

# Li Ion Conduction Behavior of Hybrid Polymer Electrolytes Based on PEMA

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**ABSTRACT:** Poly(vinyl chloride)/Poly(ethyl methacrylate) (PVC)/(PEMA)-based blend polymer electrolytes comprising a combination of PC (Propylene carbonate) as a plasticizer and LiClO<sub>4</sub> as a salt have been prepared by solvent casting technique with varying salt concentration ratios systematically. The prepared electrolytes were subjected to X-ray diffraction, Fourier transform infrared spectroscopy, conductivity studies, thermogravimetric/dif-

ferential thermal analysis and Scanning electron microscopic studies. PVC/PEMA polymer blend electrolyte with 8 wt % of lithium salt exhibited ionic conductivity of the order of 10<sup>-3</sup> S/cm at room temperature. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2802–2806, 2008

**Key words:** PVC/PEMA; blends; X-ray diffraction; FTIR; thermogravimetric analysis

## INTRODUCTION

Recently, there has been an increasing need for rechargeable batteries of high specific energy for portable electronic equipment. Among them, lithium-polymer batteries are now being widely investigated and developed.<sup>1,2</sup> Polymer electrolytes are expected to produce safe, high energy density, and flexible lithium polymer batteries. Poly(ethylene oxide)-based polymer electrolytes are the most commonly studied.<sup>3,4</sup> These electrolytes exhibit conductivity in the range from 10<sup>-8</sup> to 10<sup>-5</sup> S/cm at room temperature. This excludes practical application at ambient temperature.<sup>5</sup> On the other hand, Poly(acrylonitrile) (PAN)-based electrolytes offer high ionic conductivity at room temperature (10<sup>-3</sup> S/cm), good electrochemical stability and appreciable transference number (0.6).<sup>6,7</sup> The ionic conductivity of poly(methyl methacrylate) (PMMA) gel electrolytes remain very close to that of 10<sup>-3</sup> S/cm at room temperature.<sup>8,9</sup> Polymer electrolyte based on PVC offered low ionic conductivity at ambient temperature.<sup>10,11</sup>

The choice of individual components in the electrolyte material is crucial. Their chemistry and compatibility with each other and with the electrodes will affect both the mechanical and electrochemical properties of the material. The amount of salt chosen to improve the conductivity has been expected to

maximize the ionization through extensive delocalization.

PEMA is one of the host polymers. The kinetics and the mechanical strength have been studied by Han et al.<sup>12</sup> and they reported that PEMA-based polymer electrolyte showed better mechanical strength and higher ionic conductivity.

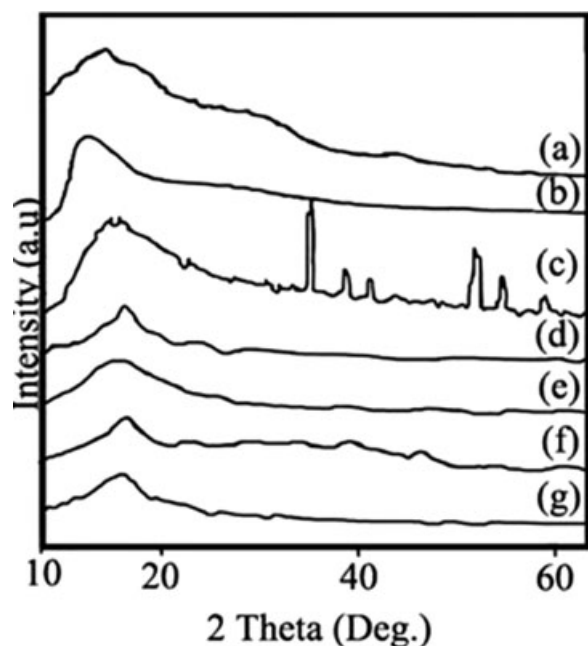
The use of PVC as a polymer electrolyte matrix allows the formation of homogeneous hybrid films in which the salt and the plasticizers are molecularly dispersed; however, PVC is inactive in the ionic transport mechanism, but simply a matrix of structural stability. In the present work, PEMA has been blended with PVC to prepare a homogeneous polymer electrolyte with a view to investigate the effect of salt concentration in the ionic conductivity and the results are discussed in detail.

## EXPERIMENTAL

PVC and PEMA (both from Aldrich) were dried under vacuum at 80°C for 24 h. Reagent grade anhydrous lithium perchlorate was used after drying in vacuum at 110°C for 24 h. The plasticizer propylene carbonate (PC) (from Aldrich) was used as supplied. Polymer electrolytes were prepared by dissolving appropriate amount of the corresponding constituents in Tetrahydrofuran (THF). All the electrolytes were prepared by the solvent casting technique. The films were further dried under vacuum for 24 h at 60°C.

Thin films thus obtained were subjected to XRD and FTIR studies to investigate the complexation behavior and the nature of crystallinity of the

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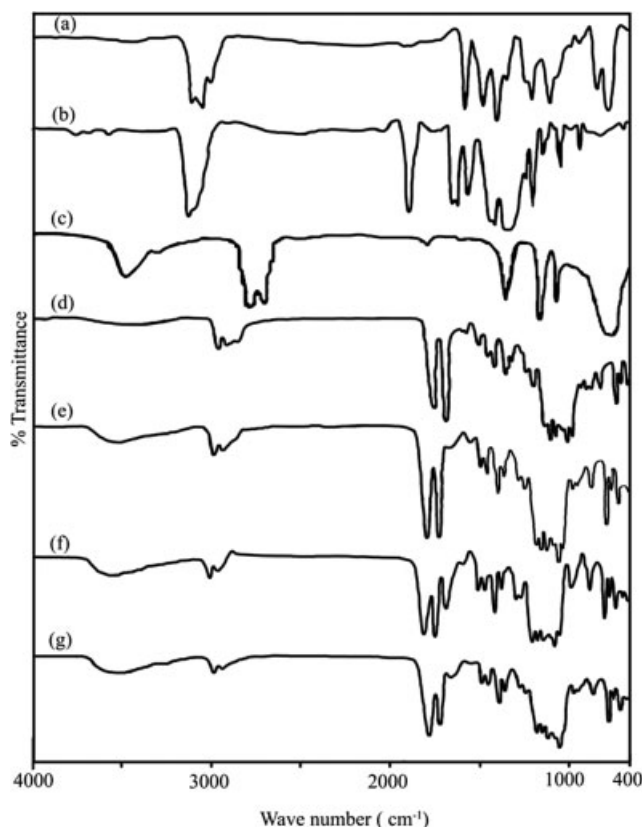
**Figure 1** X-ray diffraction patterns of (a) Pure PVC, (b) Pure PEMA, (c)  $\text{LiClO}_4$ , (d) PVC(5)-PEMA(20)- $\text{LiClO}_4$ (4)-PC(71), (e) PVC(5)-PEMA(20)- $\text{LiClO}_4$ (6)-PC(69), (f) PVC(5)-PEMA(20)- $\text{LiClO}_4$ (8)-PC(67), and (g) PVC(5)-PEMA(20)- $\text{LiClO}_4$ (10)-PC(65).

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  $10^\circ\text{C}$  per minute from room temperature to  $400^\circ\text{C}$ . 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 40 Hz–100 KHz with a signal amplitude of 10 mV.

## RESULTS AND DISCUSSION

### X-ray diffraction study

XRD patterns for pure PVC, PEMA,  $\text{LiClO}_4$  and their complexes are shown in Figure 1. Addition of salt contents induced the structural change in the polymer blend electrolytes. The characteristic peaks at  $2\theta = 13^\circ$  for PVC and  $18.6^\circ$  for PEMA are revealed from Figure 1(a and b), respectively. With increasing salt concentration, the intensity of PVC and PEMA peaks decreases and these peaks appeared as one broad peak in the complexes. In Figure 1(c) the diffraction peaks indicate the crystalline phase of  $\text{LiClO}_4$ . Diffraction pattern of the complexes reveal the amorphous nature even after  $\text{LiClO}_4$  is incorporated, which is responsible for higher conductivity. These observations apparently reveal that the polymer undergoes significant structural reorganization.

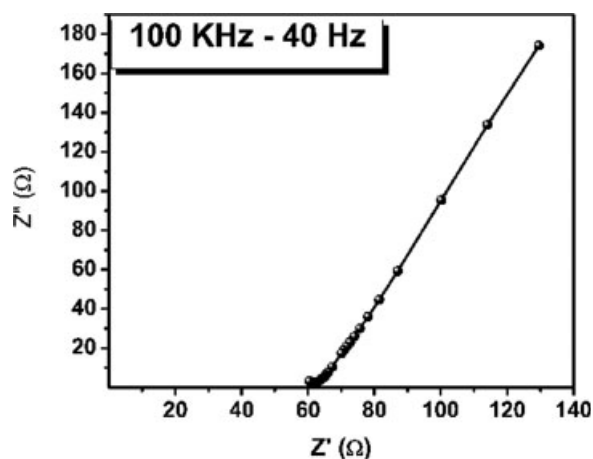


**Figure 2** FTIR Spectra of (a) Pure PVC, (b) Pure PEMA, (c)  $\text{LiClO}_4$ , (d) PVC(5)-PEMA(20)- $\text{LiClO}_4$ (4)-PC(71), (e) PVC(5)-PEMA(20)- $\text{LiClO}_4$ (6)-PC(69), (f) PVC(5)-PEMA(20)- $\text{LiClO}_4$ (8)-PC(67), and (g) PVC(5)-PEMA(20)- $\text{LiClO}_4$ (10)-PC(65).

The peaks corresponding to  $\text{LiClO}_4$  are found absent in the polymer complexes, which indicate the absence of excess salt in the polymer complexes.

### FTIR studies

FTIR spectra of pure PVC, PEMA,  $\text{LiClO}_4$  and their complexes are shown in Figure 2. The transmittance



**Figure 3** Impedance diagram for PVC-PEMA- $\text{LiClO}_4$ -PC (5-20-8-67 wt %) at 301 K.

TABLE I  
Ionic Conductivity Values of PVC-PEMA-LiClO<sub>4</sub>-PC Systems for  
Different Salt Concentrations

Film	Composition (wt %)	Ionic conductivity (10 <sup>-3</sup> S/cm)				
		301 K	311 K	321 K	331 K	341 K
B1	5-20-4-71	0.202	0.243	0.296	0.327	0.368
B2	5-20-6-69	0.913	0.937	0.993	1.072	1.201
B3	5-20-8-67	3.454	3.878	4.043	4.578	5.588
B4	5-20-10-62	1.731	1.954	2.230	2.780	2.801

bands at 605, 636 cm<sup>-1</sup> and 923, 959, 1035, 1075, 1192 cm<sup>-1</sup> are assigned to C—Cl and C—C stretching vibrations of peaks of PVC. In PEMA, the transmittance bands at 2982, 2939, and 2910 cm<sup>-1</sup> are due to the C—H stretching vibration of the methylene, (C) CH<sub>3</sub> and ethylene (O) C<sub>2</sub>H<sub>5</sub> groups that overlap. The two bands at 1240 and 1261 cm<sup>-1</sup> are associated with different vibrations of the ester group. The FTIR spectrum of the LiClO<sub>4</sub> salt is given in the Figure 2. The band at 625 cm<sup>-1</sup> corresponds to ClO<sub>4</sub><sup>-</sup>. The broad band of medium intensity at >500 cm<sup>-1</sup> is due to ClO<sub>4</sub><sup>-</sup>, which has become infrared active.<sup>13</sup>

The vibrational peaks of PVC (771, 923, 1035, 1776 cm<sup>-1</sup>), PEMA (755, 850, 1151, 1250, 1473, 2982 cm<sup>-1</sup>), and LiClO<sub>4</sub> (1463, 2924 cm<sup>-1</sup>) are shifted to (777, 915, 1026, 1790 cm<sup>-1</sup>), (748, 860, 1146, 1236, 1482, 2987 cm<sup>-1</sup>) and (1448, 2940 cm<sup>-1</sup>) in the polymer complexes, respectively.

It is also found that some of the peaks disappear in the complexes such as (1075, 1192, 1807, 2811, 2939 cm<sup>-1</sup>). In addition to this, few new peaks are observed at (940, 1052, 1114, 1600 cm<sup>-1</sup>) in the polymer complexes. The above analysis confirms the complex formation.

### Conductivity studies

The ionic conductivity of the polymer electrolytes mainly depends on the actual concentration of conducting species and their mobility. The room temperature conductivity of the polymer electrolytes are measured by knowing the values of the bulk resistance  $R_b$ , area  $A$ , and thickness  $l$  of the film by applying the equation  $\sigma = l/R_b A$ . The typical impedance plot of PVC(5)-PEMA(20)-PC(67)-LiClO<sub>4</sub>(8) wt % is shown in Figure 3. In the impedance response behavior, the disappearance of the high frequency semicircular portion indicates that the current carriers are ions and this leads to the conclusion that the total conductivity is mainly due to the ion conduction. Table I, shows the ionic conductivity values of PVC(5)-PEMA(20)-PC(Y)-LiClO<sub>4</sub>(X wt %) systems for different salt concentrations (where  $Y = 71, 69, 67, \text{ and } 62$  and  $X = 4, 6, 8, \text{ and } 10$  wt %). From the Table I, it is observed that the conductivity value

increases with temperature. This can be explained with the help of free volume theory.<sup>14</sup>

As a general trend, at low salt concentration there is a build-up of charge carriers that results in an increase in ionic conductivity. The highest ionic conductivity of the polymer film is found at a salt concentration of 8 wt % over the range of temperature investigated. At high salt concentrations, the build-up of charge carriers is offset by the retarding effect of ion clouds. Thus, the ionic conductivity decreases as this latter effect begins to dominate. The conductivity decreases when the ratio of LiClO<sub>4</sub> is 10 wt %. This may be due to the restricted mobility of charge carriers in the more rigid matrix. The maximum ionic conductivity value  $3.454 \times 10^{-3}$  S/cm has been obtained for PVC(5)-PEMA(20)-PC(67)-LiClO<sub>4</sub>(8) wt % polymer complex. This value is better than the value  $2.482 \times 10^{-5}$  S/cm reported by Rajendran and Uma<sup>15</sup> for the PMMA-based polymer electrolyte.

Figure 4 shows the temperature dependent ionic conductivity plot, which explains that the conductivity increases with increase in temperature for all the polymer electrolytes; and the conductivity temperature plots show nonlinearity. Such features are generally observed for high viscous electrolytes or much amorphous polymeric systems. This cannot be

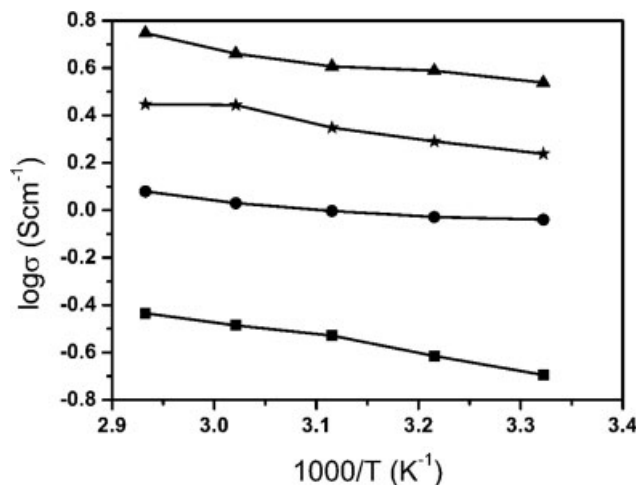
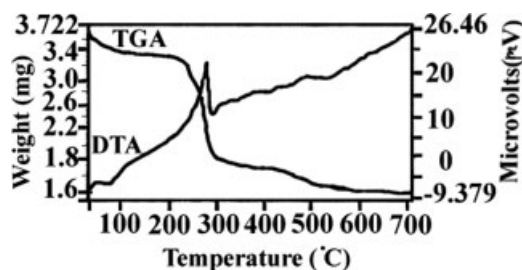


Figure 4 Arrhenius plot of PVC-PEMA-LiClO<sub>4</sub>-PC complexes for different concentrations.



**Figure 5** TG/DTA curves of PVC(5)-PEMA(20)-LiClO<sub>4</sub>(8)-PC(67) complex.

described by Arrhenius relationship but possible by the VTF expression based on the free volume concept.<sup>16</sup> It supports the idea of ionic transport taking place through the plasticizer-rich phase.

#### TG/DTA analysis

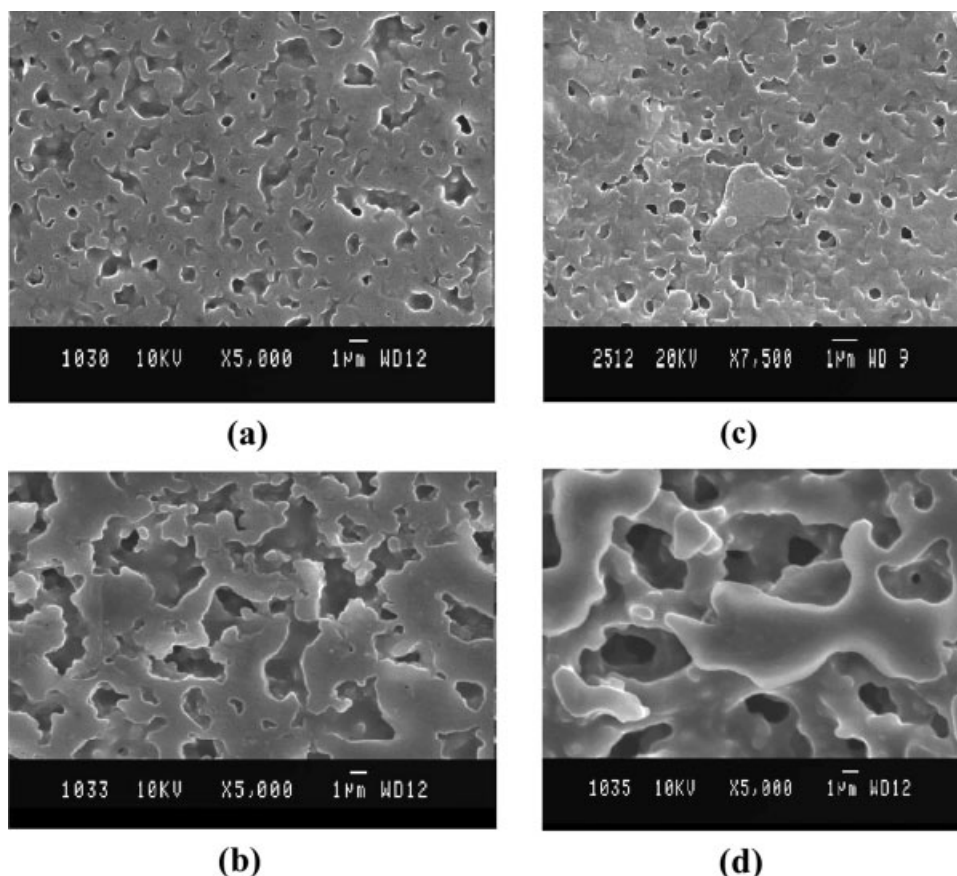
Figure 5 shows the TG/DTA traces of PVC(5)-PEMA(20)-PC(67)-LiClO<sub>4</sub> (8 wt %) polymer electrolyte, which shows maximum conductivity value. An endothermic peak was observed at 35°C and corresponding about 2% of weight loss is attributed to the presence of moisture in the samples.<sup>17–19</sup> The

film starts decomposing at 231°C followed by an exothermic peak, which indicates that the film is stable up to 231°C.<sup>20</sup> The DTA trace shows an exothermic peak around 260°C, which corresponds to the melting point of PEMA polymer host.

It is clear from these observations, that the PEMA based hybrid polymer electrolytes, which contain LiClO<sub>4</sub> as salt can be operated up to 231°C.

#### SEM analysis

Figure 6 shows the scanning electron micrographs of PVC(5)-PEMA(20)-PC(67)-LiClO<sub>4</sub> (X wt %), where X = 4, 6, 8, and 10. It is observed that ordered and almost spherical grains are uniformly distributed in PVC-PEMA-PC-LiClO<sub>4</sub> (4, 6, and 10 wt %) 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-PEMA-PC-LiClO<sub>4</sub> (8 wt %) Figure 6(c). The microstructure is disordered throughout the sample and the pore size is smaller. These results suggest that PVC-PEMA-PC-LiClO<sub>4</sub> (8 wt %) has higher solvent retention ability since the pores in microstructure occur due to solvent



**Figure 6** SEM analysis of (a) PVC(5)-PEMA(20)-LiClO<sub>4</sub>(4)-PC(71), (b) PVC(5)-PEMA(20)-LiClO<sub>4</sub>(6)-PC(69), (c) PVC(5)-PEMA(20)-LiClO<sub>4</sub>(8)-PC(67), and (d) PVC(5)-PEMA(20)-LiClO<sub>4</sub>(10)-PC(65).



removal.<sup>21,22</sup> SEM results are consistent with the view that higher conductivity in PVC-PEMA-PC-LiClO<sub>4</sub> (8 wt %) based polymer blend electrolyte arises from the increased amorphicity of the blend polymer electrolytes.

### CONCLUSION

The ionic conductivity behavior of plasticized PVC/PEMA blends containing various concentrations of LiClO<sub>4</sub> has been studied. PVC(5)-PEMA(20)-PC(67)-LiClO<sub>4</sub> (8 wt %) polymer film exhibits maximum ionic conductivity ( $3.454 \times 10^{-3}$ ) among the various blends studied. XRD and FTIR studies are used to confirm their structural status and complexation behavior of the blend polymer electrolyte. TG/DTA analysis reveals that the electrolyte is thermally stable up to 231°C, which is fairly higher than the operating temperature of lithium polymer batteries. The optimized polymer electrolyte can be used as an electrolyte in the fabrication of Li batteries.

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