CHAPTER - V

STUDIES ON PMMA-PVA BLEND ELECTROLYTES

5.1. INTRODUCTION

A variety of dielectric materials, such as polymers, glasses, ceramics and their combinations may be useful as solid electrolytes for lithium rechargeable batteries. Among these materials, polymers have received considerable attention in the last two decades because of their low density, manufacturability and capacity to accommodate volume changes as compared to true rigid inorganic solid electrolytes. The ability of polymer alkali metal complexes to conduct ions and the possible use of polymeric materials in thin films make them promising for solid electrolytes in battery applications. Thus the electrochemical applications have stimulated worldwide interest in metal salt solvating macromolecules. Intensive efforts have been made by various academic and industrial laboratories to develop practical solid polymer electrolytes (SPE) for lithium batteries [1]. The major obstacle in developing a successful SPE’s is the low ionic conductivity at ambient temperature. The ionic conductivity occurs in the amorphous phase of the polymer [2]. The amorphousness percentage of a polymer depends on its average molecular weight (MW), its stereoregularity (tacticity) of its monomeric unit chains, its thermal history and temperature [3]. Various research groups are involved to develop different approaches, which gave improved conductivity. Some of the approaches include

1. Cross-linking of two polymers [4,5].
2. Identifying new polymer host [6-8].
4. Composite polymer electrolytes [12-14].

5. Blending of two polymers [15,16]

For a solid polymeric ionic conductor at ambient temperature, MW is a critical variable to be considered; when it has certain low value, its mechanical properties will not be so good. An approach to overcome this problem has been by mixing of polymers [17]. The miscibility of polymers is generally attributed to intermolecular hydrogen bonding and several theoretical [18] and experimental studies have been reported on this subject. A hydroxyl group (-OH) can act both as a donor and as an acceptor and it forms a basis of hydrogen bonding in several polymer systems. In binary polymer system, chemical modification of either or both of them can be brought about by introducing functional groups which enhance hydrogen bonding and therefore increase miscibility. Such a possibility is of particular interest in view of the technological importance of polymer blends [19]. PVA is a semicrystalline polymer with carbon chain backbone with hydroxy groups attached to the methane carbons. These OH groups can be a source of hydrogen bonding and hence assist in the formation of polymer blends [20,21]. These blends are important because of their potential application as electrolytes or matrices in batteries and other electrochemical devices. The solid state process like grinding and hot pressing may affect the thermal cycling behaviour of the blend. Attempts are still being made in this area with the objective of restoring the flexibility and improved strength and to achieve superior surface property [22].

In the present study, new plasticized polymer electrolyte composed of PMMA-PVA blend as the host polymer, LiClO$_4$ as the doping salt and DMP as the plasticizer
was prepared and characterised to arrive an appropriate blend composition on the basis of high conductivity achievable with the film when it is dry with good dimensional stability.

**5.2. STATUS OF PREVIOUS WORK**

Yamamoto et al [23] have studied polymer electrolyte systems based on PVA. The films obtained from PVA-lithium salt solutions exhibited relatively high conductivities ($10^{-5} - 10^{-3.5}$ S cm$^{-1}$ at 293K) for a polymer salt system. Every et al [24] studied the ion mobility in PVA based polymer electrolytes, which is determined by NMR spectroscopy. They prepared solvent free polymer electrolytes of PVA and LiCF$_3$SO$_3$, which has shown conductivities in the range of $10^{-8} - 10^{-4}$ S cm$^{-1}$ with Arrhenius temperature dependence below the glass transition temperature. The activation energies obtained for the conductivity data are approximately five times larger than those obtained from the linewidth measurements by NMR spectroscopy. Gupta et al [25] have studied the electrical conductivity and dielectric relaxation in PVA complexes with acid salts (Phosphoric acid –H$_3$PO$_4$).

Bao et al [26] have studied PVA-Li salt complexes and found that despite, exhibiting single ion conduction these complexes suffer from ionic conductivity in the absence of suitable plasticizer.

The conductivity of PVA polymer complexes also shows high values by blending PVA with other suitable polymer. Mishra and Rao has blended PVA with PEO to obtain complexes with high conductivity [27].

In order to improve the mechanical stability of polymeric electrolytes Weston and Steel [28] mixed PEO-LiClO$_4$ polymer complex with ν alumina powder.
but they could not observe any enhancement in conductivity. However, Croce et al. [29] successfully applied this approach to polymer electrolytes to improve both mechanical stability and ionic conductivity. They reported that the incorporation of $\nu$-Al$_2$O$_3$ system is as high at $10^{-4}$ S/cm at 103K.

5.3. PROCEDURE

The appropriate weights of PMMA, PVA and LiClO$_4$ were dissolved in distilled Dimethyl formamide (DMF) followed by the addition of plasticizer DMP. The solution was then stirred continuously until the mixture took a homogeneous viscous liquid appearance. The resulting solution was poured on a glass plate and the DMF was allowed to evaporate in air at room temperature. This procedure provided mechanically stable, free standing and flexible films with thickness between 90 and 200 $\mu$m. The films were further dried for 24 h to remove any trace of DMF.

Perkin-Elmer Paragon 500 grating IR spectrophotometer was used for FTIR measurement. X-ray diffraction analysis was performed in the $2\theta$ range between 5$^0$ and 75$^0$. Impedance of the film was studied over the frequency range 40Hz – 100kHz using a LCZ meter. For temperature dependent ionic conductivity measurements, a thermocouple (chromel-alumel) was held in close proximity to the sample environment inside the cell. Measurements were performed in the temperature range from 303 K to 373K.

5.4. RESULTS AND DISCUSSIONS

5.4.1. X-ray diffraction

X-ray diffraction (XRD) pattern of all the polymer complexes are shown in Fig.5.1. The $d$ values (in $\AA$) and the relative intensities of all the major peaks are also
listed in Table 5.1. The following general observations can be made on the basis of Fig 5.1 and Table 5.1.

1. The X-ray diffraction analysis reveals that the film consisting PMMA (7.5)-PVA(17.5)-LiClO₄(8)-DMP(67) shows less crystallinity compared to other complexes.

2. The diffraction peaks appearing at 2θ ≈ 21° and 47° are assigned to PVA. These reflections are consistent with literature reports on semicrystalline PVA.[30]

3. The peaks belonging to PVA appear on the diffractogram (Film F52) with some shifts and less intense compared to other complexes which indicate the presence of low degree crystalline ordering. These results can be interpreted by considering the Hodge et al [31] criterion, which establishes a correlation between the height of the peak and the degree of crystallinity.

4. No peaks corresponding to pure LiClO₄ appeared in the complex which indicate the complete dissolution of salt in the polymer matrix and no excess salt present in the complex.

From XRD characterisation studies it is found evidence for the presence of induced crystalline ordering of PVA in the presence of PMMA.

5.4.2 FTIR studies

Infrared spectroscopy has been used to characterize the chain structure of polymers and has led the way in interpreting the reactions of multifunctional monomers including rearrangements and isomerizations. The end groups, branches, crosslinks and other structural manifestations of the chain have been detected and identified by IR.
Fig. 5.1 XRD Spectra of
(a) Pure PMMA, (b) PVA (c) LiClO$_4$.
(d) PMMA (25)% LiClO$_4$ (8)% DMP (67)
(e) PMMA (17.5) % PVA (7.5) % LiClO$_4$ (8) % DMP (67)
(f) PMMA (7.5) % PVA (17.5) % LiClO$_4$ (8) % DMP (67)
(g) PVA (25) % LiClO$_4$ (8) % DMP (67)
Table-5.1

d values (in Å) of characteristic peaks observed in the XRD patterns of polymer samples

<table>
<thead>
<tr>
<th>Pure PVA</th>
<th>Pure LiClO₄</th>
<th>Polymer complex</th>
<th>PVA:PMMA</th>
<th>PVA:PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.5:17.5</td>
<td>17.5:7.5</td>
</tr>
<tr>
<td>4.58 (815)</td>
<td>11.042 (888)</td>
<td>6.846 (320)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.983 (592)</td>
<td>4.247 (708)</td>
<td>4.300 (248)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.864 (421)</td>
<td>3.914 (315)</td>
<td>3.383 (170)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.630 (382)</td>
<td>2.875 (133)</td>
<td>2.547 (96)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.437 (305)</td>
<td>2.307 (65)</td>
<td>2.245 (58)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.855 (441)</td>
<td>1.937 (58)</td>
<td>1.762 (47)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.736 (328)</td>
<td>1.661 (63)</td>
<td>1.605 (43)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.296 (195)</td>
<td>1.290 (35)</td>
<td></td>
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</table>
Fig. 5.2 shows the comparison of FTIR spectra of polymer complexes with those of pure PVA, PMMA and LiClO₄.

In the infrared spectra of PVA, stretching vibrations of hydroxyl groups appear at 3576 cm⁻¹ (3400-3600 cm⁻¹ region) along with few weaker absorptions below and above this frequency. The IR spectra in the polymer complex has its hydroxyl band at lower wavenumber when compared with that of pure PVA. This displacement is a strong indication of specific interactions in the polymer blend. The absorption peak appearing at 1712 cm⁻¹ in PVA rich blend is due to the C=C stretching of unhydrolyzed acetate groups present in the PVA [30]. The IR spectra of the complex show sharp peaks at 3475, 1389 and 1288 cm⁻¹. These peaks are assigned to the C-O-H stretching, CH₂ asymmetric bending and C-O bending deformation of PVA.

The peak appearing at 1736 cm⁻¹ in pure PMMA is assigned to C=O stretching which is shifted to 1731 cm⁻¹ in the PMMA-LiClO₄ complex. The addition of PVA in the complex broadens this absorption band. These observation associated with the reliable carboynl band implies the interactions between the polymers PMMA and PVA. The vibrational bands at 2951 and 1389 cm⁻¹ are assigned to CH₃ asymmetric stretching and O-CH₃ deformation of PMMA respectively. The bands at 1483, 1377, 947 and 750 cm⁻¹ are assigned to CH₂ scissoring, twisting, wagging and rocking modes of PMMA.

The strong band at about 940 cm⁻¹ is assigned to the totally asymmetric (v) vibration of the perchlorate anion [32]. The frequency of this band is sensitive to the ion association since the polarising effect of the counterion in an ion pair or multiple ion aggregate leads to an upshift of this frequency as compared with the unperturbed anion. From the IR spectra of the complexes it is observed that this band is found at
Fig. 5.2 FTIR Spectra of
(a) Pure PMMA, (b) LiClO₄, (c) PVA
(d) PMMA (25) - LiClO₄ (8) - DMP (67)
(e) PMMA (17.5) - PVA (7.5) - LiClO₄ (8) - DMP (67)
(f) PMMA (7.5) - PVA (17.5) - LiClO₄ (8) - DMP (67)
(g) PVA (25) - LiClO₄ (8) - DMP (67)
930 cm\(^{-1}\) for the film (F53) and for other complexes, it is shifted to higher frequency indicating the presence of more free (completely solvated) anions in the film (F53) compared to other complexes. The carbon-oxygen stretch band of the methyl esters appearing at 1039 cm\(^{-1}\) for pure DMP is found absent in the complexes.

The absorption intensity of the peak corresponding to 2038 cm\(^{-1}\) is 89% for the polymer complex containing 7.5wt% of PVA. Increasing the PVA content (17.5wt%) in the blend composition the intensity of this band decreases to 57% for further addition of PVA increases the intensity (78%) of the band. From this observation if may be concluded that the film F53 is less ordered than the other films [33]. The maximum value of conductivity is also observed for this combination.

The absorption bands of pure PMMA (3410, 3220, 3010, 2645, 1305 and 1055 cm\(^{-1}\)), PVA (3787, 1879, 1586, 1549 and 1408 cm\(^{-1}\)), LiClO\(_4\) (3433 and 1089 cm\(^{-1}\)), and DMP (1728 and 1434 cm\(^{-1}\)) are found absent in the complexes. The vibration peaks of LiClO\(_4\) (2360, 1636 and 1146 cm\(^{-1}\)) and DMP (840, 746 and 1124 cm\(^{-1}\)) are get shifted to (2359, 1649 and 1142 cm\(^{-1}\)) and (844, 750 and 1141 cm\(^{-1}\)) respectively in the polymer complexes.

These results suggest that homogeneous polymer electrolytes are formed over all the blend compositions.

5.4.3. Conductivity studies

Fig 5.3 shows the a.c. impedance diagram of the SS-SPE-SS. (SPE-Solid polymer electrolyte, SS-Stainless steel). In the impedance response behaviour, only a linear spike is detected with no sign of high frequency semicircle in the complex impedance plot which could be associated with the following reasons.
Fig. 5.3 Impedance plot (Z' Vs Z'') of PMMA (7.5)-PVA(17.5)-LiClO₄(8)-DMP(67) at 303K
1. The lack of gel homogeneity due to crystalline phase separation
2. The contact state between the particles becomes poor and thus large contact resistance will appear.

The ionic conductivity of a polymer electrolyte depends on the actual concentration of the conductivity species and their mobility. The low ionic conductivity in a polymer complex results from the crystalline phase that affects the mobility of ions. The conductivity values obtained for the dry plasticized films are summarized in Table 5.2. In order to investigate the effect of PMMA composition in the blend on ionic conductivity behaviour, the concentration of the salt and the plasticizer are fixed. It is found that all the blend electrolytes exhibit significantly higher conductivity than PVA-LiClO₄ complexes. The conductivity value of PMMA (7.5)-PVA (17.5)-LiClO₄ (8)-DMP (67) electrolyte system presented in this work is estimated as 0.06×10⁻³ S/cm at 303K. This value is higher than the value 10⁻⁸ to 10⁻⁴ S/cm reported by Every et al [24] for PVA-LiCF₃SO₃ system. The higher ionic conductivities of PMMA/PVA blend electrolytes compared to the other complexes may be due to (1) the higher degree of amorphous character stemming from the presence of PMMA in the blend and (2) the enhancement of the ionic mobility by the addition of high dielectric constant (8.11) and low molecular weight (194 g/mol) DMP as plasticizer. The increase in conductivity by the addition of plasticizers may be due to the existence of separate ionic pathways for the migration of free lithium ions through the plasticizer. Li⁺ ions may prefer to conduct through these new paths because the medium is less viscous, thus enhancing the mobility of ions. It is also found that with an increasing PMMA content (>17.5wt%),
Table 5.2.
Conductivity values of PVA-PMMA-LiClO$_4$-DMP polymer complexes

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sample</th>
<th>$\sigma$ (x $10^{-3}$ S/cm)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>303K</td>
</tr>
<tr>
<td>25-0-8-67</td>
<td>F51</td>
<td>0.017</td>
</tr>
<tr>
<td>17.5-7.5-8-67</td>
<td>F52</td>
<td>0.060</td>
</tr>
<tr>
<td>7.5-17.5-8-67</td>
<td>F53</td>
<td>0.048</td>
</tr>
<tr>
<td>0-25-8-67</td>
<td>F54</td>
<td>0.041</td>
</tr>
</tbody>
</table>
the conductivity gets decreased. A high PMMA content imparts high viscosity and makes the mixture more like a rubbery transport solid. Increase in viscosity could be also realized as a macroscopic interactive effect between the polymer and the solution which affects the mobility. Similar observations are also reported by Such et al [34] and Bajpai et al [35] for PMMA-PEO blend. A high PMMA content imparts high viscosity and makes the mixture more like a rubbery transport solid. Increase in viscosity could be also realised as a macroscopic interactive effect between the polymer and the solution which affects the miscibility. Agnihotry et al [36] reported that complexes with PMMA content greater than 20 wt% are more like highly viscous liquids. Hence it is found that the optimum blend composition for PMMA-PVA is 7.5 and 17.5 wt% respectively considering both the mechanical stability and ionic conductivity.

The temperature dependence of the ionic conductivity has been described by Vogel-Tamman-Fulcher equation

\[ \sigma = \sigma_0 \exp \left[ \frac{B}{T - T_0} \right] \]

This equation proposes that ionic conductivity is only prevalent above a temperature \( T_0 \), which is often related to the glass transition temperature \( T_g \) of the system. Consequently polymer relaxation’s appear to influence the conductivity of the electrolyte. The temperature dependence of the conductivities of the PMMA-PVA blend electrolytes can be approximated by Arrhenius behaviour (Fig 5.4). The PVA electrolytes studied by Yamamoto and coworkers [23] showed similar conductivity behaviour. This observation seems to indicate that the conduction mechanism is not entirely attributable to the segmental motions of the polymer and is more likely to involve ion hopping between static sites or limited motions of parts of the polymer.
Fig. 5.4 Temperature dependence on ionic conductivity
(a) PMMA (25) - LiClO₄ (8) - DMP (67)
(b) PMMA (17.5) - PVA (7.5) - LiClO₄ (8) - DMP (67)
(d) PMMA (7.5) - PVA (17.5) - LiClO₄ (8) - DMP (67)
(d) PVA (25) - LiClO₄ (8) - DMP (67)
chain. Alternatively, conduction might be due to proton motion by Grotthius type mechanism involving the polymer hydroxy groups with some release of protons being generated by a lithium hydrolysis reaction.

5.5 CONCLUSIONS

The following conclusions are arrived at based on the present work.

1. The polymer electrolytes comprising PMMA/PVA blend polymer have been prepared.

2. The complex formation in polymer electrolyte system has been confirmed from XRD and FTIR studies.

3. The conductivity of PVA based electrolyte is increased by blending this polymer with PMMA (7.5 wt%). The higher conductivities observed in the polymer membranes are due to the lower degree of crystallinity of PVA which is confirmed from XRD studies.

4. The temperature dependence of the polymer electrolyte films obeys Arrhenius relation.
REFERENCES


