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Studies on solid polymer electrolyte based on PEO/PVC blends

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Abstract Novel polymer blend electrolyte was prepared using poly (ethylene oxide), poly(vinyl chloride) and lithium perchlorate ($LiClO_4$) as the complexing salt by employing solvent casting technique. The prepared films were subjected to XRD, FTIR, a.c. impedance spectroscopy and thermogravimetry / differential thermal analysis (TG/DTA). Quantitative analysis of the FTIR spectra provides the specific interactions between the constituents. The thermal stability of the film is found using TG/DTA studies. The maximum conductivity value of PVC (25)–PEO(75)–$LiClO_4$(8) film is found as 1.32×10^{5} S/cm at room temperature. As the PVC concentration increases in the electrolyte, the conductivity is found to decrease. The temperature dependent ionic conductivity is also carried out in the temperature range 303–333K and the results are discussed.

Keywords Polymer blend, FTIR, ac impedance spectroscopy, thermal studies

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1. Introduction

In the last couple of decades, solid polymer electrolytes (SPEs) have attracted considerable attention due to their interesting properties such as ease of preparation of thin film and other forms, wide range of composition and hence control of properties, good electrode-electrolyte interfacial contacts, high value of ionic conductivity as well as their wide application potentials in high energy density batteries, electrochromic displays, sensors and fuel cells [1,2]. Poly (ethylene oxide), in particular, is an exceptional polymer which makes complexes with high concentrations of a wide variety of salts to form polymeric electrolytes [3]. The complexes of PEO with a number of alkali salts such as $LiBF_4$,

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$LiPF_6$, $LiB(C_6H_5)_4$ [4], LiSCN [5], $LiSO_3CF_3$ and $LiClO_4$ [6] are reported. Even though these electrolytes give good conductivity above their melting temperature *i.e.* above 60°C appreciable conductivity could not be attained at room temperature due to the crystalline nature of PEO, which is a major obstacle in the context of ionic conductivity. To minimize the crystallization, works have been done by incorporating ceramic fillers into the PEO matrix.

The main thrust of the current research in SPE is to develop the electrolytes that show high conductivity and give better mechanical properties. Enhancement in ionic conductivity could be attained by blending of polymers [7], cross linking [8], insertion of ceramic fillers [9], plasticization [10], *etc.* Among the various methods polymer blending is a feasible approach in which one conducting component acts as a plasticizer to reduce the non conductive crystalline phase of the other leading to an increase in the ionic conduction.

Proof of the blend concept was first demonstrated by Rhoo *et al* [11] on PVC/PMMA blend polymer electrolytes, further the characteristics of a Lithium-ion polymer battery that employ a PVC/PMMA polymer electrolyte was reported by Kim *et al* [12]. Many workers conceived this idea and worked on different blends such as PVC/PMMA, PVdF/ PMMA, PAN/ PEO [13-17] to find an appropriate blend which would be suitable for lithium battery applications.

In the present work we have prepared blend electrolytes consisting of polymers PVC, PEO and $LiClO_4$ as the salt in different weight ratios and investigations on conductivity, complexation and thermal stability have been carried out. PVC which acts as a mechanical stiffener, is used in order to increase the thermal stability and mechanical stability of the polymer electrolyte. It is well known that the thermal stability of PEO based electrolytes bereft of ceramic oxides is not good. Hence to increase the thermal stability of PEO based polymer electrolyte PVC has been incorporated.

2. Experimental Studies

PVC ($M_w = 1.5 \times 10^5$), PEO ($M_w = 1 \times 10^5$) and $LiClO_4$ purchased from Aldrich were used in this study. All the electrolytes were prepared by the solvent casting technique. The solutions for film cast were prepared by dissolving appropriate amounts of PVC, PEO and $LiClO_4$ together in anhydrous THF. The solution was stirred continuously for 10 hours until a homogeneous suspension was obtained. The resulting homogeneous mixture was cast on the Teflon-bushes, allowing THF to evaporate slowly in an argon atmosphere at room temperature and then at 40°C for an hour for complete evaporation of residual solvent if any. The resulting films were visually examined for its dryness and free standing nature. Chemical storage, film casting and cell assemblies were performed in a vacuum atmosphere.

3. Results and discussion

3.1 X-ray diffraction studies :

Figure 1 shows the XRD patterns of PVC-PEO-$LiClO_4$ complexes and those of pure PVC, PEO and $LiClO_4$. It is seen that PVC exhibits amorphous phase. The XRD pattern of pure PEO (Figure 1b) indicates two crystalline peaks at 19.7° and 23.9° [18]. The peaks

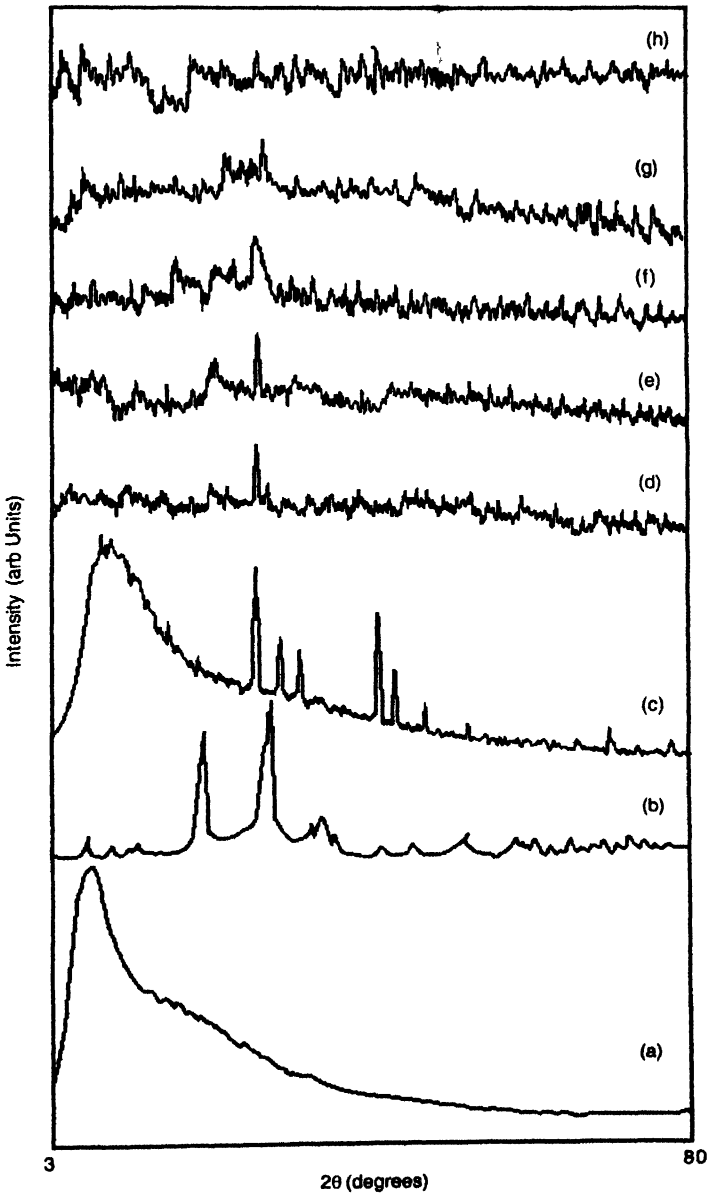

Figure 1. XRD plots for Pure (a) PVC ; (b) PEO ; (c) $LiClO_4$; (d) PVC:PEO:$LiClO_4$ (0:100:8); (e) PVC:PEO:$LiClO_4$ (25:75:8) ; (f) PVC:PEO:$LiClO_4$ (50:50:8) ; (g) PVC:PEO:$LiClO_4$ (75:25:8) and (h) PVC:PEO:$LiClO_4$ (100:0:8).

appearing in pure PEO are observed in the complexes S_1 and S_2 with lesser intensities and are found to be absent in other complexes. This is in accordance with the concentration of PEO in the complex. Most of the peaks pertaining to $LiClO_4$ disappear in the polymer complex, which indicates the complexation of lithium salt with the polymer electrolyte.

3.2 FTIR studies :

FTIR studies on blends are useful to identify miscibility of the polymers used for blending. Figure 2(a-h) depicts the FTIR spectra of pure PVC, PEO, $LiClO_4$ and complexes respectively. Figure 2(d) gives the spectrum of pure PVC+$LiClO_4$ complex.

The γ (C-Cl) stretching vibration of pure PVC appearing at 610 cm^{-1} is shifted to 692 cm^{-1} in the complex. The other CH_2 bending vibrations like CH_2 wagging, CH_2 twisting and δ_{sym} CH_2 deformation which appear at 1254, 1333 and 1428 cm^{-1} in pure PVC are shifted to 1258,1328 and 1419 cm^{-1} respectively. Some peaks present in pure PVC (2360, 1734, 1559, 966, 494 cm^{-1}) are found to be absent in the complexes.

Figure 2(h) elucidates the spectrum of PEO+$LiClO_4$. The peaks at 930, 820 cm^{-1} are assigned to CH_2 rocking vibrations and may be attributed to the gauche form. The broad peak at 1130 cm^{-1} in the pure PEO shifts to 1145 cm^{-1} in the complex. The peak at 1105 cm^{-1} is shifted to 1110 cm^{-1} corresponding to C-O-C stretching vibration. Vibrational peaks of PEO appearing at 2900, 1600, 1325, 1225 cm^{-1} are absent in the polymer complexes.

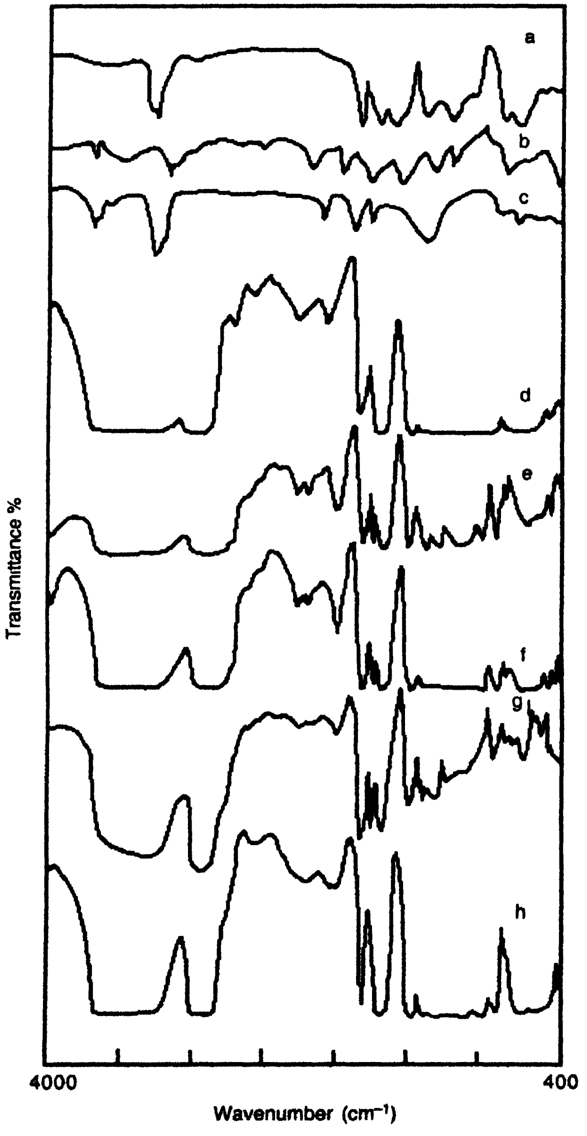

Figure 2. FTIR plots for Pure (a) PVC; (b) PEO; (c) $LiClO_4$; (d) PVC:PEO:$LiClO_4$ (0:100:8) ; (e) PVC:PEO:$LiClO_4$ (25:75:8); (f) PVC:PEO:$LiClO_4$ (50:50:8) ; (g) PVC:PEO:$LiClO_4$ (75:25:8) and (h) PVC:PEO:$LiClO_4$ (100:0:8)

The band at 470 cm^{-1} in pure $LiClO_4$ is assumed to be replaced by two bands at 479 and 434 cm^{-1} indicating two kinds of environment for the ClO^-_4 ion in the complex. The vibrational peaks 1610, 1300, 1070, 750 cm^{-1} of $LiClO_4$ are found to be absent in the polymer complexes.

In addition, some new peaks at 2237, 2162, 1965, 1800, 1725, 1620, 1469, 1031 cm^{-1} are observed in the polymer complexes other than those of the starting materials *viz.* PVC, PEO, $LiClO_4$ which proves the complexation of the system.

3.3 Conductivity studies :

The polymer electrolyte films were sandwiched between two stainless steel (SS) blocking electrodes. The ionic conductivities of the polymer electrolytes were calculated from the bulk resistance obtained from the isotherm. Measurements were made by complex impedance analyzer in the frequency range 40 Hz-100 KHz. The ionic conductivity values of PVC-PEO-$LiClO_4$ electrolyte films were obtained in the temperature range 303-333K and are tabulated in Table. The maximum conductivity has been obtained for the film S_1 (Table 1). But it has poor mechanical stability. Hence, the film S_2 having good mechanical stability may be used for the battery application. The room temperature conductivity of S2[PVC(25)-PEO(75)-$LiClO_4$)] is estimated as 1.32×10^{-5} S/cm. Figure 3 represents the variation of the logarithm of electrical conductivity (logσ) with inverse absolute temperature for various polymer electrolytes with fixed concentration of $LiClO_4$. It is evident from the table that as the temperature increases the conductivity also increases for the polymer complexes. This can be explained by free volume model [19]. As the temperature increases the free volume increases which leads to increase in ion mobility and segmental mobility that will assist ion transport and virtually compensate for the retarding effect of the ion clouds. The graphs in Figure 3 show an unique nature suggesting no linear dependence which suggest that ion cloud follow Williams-Landel-Ferry (WLF) mechanism [20], in otherwords ion transport in polymer electrolyte is dependant on segmental motion [21].

Table 1. Conductivity values of PVC: PEO:$LiClO_4$

	Composition	Conductivity values x 10^{-5} S/cm		
Film	PVC:PEO:$LiClO_4$	303 K	318 K	333 K
S_1	0 : 100 : 8	4.587	22.290	89.170
S_2	25 : 75 : 8	1.322	2.401	10.440
S_3	50 : 50 : 8	0.409	0.676	1.529
S_4	75 : 25 : 8	0.115	0.123	0.127
S_5	100 : 0 : 8	0.002	0.011	0.013

3.4 Thermal analysis :

Thermal analysis of PVC-PEO-$LiClO_4$ (film S_2) is shown in Figure 4. The DTA curve shows a small endothermic peak at 64.4°C which indicates the melting of the polymer. It can be seen from TG curve that the film looses its weight gradually on increasing the temperature. A well defined exothermic peak is seen around 302°C indicating the decomposition of polymer electrolytes. Consistent with this thermal event, the weight decreased rapidly from 265°C. The first and second decomposition of the film take place between 50-80 and 250-280°C respectively. Weight losses of the polymer electrolyte at 100, 200 and 300°C are found as 7, 11 and 28% respectively. The weight losses may be due to the evaporation of the moisture and solvent.

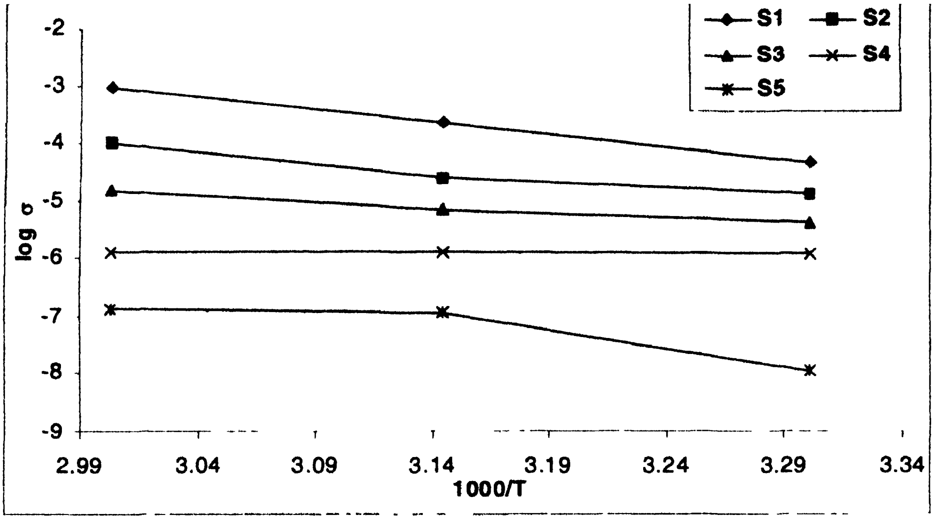

Figure 3. Arrhenius plot of log σ against reciprocal temperature of PVC:PEO:$LiClO_4$.

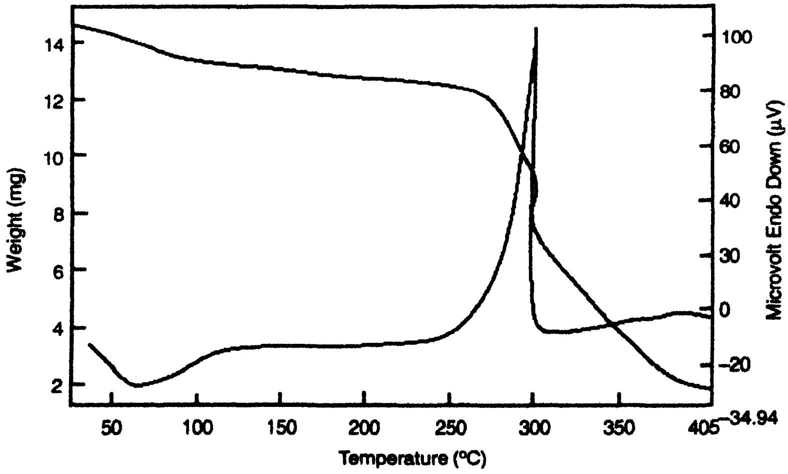

Figure 4. TG/DTA curve for PVC: PEO: $LiClO_4$ (25:75:8).

4. Conclusion

Five different compositions of PVC-PEO-$LiClO_4$ polymer electrolyte systems have been prepared and the polymer electrolyte (film S_2, *i.e.* PVC/PEO, 25/75) is found to be the best film on the basis of both conductivity and mechanical stability. The film is found stable upto 250°C and then the film losses its weight gradually till 265°C beyond which the polymer electrolyte loses weight drastically because of onset of degradation. As the film S_2 possesses desirable properties, it can be used for Li battery applications.

References

[1] M B Armand, J M Chabagno and M Duclot in *Second Intern Meeting on Solid Electrolytes*, St Andrews, Scotland, p2022 (1978)

[2] F M Gray *Solid Polymer Electrolyte-Fundamentals and Technological Applications* (Germany VCH, Weinheim) (1991)

[3] D W Kim, J R Park and H W Rhee *Solid State Ionics* **83** 49 (1996)

[4] W Wieckzorek and J R Stevens *J Phys Chem.* **B 101** 1529 (1997)

[5] J Przyluski and W Wieczorek *Solid State Ionics* **36** 165 (1989)

[6] J Y Cherng, M Z A Munshi, B B Owens and W H Smyrl *Solid State Ionics* **28** 857 (1988)

[7] H J Rhoo, H T Kim, J K Park and T S Hwang *Electrochim Acta* **42** 571 (1997)

[8] H T Kim, K B Kim, S W Kim and J K Park *Electrochim Acta* **45** 4001 (2000)

[9] H Hong, C Liquan, H Xuejie and X Rongjian *Electrochim Acta* **37** 1671 (1992)

[10] D Peramunage, D M Pasquariello and K M Abraham *J Electrochim Soc* **142** 1789 (1995)

[11] O Bohnke, G Frand, M Rezrazi, C Rousselot and C Truche *Solid State Ionics* **66** 97 (1993)

[12] M Alamgir and K M Abraham *J Electrochem Soc* **140** 196 (1993)

[13] T Mani and J R Stevens *Polymer* **33** 834 (1992)

[14] M B Armand in J R Mac Callum, C A Vincent (Eds) *Polymer Electrolyte Reviews* (Amsterdam Elsevier) p1 (1987)

[15] E A Reitman, M L Kaplan and R J Cava *Solid State Ionics* **17** 67 (1985)

[16] P R Sorenson and T Jacobson *Eletrochim Acta* **27** 1675 (1982)

[17] D Fauteux and C Robitaille *J Electrochem Soc* **133** 307 (1986)

[18] K Such, Z Florianczyk, W Wieczorek and J Przytuski *Second Int Symposium on Polymer Electrolytes* (1989)

[19] M Rathner and D F Shriver *Chem Rev* **88** 109 (1988)

[20] M L Williams, R F Landell and J D Ferry *J Am Chem Soc* **77** 3701 (1955)

[21] Y Okamoto, T F Ych, H S Lee and T A Skotheimk *J Polym. Sci Part A Polym. Chem.* **31** 2573 (1993)