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Preparation and Characterization of PVC – PEO Based Polymer Blend Electrolytes Complexed With Lithium Perchlorate

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Abstract:- Polymer blend electrolyte films, based on polyvinyl chloride (PVC), polyethylene oxide (PEO) as a host polymer complexed with lithium perchlorate ($LiClO_4$) as salt were prepared using solution – casting technique. Tetrahydrofuran (THF) was used as a solvent. The complexations of these films were examined by Fourier transform infrared (FTIR) spectroscopy. The increase in amorphicity with increase in PVC content was observed through XRD studies. The ionic conductivities of the prepared samples were measured using AC impedance analyser in the frequency range of 1Hz – 10MHz. Among the three blend ratios studied, PVC (37.5%) – PEO (37.5%) – $LiClO_4$ (25%) exhibited a maximum ionic conductivity as 6.5 x 10^{-6} Scm^{-1} at room temperature. This was supported through XRD, FTIR and SEM studies.

Keywords:- Polymer blend electrolytes; ionic conductivity; amorphicity; complexation.

I. INTRODUCTION

The field of polymer engineering has become the driving force in the advances in battery technology with the emergence of the 21st century. This requires the availability of solid polymer electrolyte films with adequate conductivity, good mechanical property, electrochemical stability and ease of processing **[1, 2]**. The most commonly studied solid polymer electrolyte membranes are complexes of Li salts with a high molecular weight polyethylene oxide (PEO) **[3]**. PEO excels as a polymer host because of its high solvating power for lithium ions and its compatibility with the lithium electrode **[4]**. However, high ionic conductivity (10^{-3} – 10^{-4} Scm^{-1}) of most PEO – based polymer electrolytes is achieved at the temperature range of 80 – 100 ^0C **[3 – 7]**, while at low temperature PEO exhibits low conductivity (10^{-7} – 10^{-8} S/cm) because of the high crystallinity of PEO **[6, 7]**.

Many intensive efforts have been devoted to increase the ionic conductivity of PEO – based polymer electrolytes **[8]**. The most common method is the addition of liquid plasticizers to the polymer matrix. This plasticized polymer electrolytes, exhibit higher ionic conductivity of the order of 10^{-3} Scm^{-1} **[9]**. But the plasticized polymer electrolytes have drawbacks such as solvent volatility, increased reactivity with lithium metal electrode and poor mechanical properties at high degree of polarization **[8]**.

To overcome the drawbacks of liquid plasticizers, there are other methods to increase the ionic conductivity of PEO – based solid polymer electrolytes. It is by the introduction of inorganic fillers such as SiO_2, Al_2O_3, TiO_2 etc., **[10 – 15]**.

Polymer blending is one of the most feasible techniques for the above said purpose. This technique has the advantages from other techniques like easy preparation and control of the physical properties within the miscibility compositional regime **[16 – 19]**. In the present work, we have made an attempt to prepare and characterize PVC – PEO based blend polymer electrolyte membrane complexed with $LiClO_4$.

The polymer PVC is chosen for blending because of its excellent miscibility and compatibility properties with various low or high molecular weight polymers as well as providing good mechanical strength. This is due to its lone pair of electron from the chlorine atom which can act to stiffen the backbone of the polymer. Besides, the inexpensive PVC can well solvated with the inorganic salts **[20, 21]**.

Polyethylene oxide is the most widely used interesting material because of its high chemical and thermal stability. PEO is a semi-crystalline polymer, possessing both amorphous and crystalline phases at room temperature **[22]**. Lithium perchlorate ($LiClO_4$) is chosen as it fulfils the electrochemical stability criteria and it has a low lattice energy (723 $KJmol^{-1}$) which is favourable for polymer – salt complexation **[23]**.

In this work, the weight ratio of $LiClO_4$ remains fixed in all the samples and the PVC is blended with PEO and their composition is varied at different weigh ratios, so that we can find the optimum ratio of PVC and

PEO that exhibits the highest ionic conductivity. The structural (XRD), complexation (FTIR), morphological (SEM) studies of these polymer blend electrolytes with different weight ratios of PVC and PEO are reported.

II. EXPERIMENTAL

A. Materials

In this study, PVC with an average molecular weight of 45,000 gmol^{-1} (Aldrich, USA), PEO with an average molecular weight of 1,00,000 gmol^{-1} (Alfa Aeson, India), inorganic salt $LiClO_4$ (Aldrich, USA) and the solvent tetrahydrofuran (Merck, India) were used without any further purification. Solvent casting technique was employed to prepare the polymer blend electrolytes used in this study.

B. Preparation of Polymer Blend Electrolytes

Different weight ratios of PVC/PEO blend and $LiClO_4$ were dissolved separately in THF and these solutions were then mixed together and stirred for 24 hours at room temperature to obtain a homogenous mixture. The solution was then poured into a petri dish and allowed to evaporate at room temperature for one day. Then the samples were placed inside a vacuum oven at 65^{0}C for 24 hours to remove any traces of solvent. This procedure yields mechanically stable and free standing films of average thickness of the order of mm. The compositions of the films are PVC (25%) – PEO (50%) – $LiClO_4$ (25%), PVC (37.5%) – PEO (37.5%) – $LiClO_4$ (25%) and PVC (50%) – PEO (25%) – $LiClO_4$ (25%).

C. Characterization Techniques

The amorphicity of polymer blend electrolytes was investigated using XRD. The XRD patterns were recorded using XPERT – PRO system, over the range of 2θ from 10^0 to 80^0 at room temperature. FTIR analysis was performed with SHIMADZU – 8400S FTIR spectrometer in the wave number region between 4000 cm^{-1} and 400 cm^{-1}, with a resolution of 4 cm^{-1}. The surface morphology was investigated through Scanning Electron Microscopy. The SEM images were obtained using HITACHI system. The impedance measurements were performed using a computer based phase sensitive multimeter (PSM 1735) in the frequency range of 1 Hz to 10 MHz at room temperature. The measurements were done by sandwiching the electrolyte film between two golden plated electrodes.

III. RESULTS AND DISCUSSION

A. X – ray Diffraction Studies

The X-ray diffraction patterns of pure PVC, PEO, $LiClO_4$ and their complexes are shown in **figures from 1(a) to 1(j)** respectively. The X-ray diffraction pattern for PVC is shown in **Fig. 1a**. PVC generally exhibits an amorphous phase **[24]**, but some of the crystalline peaks are observed at 16.6º and 25.4º of 2θ for the sample used in the present study. The incorporation of lithium salt into the PVC matrix causes a shift in the Bragg peaks from 16.6º to 17º and from 25.4º to 26.3º as observed in **Fig. 1d**. This behaviour demonstrates that the complexation has occurred between the salt and the polymer **[25, 26]**.

Table I: Values of crystallite size (D_P), Bragg's angle (2θ) and FWHM (β) for PEO and PVC – PEO blends.

Sample Name	2θ (deg)	β (rad)	D_P (nm)
Pure PEO	23.2	0.0115	12.850
PVC (25%) – PEO (50%)	23	0.0174	8.490
PVC (37.5%) – PEO (37.5%)	23	0.0218	6.776
PVC (50%) – PEO (25%)	26	0.0218	6.815

The XRD pattern of pure PEO is shown in Fig. 1b which contains two strong crystalline peaks at 19.1º and 23.2º. The higher intensity of these diffraction lines is suggesting that the PEO is intrinsically crystalline polymer with high crystallinity **[27]**. The intensity of these peaks of crystalline PEO decreases with increasing PVC content as shown in **figures 1(e – g)**. The PEO peaks become relatively broader as well as less prominent/feeble when the PVC content is greater than PEO in the blend. Thus, the higher PVC content supports the increase of the amorphous nature of PVC-PEO blends **[28]**.

The diffraction pattern of pure $LiClO_4$ is shown in **Fig. 1c**. The presence of sharp diffraction peaks in $LiClO_4$ indicates the crystalline nature of the salt. In the Fig. 1c, a strong peak is observed at 31.6º and the minor peaks are found at 35.8º and 39.6º. The absence of these sharp peaks pertaining to $LiClO_4$ is observed in the XRD patterns of polymer blend complexes as shown in **figures 1(h – j)**, and there is no additional peaks observed in the complex which confirmed the complexation of lithium salt with PVC – PEO blend electrolyte **[29]**.

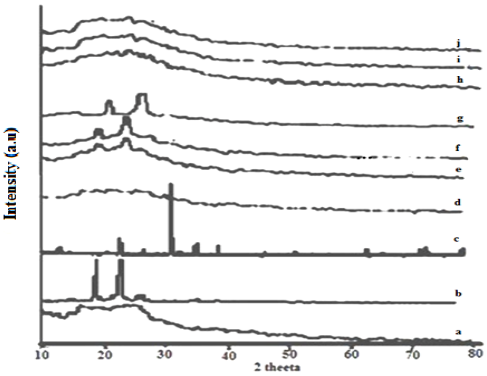


Fig. 1: XRD Pattern of a) Pure PVC, b) Pure PEO, c) Pure $LiClO_4$, d) PVC – $LiClO_4$, e) PVC (25%) – PEO (50%),
f) PVC (37.5%) – PEO (37.5%), g) PVC (50%) – PEO (25%), h) PVC (25%) – PEO (50%) – $LiClO_4$,
i) PVC (37.5%) – PEO (37.5%) – $LiClO_4$, j) PVC (50%) – PEO (25%) – $LiClO_4$

The crystallite size (D_p) has been calculated for PEO and its blends with PVC using Scherrer's formula

$$D_p = \frac{0.94\lambda}{\beta_{1/2}cos\theta} \qquad \ldots (1)$$

And their values are given in **Table I**. □ is the X-ray wavelength. The values of 2□ and FWHM (□) are also included in the table. It can be seen from the values of crystallite size that the crystallinity of pure PEO was decreasing on blending with pure PVC. The reduction of crystallinity is found to be higher for the blend PVC (37.5%) – PEO (37.5%) which in turn being more amorphous than pure PEO and the other blends.

B. FTIR Spectroscopy

The FTIR spectrum of pure samples of PVC, PEO and $LiClO_4$ are given in **Fig. 2**. It also includes the spectrum of polymer electrolyte PVC – $LiClO_4$ and polymer blend electrolyte PVC – PEO – $LiClO_4$. The vibrational peaks of all the samples are given in **Table II** along with the vibrations of constituent groups of polymer and salt.

The recorded FTIR spectrum of pure PVC in **Fig. 2a** is comparable with earlier reports of Rinaldi et al., **[30]** and Rajendran et al., **[29]**. The PVC spectrum consists of CH_2 asymmetric stretching vibration modes at 2972 cm^{-1} and 2910 cm^{-1}. The symmetric CH_2 stretching vibration is observed at 2868 cm^{-1}. The intense peak at 1425 cm^{-1} is due to the deformation of CH_2. The CH_2 wagging and CH_2 twisting is observed at 1253, 1332 and 1197 cm^{-1}. The C – C stretching vibration is occurred at 1064 cm^{-1} and CH_2 rocking vibration is appeared at 962 cm^{-1} and the stretching mode of C – Cl is at 692, and at 615 cm^{-1}.

The FTIR spectrum of pure PEO is shown in **Fig. 2b** and it has CH_2 asymmetric stretching vibration peak at 2922 cm^{-1}. The CH_2 symmetric stretching vibration peak is observed at 2856 cm^{-1}. The weak absorption peaks at 1735 cm^{-1} corresponding to C = O stretching and C = C stretching vibration at 2376 cm^{-1} are observed. The vibration peak at 1462 cm^{-1} corresponds to the CH_2 deformation and the peaks at 1344, 1228 cm^{-1} are corresponding to CH_2 wagging vibrations of PEO. The crystalline PEO phase in the XRD is confirmed by the presence of triplet peak of the C – O – C stretching vibration at 1101 cm^{-1} **[31]**. The presence of two peaks at 960, 842 cm^{-1} are the characteristic peaks in supporting the gauche conformation of [-CH_2-CH_2-] group as needed for a helical conformation of pure PEO **[26]**.

Table II: The vibrational modes and their assignment for PVC, PEO, $LiClO_4$ and PVC – PEO – $LiClO_4$ systems

Pure PVC		Pure PEO		Pure $LiClO_4$		PVC (37.5%) – PEO(37.5%) – $LiClO_4$	
Wave number	Assignments	Wave number	Assignments	Wave number	Assignments	Wave number	Assignments
2972 cm^{-1} and 2910 cm^{-1}	CH_2 asymmetric stretching	2922 cm^{-1}	CH_2 asymmetric stretching			2910 cm^{-1}	CH_2 asymmetric stretching
2868 cm^{-1}	Symmetric CH_2 stretching	2856 cm^{-1}	CH_2 symmetric stretching				

	vibration						
1425 cm^{-1}	Deformation of CH_2	2376 cm^{-1}	C = C stretching				
		1735 cm^{-1}	C = O stretching				
1253, 1332 and 1197 cm^{-1}	CH_2 wagging and CH_2 twisting	1462 cm^{-1}	CH_2 deformation				
		1344, 1228 cm^{-1}	CH_2 wagging vibrations				
1064 cm^{-1}	C – C stretching	1101 cm^{-1}	C – O – C stretching			1093 cm^{-1}	C – O – C stretching
962 cm^{-1}	CH_2 rocking	960, 842 cm^{-1}	Gauche conformation of [$-CH_2-CH_2-$]			954 cm^{-1}	CH_2 rocking
692 and 615 cm^{-1}	Stretching mode of C – Cl			630 cm^{-1}	Coordinated ClO^-_4 ion vibration	688 and 623 cm^{-1}	Stretching mode of C – Cl

FTIR spectrum of pure $LiClO_4$ is shown in **Fig. 2c**. The peak observed at 630 cm^{-1} corresponds to coordinated ClO^-_4 ion vibration.

The FTIR spectrum of the sample PVC (75%) – $LiClO_4$ (25%) is shown in **Fig. 2d**. A close look on **Fig. 2a** and **Fig. 2d** reveals that the CH_2 symmetric vibration of pure PVC found at 2868 cm^{-1} is absent for PVC – $LiClO_4$ complex. The intense CH_2 deformation observed at 1425 cm^{-1} for PVC is shifted to 1435 cm^{-1} and CH_2 wagging deformation peaks observed at 1332, 1197, 962 cm^{-1} in PVC are shifted to 1330, 1193, 964 cm^{-1} for the complex. These observations indicated a good complex formation between PVC and $LiClO_4$.

The FTIR spectra of the blends for different weight ratios of PVC and PEO are given in **figures 2(e – g)**. The intense CH_2 asymmetric vibration peak of PVC becomes broader against the increase of PEO content. The CH_2 symmetric vibration peak 2868 cm^{-1} of PVC is disappeared for the blend PVC (25%) – PEO (50%) and shifted to 2893 cm^{-1} for PVC (37.5%) – PEO (37.5%). It is shifted to 2887 cm^{-1} for PVC (50%) – PEO (25%). The weak C = O stretching vibration peak 1735 cm^{-1} of PEO is shifted to 1728 cm^{-1} for PVC (37.5%) – PEO (37.5%) and it is disappeared for PVC (50%) – PEO (25%). Further, the C = O stretching peak is shifted to 1724 cm^{-1} for PVC (25%) – PEO (50%). The CH_2 deformation peak observed at 1425 cm^{-1} for PVC is shifted to 1465 cm^{-1} for the blend PVC (25%) – PEO (50%) and to 1467 cm^{-1} for PVC (37.5%) – PEO (37.5%). But for the blend PVC (50%) – PEO (25%), the said peak has not shifted and appeared with reduced intensity. Thus, the blend PVC (37.5%) – PEO (37.5%) is found to be more compatible as all the vibrational modes of PVC undergo a significant shift in this composition. It can also be stated that there is complexation between PVC and PEO and it is stronger for the said composition of PVC (37.5%) and PEO (37.5%) of the blend.

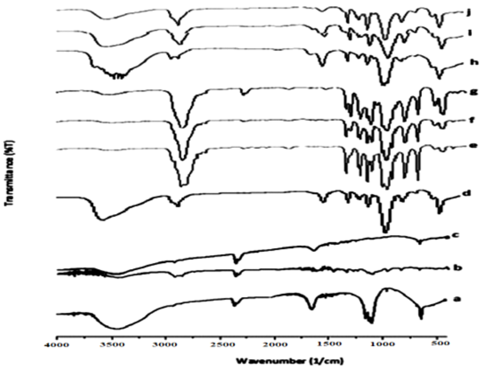


Fig. 2: FTIR Spectra of a) Pure PVC, b) Pure PEO, c) Pure $LiClO_4$, d) PVC – $LiClO_4$, e) PVC (25%) – PEO (50%), f) PVC (37.5%) – PEO (37.5%), g) PVC (50%) – PEO (25%), h) PVC (25%) – PEO (50%) – $LiClO_4$, i) PVC (37.5%) – PEO (37.5%) – $LiClO_4$, j) PVC (50%) – PEO (25%) – $LiClO_4$

The spectra of PVC – PEO polymer blends with $LiClO_4$ complexes are shown in **figures 2(h – j)**. A comparison of **Fig. 2(e – g)** and **Fig. 2(h – j)** shows that there is complex formation between PVC – PEO blend and the lithium salt. The CH_2 asymmetric vibration peak 2910 cm^{-1} of PVC is observed for each polymer blend electrolytes but their intensity decreases with the increase of PVC content. The observed CH_2 deformation peak 1425 cm^{-1} of the blends is shifted to lower frequency due to the addition of salt. The C – O – C stretching vibration peak 1097 cm^{-1} of PVC – PEO blends is shifted to 1093 cm^{-1} and becomes broader for PVC (37.5%) – PEO (37.5%) – $LiClO_4$ (25%). The CH_2 rocking vibration peaks at 962 and 842 cm^{-1} of PVC – PEO blends are shifted to 954, 837 cm^{-1} for PVC (37.5%) – PEO (37.5%) – $LiClO_4$ (25%) and to 956, 835 cm^{-1} for the other ratios of PVC and PEO. Similarly, the C – Cl stretching vibration peaks 692, 636 cm^{-1} of PVC – PEO blends are shifted to 688, 623 cm^{-1} for PVC (37.5%) – PEO (37.5%) – $LiClO_4$ (25%) and to 680, 624 cm^{-1} for the other ratios of PVC and PEO.

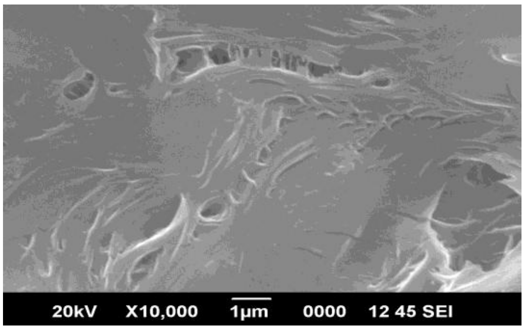
From the above observed changes in the vibrational frequencies of CH_2 asymmetric vibration, deformation, C – O – C stretching and C – Cl stretching of PVC it can be stated that there is complex formation between the blends and $LiClO_4$ salt. Also, there is interaction between the Li^+ ions and the ether oxygen of PEO which forms the transient cross linking complex which weakens C – O – C vibrations and decreases the crystallinity of PEO **[32]**.

C. SEM Studies

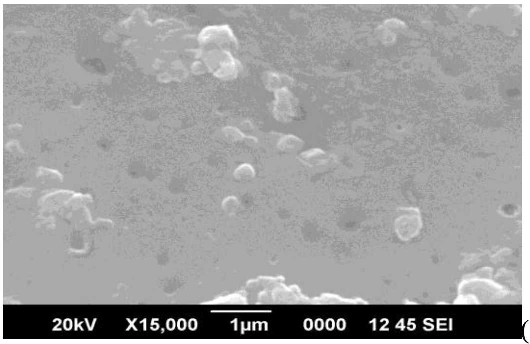
The electronic properties of PVC/PEO films are intricately linked to the morphology; a smoother, more dense film will generally be more conductive, as it is likely to be less porous and more ordered, which can facilitate charge transport through the film. In trying to understand the role that the ionic conductivity plays in producing such electrochemically active polymer films, electron microscopy is used to investigate the surface morphology **[33]**.

The surface morphology of PVC – PEO polymer blends and their complexes with $LiClO_4$ are given in **Fig. 3a – 3f**. Pure PVC shows a smooth surface morphology where as PEO with a rough surface having several crystal domains as observed by Wenjing Li et al. **[34]** and Yan-Jie-Wang et al. **[35]** respectively.

The **Fig. 3a** shows the micrograph of PVC (25%) – PEO (50%). The **Fig. 3b** is the SEM image of PVC (37.5%) – PEO (37.5%) blend, which shows a smooth surface morphology when compared with that of earlier system. This indicated the disappearance of the PEO crystalline phase in the blend. The micrograph given in **Fig. 3c** is of the blend PVC (50%) – PEO (25%) which had different size of pores in smooth surface. These pores are corresponding to the interconnected networks of polymers which would be created due to the solvent evaporation **[27]**.



(a)



(d)

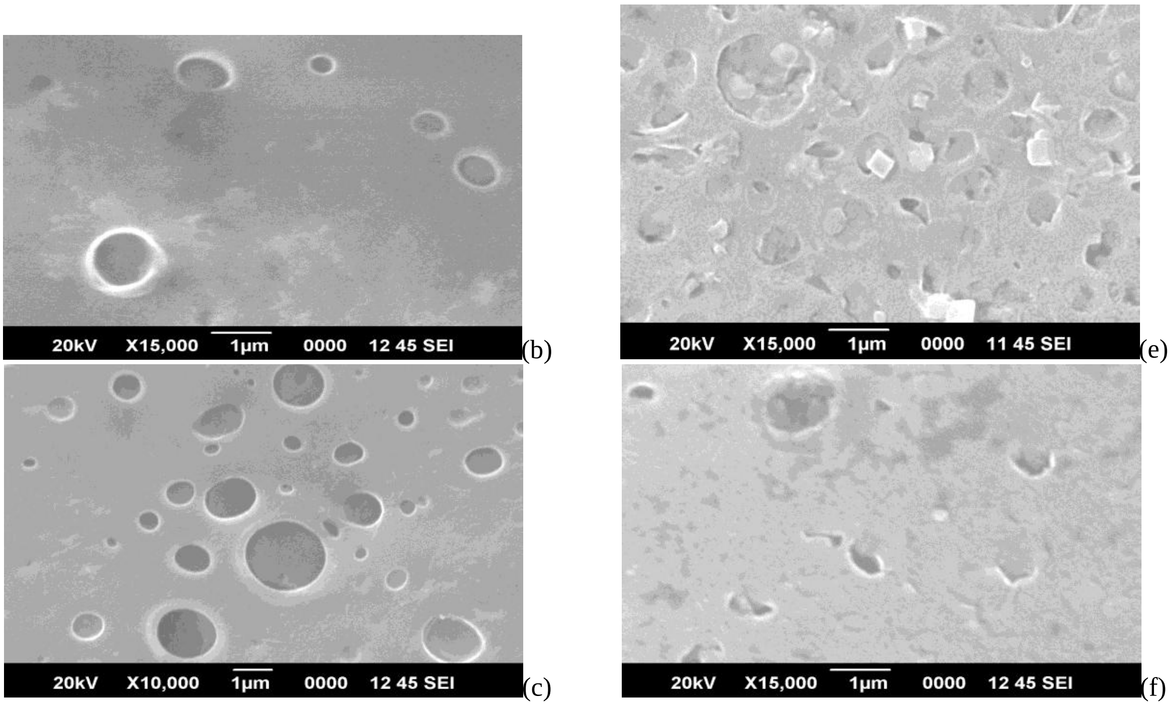


Fig. 3: SEM images of a) PVC (25%) – PEO (50%). b) SEM image of PVC (37.5%) – PEO (37.5%),

c) SEM image of PVC (50%) – PEO (25%), d) SEM of PVC (25%) – PEO (50%) – $LiClO_4$ (25%), e) SEM of PVC (37.5%) – PEO (37.5%) – $LiClO_4$ (25%), f) SEM of PVC (50%) – PEO (25%) – $LiClO_4$ (25%)

The micrographs of blended polymer electrolyte PVC – PEO – $LiClO_4$ with different ratios of PVC and PEO are shown in **figures 3d to 3f**.

The micrograph given in **Fig. 3d** is of PVC (25%) – PEO (50%) – $LiClO_4$ (25%). It shows a smooth surface with micropores which indicates the immiscibility of PVC with PEO and $LiClO_4$. This has led to a lower ionic conductivity 1.68 x 10^{-9} Scm^{-1}. This observed lower ionic conductivity can be attributed to the presence of lesser number of pathways for ion transportation.

The SEM micrograph of PVC (37.5%) – PEO (37.5%) - $LiClO_4$ (25%) is given in **Fig. 3e** and it shows a smooth surface with more craters of different sizes. This is due to the favour of the formation of free ions in the system due to increased concentration of PVC form 25 wt% to 37.5 wt% and decreased concentration of PEO from 50 wt% to 37.5 wt%. This change in concentrations of PEO and PVC has unfavoured the ion pair formation and favoured the complex process of interaction between the tetrahydrofuran, $LiClO_4$, PVC and PEO during the evaporation **[26, 36, 37, 38]**. Thus, the enhancement in porosity/craters has been attributed to the enhancement of free ion formation and hence to the enhancement of ionic conductivity from 1.68 x 10^{-9} Scm^{-1} to 6.5 x 10^{-6} Scm^{-1}.

Further increase of PVC content to 50 wt% and the reduction of PEO content to 25 wt% in the PVC – PEO – $LiClO_4$ system have resulted in the reduction in ionic conductivity from 6.5 x 10^{-6} Scm^{-1} to 3.65 x 10^{-9} Scm^{-1}. The micrograph of the said system given in **Fig. 3f** shows a surface morphology with pores and cracks of different sizes. But the number of pores and cracks are lesser when compared with the previous system which showed a higher ionic conductivity. This is due to the unfavour of the formation of free ions in the system due to the increase of PVC concentration from 37.5 wt% to 50 wt% and the decrease of PEO concentration from 37.5 wt% to 25 wt%. As the interaction among the species, PEO, PVC, $LiClO_4$ and tetrahydrofuran, is concentration dependent, the change in the concentration of polymers has reduced the free ion formation and their transportation due to the alteration in the phase of the system.

A close look on the micrographs reveals that the surface roughening decreases gradually against the increase of PVC content. This is attributed to the fact that PVC has served as a plasticizer for PEO as concluded in FTIR and XRD studies. The difference in morphology of the films is consistent with the significant differences in the ionic conductivities of these films.

D. Ionic Conductivity Studies

The impedance spectra of polymer blend electrolytes with different compositions are shown in **Fig. 4(a – d)**. The impedance plots comprise of distorted semicircle in high frequency region followed by an inclined spike in the lower frequency region. The semicircle is due to bulk properties and the spike is to the ion diffusion in polymer electrolyte. The intercept of semicircle with real axis in the low frequency region gives rise to bulk resistance R of the material.

The ionic conductivity of PVC – PEO - $LiClO_4$ systems is calculated by the following equation

$$\sigma = \frac{t}{R_b A} \qquad \dots (2)$$

Where t is the thickness of the sample, A is the area of the electrode and R_b is the bulk resistance of the material. It is evident from the Cole-Cole plots of polymer blend electrolytes with different compositions of PVC and PEO that the intercept of the semicircle (bulk resistance) on the real axis decreases as well as increases with increasing composition of PVC. It has been found that the ionic conductivity has been enhanced at a particular composition of PVC and PEO and has been suppressed at the other compositions.

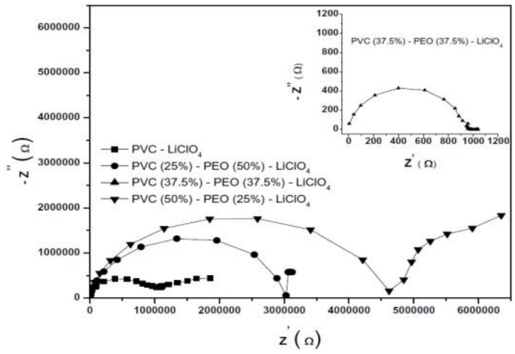


Fig. 4: AC Impedance Plots for a) PVC – $LiClO_4$,
b) PVC (25%) – PEO (50%) – $LiClO_4$ (25%)
c) PVC (37.5%) – PEO (37.5%) – $LiClO_4$ (25%),
d) PVC (50%) – PEO (25%) – $LiClO_4$ (25%)

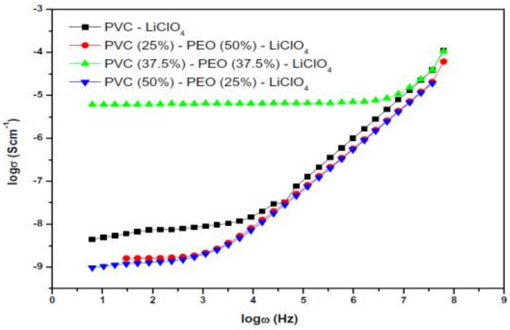


Fig. 5: Frequency dependence spectrum of PVC – PEO – $LiClO_4$ system

According to the previous reports, the conductivity of pure PVC is of the order 10^{-11} Scm^{-1} and pure crystalline PEO is of 10^{-9} Scm^{-1} **[30]**. Pure PEO has crystalline degree at room temperature **[39]**. It implies that PEO based polymer electrolyte has a very low ionic conductivity at room temperature. The amorphous phase contributes to the conductivity and the material has better ionic conductivity.

The ionic conductivity of the sample PVC (25%) – PEO (50%) – $LiClO_4$ (25%) has been determined as 1.68×10^{-9} Scm^{-1}. When the PVC content is increased to 37.5% followed by a reduction in the PEO content from 50% to 37.5% the conductivity increases to 6.5×10^{-6} Scm^{-1}. The increase in ionic conductivity with the increase of composition of PVC is attributed to a reduction in crystallinity of PEO. The coordination interactions of the ether oxygen of PEO with Li^+ cations which result in a reduction in crystallinity of PVC/PEO mixture are responsible for the increase in ionic conductivity. The interactions between Li^+ cations and polymer blends have been proved by FTIR analysis. A polymer chain in the amorphous phase is more flexible which results in an increase in segmental motion of the polymer, which facilitates higher mobility of ions **[22]**. A reduction in crystallinity of PVC/PEO electrolytes at higher concentration of PVC can also be seen from the XRD analysis that shows a broadening and decrement in the intensity of Bragg's peaks which results in the dominant amorphous phase in the electrolytes.

A further increase of PVC content to 50% in the PVC – PEO – $LiClO_4$ system shows a decrease in the ionic conductivity from 6.5×10^{-6} Scm^{-1} to 3.65×10^{-9} Scm^{-1}. The fall of ionic conductivity is due to excessive cross – linking effect which was reported by Kumara et al. **[44]**. When the loading of PVC is higher, it will lead to high degree of cross – linking between PVC and PEO which in turn increases the viscosity by forming entanglements within the polymer chain. Due to the entanglements, the favorable condition for ionic conduction (i.e., free voids) gets reduced which will restrict the mobility of charge carriers. This will lead to the decrement in the ionic conductivity of the polymer electrolyte.

1) Frequency Dependent Conductivity: The conductivity is calculated as a function of frequency from the real and imaginary parts of the impedance data. **Fig. 5** shows the frequency dependent conductivity spectra of PVC – $LiClO_4$ and PVC – PEO – $LiClO_4$ samples at room temperature. It is observed from the Fig. 5 that the frequency dependence of conductivity shows two regimes i) the low frequency plateau region and ii) the high frequency dispersion region. The low frequency plateau region corresponds to the frequency independent conductivity σ_o (or) σ_{dc}. The value of σ_o is obtained by extrapolating the plateau to the lower frequency **[41]**. The frequency dependence of conductivity in the high frequency dispersion region for polymer blend electrolytes at room temperature are analysed using the universal Jonscher's power law relation **[42]**.

$$\sigma(\omega) = \sigma_o + A\omega^n \qquad \text{… (3)}$$

Where σ_o is the limiting zero frequency conductivity and A is the pre-exponential constant. ω is the angular frequency and n is the power law exponent where $0 < n < 1$. Using the above equation, the fitting parameters σ_o, A and n are obtained and is given in **Table III**.

The values of σ_o obtained from the Jonscher's power law relation are found to be almost equal to the values of conductivity obtained from the cole-cole plot and are given in **Table III**. Further, the value of σ_o is higher for the system with equal content of PVC and PEO with $LiClO_4$ when compared with the other compositions. This revealed that the variation of conductivity is reflected in the mechanism of charge transport and interactions among the charge carriers. According to the jump relaxation model **[43]**, at low frequencies, ions jump from one site to its neighbouring vacant site. While at higher frequencies, due to the short time periods, the probability for ions to go fall back to their original sites increases. More hoping of ions is responsible for the higher conductivity in lower frequencies.

Table III: Comparison of parameters obtained from fit the experimental data to $\sigma(\omega) = \sigma_o + A\omega^n$ of PVC – PEO – $LiClO_4$ at room temperature

Sample Name	σ (Scm^{-1}) obtained from cole-cole plot	σ_o (Scm^{-1})	A	n	ω_p
PVC – $LiClO_4$	5.21×10^{-9}	4.395×10^{-9}	9.96×10^{-13}	1.00	4.412×10^3
PVC (25%) – PEO (50%) – $LiClO_4$	1.68×10^{-9}	1.59×10^{-9}	3.95×10^{-13}	1.029	3.185×10^3
PVC (37.5%) – PEO (37.5%) – $LiClO_4$	6.50×10^{-6}	6.11×10^{-6}	2.46×10^{-11}	0.776	8.960×10^6
PVC (50%) – PEO (25%) – $LiClO_4$	3.65×10^{-9}	1.008×10^{-9}	8.90×10^{-13}	0.971	0.920×10^3

The hopping frequency of the charge carrier (ω_p) can be estimated by the following equation,

$$\omega_p = \left(\frac{\sigma_0}{A}\right)^{1/n} \qquad \text{… (4)}$$

The value of ω_p is used to analyze the charge carrier mobility - in PVC – PEO – $LiClO_4$ system. In the present study, the value of ω_p increased with the increase of PVC content from 25% to 37.5%, which indicated the enhancement of both the mobility of ions and the number of charge carriers.

IV. CONCLUSION

PVC – PEO based polymer blend electrolytes complexed with $LiClO_4$ were prepared using solution – casting technique at three different blend ratios. The structural properties of these films were examined by X – ray diffraction patterns and Fourier Transform Infrared (FTIR) Spectroscopy. XRD studies revealed the amorphous nature of the polymer – blend salt complexes. FTIR studies confirmed the complexation in polymer blend and blend electrolytes. The higher ionic conductivity at room temperature, 6.5×10^{-6} Scm^{-1}, was observed for the system PVC (37.5%) – PEO (37.5%) – $LiClO_4$ (25%). This was supported through XRD, FTIR and SEM studies. The DC conductivity values estimated from Jonscher's power law and Cole-Cole plot were found to be almost equal.

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REFERENCES

[1]. F.M. Gray, Polymer electrolytes, Cambridge, UK: The Royal Society of Chemistry, 1993.
[2]. X. Hou, K.S. Siow, "Novel Interpenetrating Polymer Network electrolytes", *Polymer,* Vol. 42, pp.4181, Apr. 2001.
[3]. J.-H. Ahn, G.X. Wang, H.K. Liu, S.X. Dou, "Nanoparticle-dispersed PEO polymer electrolytes for Li batteries", *J. Power. Sources*, Vol. 119-121, pp. 422-426, Jun. 2003.
[4]. M. Alagmir, K.M. Abraham, Lithium batteries, new materials, development and prospective, In: Postoia G (eds), Amsterdam, Elsevier, 1994.
[5]. Abraham, K. M., "Applications of electro active polymers", In: Scrosati B (eds), London, U.K., Chapman and Hall, 1993.

[6]. M. Kovac, M. Gaberscek, J. Grdadolnik, “The effect of plasticizer on the microstructural and electrochemical properties of a $(PEO)_nLiAl(SO_3Cl)_4$ system”, *Electrochim. Acta*, Vol. 44, pp.863-870, Oct. 1998.

[7]. M. B. Armand, J.M. Chabagno, M.J. Duclot, Fast ion transport in solids, In: Vashista P, Shenoy GK (eds), New York, North-Holland, 1997.

[8]. M. M.E. Jacob, E. Hackett, E.P. Giannelis, “From nanocomposite to nanogel polymer electrolytes”, *J. Mater. Chem*. Vol. 13, pp.1-5, Nov. 2003.

[9]. J.Y. Song, Y.Y. Wang, C.C. Wan, “Review of gel-type polymer electrolytes for lithium-ion batteries”, *J. Power. Sources*, Vol. 77, pp.183-197, Mar. 1999.

[10]. L.Z. Fan, C-W. Nan, S.J. Zhao, “Effect of modified SiO_2 on the properties of PEO-based polymer electrolytes”, *Solid State Ionics*, Vol. 164, pp.81-86, Oct. 2003**.**

[11]. S. Zhang, J.Y. Lee, L. Hong, “Li^+ conducting ‘fuzzy’ poly (ethylene oxide)–SiO_2 polymer composite electrolytes*”, J. Power. Sources*, Vol. 134, pp.95-102, May 2004.

[12]. M. Nookala, B. Kumar. S. Rodrigues, “Ionic conductivity and ambient temperature Li electrode reaction in composite polymer electrolytes containing nanosize alumina”, *J. Power. Sources*, Vol. 111, pp.165-172, Sep. 2002.

[13]. X.M. Qian, N.Y. Gu, Z.L. Cheng, X.R. Yang, E.K. Wang, S.J. Dong, “Impedance study of $(PEO)_{10}LiClO_4$–Al_2O_3 composite polymer electrolyte with blocking electrodes”, *Electrochim. Acta*, Vol. 46, pp.1829-1836, Mar. 2001.

[14]. T. Liu, J.Y. Lee, L. Hong, “Morphology, crystallinity, and electrochemical properties of **in situ** formed poly (ethylene oxide)/TiO_2 nanocomposite polymer electrolytes”, *J. Appl. Polym. Sci.*, Vol. 89, pp.2815-2822, Jun. 2003.

[15]. S. Rajendran, O. Mahendran, R. Kannan, “Characterisation of $[(1-x)$ PMMA–xPVdF$]$ polymer blend electrolyte with Li^+ ion”, *Fuel*, Vol. 81, pp.1077-1081, May 2002.

[16]. Z. Ahmad, N.A. Al-Awadi, F. Al-Sagheer, “Morphology, thermal stability and visco-elastic properties of polystyrene–poly (vinyl chloride) blends”, *Polym. Degrad. Stabil.,* Vol. 92, pp.1025-1033, Jun. 2007.

[17]. M. Tang, W.R. Liau, “Solvent effect on the miscibility of poly (4-hydroxystyrene)–poly(ethylene oxide) blends”, *Eur. Polym. J.,* Vol. 36, pp.2597-2603, Dec. 2000.

[18]. K. Pielichowski, I. Hamerton, “Compatible poly(vinyl chloride)/chlorinated polyurethane blends: thermal characteristics”, *Eur. Polym. J.,* Vol. 36, pp.171-181, Jan. 2000.

[19]. A.M. Rocco, R.P. Pereira, M.I. Felisberti, “Miscibility, crystallinity and morphological behavior of binary blends of poly(ethylene oxide) and poly(methyl vinyl ether–maleic acid)”, *Polymer*, Vol. 42, pp.5199-5205, Jun. 2001.

[20]. A. Alamgir, K.M. Abraham, “Li Ion Conductive Electrolytes Based on Poly (vinyl chloride)”, *J. Electrochem. Soc.,* Vol. 40, pp.L96-L97, Mar. 1993.

[21]. T. Uma, T. Mahalingam, U. Stimming, “Solid polymer electrolytes based on poly (vinylchloride)–lithium sulphate”, *Mat. Chem. Phys.,* Vol. 90, pp.239-244, Apr. 2005.

[22]. R. Kirankumar, M. Ravi, Y. Pavani, S. Bhavani, A.K. Sharma, V.V.R. Narasimha Rao, “Investigations on the effect of complexation of NaF salt with polymer blend (PEO/PVP) electrolytes on ionic conductivity and optical energy band gaps”, *Physica B: Condensed Matter*, Vol. 406, pp.1706-1712, Apr. 2011.

[23]. Th. Joykumar Singh, S.V. Bhat, “Increased lithium-ion conductivity in $(PEG)_{46}$ $LiClO_4$ solid polymer electrolyte with δ-Al_2O_3 nanoparticles”, *J. Power Sources*, Vol. 129, pp.280-287, Apr. 2004.

[24]. S. Sejal, Q. Anjum, D. Singh, **N.L.** Singh, K.P. Singh, V. Shrinet, Dielectric properties and surface morphology of proton irradiated ferric oxalate dispersed PVC films”, *Ind J Pure and Appl Phys*., Vol. 46, pp.439-442, 2008.

[25]. S. Rajendran, R. Babu, K. Kanimozhi, “Studies on solid polymer electrolyte based on PEO/PVC blends”, *Ind J Phys.,* Vol. 81, pp.539-545, 2007.

[26]. S. Ramesh, A.K. Arof, “Structural, thermal and electrochemical cell characteristics of poly (vinyl chloride)-based polymer electrolytes”, *J. Power. Sources*, Vol. 99, pp.41-47, Aug. 2001.

[27]. I.E. Animista, A.L. Kruglyashov, “Morphology and ionic conductivity of poly (ethylene oxide)–poly (vinyl acetate)–$LiClO_4$ polymer electrolytes”, *Solid State Ionics*, Vol. 106, pp.321-327, Feb. 1998.

[28]. A. Chandra, R.C. Agarwal, Y.K. Manipal, “Ion transport property studies on PEO–PVP blended solid polymer electrolyte membranes”, *J Phys D: Appl Phys*., Vol. 42, pp.135107, Jul. 2009.

[29]. S. Rajendran, R. Babu, P. Sivakumar, “Investigations on PVC/PAN composite polymer electrolytes”, *J. Membr. Sci*., Vol. 315, pp.67-73, May 2008.

[30]. R.W. Rinaldi, R. Matos, A.F. Rubira, O.P. Ferrira, E.M. Girotto, "Electrical, spectroscopic, and thermal properties of blends formed by PEDOT, PVC, and PEO", *J. Appl. Polym. Sci.*, Vol. 96, pp.1710-1715, Mar. 2005.

[31]. S. Rajendran, M. Ramesh Prabhu, M. Usha Rani, "Characterization of PVC/PEMA Based Polymer Blend Electrolytes" *Int. J. Electrochem. Sci.*, Vol. 3, pp.282-290, 2008.

[32]. D. Zhou, X. Mei, J. Ouyang, "Ionic Conductivity Enhancement of Polyethylene Oxide-LiClO4 Electrolyte by Adding Functionalized Multi-Walled Carbon Nanotubes", *J. Phys. Chem. C*, Vol. 115, pp.16688–16694, Jul. 2011.

[33]. Ch. V. Subba Reddy, Q-Y, Zhu, L-Q, Mai, W. Chen, "Electrochemical studies on PVC/PVdF blend-based polymer electrolytes", *J. Sol. Stat. Electrochem.*, Vol. 11, pp.543-548, Mar. 2007.

[34]. W. Li, J.K-Kocsis, R. Thomann, "Compatibilization effect of TiO_2 nanoparticles on the phase structure of PET/PP/TiO_2 nanocomposites", *J. Polym. Sci. Part B: Polym. Phys.*, Vol. 47, pp.1616-1624, Jul. 2009.

[35]. Y-J, Wang, Y. Pan, L. Wang, M-J. Pang, L. Chen, "Characterization of (PEO)$LiClO_4$-$Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ composite polymer electrolytes with different molecular weights of PEO", J. *Appl. Polym. Sci.*, Vol. 102, pp.4269-4275, Sep. 2006.

[36]. M.Y.A. Rahman, A. Ahmad, T.K. Lee, Y. Farina, H.M. Dahlan, "Effect of Ethylene Carbonate (EC) Plasticizer on Poly (Vinyl Chloride)-Liquid 50% Epoxidised Natural Rubber (LENR50) Based Polymer Electrolyte", *Mater. Sci. App*., Vol. 2, pp.817-825, Jul. 2011.

[37]. H. M. Dahlan, A.G. Harun, R. Mamat, "Production of Liquid Epoxidised Natural Rubber (ENR) by Photochemical Technique", *Journal Sains Nuklear Malaysia*, Vol. 17, pp. 1-13, 1999.

[38]. R. Vickraman, V. Aravindan, M. Selvambikai, N. Shankarasubramanian, "Ionic transport, thermal, XRD, and phase morphological studies on $LiCF_3SO_3$-based PVC–PVdF gel electrolytes", *Ionics*, Vol. 15, pp.433-437, Aug. 2009.

[39]. D.K. Pradhan, R.N.P. Choudry, B.K. Samantary, N.K. Karan, R.S. Katiyar, "Effect of Plasticizer on Structural and Electrical Properties of Polymer Nanocompsoite Electrolytes", *Int. J. Electrochem. Sci.*, Vol. 2, pp.861-871, Oct. 2007.

[40]. R. Kumar, A. Subramania, A, N.T. Kalyana Sundaram, G. Vijaya Kumar, I. Baskaran, "Effect of MgO nanoparticles on ionic conductivity and electrochemical properties of nanocomposite polymer electrolyte", *J. Membr. Sci.*, Vol. 300, pp.104-110, Aug. 2007.

[41]. W.K. Lee, B.S. Lim, J.F. Liu, A.S. Nowick, "ac conductivity in ionically conducting crystals and glasses", *Solid State Ionics*, Vol. 53-56, pp.831-836, Jul. – Aug. 1992.

[42]. A.K. Jonscher, "The 'universal' dielectric response", *Nature*, Vol. 267, pp.673-679, Jun. 1977.

[43]. B. Natesan, N.K. Karan, R.S. Katiyar, "Ion relaxation dynamics and nearly constant loss behavior in polymer electrolyte", *Physical Review. E, Statistical, Nonlinear, and Soft Matter Physics*, 74 (4 Pt 1):042801, 2006.