CHAPTER VIII

EFFECT OF CERAMIC FILLER

8.1. Introduction

Polymeric complexes with inorganic salts have widely been studied as solid electrolytes because of their potential importance in the development of solid state batteries, electrochromic devices and electrochemical sensors [1–3]. At the beginning of this area, most efforts were made to investigate lithium ion conducting polymer electrolytes based on a linear polyethylene oxide (PEO) because of its easy coordination with alkali metal ions. However, such problems as the unsatisfied morphological characteristics and insufficient mechanical property of linear PEO polymer electrolytes in high-temperature regions have been proposed for practical applications of the polymer electrolytes. To overcome these problems, composite polymer electrolytes with inert ceramic fillers were explored by Weston and Steele initially [4].

The addition of nanoscale inorganic fillers, such as alumina (Al₂O₃), silica (SiO₂), titania (TiO₂), to the polymer electrolyte resulted in the improvements of transport properties as well as mechanical and electrochemical properties [5–9]. Particularly, the TiO₂ nanoparticles in the polymer electrolyte were confirmed to play useful roles in increasing the ionic conductivity and the cation transference number [10], which were not attributable to the polymer segmental motion but probably to the dipole interaction of TiO₂ with the polymer component [11].
In this work, we investigated the preparation of PVC/PEMA based composite polymer blend electrolytes composed of LiClO$_4$ as a salt and TiO$_2$ as a ceramic filler. This study focuses on improvement of the ionic conductivities of polymer electrolytes by the addition of TiO$_2$ nanoparticles. The effects of the TiO$_2$ nanoparticles on the performance of polymer electrolytes are presented and discussed.

### 8.2. Experimental Section

PVC and PEMA (both from Aldrich) were dried under vacuum at 80°C for 24 hours. Reagent grade anhydrous lithium perchlorate was used after drying in vacuum at 110°C for 24 hours. The plasticizer propylene carbonate (PC) (from Aldrich) was used as supplied. The nano sized TiO$_2$ (Aldrich) was used as a ceramic filler. All the electrolytes have been prepared by the solvent casting technique. Appropriate quantities of PVC, PEMA and LiClO$_4$ are dissolved by adding in sequence to tetrahydrofuran (THF) and stirred for 24h. The resulting solution is poured on to a glass plate and the THF is allowed to evaporate in air at room temperature for several hours. The films are further dried at 60º C for 24 hours in vacuum to remove any traces of THF.

Thin films thus obtained were subjected to XRD and FTIR studies to investigate the complexation behaviour and the nature of crystallinity of the polymer electrolytes using Bruker (D8 Advance) diffractometer and Perkin-Elmer (Paragon 500 grating) IR spectrophotometer respectively. Thermal stability of the film was also characterized by TG/DTA at a heating rate of 10ºC per minute from
room temperature. The electrical conductivity of polymer complexes was measured from impedance plots at different temperatures using Keithley 3330 LCZ meter. The impedance measurement was recorded in the frequency range 40Hz-100 kHz with a signal amplitude of 10mV. Scanning Electron Microscope (JEOL, JXA-840 Japan) was used for micro structural studies.

8.3. Results and Discussion

8.3.1 X-ray Diffraction

X-ray diffraction patterns of pure PVC, PEMA, LiClO$_4$ and PVC(5)-PEMA(20)-PC(67)-LiClO$_4$(8) with X % of TiO$_2$ (where X= 0,5,10,15,20) in the total polymer weight are shown in the figure 8.1. The characteristic peaks at $\theta = 13^\circ$ for PVC and $18.6^\circ$ for PEMA are revealed from fig 8.1(b) and 8.1(a) respectively. Addition of salt and plasticizer, the intensity of PVC and PEMA peaks decreases and these peaks appeared as one broad peak in the complexes. The addition of plasticizer induces significant disorder in the polymer structure, resulting in lower crystallinity. The nano sized TiO$_2$ dispersed emulsion can penetrate the space between the polymer chains and consequently, the homogeneously dispersed ceramic filler in the matrix prevents or retards crystallization of the polymers due to its large surface area. The intensity of the peaks abruptly decreases in the composite electrolytes. No peaks have appeared corresponding to the salt in the complexes, which confirms the amorphous nature of the electrolytes. These observations illustrate that the polymer electrolytes have turned to an amorphous phase.
8.3.2 FTIR Analysis

Polymer complexes with ionic salt have been characterized by FTIR spectroscopy. This technique provides a powerful means to characterize the organic and inorganic components and their composition formation. FTIR spectra of composite polymer complexes are shown in figure 8.2. The peak at 1725 cm\(^{-1}\) represents the carbonyl stretching vibration of PEMA. In PEMA, the peaks at 2982, 2939 and 2910 cm\(^{-1}\) are due to the methylene, (C) CH\(_3\) and ethylene (O) C\(_2\)H\(_5\), groups which overlap [12]. Peaks at 2963 and 1329 cm\(^{-1}\) are assigned respectively to asymmetric C-H methylene group vibration and in-plane CH deformation of PVC. Further the peaks at 954 and 630 cm\(^{-1}\) are assigned to trans CH rocking and cis-CH wagging of PVC. The peak at 1777 cm\(^{-1}\) represents the CH\(_3\)-C- vibration of propylene carbonate. The frequency of C=O at 1785 cm\(^{-1}\) indicates the interaction of the plasticizer with LiClO\(_4\). The weak intensity peak appearing at 507 cm\(^{-1}\) is assigned to [13] respectively.

The vibrational peaks at 1776, 1254, 959, 847, 693 cm\(^{-1}\) of pure PVC, 1473,1250,1157,1032,777 cm\(^{-1}\)of pure PEMA, 2924,1378, cm\(^{-1}\) of pure LiClO\(_4\), 1650 cm\(^{-1}\) of pure TiO\(_2\) are shifted to 1789,1266,972,861,713 cm\(^{-1}\), 1482,1266,1173,1025,792 cm\(^{-1}\), 2936,1389 cm\(^{-1}\) and 1660 cm\(^{-1}\) respectively.

It is also found that some of the peaks appearing in the pure polymers and salts get disappeared in the complexes such as 2910, 1807, 1400, 1087,923, 632 cm\(^{-1}\). In addition to this, few new peaks are observed at 1532, 1142 and 1173 cm\(^{-1}\) in polymer complexes. Shifting of peaks and formation of new peaks in electrolyte
systems suggest the polymer-salt interaction in PVC/PEMA blend based composite polymer electrolytes.

**8.3.3 Conductivity Studies**

Figure 8.3 shows the complex impedance plot of PVC(5)-PEMA(20)-PC(67)-LiClO$_4$(8) with 15 wt % of TiO$_2$ of the total polymer weight at various temperatures. This plot shows linear spikes. The disappearance of the high frequency semicircular portion in the polymer complex impedance plot indicates that the current carriers are ions and the total conductivity is the result of ion conduction. The bulk resistance of the electrolyte was measured by extrapolating the intercept of this plot on the real axis. The electrical conductivity of the electrolyte was calculated for the known values of bulk resistance ($R_b$), area (A) and the thickness (t) of the film using the formula $\sigma = \frac{l}{R_bA}$.

From the Table 8.1, it is seen that the addition of inorganic fillers leads to an increase in the ambient temperature conductivity up to 15 wt% of TiO$_2$ in the total polymer weight and then the ionic conductivity decreases due to higher concentration of ceramic fillers. The result reveals that the addition of small particle size ceramic powders enhances the degree of amorphicity of the polymer electrolyte. Indeed, one may surmise that the presence of high dispersed particles in the polymer matrix may affect the crystallization rate by preventing the agglomeration of the polymer chains. Further, the particle size and content of the ceramic additive appear to be a critical factor. It is also seen that a reasonably high
concentration of the filler is also necessary to affect the recrystallization rate of the polymer host.

The temperature dependence of the ionic conductivity of PVC(5)-PEMA(20)-PC(67)-LiClO$_4$(8)-X% of TiO$_2$ (where X= 0,5,10,15,20) in the total polymer electrolyte is shown in the figure 8.4. From the plot it has been observed that as temperature increases the conductivity values also increase for all the compositions. The non-linearity in Arrhenius plots indicates that ion transport in polymer electrolytes is dependent on polymer segmental motion. The curvature behaviour of the plots suggests that the data can be better described by the Vogel–Tamman–Fulcher (VTF) relation [14-16], which described the transport properties in a viscous matrix. It supports the idea that the ion moves through the plasticizer-rich phase.

8.3.4 TG/DTA Analysis

The TG/DTA thermograms of PVC(5)-PEMA(20)-PC(67)-LiClO$_4$(8)-X% of TiO$_2$ (where X= 0,5,10,15,20) composite systems are shown in figure 8.5 (a-e). In fig 8.5 (a), the DTA curve shows a small exothermic peak in the temperature range 50-70°C indicating the melting of the polymer film and it exhibits a linear trend towards its decomposition temperature at 291°C. This peak is concurrent with the TG curve. The first and second decomposition of the film take place in between 60-70°C and 200-230°C (Table 8.2) respectively and the corresponding weight losses were 8 and 16% (fig 8.5 (a)) at various temperatures of 100 and 200°C respectively.
In the DTA curve (fig 8.5 (b)), the melting of the polymer film is observed in the temperature range 55-65°C which is indicated by a small endothermic peak. Followed by it, there is no other peak till 280°C. This trend is accompanied by a rapid weight loss of the film E2. The thermal stability of the polymer film is found to be poor. The exothermic peak occurred at 280°C corresponds to the decomposition of the polymer electrolyte. The first and second decomposition of the film take place in between 50-60°C and 220-300°C respectively and the corresponding weight losses were 16 and 30% at various temperature of 100°C and 200°C respectively.

In the DTA curve (fig 8.5 (c)), the polymer film exhibits a linear trend beyond 40-60°C at which an endothermic peak is observed. This peak is clearly indicating the melting of the polymer film. A large exothermic peak observed at 295°C indicates the final decomposition of the polymer film which is supported by the TG curve wherein the weight loss of the film is gradually decreasing. From the DTA and TG curves, it can be seen that, the film is thermal stable in the temperature range 230-250°C. The first and second decomposition take place in the temperature range 50-60°C and 236°C respectively and the corresponding weight losses were 12 and 13% at various temperatures of 100 and 200°C respectively.

In the DTA curve (film E4), the polymer film exhibits a linear trend beyond 40-70°C at which an endothermic peak is observed. This peak is indicating the presence of moisture at the loading of the samples. A sharp exothermic peak
observed at 292°C indicates the final decomposition of the polymer film which is accompanied by the TG curve wherein the weight loss of the film is continuously decreasing. From the DTA and TG curves, it can be seen that, with the increase in the temperature, the film E4 losses its weight continuously showing its poor thermal stability. The first and second decomposition of the film take place in between 40-60°C and 220-240°C respectively and the corresponding weight losses were 13 and 30% at various temperatures of 100 and 200°C respectively.

In DTA curve (fig 8.5 (e)), an endothermic peak observed in the temperature range 55-70°C indicates the melting of the polymer film. A clear, larger exothermic peak is noticed in the temperature range 330-390°C confirming the decomposition of the polymer film. The TG curve indicates no appreciable weight loss till 250°C. The thermally stable of the polymer film is found to be 250°C from the TG curve. The first and second decomposition take place at 60°C and 250°C respectively and the corresponding weight losses were 9 and 25% at various temperature of 100 and 200°C respectively.

The conductivity value has been found to be maximum (7.179 x 10⁻³ S/cm) for the film E4 compared to other films. Hence, the film E4 is found to be superior among the other films on the basis of the both thermal stability and conductivity.

8.3.5. SEM Analysis

The Scanning electron micrographs of 0, 5, 10, 15, and 20 wt% of TiO₂ based PVC(5) PEMA (20) – LiClO₄ (8) – PC (67) polymer electrolyte system are shown in figure 6 (a – c). These dispersed TiO₂ particles play an active role
in the growth of microstructures resulting in completely different morphology. The interaction of nano filler on the gel electrolyte may provide additional mechanism of ionic conductivity enhancement along the particle – gel electrolyte interface. No spherullitic structure due to crystalline phase is observed in figure 8.6 (a – c). It confirms the amorphous nature of the developed electrolytes. But significant differences are observed due to the addition of TiO$_2$ nano filler. Addition of ceramic filler at 15 wt % shows smooth surface with some nanoscale pores. As the content of TiO$_2$ increases (fig 8.6 (c)) the film surface becomes rough. Also it is found that in figure 8.6 (c), the grain size increases, with a reduction in the number of grain aggregates, that tend to restrict the ionic movement. In consequent to this the conductivity is found decreasing.

8.4. Conclusion

The salt-in-polymer electrolytes prepared from the PVC/PEMA show a strong enhancement of the ionic conductivity by the addition of TiO$_2$ nanoparticles. The ionic conductivity of the resulting composite polymer electrolyte is better than the blend polymer electrolyte [20]. The temperature dependent ionic conductivity plot of the composite films seems to obey the VTF relation. The thermal stability of the polymer film E4 is found to be 260ºC from the TG curve. The optimized polymer electrolyte can be used as an electrolyte in the fabrication of Li batteries.
Figure 8.1. X-ray diffraction patterns of (a) Pure PEMA (b) Pure PVC (c) LiClO$_4$, (d) PVC (5)-PEMA (20)-LiClO$_4$ (8)-PC (67)-TiO$_2$(0), (e) PVC (5)-PEMA (20)-LiClO$_4$ (8)-PC (67)-TiO$_2$(5), (f) PVC (5)-PEMA (20)-LiClO$_4$ (8)-PC (67)-TiO$_2$(10), (g) PVC(5)-PEMA(20)-LiClO$_4$(8)-PC(67)-TiO$_2$(15), (h) PVC(5)-PEMA(20)-LiClO$_4$(8)-PC(67)-TiO$_2$(20)
Figure 8.2. FTIR spectra of (a) Pure PVC (b) Pure PEMA (c) LiClO₄, (d) PVC (5)-PEMA (20)-LiClO₄ (8)-PC (67)-TiO₂(0), (e) PVC (5)-PEMA (20)-LiClO₄ (8)-PC (67)-TiO₂(5), (f) PVC (5)-PEMA (20)-LiClO₄ (8)-PC (67)-TiO₂(10), (g) PVC(5)-PEMA(20)-LiClO₄(8)-PC(67)-TiO₂(15), (h) PVC(5)-PEMA(20)-LiClO₄(8)-PC(67)-TiO₂(20)
Figure 8.3. Impedance diagram for PVC(5)-PEMA(20)-LiClO₄(8) -PC(67)-
TiO₂(15) wt% at various temperatures.
Figure 8.4. Arrhenius plot of PVC(5)-PEMA(20)-LiClO₄(8)-PC(67)- TiO₂(X wt %) (where X= 0, 5, 10, 15, 20) composites.
Figure 8.5. (a). TG/DTA curves of PVC(5)-PEMA(20)-LiClO$_4$(8)-PC(67)-TiO$_2$ (0 wt %)

Figure 8.5. (b). TG/DTA curves of PVC(5)-PEMA(20)-LiClO$_4$(8)-PC(67)-TiO$_2$ (5 wt %)
Figure 8.5. (c). TG/DTA curves of PVC(5)-PEMA(20)-LiClO₄(8)-PC(67)-TiO₂(10 wt %)

Figure 8.5. (d). TG/DTA curves of PVC(5)-PEMA(20)-LiClO₄(8)-PC(67)-TiO₂(15 wt %)
Figure 8.5. (e). TG/DTA curves of PVC(5)-PEMA(20)-LiClO₄(8)-PC(67)-
TiO₂(20 wt %)
Figure 8.6 SEM images of (a) PVC-PEMA-PC-LiClO$_4$-TiO$_2$ (5:20:67:8:0) wt%, (b) PVC-PEMA-PC-LiClO$_4$-TiO$_2$ (5:20:67:8:15) wt%, (c) PVC-PEMA-PC-LiClO$_4$-TiO$_2$ (5:20:67:8:20) wt%.
Table 8.1

Ionic conductivity values for PVC(5)-PEMA(20)-PC(67)-LiClO$_4$(8)-TiO$_2$(X wt%) (where X= 0, 5, 10, 15, 20) system

<table>
<thead>
<tr>
<th>Film</th>
<th>TiO$_2$ ratio</th>
<th>Ionic conductivity x 10$^{-3}$ S cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>301K</td>
</tr>
<tr>
<td>E1</td>
<td>0</td>
<td>3.454</td>
</tr>
<tr>
<td>E3</td>
<td>10</td>
<td>5.812</td>
</tr>
</tbody>
</table>
Table 8.2. TG/DTA results of the prepared samples

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Decomposition range (ºC)</th>
<th>% wt loss (±2% at various temperatures (ºC))</th>
<th>Endothermic peaks (ºC)</th>
<th>Exothermic peaks (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First</td>
<td>Second</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>E1</td>
<td>60-70</td>
<td>200-230</td>
<td>8</td>
<td>16</td>
</tr>
<tr>
<td>E2</td>
<td>50-60</td>
<td>220-300</td>
<td>16</td>
<td>30</td>
</tr>
<tr>
<td>E3</td>
<td>50-60</td>
<td>230-250</td>
<td>12</td>
<td>13</td>
</tr>
<tr>
<td>E4</td>
<td>40-60</td>
<td>220-240</td>
<td>13</td>
<td>30</td>
</tr>
<tr>
<td>E5</td>
<td>55-70</td>
<td>230-250</td>
<td>9</td>
<td>25</td>
</tr>
</tbody>
</table>

Reference

