

Characterization of PVC/PEMA Based Polymer Blend Electrolytes

S. Rajendran*, M. Ramesh Prabhu, M. Usha Rani

Department of Physics, Alagappa University, Karaikudi 630 003, India

*E-mail: sraj54@yahoo.com

Received: 1 September 2007 / Accepted: 29 December 2007 / Online published: 20 January 2008

Polymer electrolyte membranes comprising of poly (ethyl methacrylate)/ poly (vinyl chloride), propylene carbonate (PC) as plasticizer and LiClO₄ as salt were prepared by solvent casting technique. XRD, FTIR and SEM studies have been made to investigate the structural, complexation and variation in film morphology of the polymer electrolyte. The maximum ionic conductivity value 3.454×10^{-3} S/cm has been observed for PVC (5)-PEMA (20)-PC (67) - LiClO₄ (8 wt %) system at 303K using ac impedance spectroscopic technique. Also, the TG/DTA studies showed the thermal stability of the film.

Keywords: Polymer blend; FTIR; XRD; Thermal and conductivity studies

1. INTRODUCTION

In the recent years, there has been a tremendous interest in the preparation of polymer electrolytes with high ionic conductivity, good mechanical strength and thermal stabilities because these polymer electrolytes play a major role in solid-state batteries, electrochromic windows, sensors, fuel cells etc., [1]. Earlier, solution type electrolytes consisted of polymers such as PEO and PPO or their blend complexes with suitable salts (LiClO₄, LiCF₃SO₃, etc) [2]. However they showed poor room temperature conductivity ($\approx 10^{-8}$ Scm⁻¹). In the past two decades different polymer hosts, such as PMMA [3], PAN [4], PVC [5], PVdF [6] had been studied as the gel-forming polymer matrix. Comparing with other polymer electrolytes, this plasticized or gelled polymer electrolytes possess higher room temperature ionic conductivity of about 10^{-3} Scm⁻¹ and could be useful for lithium and lithium-ion battery application.

Poly (vinyl chloride) (PVC) can act as a mechanical stiffener in the electrolyte due to its immiscibility with the plasticizer. A PVC-based polymer electrolyte system plasticized with ethylene carbonate and propylene carbonate has been reported [7] to be applicable to lithium metal and lithium-

ion secondary batteries [8]. The use of poly (ethyl methacrylate) (PEMA) as a host polymer was first reported by Han et al. [9] and Fhamy et al. [10]. In the present work, polymer electrolytes are prepared with the different weight ratios of PEMA and PVC for the constant weight percentage of PC and LiClO_4 .

2. EXPERIMENTAL PART

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. Polymer electrolytes were prepared by dissolving appropriate amounts of the corresponding constituents in anhydrous Tetrahydrofuran (THF). All the electrolytes were prepared by the solvent casting technique. The cast films were allowed to stand in air at room temperature to allow slow evaporation of THF. Residue of remaining THF was removed by further drying vacuum at 24 hrs at 60°C .

The XRD equipment used in this study was JEOL, JDX 8030 X-ray diffractometer. FTIR ABB BOMEN MB104 IR spectrophotometer measurements were made in the range $400\text{--}4000\text{ cm}^{-1}$. The electrical conductivity of polymer complexes were measured from impedance plots at different temperatures using Keithley 3330 LCZ meter. Scanning Electron Microscope (JEOL, JXA-840 Japan) was used for micro structural studies.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction

Fig 1 shows the X-ray diffraction patterns of pure PEMA, PVC and LiClO_4 . Fig 2 shows XRD pattern of $[(25-x)\text{ PVC} - x\text{ PEMA}] - \text{PC} - \text{LiClO}_4$ with $x = 0, 5, 10, 15, 20, 25$ complexes respectively. The diffraction peak of pure PEMA was observed at $2\theta = 18.6^\circ$ and that of PVC at $2\theta = 13^\circ$. In polymer complexes, these pure peaks of PEMA and PVC appeared as one broad peak with less intensity. It may be due to the incorporation of LiClO_4 and the plasticizer (PC), which would have disturbed the crystalline region and increased the amorphous phase. Diffraction pattern of the complexes reveal the amorphous nature, which is responsible for higher conductivity. These observations apparently reveal that the polymer undergoes significant structural reorganization while adding plasticizer and salt. No peaks corresponding to pure LiClO_4 were observed in the polymer complexes, revealing absence of excess salt in the polymer complexes.

3.2. FTIR Studies

FTIR spectra of pure PEMA, PVC and LiClO_4 are shown in fig.3, and their polymer complexes are depicted in fig 4. The characteristic bands of PVC can be classified into three regions. The first is called the C-Cl stretching region in the range from $600\text{--}700\text{ cm}^{-1}$. The second region is called C-C

stretching in the range from $900\text{--}1200\text{ cm}^{-1}$. The third region is $1250\text{--}2970\text{ cm}^{-1}$ in PVC (numerous C-H modes). The frequency occurred at around 1725 cm^{-1} is assigned to the carbonyl stretching vibration of PEMA. In the region $2900\text{--}3000\text{ cm}^{-1}$, namely at 2982 , 2939 and 2910 cm^{-1} are due to the C-H stretching vibration of the methylene, (C) CH_3 and ethylene (O) C_2H_5 groups which overlap [11]. The two bands at 1240 and 1261 cm^{-1} are associated with different vibrations of the ester group. Frequency at 1483 cm^{-1} is assigned to $-\text{CH}_3$ asymmetric bending of plasticizer such as propylene carbonate.

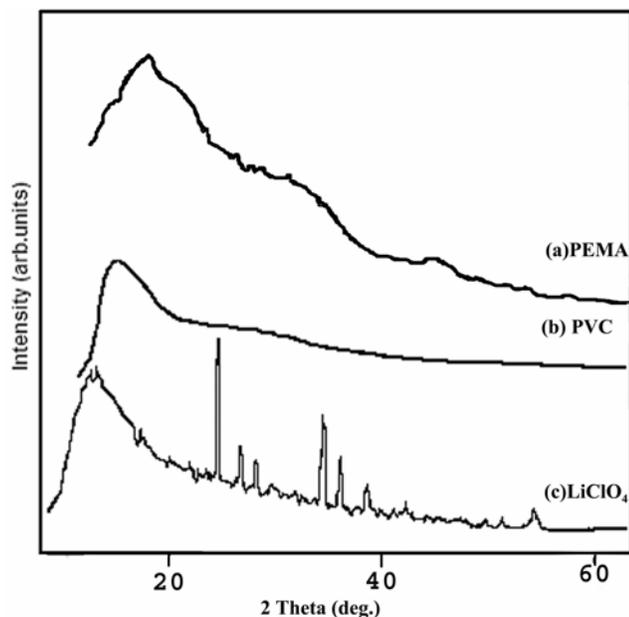


Figure 1. XRD pattern of pure (a) PVC, (b) PEMA, (c) LiClO_4 .

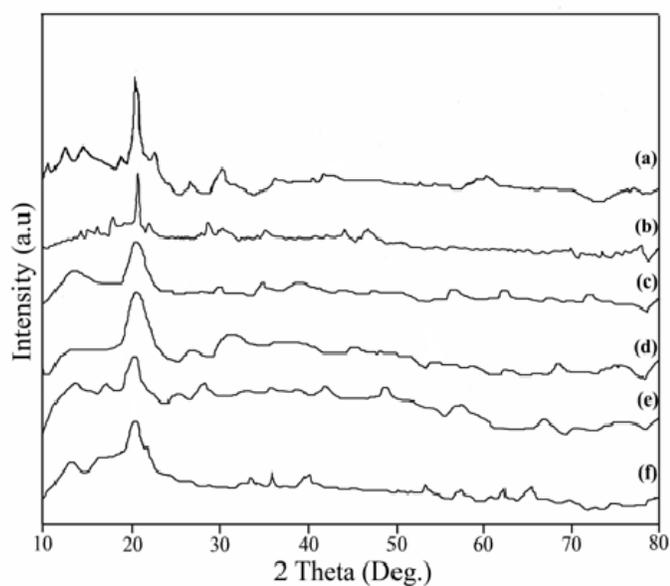


Figure 2. XRD pattern of $[(25-x)\text{ PVC} - x\text{ PEMA}]\text{-PC (67) -LiClO}_4(8)$ polymer complex with $x = 0, 5, 10, 15, 20, 25$.

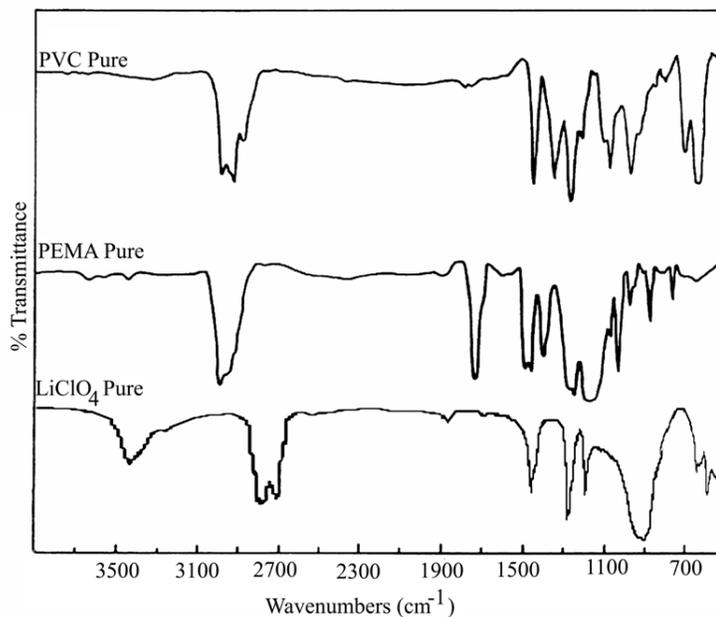


Figure 3. FTIR spectra of pure (a) PVC, (b) PEMA, (c) LiClO₄.

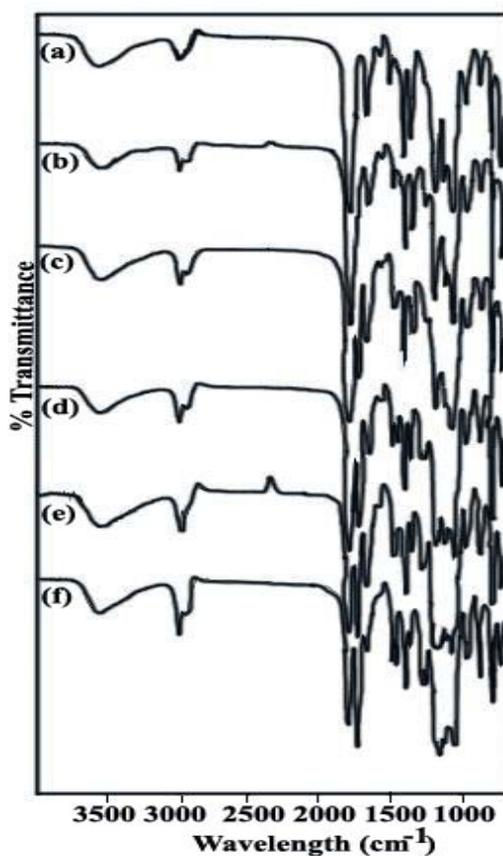


Figure 4. FTIR spectra of [(25-x) PVC - x PEMA]-PC-LiClO₄ polymer complex with x = 0, 5, 10, 15, 20, 25.

The vibrational peaks of PEMA (646, 755, 850, 1157 and 1473 cm^{-1}), PVC (693, 771, 959, 1035, 1254 and 1479 cm^{-1}) and LiClO_4 (1366, 1378 and 2924 cm^{-1}) are shifted to (660, 748, 860, 1179 and 1483 cm^{-1}), (711, 777, 966, 1049, 1270 and 1483 cm^{-1}) and (1353, 1388 and 2942 cm^{-1}) in the polymer electrolytes, respectively. In addition to that, a few new peaks at 1115 and 1447 cm^{-1} , which corresponds to C-O stretching and asymmetrical bending vibrations of the methyl C-H bond, are found in the electrolytes. Shifting and formation of new peaks suggest the polymer-salt interaction in PEMA based gel polymer electrolytes.

3.3. Conductivity measurements

The ionic conductivity of PEMA and PVC based hybrid polymer electrolytes is calculated from $\sigma = l/R_b A$, where 'l' the thickness of the film, 'A' the area of the film and R_b the bulk resistance of the material which is obtained from the intercept on the real axis at the high frequency end of the Nyquist plot of complex impedance.

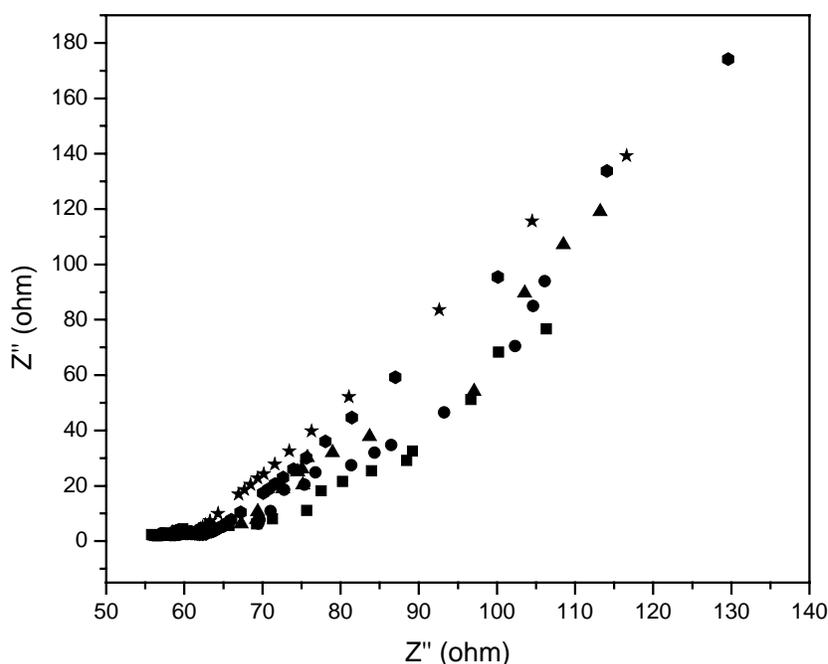


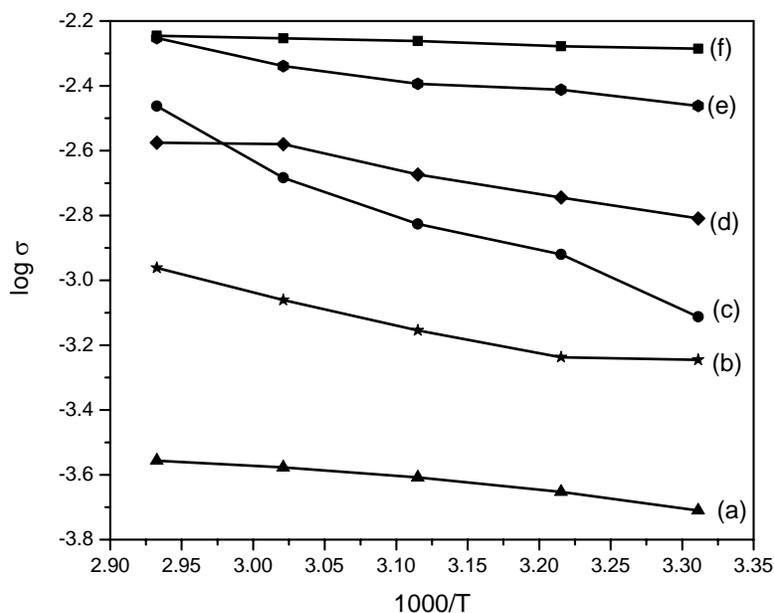
Figure 5. Typical impedance plot of PVC (5) - PEMA (20) - PC (67) - LiClO_4 (8 wt %) at 303 K.

Fig.5 shows the complex impedance diagram of PEMA (20)-PVC (5)-PC (67)- LiClO_4 (8) wt % at the room temperature. The disappearance of semicircular portion in the high frequency region of complex impedance plot indicates that the conduction is mainly due to the ions [12]. The conductivity data for hybrid polymer electrolytes containing different weight ratios of PEMA-PVC-PC- LiClO_4 are presented in Table.1. From the table we can see that the conductivity value increases with temperature

Table 1. Ionic conductivity values of PEMA-PVC-PC-LiClO₄ (8 wt %) polymer electrolyte system

Composition of PEMA-PVC-PC	Conductivity values of PEMA-PVC-PC-LiClO ₄ (8wt %) system ($\times 10^{-3}$ S/cm)				
	302K	311K	321K	331K	341K
A ₀ (0-25-67)	0.195	0.223	0.246	0.264	0.278
A ₁ (5-20-67)	0.568	0.579	0.701	0.869	1.091
A ₂ (10-15-67)	0.771	1.201	1.493	2.073	3.448
A ₃ (15-10-67)	1.552	1.799	2.117	2.632	3.048
A ₄ (20-5-67)	3.454	3.876	4.042	4.578	5.588
A ₅ (25-0-67)	4.446	4.545	4.717	4.808	4.902

From Table 1 (film A5) shows higher conductivity compared with other electrolytes, but exhibits gelly nature and poor mechanical stability. Less quantity of PVC (5) with PEMA (20) has given appreciable conductivity with good mechanical stability. The poor ionic conductivity at high PVC content is caused mainly by the low electrolyte content (Film A₀). From these observations, it is concluded that PEMA, PVC (20:5) electrolyte (film A₄) exhibits appreciable conductivity with adequate mechanical stability.

**Figure 6.** Temperature dependence of ionic conductivity for [(25-x) PVC-x PEMA]-PC-LiClO₄ polymer complex with x= 0, 5, 10, 15, 20, 25.

The temperature dependent ionic conductivity plots are shown in Fig.6. The Arrhenius plots suggest that the ion transport in polymer electrolytes depends on the polymer segmental motion. Figure 6 explains that . The ionic conduction in the polymer electrolyte system obeys the VTF (Vogel-

Tamman-Fulcher) relation, which describes the transport properties in a viscous matrix. [13]. The increase of conductivity with temperature is interpreted as being due to a hopping mechanism between co-ordination sites, local structural relaxations and segmental motion of polymers. As the amorphous region progressively increases, however, the polymer chain acquires faster internal modes in which bond rotation produces segmental motion. This in turn, favors the hopping of inter-chain and intra-chain ion movements and the conductivity of the polymer electrolyte becomes high.

3.4. Thermal analysis

The thermal stability of the polymer electrolyte is also an important parameter to guarantee acceptable performances in lithium batteries. Fig 7(a-c) shows the traces of TG/DTA of polymer electrolytes. It is observed from Fig 7(a), for the film a first decomposition is observed at the temperature 45°C with a weight loss of 8% and is attributed to the presence of moisture at the time of loading the sample. The film starts complete decomposition at 265°C, which indicates the film is stable up to 265°C. the DTA traces shows an exothermic peak around 230°C indicating the decomposition of PEMA as evidenced by rapid weight loss observed in the TG curve.

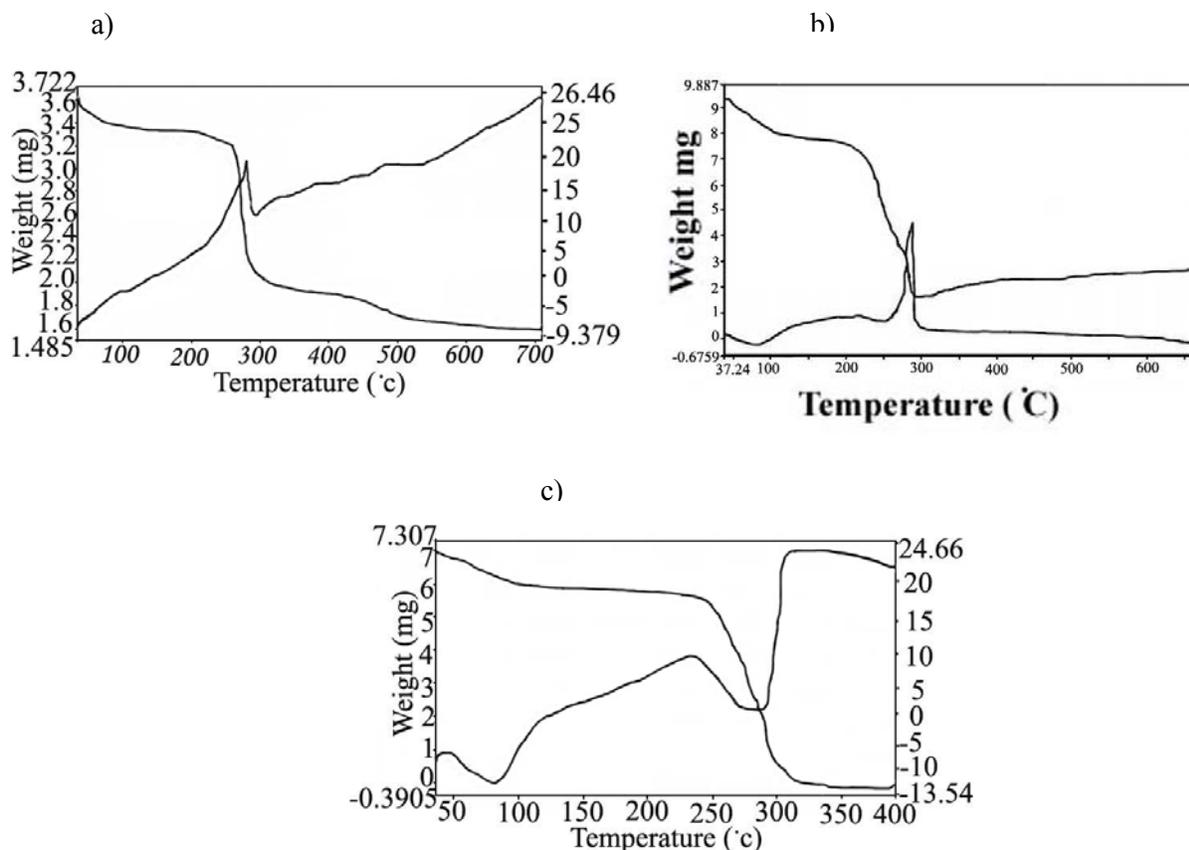


Figure 7. TG/DTA plots for [(25-x) PVC – x PEMA]-PC-LiClO₄ polymer complex with x= 0, 5, 10, 15, 20, 25.

On the other hand, for the film Fig 7(b) & (c) a similar decomposition peak was observed around 90°C and 85°C with a weight loss of about 12% and 10%. And the films start complete decomposition at 231°C and 245°C. As mentioned earlier, a similar exothermic peak appears in the DTA traces for both the films. This indicates the complete decomposition of the polymer electrolyte film, which is in good agreement with the TG curve. From the above discussion, it is concluded that the thermal stability limit of the polymer blend electrolyte is about 210°C.

3.5. SEM Analysis

Fig 8 (a, b&c) shows SEM images of polymer electrolytes at different blending ratios (film A₀, A₄&A₅) respectively. The pores in the micrographs indicate the occurrence of phase-separation in the polymer electrolytes. The several pores or craters, which have formed on the surface, are due to the rapid evaporation of the solvent (THF). The difference in the pore size is related with the difference in the driving force for phase separation [14].

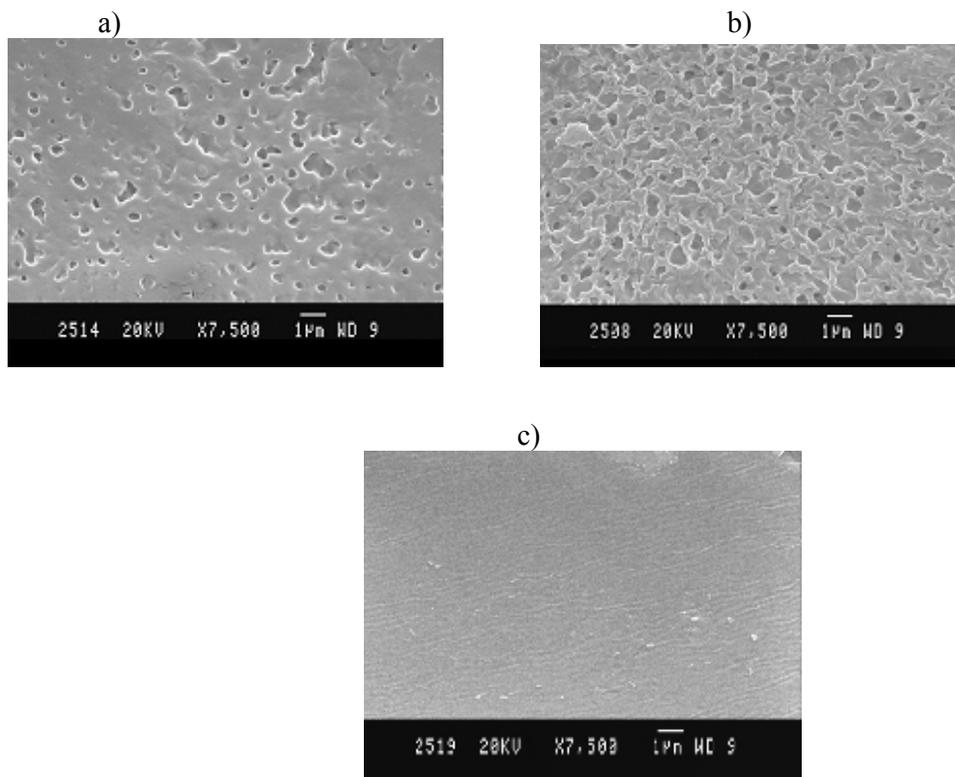


Figure 8. SEM images of PVC-PEMA-PC-LiClO₄ polymer electrolytes where (a) = (25:0:67:8 wt %), (b) = (5:20:67:8 wt %) and (c) = (0:25:67:8 wt %)

The dual compatibility of PEMA towards both PVC and the plasticizer tend to lessen the driving force for separation of the PVC phase and leads to better development of the film. In PVC

polymer electrolytes is coagulated at the beginning stage of phase separation before a large electrolyte rich phase is developed. Thus the resulting film has distinct phases, viz., a PVC rich phase and plasticizer rich phase (film A₀). But PEMA (25) rich compositions, the phase separation is less and more homogeneous solutions tend to form and because of this the conductivity is also increased (film A₅).

4. CONCLUSIONS

PEMA based polymer electrolytes were prepared by solvent casting technique. The complex formation in PEMA –PVC-PC-LiClO₄ system has been confirmed from XRD and FTIR studies. All electrolytes show appreciable conductivity even at room temperature. Maximum conductivity (3.454×10^{-3} S/cm) at room temperature with good mechanical stability has been observed for PVC (5)-PEMA (20)-PC (67)-LiClO₄ (8 wt %) system among the various compositions studied. Higher conductivity in this composition could be attributed to the higher amorphicity. Good thermal stability of these polymer electrolyte systems up to 230°C was confirmed by TG/DTA analysis. Since the polymer electrolyte (film A₄) exhibits maximum conductivity value and good thermal stability, this can be used as an electrolyte in lithium batteries and other electrochemical devices.

References

1. C. Vincent and B. Scrosati, *Modern Batteries: an introduction to electrochemical power sources*, John Wiley and sons, Inc, New York (1997)
2. C. Vincent, *Solid state ion.*, 134(2000)159
3. K.S.Kim, K.S. Kum, H.W. Cho, B. Woncho, W.H.Rhee, *J.Power sources.*, 124(2003)221
4. M.Watanabe, M.Kanba, Nagaoka, I.Shinohara, *J.Polym Sci Poly Phys Ed.*, 21(1983)939
5. A.M.Sukeshini, A. Nishimoto, M.Watanabe, *Solid State Ionics.*, 86-88 (1996) 385
6. E.Tsuchida, H.Ohno, E.Tsunemi, *Electrochim Acta.*, 28(1983)833
7. A.M.Stephan, T.Premkumar, N.G.Renganathan, S.Pitchumani, R.Thirunakaran, N.Muniyandi, *J.Power sources.*, 89(2000)80
8. M.Alamgir, K.M.Abraham, *J. Electrochem Soc.*, 140(1993)L96
9. H.S.Han, H.R.Kang, S.W.Kim, H.T.Kim, *J.Power sources.*, 122(2002)461
10. M.T.Ahmed, T.Fahmy, *Polym. Testing.*, 20(2000)477
11. T.Fahmy, M.T. Ahmed, *Polymer testing* 20 (2001)477.
12. M.Watanabe, K. Sanui, N. Ogata, T. Kobayashi, Z. Ohbaki, *J.Appl.phys.* 57(1) (1985) 123.
13. S. Rajendran, T. Uma, T. Mahalingam, *Eur.polym.J* 36(2000) 2617.
14. H.J. Rhoo, H.T. Kim, J.K. Park, T.S. Hwang, *Electrochim. Acta* 42(1997)15