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Studies on PVC-PEO blend polymer electrolytes

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ABSTRACT

Polymer electrolyte systems consisting of poly (vinyl chloride) (PVC), poly (ethylene oxide) (PEO) as host polymers, lithium perchlorate (LiClO_4) as inorganic salt and ethylene carbonate (EC) as plasticizer are prepared. The ionic conductivities of polymer electrolyte systems containing various salt concentrations are investigated by using impedance spectroscopy technique at various temperatures. The maximum ionic conductivity is found to be $2.39 \times 10^{-6} \text{ S cm}^{-1}$ at room temperature for polymer electrolyte system containing 20 wt% of LiClO_4 salt. Thermal stability of the various polymer electrolytes are examined by thermogravimetric/differential thermogravimetric analysis. The complex formation between polymer and salt has been confirmed in the polymer electrolytes by using X-ray diffraction studies. © 2012 Trade Science Inc. - INDIA

KEYWORDS

Ionic conductivity;
Polymer electrolytes;
Plasticizer;
Poly (vinyl chloride);
Poly(ethylene oxide);
Impedance spectroscopy

INTRODUCTION

Polymer electrolytes with high ionic conductivity have potential applications as an electrolyte in solid state batteries. Therefore development of such systems is one of the main objectives in polymer research^[1-4].

The electrochemical stability and compatibility of polymer electrolytes with electrode materials play very important role in electrochemical devices. Plasticized PVC based blend polymer electrolytes have been proposed for application in lithium batteries due to their beneficial effects on stability of Li-electrolyte interface^[5]. The cyclability of lithium battery affected due to uncontrolled passivation phenomenon. The formation of passive layer between lithium electrode and polymer electrolytes increases with passage of time^[6,7]. The nature

of the layer formed between lithium electrode and polymeric electrolyte depends on the purity and composition of the electrolyte. The passive layer between the lithium electrode and polymeric electrolyte will show solid phase behavior if such layer having properties of solid lithium ionic conductor.

In the present study, an attempt has been made to prepare various plasticized PVC-PEO blend polyelectrolyte systems containing LiClO_4 as inorganic salt in order to manifest higher ionic conductivity and good thermal stability. We present the results of our study on these polymer electrolyte systems, subjected to a. c. impedance analysis for conductivity measurements, thermogravimetric/ differential thermal analysis for thermal stability and XRD studies for structure elucidation of the material.

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The use of PVC with PEO is mainly attributed to the presence of lone pair electrons with chlorine atom which result in easy solvation of inorganic salts. There are various types of polymer blend electrolytes but those containing PVC as one of their component is one of the most important on basis of scientific as well as commercial point of view^[8-10]. In addition PVC is inexpensive and commercially available material.

EXPERIMENTAL

Sample preparation

Poly(vinyl chloride) (PVC, average mol. wt. 1.5×10^5) (Aldrich, USA) and poly(ethylene oxide) (PEO, average mol. wt. 1.5×10^5) (Aldrich, USA) dried at 100°C for 12 h were used in the present study. The plasticizer ethylene carbonate (EC), was used as such without any further purification. Special grade tetrahydrofuran (THF, E. Merck, Germany) was used as received.

PVC-PEO blend polymer electrolyte systems of various compositions were prepared by dissolving appropriate quantities of PVC, PEO, LiClO_4 salt in predistilled THF solvent. Polymer electrolyte films of various compositions were prepared by using solution cast technique. LiClO_4 was dried for 48h at 70°C temperature under vacuum. PVC and LiClO_4 were dissolved in THF solvent. EC plasticizer was incorporated in appropriate amount into the salt containing polymers solution. The resulting solutions of various compositions were magnetically stirred at room temperature for about 12 h to obtain homogeneous solutions and after stirring at room temperature these solutions were further stirred at 40°C for about 4 h. Then films of desired compositions and thickness ($150 \mu\text{m}$) were obtained by casting the films on polypropylene dishes. The solvent of the films were allowed to evaporate at room temperature. After evaporation at room temperature, the films were dried further at 30°C temperature in vacuum oven to ensure complete evaporation of solvent. All operations were performed in a glove box under argon atmosphere and all samples were stored inside desiccators to minimize chances of contamination.

Sample characterization

The prepared samples of polymer electrolyte sys-

tems were subjected to a. c. impedance measurements at various temperatures. The measurement of ionic conductivity was carried out by sandwiching the polymer electrolyte films between two polished stainless steel disk electrodes of diameter 8 mm which acted as blocking electrode for ions. The electrodes with sample were sealed in an air tight container. The polymer electrolyte samples were cut into pieces with diameter of about 15 mm. The study was carried out in the frequency range 1 mHz to 100 KHz. The temperature dependent conductivity of these samples was performed at 5°C intervals in the temperature range of $20-70^\circ\text{C}$.

Thermogravimetric analysis was carried out in order to evaluate the thermal stability of the films in terms of percentage weight loss. The films were subjected to thermogravimetric and differential thermal analysis (TG/DTA) using Perkin Elmer (pyres diamond) TG/DTA with a heating rate of $10^\circ\text{C}/\text{min}$ in argon atmosphere. The samples of various compositions were heated from 5°C to 250°C . The polymer electrolyte samples were subjected to phase analysis at room temperature using X-ray diffractometer (XRD) [Bruker (D-8 Advance)].

RESULTS AND DISCUSSION

Conductivity studies

Various polymer electrolytes have been subjected to ionic conductivity measurement at different temperatures in order to find out the influence of temperature on ionic conductivity of these electrolytes. Figure 1 presents the variation of logarithm of ionic conductivity with inverse absolute temperature for different PVC-PEO- LiClO_4 -EC complexed polymer electrolytes. The higher conductivity of plasticized systems may be due to its amorphous nature. From measurement of ionic conductivity values at different temperatures it can be found that ionic conductivity values increases with increase in temperature. The increase in ionic conductivity with temperature is in agreement with the theory^[11]. The increase in ionic conductivity with increase in temperature is due to the fact that at low temperature ionic mobility and segmental motions of polymer chains are restricted due to strong salt polymer association. While at higher temperature ionic conductivity increases due to decrease in salt polymer association and increased thermal seg-

mental motion of polymer chains in the electrolytes, having completely amorphous nature which leads to increase in the free volume thereby facilitating Li-ion conduction through the polymeric system^[12]. The enhancement in ionic conductivity with increase in temperature can also be linked with increase in chain flexibility due to decrease in viscosity^[13]. No abrupt changes have been observed, which indicates that all samples exhibit completely amorphous structure^[14]. It can also be observed from conductivity-temperature plots that all these samples follows Arrhenius rule. The variation of conductivity with temperature can be explained according to Arrhenius relation.

$$\sigma = \sigma_0 \exp(-E_a/KT)$$

where E_a , K and σ_0 represent activation energy, Boltzmann constant and pre exponential factor, respectively. The maximum ionic conductivity at 303 K (30 °C) is found to be $2.39 \times 10^{-6} \text{ S cm}^{-1}$ for PVC-PEO-LiClO₄-EC complex polymer electrolyte system.

The nature of cation transport in these systems seems to be very similar to that in ionic crystals, because temperature dependent conductivity data follows Arrhenius behavior. It seems that ion jump from one site into another site similar to that in ionic crystals^[15,16].

It is found that activation energy shows decrease with increase in the concentration of LiClO₄ salt in complexed blend polymer electrolyte films thereby increasing the ionic conductivity. The influence of incorporation of salt on the activation energy values may be due to the formation of charge transfer complexes in the polymer electrolyte system^[14]. These charge transfer complexes provide movable ions to the system which result in the improvement of conductivity of the sample.

TABLE 1 : Activation energies of PVC-PEO-LiClO₄-EC polymer electrolyte systems.

Polymer electrolyte	Activation energy (E_a)
PVC-PEO-LiClO ₄ -EC(40-30-05-25)	0.87eV
PVC-PEO-LiClO ₄ -EC(35-30-10-25)	0.73eV
PVC-PEO-LiClO ₄ -EC(30-30-15-25)	0.60eV
PVC-PEO-LiClO ₄ -EC(25-30-20-25)	0.45eV

Figure 2 shows the plots of the electrolyte behavior with salt concentration. Figure shows that conductivity values exhibit enhancement with addition of LiClO₄ salt. The trend of ionic conductivity variation is almost similar at various temperatures. It is found that the effect of

addition of salt is pronounced at lower concentration of salt which may be due to the build up of charge carriers which leads to the improvement in the ionic conductivity of the polymer electrolyte systems. The increase in conductivity by addition of LiClO₄ salt may be due to formation of charge carrier species thereby increase in the number of movable ions.

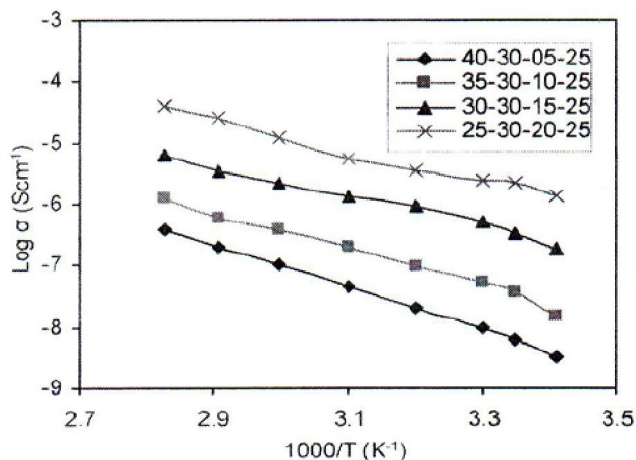


Figure 1 : Arrhenius plot of log of conductivity against reciprocal temperature for PVC-PEO-LiClO₄-EC polymer electrolytes.

Figure 3 exhibits conductance behavior with PVC content in the polymer electrolyte systems. The decrease in ionic conductivity at higher concentration of PVC may be due to lower mobility of ions^[17]. It is clear from the above discussion that polymer blend electrolytes containing PVC rich phase exhibits lower values of conductivity but higher mechanical strength. This behavior may be due to the reason that polymer blend electrolytes

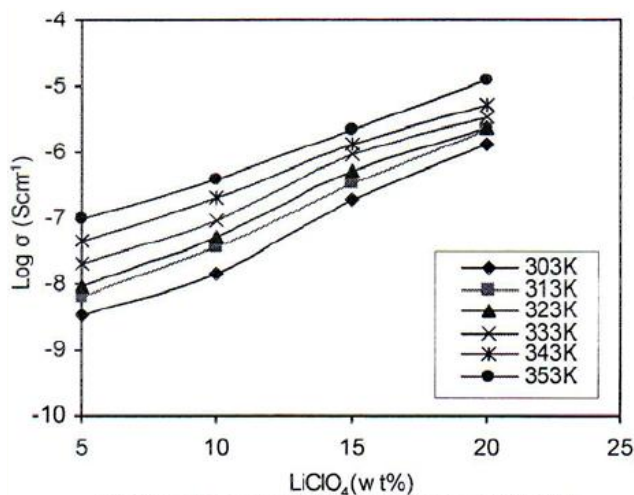


Figure 2 : Log conductivity vs. composition of PVC-PEO-LiClO₄-EC polymer electrolyte system at various temperature.

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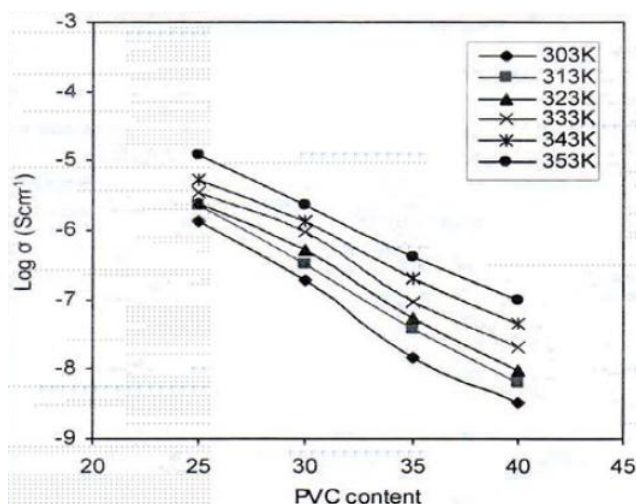


Figure 3 : Log conductivity vs. PVC content of PVC-PEO-LiClO₄-EC polymer electrolyte system.

containing PVC rich phase show solid like behavior which hindered mobility of charge carrier species thereby having lower conductivity.

TG/DTA analysis

Thermal stability is considered to be very essential property of polymer electrolyte systems to make it useful in lithium batteries in order to see their usefulness at various temperatures. TG/DTA analysis has been used to ascertain the thermal stability of polymer electrolyte systems containing lithium salt. Figures 4(a-d) show the influence of variation of LiClO₄ content on thermogravimetric and differential thermal analysis of PVC-PEO-LiClO₄-EC complexed polymer electrolyte system. Differential thermal analysis of all different samples of these polymer electrolyte systems shows broad endothermic peaks at low temperature. These peaks may be due to the evaporation of moisture present in polymer electrolyte systems due to absorption by impurities in polymer electrolytes or it would be absorbed during sample loading^[18,19]. Differential thermal analysis traces in Figures 4(a-d) shows a broad exo-

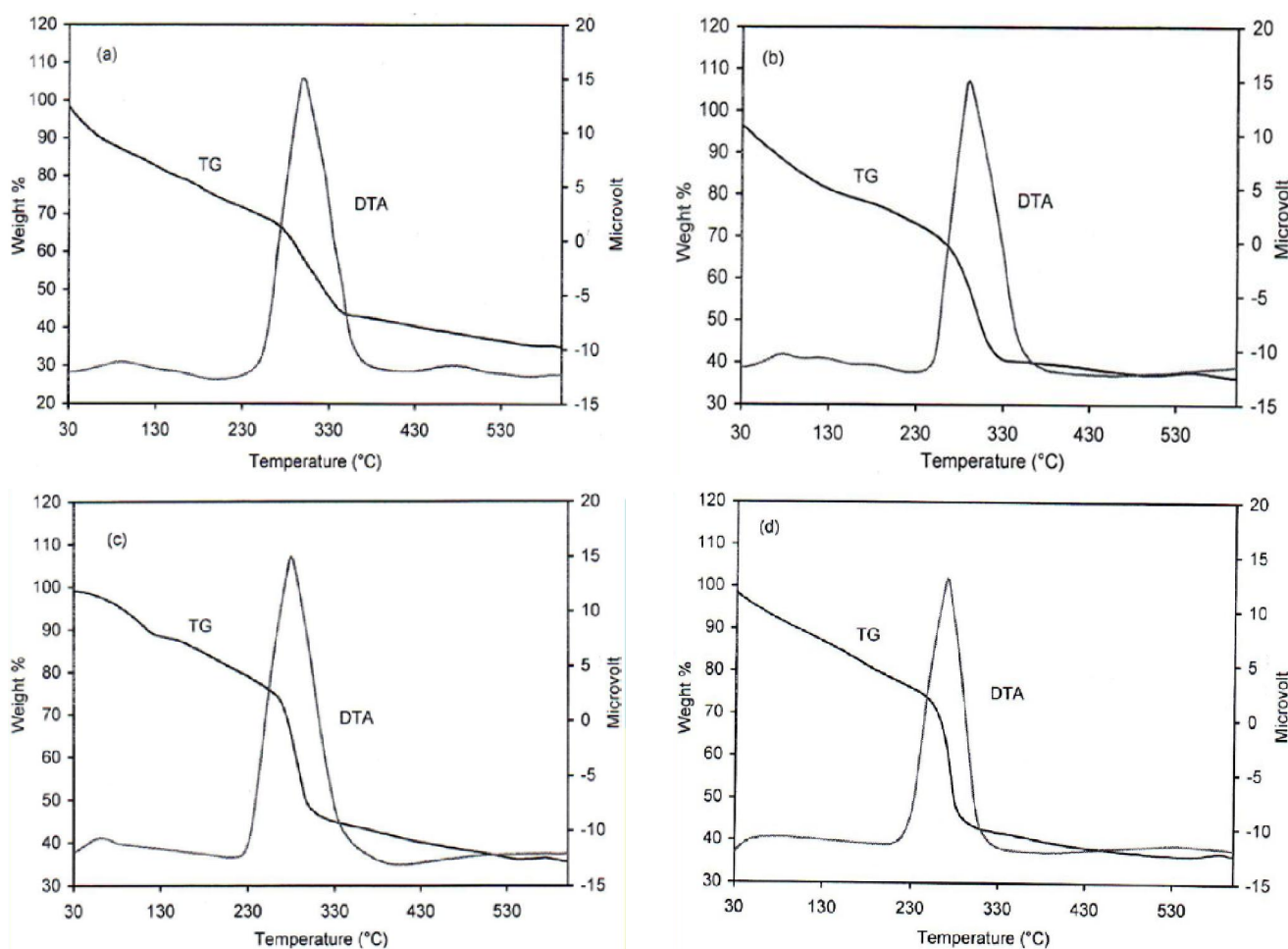


Figure 4 : TGA and DTA scans of polymer complexes; (a) PVC-PEO-LiClO₄-EC (40-30-05-25); (b) PVC-PEO-LiClO₄-EC (35-30-10-25); (c) PVC-PEO-LiClO₄-EC (30-30-15-25); (d) PVC-PEO-LiClO₄-EC (25-30-20-25).

thermic peak at 548, 543, 538 and 528 K for samples of polymer electrolytes containing 5, 10, 15 and 20% of LiClO_4 respectively. Thermogravimetric analysis traces in Figures 4(a-d) for these complexed polymer electrolyte systems exhibits a gradual weight loss up to 543, 540, 533 and 525 K respectively. While above these temperatures TGA traces show rapid weight loss for all different samples of PVC-PEO- LiClO_4 -EC polymer electrolyte system. This rapid weight loss is due to the degradation of the polymer electrolyte system^[20,21]. The irreversible thermal decomposition temperature shows decrease by addition of lithium salts which may be due to availability of Li ions in the polymer electrolyte films. The sharp variation in TG traces due to rapid weight loss is found consistent with the result of DTA.

Figures 4(a-d) reveal that with the increase in content of LiClO_4 salt in polymer electrolyte systems, degradation temperature decreases. The decrease in degradation temperature of these polymeric systems may be due to the decrease in thermal stability with the addition of LiClO_4 . It is found that these polymer electrolyte systems shows stability up to about 525 K temperature while above this temperature these polymer electrolyte samples shows thermal degradation.

It is also shown that samples containing 5% and 10% wt of LiClO_4 exhibits maximum thermal stability, which may be due to the presence of lower concentration of LiClO_4 . The temperature at which samples containing 5% and 10% LiClO_4 decomposes is 543 and 540 K respectively. Therefore it can be concluded that sample containing 5% of LiClO_4 is better as compared to the other samples from the thermal stability point of view.

XRD analysis

Figure 5 shows X-ray diffraction patterns of pure PVC, PEO, LiClO_4 and PVC-PEO- LiClO_4 -EC polymer blend electrolyte films. Figure 5(a-g) reveals that two distinct crystalline peaks appear in X-ray diffraction pattern which are for pure PEO^[22]. The intensities of these crystalline peaks of 2θ values, pertaining to PEO, reduces in complex polymer blend electrolyte films containing Li salt. Comparative studies of the XRD patterns of pure PVC, LiClO_4 salt and PVC-PEO- LiClO_4 -EC films reveals that peaks observed for 2θ values in pure PVC films are more intense as compared

to that in PVC-PEO- LiClO_4 -EC films. This shows that PVC-PEO- LiClO_4 -EC are less crystalline compared to that of LiClO_4 salt. The decrease in degree of crystallinity of PVC-PEO- LiClO_4 -EC polymer electrolytes is caused by complexation of LiClO_4 salt with PVC-PEO blend. The absence of crystalline peaks corresponding to LiClO_4 for 2θ values, in PVC-PEO complexed with LiClO_4 shows the absence of any uncomplexed LiClO_4 salt in the complexed polymeric electrolyte system. From all these, it may be confirmed that complexation of salt has taken place in the amorphous phase^[23]. Some peaks pertaining to salt and polymer disappear, while some have shifted in Figure 5(a-g) of complex polymer electrolyte system. The absence and shifting of peaks shows that interactions have taken place between the different constituents of sample films. It is clear that structural modification has occurred in the polymer electrolyte systems^[24]. The decrease in the intensities of sharp crystalline peaks at higher concentrations of Li salts manifests presence of amorphous phase in polymer electrolyte films which results in increased ionic conductivity values due to increased ionic mobility in amorphous phase.

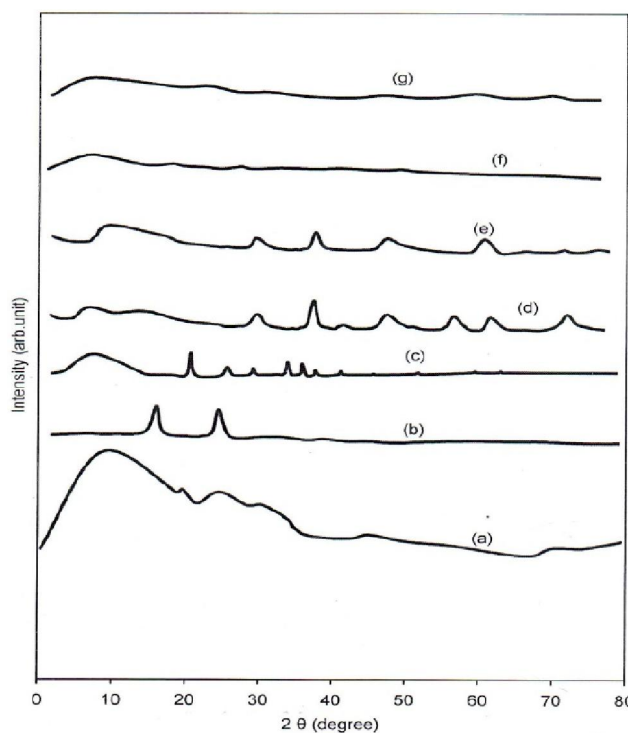


Figure 5 : XRD patterns of; (a) PVC; (b) PEO; (c) LiClO_4 ; (d) PVC-PEO- LiClO_4 -EC (40-30-05-25); (e) PVC-PEO- LiClO_4 -EC (35-30-10-25); (f) PVC-PEO- LiClO_4 -EC (30-30-15-25); (g) PVC-PEO- LiClO_4 -EC (25-30-15-25)

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CONCLUSIONS

Four different polymer electrolyte systems of PVC-PEO-LiClO₄-EC of various compositions have been prepared and subjected to ionic conductivities, thermal studies and XRD analysis. Among these four polymer electrolyte systems, PVC-PEO-LiClO₄-EC (25-30-20-25) is found to be the most suitable on basis of conductivity. The conductivity of the PVC-PEO-LiClO₄-EC (25-30-20-25) polymer electrolyte system is found to be $2.39 \times 10^{-6} \text{ S cm}^{-1}$ and the thermal stability up to 525 K. Therefore this system is found to be most suitable among all studies polyelectrolytes.

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