



Investigations on PVC/PMMA Blends with Various lithium Salts

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ABSTRACT

Hybrid, solid polymer electrolyte films consisting of poly(vinyl chloride)/poly(methyl methacrylate)-based polymer blend electrolytes comprising propylene carbonate as a plasticizer and a lithium salt LiX ($\text{X} = \text{BF}_4, \text{ClO}_4, \text{CF}_3\text{SO}_3$) are prepared by a solvent casting technique. X-ray diffraction, Fourier transform infrared spectroscopy and Differential scanning calorimeter analysis have been made to investigate the structural, complexation and variation in film morphology of the polymer electrolyte. The temperature dependence of ionic conductivity of the polymer films is explained on the basis of a free volume model. The electrolytes that contain LiBF_4 exhibit maximum conductivity.

Keywords : Polymer Electrolyte, Ionic Conductivity, XRD, FTIR, DSC, SEM.

1. Introduction

Numerous works have been carried out to optimize the polymer electrolytes to enhance ionic conductivity, thermal stability and electrochemical stability as the prerequisite for their use in lithium rechargeable batteries at ambient temperature. One of the factors that improve the ionic conductivity is reducing the crystallinity of the polymer host. Whereas there have been many reports of the physical and electrochemical properties of poly(ethylene oxide)-based electrolytes [1-3], very few studies have been made on other polymer hosts like poly(acrylonitrile) (PAN) [4,5], poly(methylmethacrylate) (PMMA) [6], poly(vinyl chloride) (PVC) [7,8] and poly(vinylidene fluoride) (PVdF) [9].

In the recent years PVC based blend electrolytes have got their popularity due to their easy processibility, inexpensive and good compatibility. Rhoo et al. [10] reported the ionic conductivity of plasticized PVC/PMMA blended polymer electrolytes. In the present study, an attempt has been made to determine the role of different anions, namely, BF_4^- , ClO_4^- and CF_3SO_3^- , on the ionic conductivity of PVC/PMMA-based polymer electrolyte. The thermal stability and the morphological analysis of these polymer electrolytes are also reported.

2. Experimental section

PVC and PMMA (Aldrich, USA) were used in this study. The plasticizer PC (from Aldrich) was used as supplied. Lithium perchlorate (LiClO_4), lithium tetrafluoro borate (LiBF_4) and lithium triflate (LiCF_3SO_3) were dried by annealing them under vacuum at 120°C , 70°C and 80°C respectively for 24 h. Polymer electrolytes were prepared by dissolving appropriate amounts of the corresponding constituents in anhydrous tetrahydrofuran (THF) and casting them as films using solvent casting technique. THF was allowed to evaporate at room temperature. After the evaporation of THF, mechanically stable films (free standing) were obtained. The films were further dried in the temperature controlled oven at 50°C for 12 h to remove the traces of THF, if any. Ionic conductivities of polymer electrolytes were evaluated from the complex impedance plot in the temperature range (301-341 K) using Keithley 3330 LCZ meter in the frequency range 40Hz-100KHz. X-ray diffractograms were studied by JEOL, JDX 8030 X-Ray Diffractometer. An IR study was made using a Perkin-Elmer (Paragon 500 grating)

IR spectrophotometer. Thermal stability of the film was also characterized by DSC at heating rate of 10°C per minute from the room temperature to 400°C . SEM analysis (JEOL, IXA-840, Japan) was employed for micro structural studies.

3. Results and discussion

3.1 X-ray diffraction studies

Figure 1 shows the X-ray diffraction pattern for pure PVC, PMMA, LiCF_3SO_3 , LiClO_4 , LiBF_4 and their complexes of $\text{PVC}(7.5)\text{-PMMA}(17.5)\text{-PC}(67)\text{-LiX}(8)$ where ($\text{X} = \text{CF}_3\text{SO}_3, \text{ClO}_4, \text{BF}_4$). From the figure, X-ray diffraction patterns of pure LiBF_4 , LiClO_4 and LiF_3SO_3 show several diffraction peaks due to the existence of crystallinity. In complexes, these peaks are completely disappeared in the complexes and it reveals the absence of excess salt in all complexes. The incorporation of LiClO_4 and the plasticizer (PC), which would have disturbed the crystalline region and increased the amorphous phase. A diffraction peak has appeared at $2\theta=13^\circ$ corresponding to pure PVC which is found absent in the complexes. It reveals that the structural modification has occurred in the system [11]. The diffraction peak of PMMA abruptly reduced in all the complexes. The shift and the decrease in the relative intensity of the peaks suggest that the complexation has occurred between the salts and the polymers.

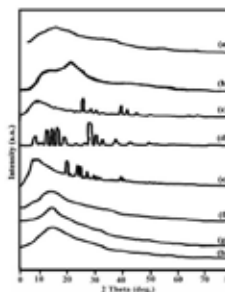


Figure 1. X-ray diffraction patterns of
(a) Pure PVC
(b) Pure PMMA
(c) LiCF_3SO_3
(d) LiClO_4

- (e) LiBF₄
- (f) PVC (7.5)-PMMA (17.5)-LiCF₃SO₃ (8)-PC (67)
- (g) PVC (7.5)-PMMA (17.5)-LiClO₄ (8)-PC (67)
- (h) PVC (7.5)-PMMA (17.5)-LiBF₄ (8)-PC (67)

3.2 FTIR analysis

FT-IR spectra of polymer complexes are shown in figure 2. 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 CH₃-C- vibration of propylene carbonate. The frequency of C=O at 1785 cm⁻¹ indicates the interaction of the plasticizer with LiClO₄. The weak intensity peaks appearing at 1027,930 and 507 cm⁻¹ are assigned to SO₃ stretching mode [12], BF₄⁻ and ClO₄⁻ [13] respectively.

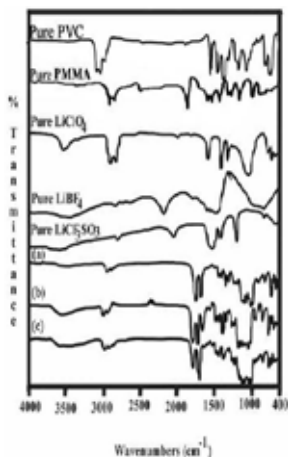


Figure 2. FTIR Spectra of

- (a) Pure PVC
- (b) Pure PMMA
- (c) LiClO₄
- (d) LiBF₄
- (e) LiCF₃SO₃
- (f) PVC (7.5)-PMMA (17.5)-LiCF₃SO₃ (8)-PC (67)
- (g) PVC (7.5)-PMMA (17.5)-LiClO₄ (8)-PC (67)
- (h) PVC (7.5)-PMMA (17.5)-LiBF₄ (8)-PC (67)

The vibrational and observed at 3010,2952,1275,1173 and 750 cm⁻¹ are assigned to CH₃ stretching vibration, CH₂ asymmetrical stretching vibration, CH₂ transformation, CH₂ twisting, CH rocking vibration of PMMA. The peak observed at 1483cm⁻¹ is assigned to CH₃ asymmetric bending of plasticizer PC.

The vibrational peaks at 1776,1334,1075,959 cm⁻¹ of pure PVC, 3410,3010,1235,760,500 cm⁻¹ of pure PMMA, 2954,1652,1463 cm⁻¹ of pure LiClO₄, 1980,1769,1545 cm⁻¹ of pure LiBF₄ and 1725,768 cm⁻¹ of pure LiCF₃SO₃ are shifted to 1793,1334,1062,972 cm⁻¹, 3554,2996,1250,778,512 cm⁻¹, 2952,1671,1445 cm⁻¹, 1966,1778,1558 cm⁻¹ and 1732,775 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 3527,3431,3220,1965,1807 cm⁻¹. In addition to this, few new peaks are observed at 2592 and 2035 cm⁻¹ in polymer complexes. Shifting of peaks and formation of new peaks in electrolyte systems suggest the polymer-salt interaction in PVC/PMMA blend based polymer electrolytes.

3.3 Conductivity measurements

The ionic conductivity of PVC/PMMA based gel polymer electrolytes containing different lithium salts, LiBF₄, LiClO₄, LiCF₃SO₃ were calculated from $\sigma = l/RbA$, where 'l' and 'A' represents the thickness and area of the film. Rb is the bulk

resistance of the gel electrolyte obtained from complex impedance measurement [14,15].

Figure 3 shows the room temperature complex impedance spectra of PVC (7.5)-PMMA (17.5)-PC (67)-LiX (8) wt % (where X= CF₃SO₃⁻, ClO₄⁻, BF₄⁻) polymer electrolyte system. According to the theoretical analysis given by Watanabe and Ogata [16] two semicircles should appear in impedance spectrum for a symmetric cell, i.e., one at higher frequencies corresponding to bulk electrolyte impedance and other at lower frequencies related to the interfacial impedance. Also it is reported [17-19] that the high frequency semicircle does not appear in practical impedance plots for plasticized polymer electrolyte membranes. The disappearance of semicircle portion indicates that the conductivity is mainly due to ions.

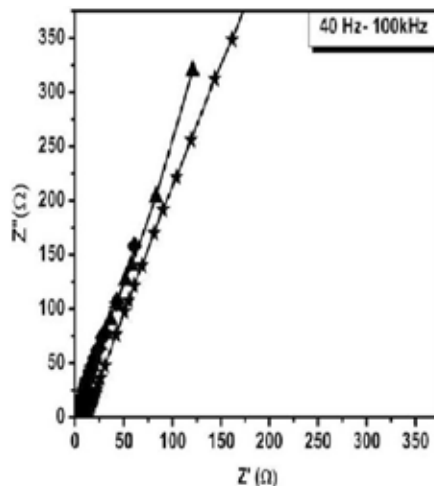


Figure 3. Impedance diagram for PVC-PMMA-LiX-PC (7.5-17.5-8-67 wt %) (where X = CF₃SO₃⁻, BF₄⁻, ClO₄⁻) at 301 K.

Figure 4, shows the conductivity versus temperature inverse plots of PVC-PMMA-PC-LiX (where X= BF₄⁻, ClO₄⁻, CF₃SO₃⁻) based hybrid polymer electrolytes respectively. The figure shows that the ionic conduction in all polymer electrolyte systems obeys the VTF (Vogel-Tammam-Fulcher) relation, which describes the transport properties in a viscous matrix [20-23]. It supports the idea that the ions move through the plasticizer rich phase, which is the conductivity medium and involves the salt.

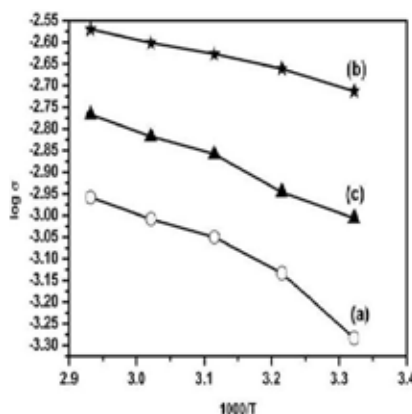


Figure 4. Arrhenius plot of PVC-PMMA-LiX-PC (7.5-17.5-8-67 wt %) (where X= CF₃SO₃⁻, BF₄⁻, ClO₄⁻) complexes.

The conductivity data for hybrid polymer electrolytes containing different salts are presented in table 1. From the table we can see that the LiBF₄ offers highest conductivity (1.932 x 10⁻³ S/cm) among the other lithium salts. Since all the anions are counter ions of strong acids the difference in conductivity is presumably due to the difference in lattice energies. LiBF₄ has the lowest lattice energy and therefore easier solvation

of Li⁺ ion by the polymer matrix, which facilitates for higher ionic conductivity. A similar observation has been reported by Immanuel et al [24].

3.4 DSC (Differential Scanning Calorimetry) studies

The Differential Scanning Calorimetry thermogram of the polymer electrolyte exhibiting maximum conductivity is given in fig. Generally the addition of lithium salts to polymer electrolyte may marginally shift the glass transition temperature (T_g) of the complex to the higher side.

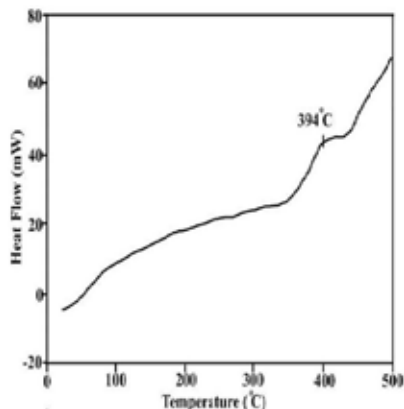


Figure 5. DSC curve of PVC (7.5)-PMMA (17.5)-LiBF₄ (8)-PC (67) complex.

The glass transition temperature (T_g) of pure PVC and PMMA are 81°C and 95°C respectively. From fig it is evident that these appear a single endothermic peak at around 75°C which clearly indicates the miscibility of the polymers. The shift in glass transition to lower side (i.e 75°C) could be attributed to the addition of plasticizer in higher amount which has accounted for the lowering of T_g. A broad exothermic peak in the range 360 to 430°C with a peak maximum at 394°C clearly indicates the melting point of the polymer membrane indicating the highest temperature of usage of the polymer electrolyte. Hence it is concluded that PVC-PMMA-PC-LiBF₄ polymer electrolyte membrane could be used effectively in the temperature range from room temperature to 394°C.

3.5 SEM analysis

Figure 6 shows the scanning electron micrographs of PVC(7.5)-PMMA(17.5)-PC(67)-LiX(8) where (X= CF₃SO₃⁻, ClO₄⁻, BF₄⁻). It is observed that ordered and almost spherical grains are uniformly distributed in PVC-PMMA-PC-LiX (X= CF₃SO₃⁻, ClO₄⁻, BF₄⁻) systems [Fig. 6(a, b, and d)] and the pore size (dark region) size is large. On the other hand

the surface morphology is uniform and the ordered spherical grain structure is absent for PVC-PMMA-PC-LiBF₄ complex. The microstructure is disordered throughout the sample and the pore size is smaller. These results suggest that PVC-PMMA-PC-LiBF₄ (8 wt %) has higher solvent retention ability since the pores in microstructure occur due to solvent removal. SEM results are consistent with the view that higher conductivity in PVC-PMMA-PC-LiBF₄ (8 wt %) based polymer blend electrolyte arises from the increased amorphicity of the blend polymer electrolytes.

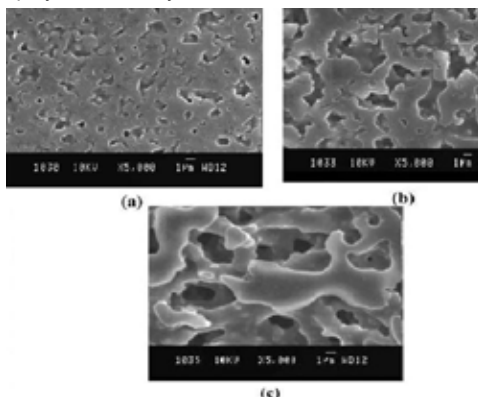


Figure 6. SEM images of PVC-PMMA-LiX-PC (7.5-17.5-8-67 wt %) (where X= CF₃SO₃⁻, ClO₄⁻, BF₄⁻) complexes.

4. Conclusions

The complex formation in PVC/PMMA system has been confirmed from XRD and FTIR studies. All electrolytes show appreciable conductivity even at room temperature. Maximum conductivity (1.932x10⁻³ S/cm) at room temperature with good mechanical stability has been observed for PVC (7.55)-PMMA (17.5)-PC (67)-LiBF₄ (8 wt %) system among the various salts studied. Good thermal stability of these polymer electrolyte systems up to 394°C was confirmed by DSC analysis. Since the polymer electrolyte exhibits maximum conductivity value and good thermal stability, this can be used as an electrolyte in lithium batteries and other electrochemical devices.

Table 1

Ionic conductivity values of PVC-PMMA-PC-LiX (where X is CF₃SO₃⁻, ClO₄⁻ and BF₄⁻) systems for different salt concentrations

Film Composition (wt %)	Ionic conductivity x 10 ⁻³ S cm ⁻¹				
	301K	311K	321K	331K	341K
S1 5:20:67:8	0.521	0.736	0.891	0.984	1.101
S2 5:20:67:8	1.932	2.178	2.356	2.501	2.689
S3 5:20:67:8	0.986	1.131	1.384	1.524	1.708

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