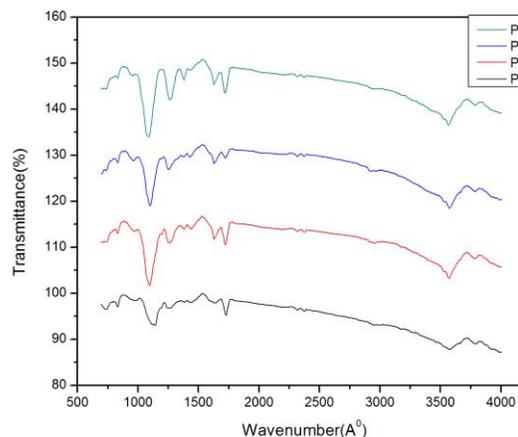
Vibrational analysis of the composition of the polymer blend electrolyte has been done by FTIR spectroscopy which is very important for the analysis of the interactions among atoms or ions in the electrolyte system. FTIR Spectra of the prepared samples were recorded from range of wavenumber 800 – 4000 cm<sup>-1</sup> with the help of Thermo Nicolet, SHIMADZU Infrared spectrometer at room temperature.

From the data it is seen that the region at 979.84 cm<sup>-1</sup> has been shifted to 964.41cm<sup>-1</sup>, 956.69cm<sup>-1</sup> which are assigned for C-H bending corresponding to PMMA. Whereas the bands at 1095.57, 1103.28, 1087.85, 1118.71 cm<sup>-1</sup> showing vibrational shift which are assigned for aliphatic C-N stretching vibration. The peaks at 1242.16, 1257.59, 1249.87, 1265.30 cm<sup>-1</sup> deals with C-H wagging of methyl methacrylate(-CH<sub>2</sub>X). And the vibrational modes at 1967.39, 2029.11, 1957.11, 2029.13 corresponds to C=O stretching vibration of PVAc respectively. It is seen that the spectral region at 1427.32, 1442.75cm<sup>-1</sup> correspond to alkyl C-H bending. Similarly the bands at 2947.23, 2954.95, 2931.80, 2939.52 cm<sup>-1</sup> corresponds to C-H stretching of PVC. The bands at 3464.15, 3425.58, 3464.15 cm<sup>-1</sup> are due to O-H stretching of THF [9].

From the assigned vibrational data a shift which stands as common thing for all polymers and plasticizers involved in this electrolyte is seen. It can be said that the variation in the vibrational bands are due to the incorporation of lithium salts into the polymer matrix. When the ratio of lithium salt increases in the polymer matrix the vibrational peaks are also showing corresponding shifts, which in turn explains the complexation of salt with the polymers[10].

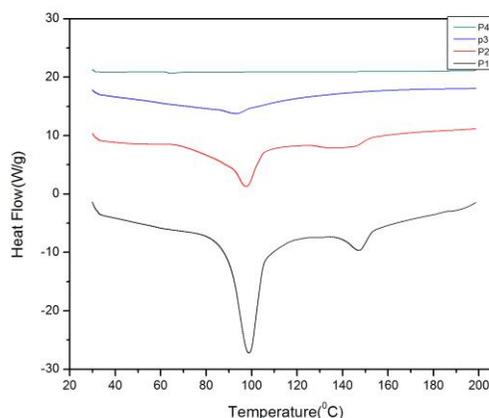
### 3.3 Differential Scanning Calorimetry

To obtain the  $T_g$  value for the prepared polymer blend electrolytes DSC thermograms were taken using DSC Q20 V24.10 Build 122 instrument in the nitrogen atmosphere at the  $5^\circ\text{C}/\text{min}$  from  $20^\circ\text{C}$  to  $210^\circ\text{C}$ . From the DSC thermogram it is noted that the  $T_g$  value seems to be  $139^\circ\text{C}$  for P1(100m% PMMA:PVC:PVAc),  $126^\circ\text{C}$  for P2 (80m%PMMA:PVC:PVAc) : 20m%LiClO<sub>4</sub>),  $93^\circ\text{C}$  for P3 (60m%PMMA:PVC:PVAc): 40m%LiClO<sub>4</sub>) and for P4(60m%PMMA:PVC:PVAc):40m%LiClO<sub>4</sub>) it is found to be  $79^\circ\text{C}$ . The decrease in  $T_g$  value indicates the interaction of  $\text{Li}^+$  ion with the polymer matrix which facilitates segmental mobility of ions. And also



**Figure 3.2. FTIR spectrograph of the polymer electrolytes P1,P2,P3 and P4**

decrease in  $T_g$  value for the higher concentration of LiClO<sub>4</sub> (P4) indicates that the present system can withstand higher temperature and offer higher conductivity [11].



**Figure 3.3 DSC thermogram of the polymer electrolytes P1,P2,P3 and P4**

### 3.4 AC impedance Analysis

A method to characterize the electrical properties of molecules and their interfaces with electronically conducting electrodes is impedance spectroscopy. It is a standard material characterization technique for various solid electrolytes. The applicability of this method to determine the electrical characteristics of materials has been enhanced by the development of the ac analysis. The ac analysis is used to study the dynamics of mobile charges in the bulk of ionic, electronic-ionic and dielectric materials.

In the present study the blocking electrodes were used for the measurement of electrical conductivity. Here the sample is sandwiched between the blocking electrodes and ac frequency is applied and the corresponding response of the sample for the applied frequency is studied from Nyquist plot, dielectric spectra, conduction spectra and loss tangent spectra etc.,

The ionic conductivity for the samples P1, P2, P3, P4 at room temperature(303K) are shown in terms of Nyquist plot in the figure. It is seen that the sample P1 shows a large semicircle region which denotes the presence of bulk resistance( $R_b$ ) which can be explained using a circuit having capacitor parallel to a resistor. This semicircle region

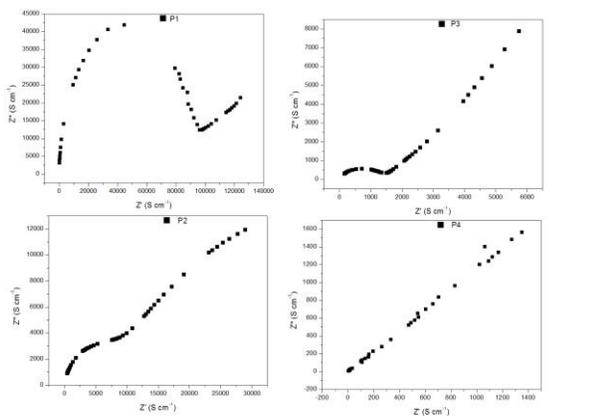
seems to be get decreased for the samples P2 and P3. For the sample P4 the semicircle region is fully disappeared which represents the low resistance which enhances high conductivity. Thus the semicircle region decreased with increase in  $\text{LiClO}_4$  content. EQ software developed by Boukamp is used here to calculate the bulk resistance ( $R_b$ ) of the polymer electrolytes from impedance plots of the low frequency side intercept on  $Z'$  axis. The ionic conductivity is calculated using the formula

$$\sigma=L/R_bA(\text{Scm}^{-1})$$

where L and A represent thickness and area of the samples respectively. It is seen that the bulk resistance value for the polymer electrolytes decreased with increase in  $\text{LiClO}_4$  content[12]. From table it is noted that the conductivity value for sample P2 and P3 is  $1.3 \times 10^{-7} \text{ Scm}^{-1}$  and  $1 \times 10^{-6} \text{ Scm}^{-1}$ , whereas for the sample P4 it seems to be  $3.5 \times 10^{-5} \text{ Scm}^{-1}$  which clarifies that the  $\text{LiClO}_4$  content played a vital role in enhancing the ionic conductivity.

#### **Tabulation 1. Compositions, calculated Tg, ionic conductivity, dielectric relaxation parameters of the prepared polymer blend electrolytes at 303K.**

Sample composition	Use d her eaft er as	T <sub>g</sub> <sup>o</sup> C	σ calcu lated from Nyq uist plot( Scm <sup>-1</sup> )	σ dc(S cm <sup>-1</sup> )	F <sub>ma x</sub> (Hz)	Rela xatio n time τ(sec )
100m% (PMMA:PVC:PV Ac)	P1	139	3.2 x 10 <sup>-8</sup>	3 x 10 <sup>-8</sup>	9 x 10 <sup>2</sup>	5.65 x 10 <sup>-3</sup>
80m% (PMMA:PVC:PV Ac):20m%LiClO <sub>4</sub>	P2	126	1.3 x 10 <sup>-7</sup>	1.3 x 10 <sup>-7</sup>	2 x 10 <sup>2</sup>	1.25 x 10 <sup>-3</sup>
60m% (PMMA:PVC:PV Ac):40m%LiClO <sub>4</sub>	P3	96	1 x 10 <sup>-6</sup>	5.8 x 10 <sup>-7</sup>	6 x 10 <sup>4</sup>	3.76 x 10 <sup>-5</sup>
40m% (PMMA:PVC:PV Ac):60m%LiClO <sub>4</sub>	P4	79	3.5 x 10 <sup>-5</sup>	3.5 x 10 <sup>-5</sup>	2 x 10 <sup>5</sup>	1.25 x 10 <sup>-6</sup>



**Figure 3.4.1 Representing Nyquist plots of the polymer electrolytes P1, P2, P3 and P4 at 303K**

### 3.5 Conductance spectra

The study of dielectric relaxation in solid polymer electrolytes is a powerful approach for obtaining information about the characteristic of ionic and molecular interactions. The complex permittivity ( $\epsilon^*$ ) or dielectric constant of a system is defined by

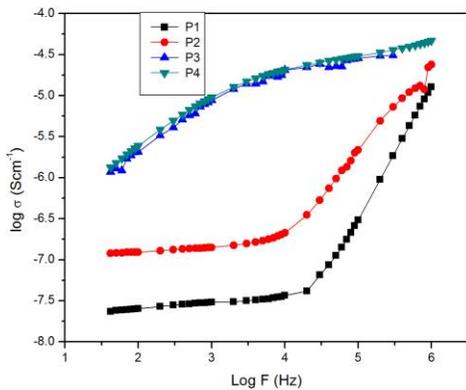
$$\epsilon - j(\sigma'/\omega\epsilon_0)$$

Where  $\epsilon$  is real part of dielectric constant,  $\epsilon''$  is imaginary part of dielectric constant,  $\omega$  is angular frequency and  $\epsilon_0$  is permittivity of free space respectively.

From the figure it was seen that the dielectric permittivity rose sharply towards low frequencies, which was due to electrode polarization effect. The low frequency dispersion region was due to accumulation of

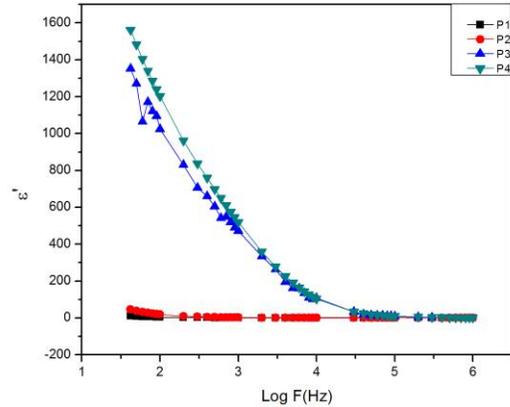
charge on electrode-electrolyte interface. At high frequencies due to high periodic reversal of applied field at the interface, the dielectric constant  $\epsilon'$  decreased with increase in frequency.

It was noted that the dielectric loss( $\epsilon''$ ) become very large( $2 \times 10^5$ ) at lower frequencies due to free charge motion. But this does not correspond to bulk dielectric process, but were due to the free charges built up at the interfaces of the electrolyte and electrode[13]. At low frequencies there was enough time for the charges to build up at the interfaces before the field changes the direction and this contributed to very large apparent values of  $\epsilon''$ . This phenomenon that's why is called as "Conductivity relaxation".

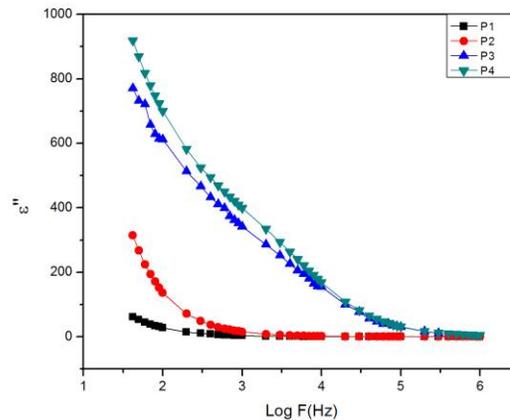


**Figure 3.4.2** representing conduction spectra of the polymer electrolytes P1,P2,

**P3 and P4 at 303K**



**Figure 3.4.3.a** Dielectric spectra of polymer blend electrolytes P1,P2,P3 and P4 at 303K



**Figure 3.4.3.b** Dielectric spectra of the polymer blend electrolytes P1,P2,P3 and P4 at 303K.

### 3.6 Loss tangent spectra

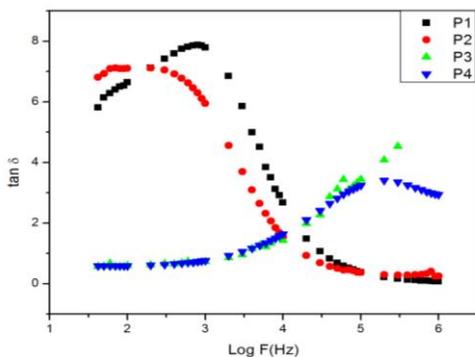
The dielectric relaxation parameter of the prepared polymer electrolytes P1, P2, P3 and P4 are obtained from the plot of  $\text{Tan } \delta$  as a function of frequency. The dielectric loss tangent was defined by the equation,

$$\text{Tan } \delta = \epsilon'' / \epsilon'$$

It is observed figure for all the samples the  $\text{Tan } \delta$  increased with increase in frequency and starts to decreased with further increase of frequency, for maximum dielectric loss the equation can be given as

$$\omega \tau = 1$$

where  $\omega$  and  $\tau$  represent the angular frequency and relaxation time of the applied electric field. The relaxation time for the polymer matrixes has been tabulated above. From table 1 the value of  $\tau$  seems to be decreased from  $5.6 \times 10^{-3}$  seconds to  $1.25 \times 10^{-6}$  seconds. This decrease in relaxation time enhances ionic conductivity. This is the reason why P4 sample exhibited highest ionic conductivity which has lowest relaxation time[14].



**Figure 3.4.4 loss tangent spectra of the polymer electrolytes P1,P2, P3 and P4 at 303K.**

### 4.Conclusion:-

The ternary blend polymer electrolytes of PMMA:PVC:PVAc:LiClO<sub>4</sub> of various compositions are prepared using solution casting technique. XRD diffractograms reveals the increase in amorphous nature with addition of LiClO<sub>4</sub>, thereby explaining the complexation of lithium ions with the polymer matrix. FTIR studies shows the variation in molecular vibrations, as the content of LiClO<sub>4</sub> gets increased in the blend, which in turn explaining the diffusivity, miscibility and complexation of Lithium ions in the prepared polymer blend electrolyte. DSC studies reveals the decrease in T<sub>g</sub> values of the (PMMA:PVC:PVAc):LiClO<sub>4</sub> system which is due to the segmental motion of Lithium ions in the polar groups of the polymer matrix. Ionic conductivity seems to be of increasing trend with increase in salt concentration, i.e for P2((80% PMMA:PVC:PVAc):20%LiClO<sub>4</sub>) the conductivity seems to be  $3.2 \times 10^{-8} \text{ Scm}^{-1}$  and for P4((40%PMMA:PVC:PVAc):60%LiClO<sub>4</sub>) the conductivity is  $3.5 \times 10^{-5} \text{ Scm}^{-1}$  at 303K. Low frequency dispersion region from the dielectric studies reveals the space charge effects arising from electrodes. From loss tangent spectra it was confirmed that the lowest relaxation time( $\tau$ ) which arise for the sample P4 favored highest ionic conductivity.

### Declaration of interests

The authors declare that they have no known competing financial interests or personal

relationships that could have appeared to influence the work reported in this paper.

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