

Ionic conductivity and FT-IR studies on plasticized PVC/PMMA blend polymer electrolytes

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Received 22 December 1999; accepted 31 December 1999

Abstract

Ionic conductivities of plasticized poly(vinylchloride) (PVC)/poly(methylmethacrylate) (PMMA) blend electrolyte films containing two different lithium salts, viz., lithium tetrafluoroborate (LiBF_4) and lithium perchlorate (LiClO_4) are studied using the AC impedance technique at 25°C, 40°C, 50°C and 60°C. A mixture of ethylene carbonate (EC) and propylene carbonate (PC) is used as the plasticizer. Pure PMMA and PMMA-rich phases exhibited better conductivity. The variation of ionic conductivity for different plasticizer contents and for different lithium salts is reported. The variation in film morphology is examined by scanning electron microscopic examination. Finally, the existence of ion–ion pairs has been identified using Fourier Transform Infrared analysis (FT-IR) measurements. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Polymer blend; Plasticizer; Dielectric loss; FT-IR; Conductivity

1. Introduction

Notwithstanding the several desirable characteristics of polymer–salt complexes, such as viscoelasticity, flexibility, electrochemical stability and conductivity, the applicability of the complexes to electrochemical power sources still poses a formidable challenge to battery scientists [1–4]. Lithium-ion conductive polymer electrolytes, in addition to possessing characteristics such as ambient temperature conductivities reminiscent of their aprotic organic solvent-based counterparts, must exhibit sufficient dimensional stability so as to function as separators. Classical polymer electrolytes derived from single, long chain, ‘dry’ polymers such as polyethylene oxide (PEO) are solids at room temperature with conductivities of the order of 10^{-8} S cm^{-1} , or at best are glutinous ones with a propensity to flow under mild stress [5]. Several new approaches have been adopted to enhance the dimensional stability and the conductivity of polymer electrolytes. They include incor-

poration of inert fillers such as $\gamma\text{-LiAlO}_2$ in the polymer film [6,7], the blending of a relatively fluid polymer, which facilitates ionic movement with a rigid one that can provide mechanical strength [5,8], and the use of a low volatile liquid of high dielectric constant as a plasticizer in the polymer host [5,9–11]. Plasticized electrolytes, sometimes called gelionic or ‘wet’ two-phase solid electrolytes, combine the advantageous mechanical properties of the polymer and the electrochemical properties of the liquid organic electrolyte [12–15]. Gelionic electrolytes based on poly(methyl methacrylate) (PMMA) [16–19] have been proposed for lithium battery application particularly because of their beneficial effects on the stabilization of the lithium–electrolyte interface [20]. The reasonable conductivity of such plasticized films is offset, however, by their poor mechanical properties at high concentrations of plasticizers such as ethylene carbonate (EC) and propylene carbonate (PC). The problem of poor mechanical strength can be circumvented by blending PMMA with a polymer such as poly(vinyl chloride) (PVC) which, because of its poor solubility in the plasticizer medium, manifests itself in a phase-separated morphology to provide a rather rigid framework in the polymer electrolyte film [21]. This paper presents the results of a study on plasticized PVC/PMMA

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Table 1
Composition of polymer, plasticizer and lithium salt

Sample	Weight of polymer (g)		Weight of plasticizer (g)		Weight of salt (g) X = LiClO ₄ , LiBF ₄
	PVC	PMMA	EC	PC	
S1	28	12	33.6	22.4	4
S2	23.3	10	37	25.0	4.7
S3	20	8.6	40	26.6	4.8
S4	17.5	7.5	42	28	5
S5	15.6	6.7	43.5	29	5.2
S6	0	25	42	28	5
S7	7.5	17.5	42	28	5
S8	12.5	12.5	42	28	5
S9	17.5	0	42	28	5

blends, which contain lithium tetrafluoroborate (LiBF₄) and lithium perchlorate (LiClO₄) as electrolyte salts.

2. Experimental

PVC and PMMA (Aldrich, USA) with an average molecular weight of 1.0×10^5 were used in this study. The plasticizers EC and PC (both from E. Merck, Germany) were used as supplied. LiClO₄ (ACS Reagent, Aldrich) and LiBF₄ (98%, Aldrich) were dried at 110°C and stored under vacuum for 48 h before use. Polymer electrolytes were prepared by dissolving appropriate amounts of the corresponding constituents in anhydrous tetrahydrofuran (THF) (E. Merck, India) and casting them as films using a doctor blade method. The cast films were allowed to stand in air at room temperature to allow slow evaporation of THF. Any remaining THF was removed by further drying of the films in an air oven at $50 \pm 1^\circ\text{C}$ for 8 h. The compositions of the films are given in Table 1.

Conductivity measurements were performed by sandwiching the cast films between two stainless-steel electrodes (ASTM 304) of diameter 1 cm and using an electrochemical analyzer EIS Model 6310A (EG&G Princeton

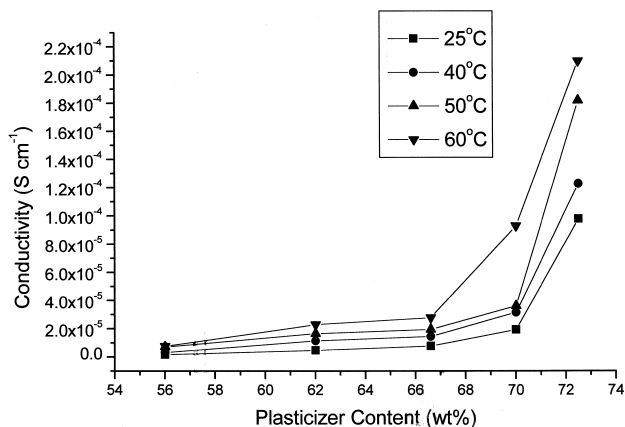


Fig. 1. Ionic conductivity as a function of plasticizer content for fixed PVC/PMMA blend ratio with lithium salt LiBF₄.

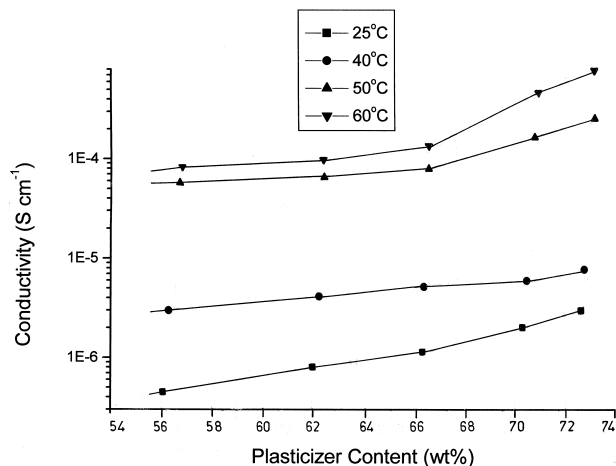


Fig. 2. Ionic conductivity as a function of plasticizer content for fixed PVC/PMMA blend ratio with lithium salt LiClO₄.

Applied Research, USA) over a frequency range of 10 Hz–100 kHz at 25°C, 40°C, 50°C and 60°C. The cast films were also subjected to Fourier Transform Infrared analysis (FT-IR) with a Perkin Elmer STA 5000, (USA) instrument. The morphology of the films was examined with a scanning electron microscope (Stereoscan 440, Leuca Cambridge, UK). In order to avoid complications due to evaporating solvent molecules during SEM imaging, the plasticizers were removed by freeze-drying without effecting any change in film morphology.

3. Results and discussion

3.1. Conductivity studies

Variations of ionic conductivity as a function of plasticizer content with LiBF₄ and LiClO₄ are shown in Figs. 1 and 2, respectively, at four different temperatures. The PVC/PMMA blend ratio of these samples was fixed at 7/3. It is evident from both sets of data that the ionic conductivity increases with increasing plasticizer content

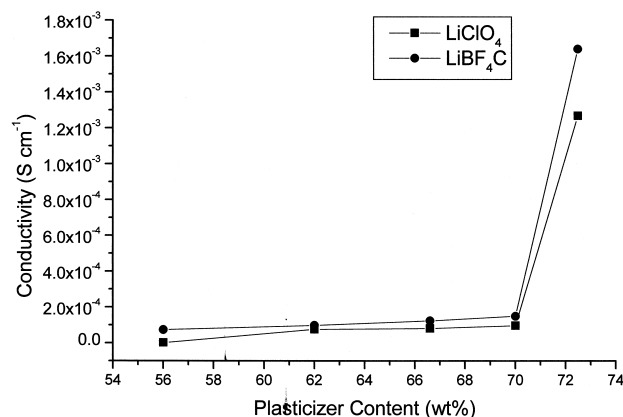


Fig. 3. Plot of ionic conductivity vs. plasticizer content for films containing 5 g of LiBF₄.

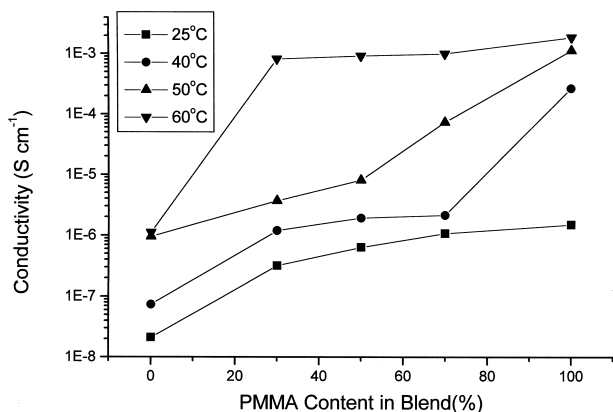


Fig. 4. Dependence of ionic conductivity on PVC/PMMA blend composition at different temperatures. Salt: LiBF_4 ; plasticizer content: 70%.

and also with increase in temperature. This can be explained in terms of two factors, namely: (i) an increase in the degree of interconnection between the plasticizer-rich phases due to an increase in the volume fraction of these phases; and (ii) increase in the free volume of the plasticizer-rich phase due to an increase in the relative amount of the plasticizer compared with that of PMMA.

The change in ionic conductivity with plasticizer content for two different lithium salts, LiClO_4 and LiBF_4 , at 50°C is compared in Fig. 3. A similar trend is found at other temperatures. The PVC/PMMA blend electrolytes containing LiBF_4 display slightly higher conductivity than the films containing LiClO_4 . In studies of PEO polymers, it has been demonstrated [25] that PEO containing LiBF_4 has a higher conductivity than PEO containing LiClO_4 . This may be attributed to the higher dissociation and the higher electronegativity of the fluoro-type lithium salt compared with the chloro-type lithium salt.

Conductivity data at different temperatures for various PMMA blend contents and with LiBF_4 and LiClO_4 are given in Figs. 4 and 5, respectively. The conductivity at any particular temperature increases with increasing PMMA content in the films. Films containing little or no PMMA have the lowest conductivities. On the other hand,

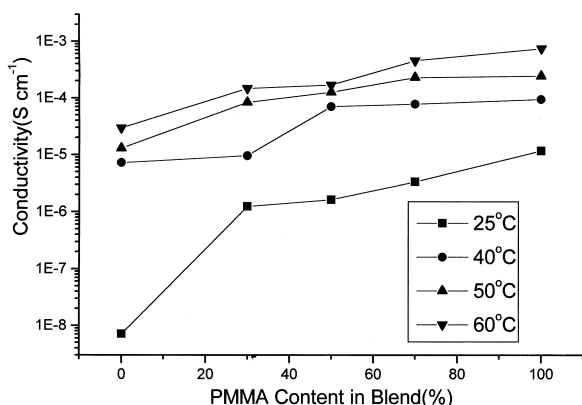


Fig. 5. Dependence of ionic conductivity on PVC/PMMA blend composition at different temperatures. Salt: LiClO_4 ; plasticizer content: 70%.

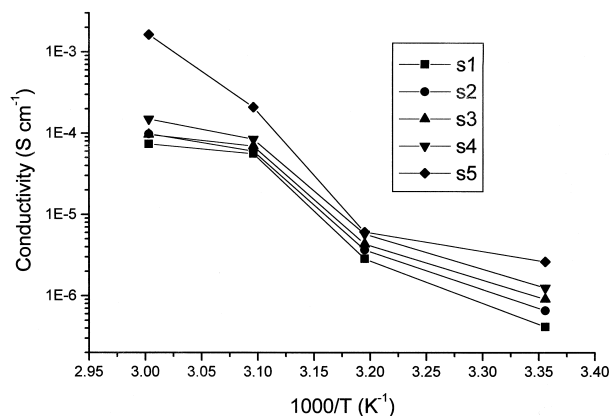


Fig. 6. Arrhenius plots for the conductivity of PVC/PMMA films containing different LiBF_4 contents. Plasticizer content: 70%.

100% PMMA films have high conductivity but no mechanical stability and no freestanding films could be obtained [21,22,24]. Films with the intermediate blend ratios 50:50 and 70:30 possess good mechanical properties with reasonable conductivity. Thus, to obtain a good freestanding film, it is necessary to add PVC. From the conductivity data, the best blend ratio of PMMA/PVC is 70:30. In electrolyte films containing PVC/PMMA, the PVC-rich phase clearly acts as a mechanical support.

Arrhenius plots of the conductivity of PVC/PMMA films (ratio 7/3) for various concentrations of LiBF_4 and LiClO_4 are presented in Figs. 6 and 7, respectively. Arrhenius plots for the conductivity of PVC/PMMA films with different plasticizer contents are shown in Fig. 8 (LiBF_4 salt) and Fig. 9 (LiClO_4 salt). The ionic conductivity follows the Arrhenius equation more or less in LiBF_4 , whereas in LiClO_4 there is a deviation. In the latter case, the conductivity may obey the Vogel–Tamman–Fulcher (VTF) equation, which describes transport properties in a viscous medium. It should be noted that the Arrhenius relation holds well at low plasticizer contents and at high temperatures, while the VTF relation is obeyed at higher plasticizer levels and low temperatures. At high levels of

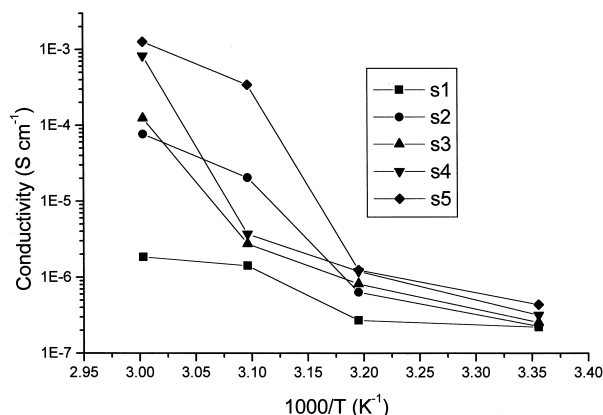


Fig. 7. Arrhenius plots for conductivity of PVC/PMMA films containing different LiClO_4 contents. Plasticizer content: 70%.

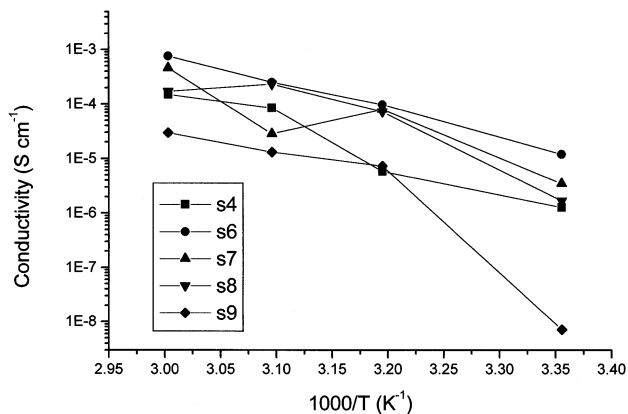


Fig. 8. Arrhenius plots for conductivity of 70/30 PVC/PMMA films with different plasticizer contents. Salt: LiBF_4 .

plasticizer, transport of ions may be expected to take place along the plasticizer-rich phase.

From these results, it is suggested that in electrolyte films containing both PVC and PMMA, the PVC-rich phase acts as a mechanical support and the plasticizer-rich phase acts as a tunnel for ionic transport. Since the PVC-rich phase is a solid-like medium, it is difficult for ions to penetrate this phase [26]. The transport of ions must occur via indirect motion along a convoluted path restricted to the plasticizer-phase, which is responsible for low conductivity at a high PVC content. A homogeneous conducting medium exists in the S6 film, which results in the direct drift of the ion. This is the reason for the relatively high ionic conductivity [22,24]. The same trend is also observed for films containing LiCO_4 (Fig. 7).

In order to prove the above phenomenon, a study was made of the dielectric loss relaxation of the blended systems. Dielectric loss (ϵ'') is the direct measure of the energy dissipated and is generally composed of contributions from ionic transport and from polarization of a charge or a dipole. The accumulation of ions at the interface between the PVC-rich phase and the plasticizer-rich

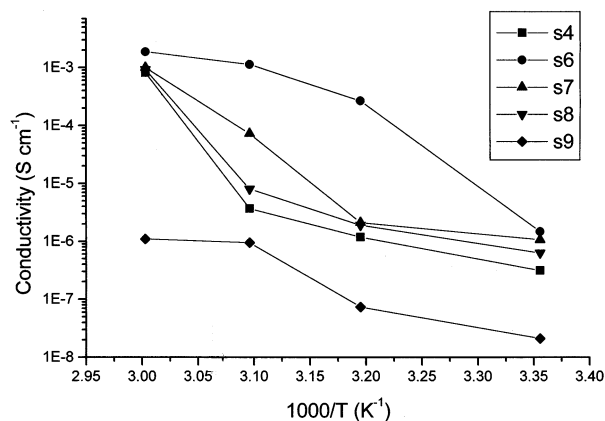


Fig. 9. Arrhenius plots for conductivity of 70/30 PVC/PMMA films with different plasticizer contents. Salt: LiClO_4 .

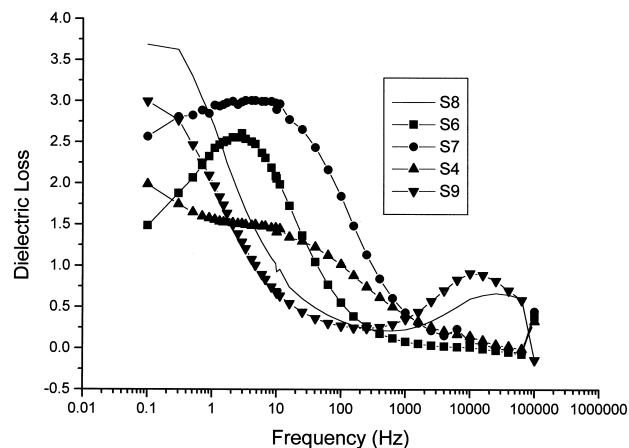


Fig. 10. Dielectric loss spectra of PVC/PMMA films with varying PMMA content (salt LiBF_4).

phase can be regarded as polarization of a macro dipole, i.e., the accumulated ionic charges, which generate a polarization peak in the dielectric loss spectra. The dielectric loss spectra for different PVC/PMMA blend ratios with fixed plasticizer content for the salt LiBF_4 are shown in Fig. 10. The plasticizer content was 70%. The polarization peaks in the high-frequency region above 10^5 Hz are more prominent for a high PVC content (S9), which is strong evidence for the prevention of the transport of ions at the interface between the PVC-rich phase and the plasticizer-rich phase. The polarization peak occurs when the stress induced by the electric field cannot be dissipated by the ionic transport at the interface. For the samples containing no PVC (S6), no polarization peak in the high-frequency region is observed. A similar trend is observed for samples containing LiClO_4 (Fig. 11).

3.2. SEM analysis

It has been suggested that [21] morphological effects are responsible for increases in conductivity. Electron micrographs of a film containing PVC only are given in

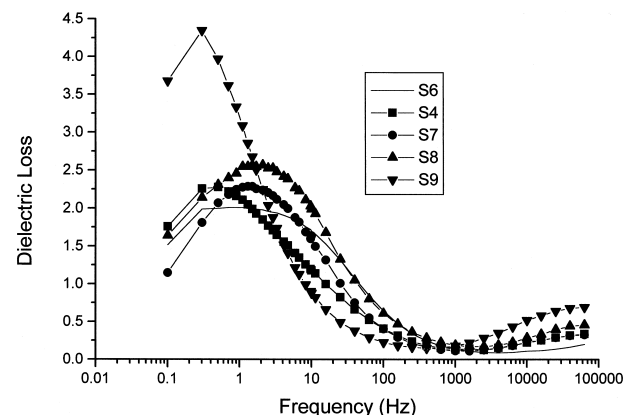


Fig. 11. Dielectric loss spectra of PVC/PMMA films with varying PMMA content (salt LiClO_4).

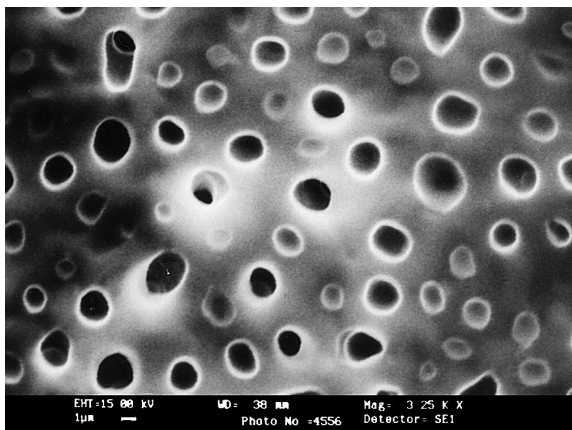


Fig. 12. Electron micrograph of PVC film cast from solution of PVC in THF.

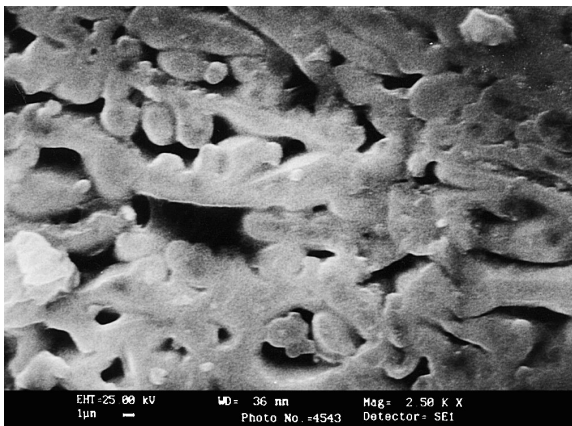


Fig. 13. Electron micrograph of PVC film soaked in PC.

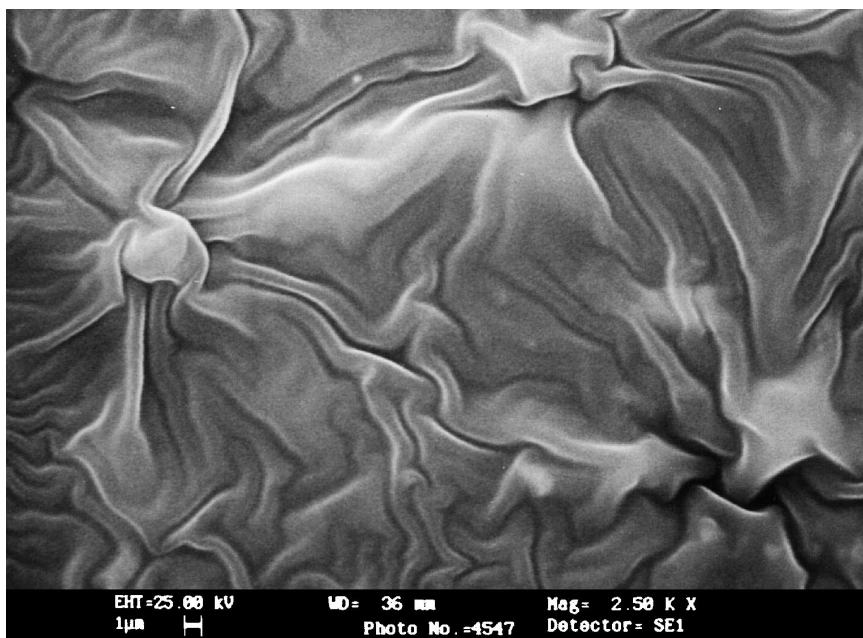


Fig. 14. Electron micrograph of a plasticized film of PVC/PMMA.

Fig. 12. The several craters, which have formed on the surface, are due to the rapid evaporation of THF used in the preparation of the film. When the above film is immersed in PC for 48 h and subsequently freeze-dried, it appears to become swollen and become segregated (Fig. 13). In other words, the addition of the plasticizer in which PVC is rather insoluble, tends to generate a more compact and phase-separated matrix of PVC. The wrinkled 'cloth-like' morphology of a blend of PVC and PMMA plasticized with EC/PC is shown in Fig. 14. The dual compatibility of PMMA towards both PVC and the plasticizer tends to lessen the driving force for separation of the PVC phase and leads to better development of the film. Finally, Fig. 15 presents an electron micrograph of the above film with added LiBF_4 .

The morphology of the polymer PVC/PMMA blend electrolytes prepared by the casting technique is affected by the immiscibility of the plasticizer with PVC. THF evaporates slowly after casting and subsequent drying. When it is concentrating during this process, due to the immiscibility of PVC, phase separation takes place and due to its segregation, a PVC-rich phase is formed. Thus, the resulting film has two distinct phases, viz., a PVC-rich phase and a plasticizer-rich phase. As discussed earlier, films containing both PMMA and PVC have craters or large pores, and in PMMA-rich compositions, the phase separation is less and more homogeneous solutions tend to form and because of this, the conductivity is also increased in blends containing more than 50 wt.% of PMMA.

3.3. FT-IR studies

FT-IR spectra of plasticized PMMA– LiBF_4 , PVC– LiBF_4 and PMMA–PVC– LiBF_4 films are presented in

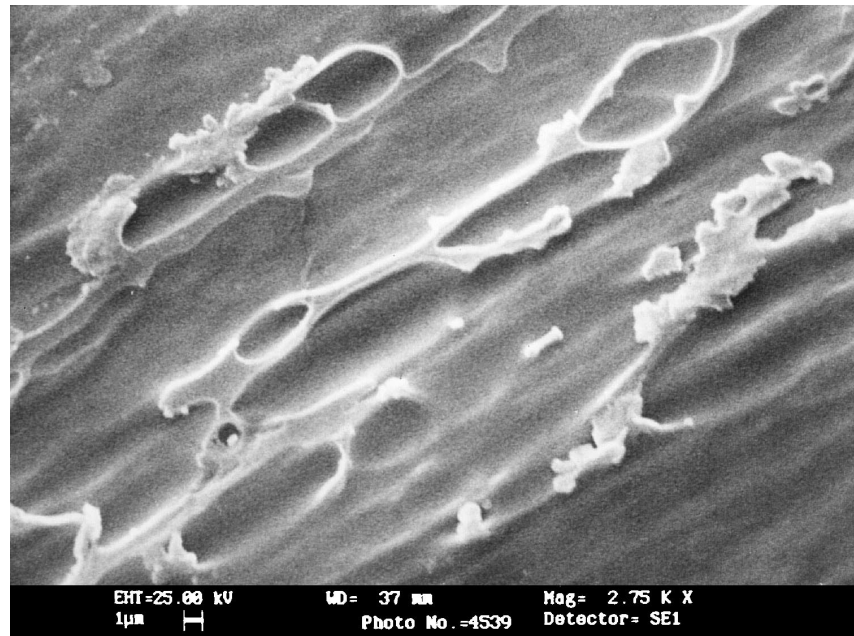


Fig. 15. Electron micrograph of plasticized film of PVC/PMMA containing LiBF_4 .

Fig. 16a to c, respectively. These data were analysed only from the angle of symmetric ring deformation region of PC; the C–O stretching and CH_2 rocking region of PC; and the C=O stretching region of PC when it acts as plasticizer containing LiBF_4 salt [21–28]. Fig. 17 displays the symmetric ring deformation region of PC. The band at 712 cm^{-1} in PC alone (Fig. 17c) is shifted in PVC +

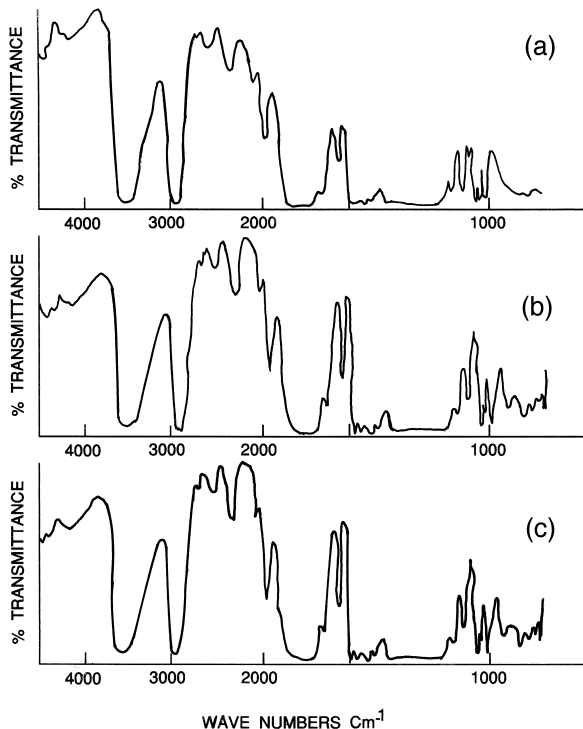


Fig. 16. FT-IR spectra of plasticized films: (a) PMMA + LiBF_4 ; (b) PVC + LiBF_4 ; (c) PMMA + PVC + LiBF_4 .

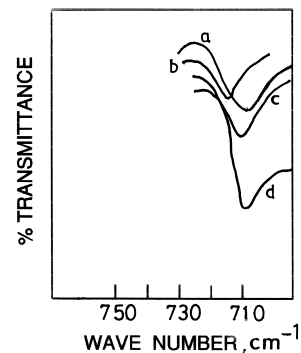


Fig. 17. Changes to symmetric ring deformation band of PC: (a) PMMA + PVC; (b) PVC + PMMA + PC/EC + LiBF_4 ; (c) PC alone; (d) PMMA + PVC + PC/EC.

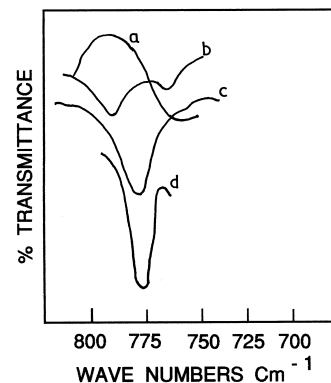


Fig. 18. Spectral bands of another ring deformation of PC: (a) PMMA + PVC; (b) PVC + PMMA + PC/EC + LiBF_4 ; (c) PC alone; (d) PMMA + PVC + PC/EC.

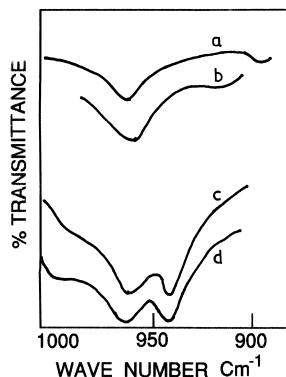


Fig. 19. Changes to the C–O stretching and CH₂ rocking regions of PC: (a) PMMA+PVC; (b) PVC+PMMA+PC/EC+LiBF₄; (c) PC alone; (d) PMMA+PVC+PC/EC.

PMMA polymer containing LiBF₄ (5 g) with EC/PC as plasticizer (Fig. 17d, 705 cm⁻¹) and also in PVC/PMMA (1:2.25 ratio) with EC/PC as plasticizer (Fig. 11b, 705 cm⁻¹). These shifts may be due to the addition of lithium tetrafluoroborate and this is consistent with earlier observations [29–32].

The spectral region of another ring deformation for PC, which occurs at the band 777cm⁻¹ is shown in Fig. 18c. This band is shifted towards 750 cm⁻¹ (Fig. 18b) in the polymer PVC + PMMA in the presence of EC/PC as plasticizer and LiBF₄ as salt. A slight shift occurs at 775 cm⁻¹ (Fig. 18b) in the case of polymer blend PVC/PMMA (1:2.25) with LiBF₄, when the ratio for PVC/PMMA is equal (1:1) with the same plasticizer and LiBF₄ the band occurs nearer to 765 cm⁻¹. This may be due to ionic association through redistribution of charge accompanying the formation of ionic pairs and aggregation [22].

The spectra in the C=O stretching and CH₂ rocking regions of PC alone (bands at 945 and 956 cm⁻¹; Fig. 19c) display the same stretching behaviour in the polymer PVC alone containing LiBF₄ salt (band at 956 cm⁻¹). In the case of polymer blend containing PVC/PMMA (1:2.25), the two bands narrow down at 965 cm⁻¹ (Fig. 19b), whereas in the PVC:PMMA (1:1) the two bands merged at 968 cm⁻¹ (Fig. 19a).

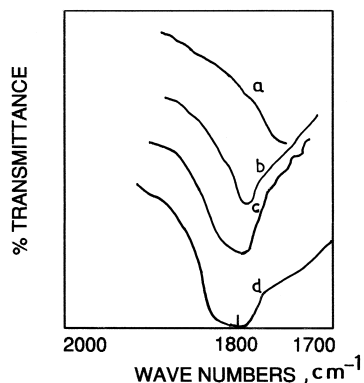


Fig. 20. C=O stretching region of PC: (a) PMMA+PVC; (b) PVC+PMMA+PC/EC+LiBF₄; (c) PC alone; (d) PMMA+PVC+PC/EC.

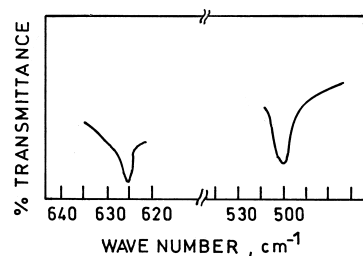


Fig. 21. FT-IR regions for BF₄⁻ (510 cm⁻¹) and ClO₄⁻ (624 cm⁻¹).

The spectra in the C=O stretching region of PC alone is broadened at 1800 cm⁻¹ (Fig. 20c). For the polymer containing PVC with PC/EC as plasticizer and LiBF₄ as salt, a narrow peak is observed at 1800 cm⁻¹ (Fig. 20b). For polymer blend PVC/PMMA (1:2.25) with EC/PC as plasticizer, a slightly broader peak occurs at 1800 cm⁻¹ (Fig. 20d). By contrast, there is no peak in PVC + PMMA (Fig. 20a). These observations show that the broad peak becomes narrower on the addition of lithium salt, a finding that is consistent with that of other studies [33–35].

The FT-IR spectra of the individual salts, viz., LiClO₄ and LiBF₄, are given in Fig. 21. The band at 625 cm⁻¹ corresponds to ClO₄⁻ and that of 440 cm⁻¹ corresponds to BF₄⁻. A broad band of medium intensity appears at 510 cm⁻¹ and can be attributed to the γ₂ mode of BF₄⁻, which has become infrared active. The band at > 500 cm⁻¹ is due to ClO₄⁻. Similar trends have been reported for a plasticized PVC/PMMA system with LiClO₄ [22].

4. Conclusions

The ionic conductivity behaviour of plasticized PVC/PMMA blends containing LiBF₄ and LiClO₄ as electrolyte salts has been studied. The conductivity of the films increases with increasing salt concentration. Although PMMA-rich phases give the highest conductivities, no freestanding films can be cast from them. On the other hand, PVC-rich phases give the lowest conductivities but provide mechanical stability to the films. At intermediate blend ratios (PVC/PMMA: 50/50 and 30/70), films with good mechanical properties and good conductivities can be obtained. Studies of electrochemical stability and compatibility with lithium metal electrodes are in progress.

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