

INVESTIGATIONS ON EFFECT OF DOUBLE PLASTICIZERS IN PEMA-PVC BASED GEL POLYMER BLEND ELECTROLYTE

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Introduction

The importance of designing suitable polymer electrolyte for lithium-polymer batteries has been well demonstrated in the recent years^[1]. Among the polymer electrolytes that are currently experimented, poly (ethyl methacrylate) PEMA based electrolyte has a special significance in view of its well known chemistry and cheaper method of processing them as laminates. In order to get PEMA amenable, choice of blending with poly (vinyl chloride) PVC has been suggested recently^[2]. The use of plasticizer in the design of polymer electrolyte has a greater preference as compared to virgin poly blending process as its approach provides several vistas to evolve predetermined polymer electrolyte laminate for electrochemical application^[3]. To understand this approach we report here the influence of plasticizers like ethylene carbonate (EC) and propylene carbonate (PC) in the poly blend of PEMA/PVC along with Li salts like LiClO₄ for evolving new protocols in the use of plasticizer for polymer electrolyte development.

Experimental Procedure

Poly (vinyl chloride) (PVC) (Aldrich) and poly (ethyl methacrylate) (PEMA) (Aldrich) and LiClO₄ (Aldrich) were dried under vacuum at 100 °C for 10 h. The polymer electrolytes of various blend ratios were prepared by solution casting technique with THF as solvent.

The solution thus obtained was cast on a glass plate and THF was allowed to evaporate slowly in air at room temperature for 48 hours. This procedure provides mechanically stable, free standing and flexible films with thickness between 1 and 2 mm. The films are further dried for 5 hours in vacuum at 60 °C to remove any trace of THF. The polymer blends of (PVC: PEMA) blend ratio with constant salt concentration are prepared with different double plasticizers concentration. Ionic conductivities of polymer electrolytes were evaluated from the complex impedance plot in the temperature range (303-343 K) using Keithley 3330 LCZ meter in the frequency range 40 Hz-400 KHz. Also, the dielectric relaxation measurements have been under taken. X-ray diffractograms of the films were studied by Bruker (D8 Advance) diffractometer. FTIR study was made using a Perkin-Elmer (Paragon 500 grating) IR spectrophotometer in the range 400-4000 cm⁻¹. Thermal stability of the film was also characterized by TG/DTA at heating rate of 10°C per minute from the room temperature to 400°C.

Result and Discussion

X-ray diffraction analysis

The X-ray diffraction analysis is a useful tool to determine the structure and crystallization of the polymer matrices^[4]. In order to investigate the effect of

double plasticizer concentrations in the PVC-PEMA-LiClO₄ system. XRD analysis has been performed, and their respective diffraction patterns of PVC, PEMA, LiClO₄ and their complexes with different double plasticizer

concentrations are shown in Fig. 1. The XRD pattern of LiClO₄ shows intense peaks at an angle 2θ = 18.36°, 23.2°, 27.5°, 32.99° and 36.58°, which reveals crystalline nature of the ionic salt (JCPDS:030-0751).

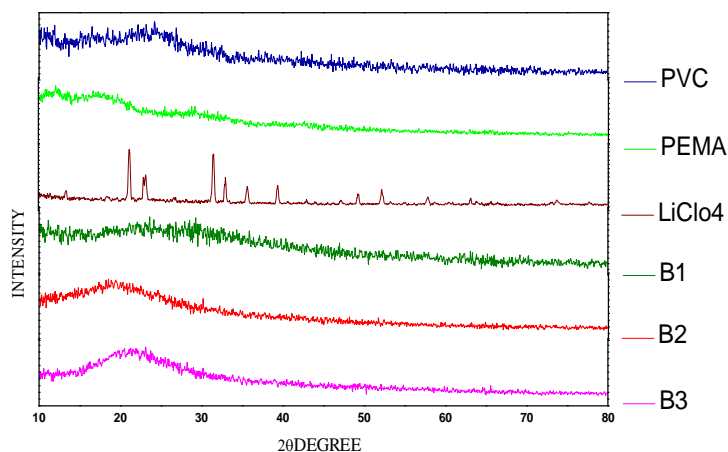


Fig. 1. XRD patterns of pure prepared electrolyte membranes

Fig. 1 shows one broad peak at an angle 2θ = 13°, which corresponds to PVC. Fig. 1 shows diffraction peak at 2θ = 18°, which is ascribed to PEMA. The diffractograms of PVC-PEMA blend with double plasticizer clearly indicate the fact that the semi crystalline nature of PVC structure is disturbed by the addition of plasticizers and salt. The increase in the amorphous nature causes a reduction in the energy barrier to the segmental motion of the polymer electrolyte. The XRD pattern shows that most of the peaks corresponding to pure LiClO₄ disappear in the blend polymer electrolytes, which reveals the complete resolution of the salts in the polymer matrix.

Conductivity Studies

The ionic conductivity of PVC/PEMA based gel polymer electrolytes containing double plasticizers (EC/PC) were

calculated from $\sigma = t/R_b A$, where 't' and 'A' represents the thickness and area of the film respectively. R_b is the bulk resistance of the gel electrolyte obtained from complex impedance measurement.

Figure 2 shows the room temperature complex impedance spectra of PVC (5) - PEMA (20) - LiClO₄ (8) wt % - PC/EC (67%) polymer electrolyte system. According to the theoretical analysis given by Watanabe and Ogata [5] 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^[6] 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.

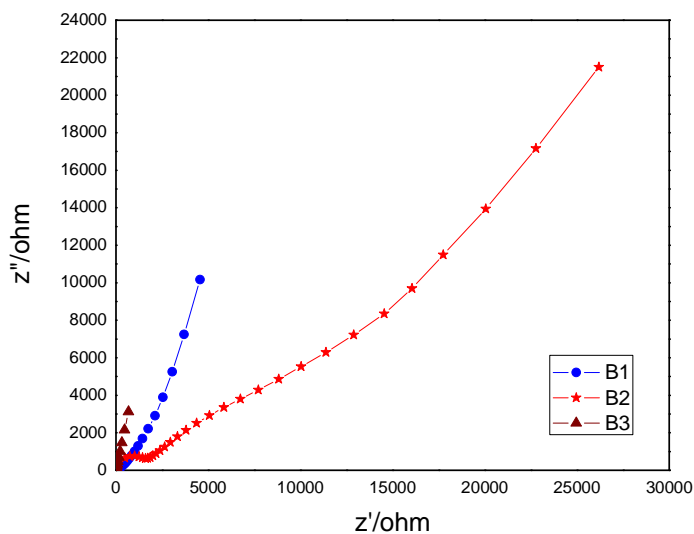


Fig. 2. Room temperature complex impedance plot of the prepared samples

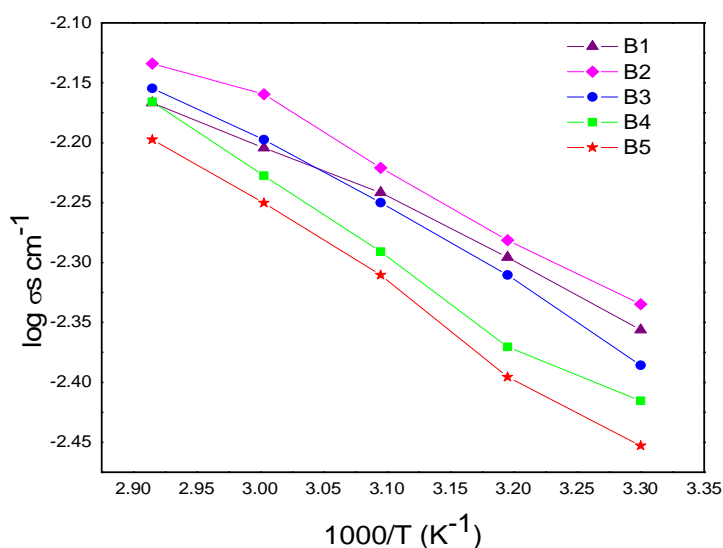


Fig. 3. Temperature dependent ionic conductivity plots of the prepared samples

Figure 3 shows the conductivity versus temperature inverse plots of PVC-PEMA-EC/PC-LiClO₄ based hybrid polymer electrolytes. 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^[7]. It supports the idea that the ions move through the plasticizer rich phase, which is the conductivity medium and involves the salt.

Table 1
Ionic conductivity values of PVC (5)/PEMA (20)/EC+PC (x)/LiClO₄ (8) wt. % of the total polymer weight

| Sample coding | PVC(5)PEMA(20) EC/PC (x) - LiClO ₄ (8) Wt.% | Ionic conductivity values (σ) $\times 10^{-3}$ Scm ⁻¹ at different temperatures (K) | | | | |
|---------------|--|--|-------|-------|-------|-------|
| | | 303 | 313 | 323 | 333 | 343 |
| B1 | 1 100/0 | 4.403 | 5.061 | 5.732 | 6.246 | 6.812 |
| B2 | 10 | 4.626 | 5.231 | 6.013 | 6.926 | 7.346 |
| B3 | 50/50 | 4.113 | 4.892 | 5.623 | 6.346 | 7.003 |
| B4 | 25/75 | 3.842 | 4.261 | 5.116 | 5.923 | 6.826 |
| B5 | 0/100 | 3.524 | 4.021 | 4.892 | 5.621 | 6.346 |

The conductivity data for hybrid polymer electrolytes containing double plasticizers are presented in Table 1. From the table we can see that the

LiClO₄ offers highest conductivity (4.626×10^{-3} S cm⁻¹) among the other gel electrolytes at 303K.

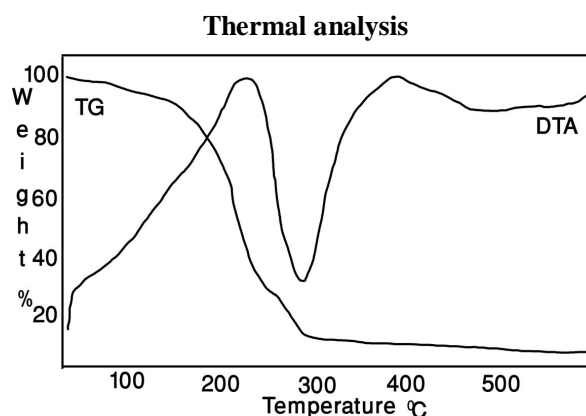


Fig. 4. TG/DTA analysis of PVC (5)-PEMA (20)-EC/PC (67)-LiClO₄ (8)

Figure 4 shows the TG/DTA traces of PVC (5)-PEMA (20)-EC/PC (67)-LiClO₄ (8) gel polymer electrolyte which shows maximum conductivity value. An endothermic peak was observed at 65°C and corresponding about 5% of weight loss is attributed to the presence of moisture in the samples. The film starts decomposing at 230°C followed by an endothermic peak, which indicates that the film is stable up to 230°C. The DTA

trace shows an endothermic peak around 288°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 LiClO₄ as salt can be operated up to 230°C.

Conclusion

PEMA based blend polymer electrolytes are prepared by solvent casting technique. The complex formation in

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PEMA-PVC-LiClO₄-EC-PC has been confirmed from XRD studies. Ionic and thermal conductivity of the polymer electrolytes were studied. The ionic conductivity of the systems at different temperatures was plotted by using the Arrhenius plot. Good thermal stability of the blend polymer electrolyte system up to 4.626×10⁻³ has been confirmed by TG/DTA analysis.

The ionic conductivity increases with increase in temperature and the highest ionic conductivity has been found to be 4.626×10⁻³ S cm⁻¹ at room temperature. This could be used as an electrolyte in lithium batteries and other electrochemical devices.

References

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