CHAPTER VII

EFFECT OF DIFFERENT PLASTICIZERS ON PVdC-co-AN BASED POLYMER BLEND ELECTROLYTES

7.1. Introduction

Since the polymer electrolytes are capable of providing a higher output voltage, higher specific heat capacity, long cycle life, improved safety and so on, their applications for Li secondary are very wide and outstanding. Hence the studies on polymer electrolytes have reasonably increased in the recent decades [1-3]. The first polymer-based solid polymer electrolyte was suggested by Armand et al. [4]. Subsequently, the solid polymer electrolytes were considered for an ideal alternate to the liquid electrolytes. Starting from 1970, PEO and alkali metal salts based solid polymer electrolytes have got great consideration [5-7]. However, their ionic conductivity at ambient temperature is very low and is yet scarcely used for practical applications at elevated current densities. Many attempts have been made to increase the room temperature ionic conductivity in the polymer matrix. These attempts include innovative polymer synthesis [8-10], cross-linking of two polymers [11-13], blending of two polymers [14, 15], formulation of plasticized polymer electrolytes [16-18], synthesis of composite polymer electrolytes by the addition of inorganic fillers [19-21] and the formation of porous electrolytes employing the phase inversion method [22-24].

Out of these above mentioned techniques, blending of another polymer with PEO has been identified to have a good compatibility. Blending can, however, have profound and sometimes unexpected effects on thermal stability, which can’t simply be predicted on the basis of the behavior of the components and their relative
properties [25]. A common approach is to add low molecular weight plasticizers to the polymer electrolytes [26]. The plasticizers impart salt solvating power and high ion mobility to the polymer electrolytes. PEO is the most interesting base materials because of its high chemical and thermal stability. It can solvate a wide variety of salts even at high concentrations [27].

On the other hand, the addition of vinylidene chloride unit with poly(acrylonitrile) (PAN) gives high mechanical stability. The ionic conductivity of PAN based electrolytes is of the order of $10^{-5} - 10^{-6}$ S cm$^{-1}$ with good thermal stability. PEO–oligomers with the copolymer of poly(vinylidene chloride) and poly(acrylonitrile) based electrolytes incorporating lithium triflate were prepared by Kim et al. [28]. They reported the conductivity of the order of $10^{-4} - 10^{-5}$ S cm$^{-1}$ with the addition of plasticizer PC. This chapter illustrates the effect of different plasticizers on PVdC-co-AN based blend electrolytes and their results have been discussed elaborately.

### 7.2. Materials and methods

The solution casting technique was used to prepare the gel polymer electrolyte films. Poly(ethylene oxide) $M_w \sim 8000$, poly(vinylidene chloride-co-acrylonitrile) $M_w \sim 150,000$ and LiClO$_4$ were purchased from Sigma–Aldrich chemicals limited, USA and they were used as received. PEO and PVdC-co-AN were dried at 50°C under vacuum for 4h to remove moisture. The salt was annealed at 60°C under vacuum for 24h. The plasticizers were also procured from Sigma–Aldrich USA. The solvent THF was acquired from E-Merck. Different gel polymer electrolytes were prepared with a constant ratio of PEO(80wt%)/PVdC-co-AN(20wt%)/LiClO$_4$(8wt%)/X(12wt%) (where X = EC, PC, gBL, DEC, DMC and DBP). The polymers, salt and plasticizer were dissolved separately and mixed together. The mixed solution was stirred for 24h
with the help of a magnetic stirrer to obtain a homogeneous mixture. The solvent THF in the solution was allowed to evaporate slowly. Finally, the homogeneous solution was cast on Petri dishes. The Petri dishes containing the solution were dried at 50°C under vacuum for 12h to remove the residual solvent. The resulting free standing films were smoothly removed from the Petri dishes and cut into required shapes. The thickness of the harvested films was in the order of about 0.3 - 0.4mm. The prepared films were subjected to various characterizations namely XRD, FTIR, a.c impedance, TG/DTA, AFM, DSC, CV, LSV and PL studies.

7.3. Results and discussion

7.3.1. X-Ray diffraction Analysis

XRD patterns of the pure and prepared complexes are shown in Fig. 7.1. The XRD pattern of pure LiClO₄ salt shows well defined peaks at angles \( 2\theta = 18.36, 23.2, 27.5, 32.99 \) and \( 36.58^\circ \) which indicate its high crystalline nature. However, these peaks disappear in the polymer blends. The intense peaks at angles \( 2\theta = 19.1 \) and \( 23.3^\circ \) confirm the semi crystalline nature of PEO. The peaks at angles \( 2\theta = 40.25, 46.76 \) and \( 67.94^\circ \) corresponding to PVdC-co-AN elucidate its crystalline nature.

From Fig.7.1, it is observed that with the addition of lithium salt and different plasticizers to the polymer blend, the intensity of these peaks decreases gradually. These observations apparently reveal that the polymer blend undergoes significant structural reorganization upon the addition of different plasticizers. The plasticizers might have induced significant disorder into the original polymers and this is attributed to the interactions between polymer and the solvents, which resulted in polymer electrolytes with much lower crystallinity. Hence, the absence of peaks pertaining to lithium perchlorate salt in the complexes indicates the complete dissolution of the salt in the polymer matrix.
7.3.2. FTIR - Studies

FTIR is a quite commonly used technique to examine the interactions in polymer blends [29, 30]. The immiscibility and the phase-separation between the blending components will be identified by the spectra of pure individual components. On the other hand, the miscibility of the components is implied by the possibility of chemical interactions between the individual polymer chains, salt and plasticizer. Generally, wave number shifts, increase or decrease in the intensity of the peaks and broadening are taken as evidence of chemical interactions between the components in a blend and are indicative of miscibility.

Fig.7.2 illustrates the FTIR spectra of pure PEO, PVdC-co-AN, salt and that of the prepared sample with different plasticizers and the Table 7.1 shows the various band assignments corresponding to the wave numbers. The broad vibrational peak around 3445 cm\(^{-1}\) in the spectra pertaining to the -OH group [31] is attributed to the water or moisture absorption which might have happened during the sample loading for the spectral analysis. The peak at 3445 cm\(^{-1}\) is shifted to the wave numbers 3454, 3451, 3454, 3455, 3448 and 3452 cm\(^{-1}\) in all the prepared complexes. The well build vibrations of C=\(\equiv\)N and C=\(\equiv\)N bands in PVdC-co-AN [31] are represented by the peaks around 2245 and 1642 cm\(^{-1}\). These two peaks are shifted to the wave numbers 2244, 2251, 2255, 2244, 2240 cm\(^{-1}\) and 1646, 1648, 1646, 1653, 1646 cm\(^{-1}\) respectively in the EC, PC, gBL, DEC, DMC and DBP based gel polymer electrolytes.

The symmetric and asymmetric C – H stretching forms of \(\text{CH}_2\) in PEO [32] is symbolized by the strong absorption band appearing around 2800 – 2950 cm\(^{-1}\) which shifts to the wave numbers 2889, 2891, 2880, 2883, 2891 and 2887 cm\(^{-1}\) in all the prepared electrolytes. The strong vibration of the ether oxygen group in PEO is indicated by the peak around 1799 cm\(^{-1}\) [33] which is shifted, to the wave numbers
1797, 1804, 1797, 1806 and 1802 cm$^{-1}$. A strong vibrational peak at 1468 cm$^{-1}$ is attributed to CH$_2$ stretching of pure PEO which is shifted to 1460, 1462, 1462, 1460, 1463 and 1462 cm$^{-1}$ respectively [34]. It can be seen that the CH$_2$ asymmetric wagging mode appearing at 1346 cm$^{-1}$ for pure PEO shifts to the wave numbers 1356, 1352, 1359, 1354,1350 and 1351 cm$^{-1}$ respectively [35]. The - CH$_2$ symmetric twisting mode is embodied by the peak near 1242 cm$^{-1}$ in pure PEO which has been shifted to the wave numbers 1254, 1249, 1249, 1247, 1242 and 1240 cm$^{-1}$ in the samples SD1, SD2, SD3, SD4, SD5 and SD6 respectively [35]. The peak relating to the antisymmetric stretching vibration of the C – O – C bridge in PEO becomes visible close to 1100 cm$^{-1}$ [36] and it is shifted in the complexes to the wave numbers 1111, 1100, 1098, 1109, 1107 and 1107 cm$^{-1}$ respectively. The peak corresponding to ClO$_4^-$ vibration is found around 625 cm$^{-1}$ which is present in all the complexes.

New peaks pertaining to the absorption at 2166, 1965, 1460 cm$^{-1}$ of EC based complex; 2744, 2359, 2165, 1965, 1462, 1245 cm$^{-1}$ of PC based complex; 2511, 2358, 1964 cm$^{-1}$ of gBL based complex; 2513, 2353, 2167 cm$^{-1}$ of DEC based complex; 2742, 2361, 1244 cm$^{-1}$ of DMC based complex and 2743, 2165, 1720 cm$^{-1}$ of DBP based complex are also present in the FTIR spectra of the complexes.

The disappearance of the few characteristic peaks of the plasticizers, the appearance of the new peaks and shift in the peaks confirm the complex formation between polymers, salt and different plasticizers.

### 7.3.3. Complex impedance analysis

The conduction mechanism is studied with the help of ac impedance spectroscopy by observing the contribution of polymeric chain, mobility and carrier generation process [37]. Fig.7.3 depicts the room temperature ionic conductivity of the prepared gel polymer electrolytes. The theoretical analysis given by Watanabe and
Ogata [38] stipulates for two semicircles to be present in the impedance spectrum of asymmetric cell. One semicircle at high frequency region embodies the bulk electrolyte impedance and the other at low frequency region corresponds to the interfacial impedance. Reports say that the high frequency semicircles will not appear in the practical impedance plots of plasticized polymer electrolyte membranes [39, 40]. This feature reveals that the conductivity in these films is established mainly by the ions and is calculated using the formula $\sigma = l/(R_b A)$, where ‘$A$’ is the area of the film surface in contact with the electrodes, ‘$l$’ is the thickness of the film and the value of bulk resistance ($R_b$) is taken on the X- intercept of the impedance plots. The film SD1 complexed with EC plasticizer is found to have maximum ionic conductivity value of $3 \times 10^{-4}$ Scm$^{-1}$ at 303 K. The rationale is clarified as follows.

In general, the influence of plasticizer in the ionic conductivity of the polymer electrolyte films is determined by its own characteristics like dielectric constants, viscosity, polymer–plasticizer interaction and ion–plasticizer interaction. In this view, the plasticizer EC possesses a high dielectric constant (89.6 at 40°C) and comparatively low viscosity (1.9 cP). This may be the reason for the high ionic conductivity of the film SD1 complexed with EC. The plasticizers would dissolve enough charge carriers and provide more mobile medium for the ions so as to enhance the conducting behaviour of the samples [41]. The conductivity is obtained in the decreasing order of the EC, PC, gBL, DEC, DMC and DBP based gel polymer electrolytes which are in accordance with their dielectric constants 89.6, 64, 42, 28, 11 and 8.4 respectively. These results agree well with the earlier reports using different plasticizers [42, 43].

The ionic conductivity values of the sample observed over the temperature range 303-353K have been plotted in Fig.7.4. It could be visualized that the
conductivity values increase with the increase of temperature regardless the nature of the sample as given in Table 7.2. This enhancement in the conductivity values with increase of temperature could be elucidated with the free volume theory [44] which assumes that when the temperature increases, the vibrational energy of a polymer segment is sufficient to push against the hydrostatic pressure imposed by its neighbouring atoms and create a small amount of space surrounding its own volume in which the vibrational motion occur. The plot of the temperature dependent ionic conductivity indicates that the ion conduction in the polymer electrolytes seems to obey the VTF (Volgel-Tamman-Fulcher) relation which describes the transport mechanism in a viscous matrix [42, 45-47]. It supports the idea that the ion moves through the plasticizer-rich phase. Because, the conducting medium i.e. the plasticizer rich phase, involves the plasticizer, salt and polymers, the characteristics of the viscous matrix are brought out.

7.3.4. Thermogravimetry/differential thermal analysis (TG/DTA)

All the physical phenomena associated with the weight changes are elaborately studied using TG/TDA. TG/DTA curves of EC, PC, gBL, DEC, DMC and DBP based PEO/PVdC-co-AN/ LiClO₄ systems have been plotted as shown in Fig. 7.5 (a-f).

Table 7.3 illustrates weight losses with temperature. It is seen from Fig. 7.5 that the initial weight loss about 2-3% is observed in the temperature range 76-88°C. This may be due to the removal of residual solvent and moisture if any. The second weight losses attributing to the structural changes in the polymers occur between 272&289°C which are 33, 35, 35, 38, 37 and 34% for the samples SD1, SD2, SD3, SD4, SD5 and SD6 respectively. Then there is no appreciable weight loss observed
until the temperature reaches around 395-405°C. Maximum thermal stability (222°C) is observed for the sample SD1.

The DTA plots of the samples exhibit endothermic peaks between 67-71°C. The second and third peaks are exothermic peaks in the range of 274-289°C and 386-395°C respectively, which are well correlated with the weight loss of all the samples observed in TG curve.

7.3.5. DSC analysis

This technique is used to measure the difference in heat flow rate between the sample and inert reference as a function of time and temperature. The processes like glass transition, melting, evaporation, etc. are associated with the endothermic heat flow, whereas, the physical events like crystallization, cure, oxidation, etc. are accompanied by an exothermic heat flow.

Fig.7.6 displays the DSC plots of the samples with various plasticizers. It is noticed that the samples SD1, SD2, SD3, SD4, SD5 and SD6 show a phase transition at 27, 28, 30, 31, 32 and 33°C which are ascribed to the glass transition temperatures of the prepared complexes accordingly. The glass transition temperature of PEO is -53 to -45°C and that of PVdC-co-AN is around 50°C. Among the different complexes, the sample prepared with EC shows a minimum $T_g$ value which attributes to its maximum ionic conductivity. The decrease in the $T_g$ value also indicates the decrease of crystallinity upon the addition of plasticizer.

7.3.6. Photoluminescence studies

The polymer electrolyte films prepared with various plasticizers were subjected to photoluminescence analysis at an excitation wavelength of 280nm. Fig.7.7 shows photoluminescence emission spectra of the prepared electrolytes. The
carrier mobility of the electrolyte is inversely proportional to the local viscosity. But the local viscosity is directly associated with the emission intensity [48, 49].

In the present study, EC based polymer electrolyte system has a minimum emission intensity as compared to other samples. This might be due to the maximum dissociation of the ionic charge carriers owing to its high dielectric constant. As the photoluminescence emission intensity decreases, the local viscosity of the surrounding polymeric media also decreases. This in turn increases the ionic mobility and hence conductivity. These results are exclusively concurring with the ionic conductivity values [Table 7.2].

7.3.7. Atomic force microscopic analysis

Atomic force microscope was used to study the two and three dimensional topographical images of the sample having a maximum ionic conductivity. Fig.7.8 (a and b) represents the topographic images. From the figures, we are able to understand that there are number of pores within the scanned area of 50 µm×50µm. These small pores of the electrolyte are responsible for the enhancement of ionic conductivity. The pores helped to ensnare the large volume of the liquid in the pores accounting for the increased conductivity. The rms roughness value is found to be 200.9 nm. The increase of pore size and smoothness might be the rationale for the increased ionic conductivity of this film which agrees with the ionic conductivity results.

7.3.8. Cyclic voltammetric test

Since high ionic conductivity is not a sufficient property to make an electrolyte useful in practical terms, the electrochemical stability of the gel polymer electrolyte film (SD1) exhibiting maximum ionic conductivity was explored using cyclic voltammetry. The cyclic voltammograms of the SS/Gel polymer electrolyte/SS
cell couple was taken at different scan rates (25 - 150mV/s) as shown in Fig.7.9. There is one poorly defined anodic peak around 0.28V and one less prominent cathodic peak near -0.09V. This may be due to the strong capacitive current [50]. These peaks are associated with the oxidation and reduction of LiClO$_4$/polymer at the anode and cathode respectively.

It is also noticed that the area of the rectangles increases with the increase of scan rates. This reveals that the voltammetric current is directly proportional to the scan rate. The poor rectangular shape with the higher scan rate could be explained that the ion species from the polymer film may confront the difficulty to enter all the vacant sites in the active electrode. This pertains to the partial rate of movement in the electrolyte [51]. The overall performance of the polymer electrolyte film as separator is highly capacitive and electrochemically reversible.

7.3.9. Linear sweep voltammetric test

The electrochemical stability window of the gel polymer electrolyte having a maximum ionic conductivity was determined by linear sweep voltammetry with a constant scan rate (50mV/s) [52] as shown in Fig.7.10. The decomposition process of the polymer electrolyte results in the onset of current in the anodic higher voltage range and cathodic low voltage range [53]. The stability window for this film is observed around -2.8 to 2.6V and also indicates that there is no decomposition of any component in this potential range.
7.4. Conclusion

The gel polymer electrolytes consisting of PEO/PVdC-co-AN/LiClO₄ with different plasticizers were prepared by solution casting technique. The reduction in the XRD peaks and the increase of amorphousity due to the addition of plasticizers were confirmed by X-ray diffraction technique. The complex formation and the interaction between polymer-plasticizer and ion-plasticizer were ascertained by FTIR analysis. The maximum room temperature ionic conductivity value is found to be $3 \times 10^{-4}$ S cm$^{-1}$ for the film prepared with EC plasticizer owing to its high dielectric constant. The two and three dimensional topographic images of the sample having a maximum ionic conductivity show the presence of number of pores which are responsible for high ionic conduction. The maximum thermal stability is found to be 222°C for the sample SD1 from TG/DTA plots. The emission peaks observed from the photoluminescence spectra were in line with the conductivity results. The CV results show a strong capacitive behaviour of the gel polymer electrolyte exhibiting maximum ionic conductivity. The electrochemical stability window has been observed to be -2.8 to +2.6V.
Fig. 7.1. XRD patterns of the pure and prepared samples.
Fig. 7.2. FTIR spectra of the pure and the prepared samples.
Fig. 7.3. Room temperature complex impedance plots of the prepared samples.
Fig. 7.4. Temperature dependent ionic conductivity plots of the prepared samples.
Fig. 7.5 (a-f). TG/DTA plots of the prepared blend electrolytes.
Fig. 7.6. DSC curves of the prepared polymer electrolytes.
Fig. 7.7. Photoluminescence spectra of the prepared complexes.
Fig. 7.8. The topographic image of the sample (SD1) having a maximum ionic conductivity, (a) 2D image; (b) 3D image.
Fig. 7.9. Cyclic voltammograms of the sample (SD1) having a maximum ionic conductivity.
Fig. 7.10. Linear sweep voltammetric plot of the sample (SD1) having a maximum ionic conductivity.
Table 7.1. Assignments of FTIR absorption bands for the prepared membranes.

<table>
<thead>
<tr>
<th>Band assignment</th>
<th>Wave number (cm$^{-1}$)</th>
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<tbody>
<tr>
<td></td>
<td>PEO</td>
</tr>
<tr>
<td>-OH group vibration</td>
<td>-</td>
</tr>
<tr>
<td>-CH$_2$ Sym Stretching</td>
<td>2884</td>
</tr>
<tr>
<td>C=O Stretching</td>
<td>-</td>
</tr>
<tr>
<td>Ether oxygen group</td>
<td>1799</td>
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<tr>
<td>C=O Stretching</td>
<td>-</td>
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<tr>
<td>-CH$_2$ Scissoring</td>
<td>1468</td>
</tr>
<tr>
<td>-CH$_2$ Wagging</td>
<td>1346</td>
</tr>
<tr>
<td>-CH$_2$ Twisting</td>
<td>1242</td>
</tr>
<tr>
<td>C–O–C Asym. Stretching</td>
<td>1100</td>
</tr>
<tr>
<td>CH$_2$ sym.rocking</td>
<td>962</td>
</tr>
<tr>
<td>-CH$_2$ rocking</td>
<td>845</td>
</tr>
<tr>
<td>ClO$_4^-$ anion</td>
<td>-</td>
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</table>
Table 7.2. Ionic conductivity values of the prepared samples.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Composition of the prepared samples in wt%</th>
<th>Conductivity values for different temperatures ( (\sigma) \times 10^{-4} \text{Scm}^{-1} )</th>
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<tr>
<td></td>
<td>PEO(64)/PVdC-co-AN(16)/LiClO_4(8)/X(12)</td>
<td>303K</td>
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<tr>
<td>SD1</td>
<td>X = EC</td>
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<tr>
<td>SD2</td>
<td>X = PC</td>
<td>1.53</td>
</tr>
<tr>
<td>SD3</td>
<td>X = gBL</td>
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</tr>
<tr>
<td>SD4</td>
<td>X = DEC</td>
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</tr>
<tr>
<td>SD5</td>
<td>X = DMC</td>
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</tr>
<tr>
<td>SD6</td>
<td>X = DBP</td>
<td>0.66</td>
</tr>
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Table 7.3. TG/DTA results of the prepared samples.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Decomposition temperature (°C)</th>
<th>Weight loss of the samples in %</th>
<th>Exothermic peaks (°C)</th>
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<tbody>
<tr>
<td></td>
<td>I</td>
<td>II</td>
<td>III</td>
</tr>
<tr>
<td>SD1</td>
<td>88</td>
<td>272</td>
<td>395</td>
</tr>
<tr>
<td>SD2</td>
<td>80</td>
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