

A study on polymer blend electrolyte based on PVC/PMMA with lithium salt

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Abstract

The new plasticised polymer electrolyte comprising the blend of poly-vinyl chloride (PVC) and poly-methylmethacrylate (PMMA) as host polymer is preferable to classical polymer for improving the ionic conductivity in the lithium rechargeable batteries. The nature of plasticizer and lithium salts have been found to influence the ionic conduction of the polymer-blended electrolytes. AC impedance analysis revealed the choice available in imparting ionic conductivity while differential thermogravimetry (DTG) and FTIR analysis have facilitated the effect of molecular interaction on host polymer matrix. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Polymer blend; Ionic conductivity; AC impedance

1. 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-methylmethacrylate (PMMA) 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 PMMA 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 polyblending process as its approach provides several vistas to evolve predetermined polymer electrolyte laminate for electrochemical application. To understand this approach we report here the influence of plasticizers like ethylene carbonate (EC), propylene carbonate (PC) and diethylphthalate (DEP) in the poly blend of PMMA/PVC along with Li salts like LiClO₄ and LiBF₄ for evolving new protocols

in the use of plasticizer for polymer electrolyte development.

2. Experimental

Commercially available PVC (ave. mol. wt. = 150,000) and custom made PMMA were blended as indicated in Table 1. Composition of the plasticizers EC, PC and DEP used are also given in Table 1. The films were cast using a doctor blade method. The cast films were subjected to XRD analysis (Jeol JDX 8030), thermal analysis (STA 1500 simultaneous thermal analysis system of Polymer Laboratories, UK), FTIR (Perkin Elmer FTIR Spectrometer PARAGON 500, UK) and EIS (EG&G Instruments, Model 6310, USA).

3. Results and discussion

Fig. 1a and b show the XRD data for the polymer blend PVC/PMMA with EC/PC and DEP as plasticizers containing LiClO₄ as salt. It is evident from Fig. 1b that crystalline nature is predominant in the case of DEP as plasticizer wherein amorphous nature is predominant in

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Table 1
Composition of plasticizer and salt

Weight of polymer (g)		Weight of plasticizer (g)		Weight of salt,	Weight of	Total weight	
PVC	PMMA	EC	PC	LiClO ₄ (g)	DEP (g)	with EC/PC	with DEP
28.0	12.0	33.6	22.4	4.0	0.223	100	44.223
23.3	10.0	37.0	25.0	4.7	0.447	100	37.447
20.0	8.60	40.0	26.6	4.8	0.670	100	34.07
17.5	7.50	42.0	28.0	5.0	0.894	100	30.07
15.6	6.70	43.5	29.0	5.2	1.118	100	28.618
0	25.0	42.0	28.0	5.0	0.894	100	30.894
7.50	17.5	42.0	28.0	5.0	0.894	100	25.694
12.5	12.5	42.0	28.0	5.0	0.894	100	30.894
25.0	0	42.0	28.0	5.0	0.894	100	30.894

EC/PC as plasticizer (Fig. 1a). Similar behaviour is observed in the case of polymer blend (PVC/PMMA) with EC/PC as plasticizer with LiBF₄ as salt (figure not given).

From the impedance measurements for the various compositions of plasticizer and salt, the variation of conductivity (25°C) using EIS (EG&G Instruments Model 6310, USA) with plasticizer content for EC/PC, with PMMA/PVC blend ratio, with plasticizer content for DEP is given in Tables 2–4, respectively. The conductivity exhibits an increasing trend when PMMA content is increased. Even though the film containing 100% PMMA and 0% PVC exhibits highest conductivity, free standing film was found to be difficult as it had poor mechanical property [3]. The films with the intermediate blend ratios 50:50 and 70:30 also showed good mechanical property with reasonable conductivity. This indicates that PVC is necessary to have a good free standing film and as per the conductivity data the blend ratio of PMMA/PVC 70:30 has been found to

be better. However, in the case of DEP as plasticizer the conductivity is poor as compared to ethylene carbonate and propylene carbonate. This trend is evident from the X-ray studies as indicated in Fig. 1a and b, wherein amorphous nature of the film formed with EC and PC as plasticizers reflects better conductivity compared with crystalline nature of the film formed with DEP as plasticizer [4].

In the electrolyte films containing both PVC and PMMA the PVC rich phase acts as a mechanical support and the plasticizer rich phase interconnected with each other acts as a tunnel for ionic transport. In the case of DEP, concentration of plasticizer could not be increased beyond the maximum level used since free standing mechanical stability film formation was found to be difficult. Moreover, tunnel for ionic transport as in the case of other plasticizer may be absent in DEP which accounts for the poor conductivity in this system. This demonstrates the influence of molecular interactions between plasticizer and the ion in deciding the conductivity level required for the chosen polymer electrolyte [5].

Fig. 2 shows the impedance data (Nyquist plot) for PVC/PMMA blend with EC/PC as plasticizer and LiBF₄ as salt. In Fig. 3 magnified view of the high frequency region of Fig. 2 is highlighted. The impedance of the polymer film was taken by placing the film in between two stainless steel electrodes and an AC voltage is applied to the cell and the frequency is varied. The equivalent circuit

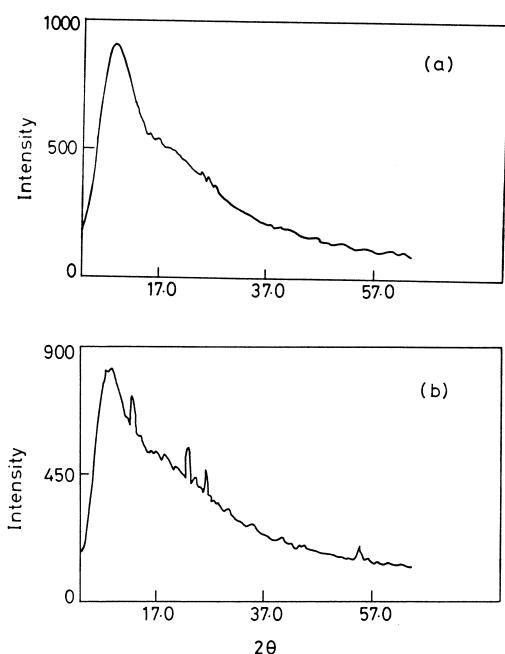


Fig. 1. XRD pattern for PVC/PMMA with EC/PC. (b) XRD pattern for PVC/PMMA with DEP as plasticizer.

Table 2
The variation of conductivity with plasticizer content at 25°C

Amount of salt (g)	Plasticizer ^a content for EC/PC (%)	Conductivity (S cm ⁻¹ × 10 ⁻⁶)
4.0	140	0.221
4.7	186	0.227
4.8	233	0.254
5.0	279	0.318
5.2	326	0.636

^a(Weight of plasticizer/Weight of polymer) × 100.

Table 3
Variation of conductivity with PMMA/PVC blend ratio at 25°C

Amount of Salt (g)	Blend ratio for		Conductivity (S cm ⁻¹ × 10 ⁻⁶)
	PMMA (%)	PVC (%)	
5.0	0	100	0.212
5.0	30	70	0.318
5.0	50	50	0.636
5.0	70	30	0.769
5.0	100	0	1.5

representing the AC response of the cell is given in Scheme 1. The electrodes become alternatively positively and negatively charged and the alternating field across the electrolyte caused the lithium ions to migrate back and forth in-phase with the voltage. The migration of lithium ions is represented by the resistor R_b . At the same time, the immobile polymer chains become polarized in the alternating field just as they would if the polymer films were devoid of mobile charges. This dielectric polarization may be represented by a capacitor C_b .

Now as the lithium ions move in the alternating field they are alternatively accumulated and depleted at each electrode. On each half-cycle ionic charge builds up with in the electrolyte near the electrodes, these charges being balanced by equal and opposite electronic charges on the electrodes themselves. Each electrode is somewhat similar to a parallel plate capacitor and may be represented by such a capacitance C_e .

The bulk polarization and ionic migration are physically in parallel. Therefore their representative components, R_b and C_b , are connected in parallel. Both are in series with the electrode capacitance, C_e and thus the electrode impedance with the blocking electrodes in the present case has been as depicted in the Scheme 1. The total impedance may be represented as

$$Z_{\text{total}}^x = R_b \left[\frac{1}{1 + (\omega R_b C_b)^2} \right] - jR_b \left[\frac{\omega R_b C_b}{1 + (\omega R_b C_b)^2} \right] + \frac{1}{\omega C_e} \quad (1)$$

At high frequencies when the impedance of the bulk resistances and capacitances are of the same magnitude

Table 4
Variation of conductivity with plasticizer (DEP) content at 25°C

Salt content (g)	DEP (g)	Conductivity (S cm ⁻¹ × 10 ⁻⁸)
4.0	0.223	2.12
4.7	0.447	0.75
4.8	0.670	0.79
5.0	0.894	6.36
5.2	1.118	3.18

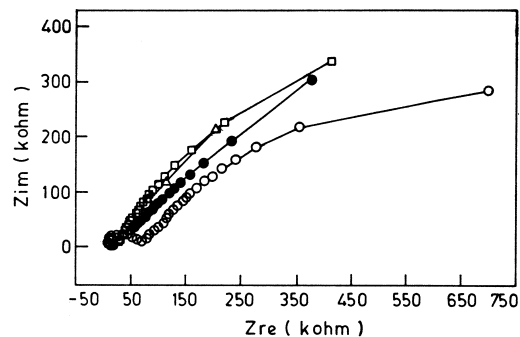


Fig. 2. The impedance data (Nyquist plot) for PVC/PMMA blend with EC/PC plasticizer. LiBF₄ concentrations: (△△△△) 0.47; (○○○○○○) 0.48; (●●●●●●) 0.50; (◇◇◇◇) 0.52.

$1/\omega C_b \approx R_b$ both the bulk resistance and capacitance are contributing factors to the overall impedance of the electrode whereas electrode capacitance C_e is insignificant $C_e \approx 10^6 C_b$. Therefore, at high frequencies the equivalent circuit reduces to a parallel $R_b C_b$ combination which gives rise to the semicircle. At low frequencies $1/\omega C_b < R_b$ and hence C_b becomes a negligible contribution to the impedance. Thus, the equivalent circuit reduces to a series combination of R_b and C_e appearing a vertical spike displaced a distance R_b along the real axis. At very low frequencies the equivalent circuit would simplify to the electrode capacitance C_e only.

As is expected the high frequency response yields information about the properties of the electrolyte. The high frequency semicircle yields the bulk resistance R_b and knowing R_b and ω_{max} the bulk capacitance C_b from $\omega_{\text{max}} R_b C_b = 1$ can be calculated. The low frequency response on the other hand carries information on the electrode/electrolyte interface. From any point on the spike the electrode capacitance can be calculated using the relationship

$$C_e = \frac{1}{Z'' \omega} \quad (2)$$

Thus, the magnitude of all the fundamental electrical properties of the cell may be obtained from the complex

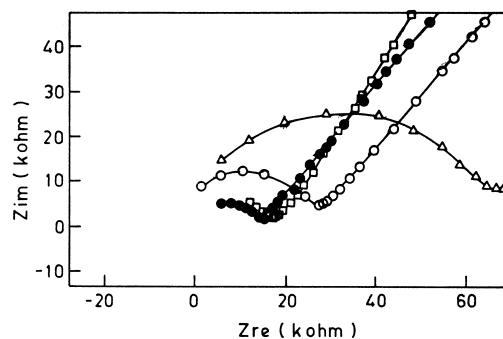
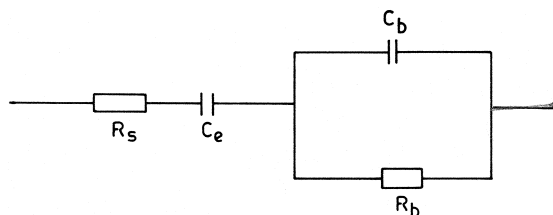


Fig. 3. The magnified view of the high frequency region of Fig. 2. LiBF₄ concentrations: (△△△△) 0.47; (○○○○○○) 0.48; (●●●●●●) 0.50; (◇◇◇◇) 0.52.



Scheme 1.

impedance data. In particular R_b is the effective DC resistance of the electrolyte can be easily obtained by simply sandwiching the electrolyte in between platinum/stainless steel electrodes.

If the electrodes and electrode/electrolyte interface were ideal, vertical spikes at the low frequency end should have been obtained. Semicircles are significantly broadened and electrode spikes at the low frequency end of the spectrum are distinctly non-vertical as it is evident from the Fig. 3. Spikes inclined at an angle of less than 90° to the real axis are obtained in the present study and this is due to roughness of the electrode/electrolyte interface. As discussed in Ref. [5] alternating electronic currents within the electrode induce parallel alternating ionic currents in the electrolyte contained within the pores. Current flow in the pores of a rough interface is similar to that of a transmission line and thus the equivalent circuit representing such pores is also similar to the transmission line and the impedance of this can be represented as

$$Z'_\omega = A'\omega\omega^{-n} \left[\cos\left(\frac{n\pi}{2}\right) - i \sin\left(\frac{n\pi}{2}\right) \right] \quad (3)$$

where A' and n are the constants and the value of n lies between 0 and 1. The above equation gives rise to a spike inclined at an angle of $n\pi/2$ to the real axis. The value of n may be correlated with the degree of roughness. Smoother interfaces lead to larger values of n . If perfectly smooth the above expression for Z'_ω reduces to that of a capacitor.

In the present case of investigation, the spike inclined at an angle to the real axis may be due to inhomogeneous

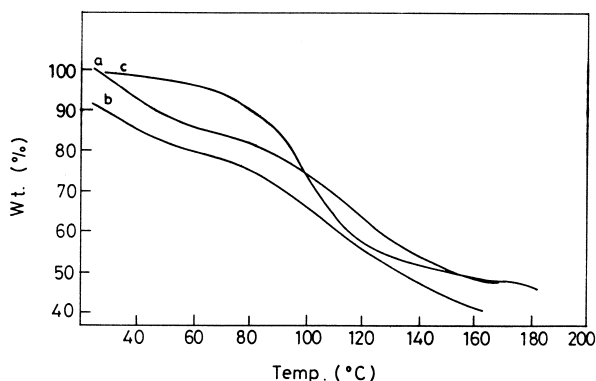


Fig. 4. TG data for different plasticizer EC/PC contents: (a) 140%, (b) 186%, (c) 326%.

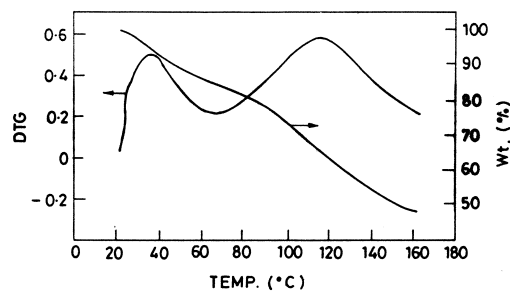


Fig. 5. TG data for plasticizer content 140% EC/PC.

distribution of salt in the polymer matrix. It also reflects the surface morphology wherein crystalline and amorphous phases are distributed unevenly. There are different grains connected with grain boundary. This surface heterogeneity is responsible for the deviation and n is large if the surface is approaching smoothness [6].

When the impedance data are compared between the two salts used (LiClO_4 and LiBF_4) LiBF_4 shows a better conductivity at the ambient temperature (LiBF_4 : $10^{-3} \text{ S cm}^{-1}$; LiClO_4 : $10^{-6} \text{ S cm}^{-1}$) for the same plasticizer EC/PC. In the case of LiClO_4 as salt in the different plasticizer, viz. in EC/PC in DEP, the conductivity is better in EC/PC ($10^{-6} \text{ S cm}^{-1}$) compared to DEP (10^{-7} to $10^{-8} \text{ S cm}^{-1}$). This may be due to more crystalline phases in the case of DEP as plasticizer which is also evident from XRD data (Fig. 1b) compared with more amorphous phases in the case of EC/PC as plasticizer (Fig. 1a).

The difference in conductivity between LiClO_4 ($10^{-6} \text{ S cm}^{-1}$) and LiBF_4 ($10^{-3} \text{ S cm}^{-1}$) may be due to the lowest T_g for LiBF_4 compared with LiClO_4 [7]. In LiBF_4 , greater ionic mobility is expected compared with LiClO_4 wherein crystallite formation is less significant.

To ascertain the thermal stability of the plasticized polymer electrolyte all the samples were subjected to thermogravimetry (TG)/differential thermogravimetry (DTG) analysis.

Typical TG data for the films containing three different plasticizer contents viz. 140%, 186%, 326% are given in Fig. 4. Figs. 5–7 depict the TG and DTG data for the

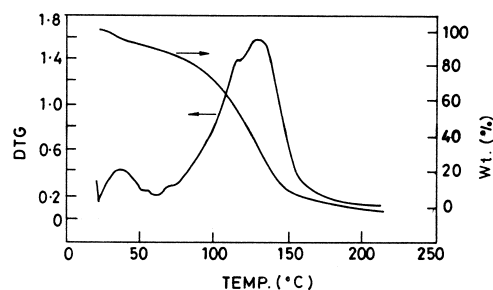


Fig. 6. TG and DTG data for plasticizer content 233%.

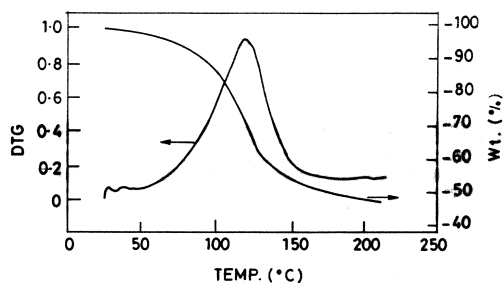


Fig. 7. TG and DTG data for plasticizer EC/PC content 326%.

plasticizer EC/PC contents. Figs. 8 and 9 show TG and DTG data for plasticizer DEP. From these data, it is seen that they decompose in a complicated way [8]. All the films exhibited a relatively small weight loss < 3% in the temperature range 50–100°C presumably due to the evaporation of residual moisture absorbed when the samples are loaded. Above 100°C, i.e., after complete dehydration no further weight loss was observed until irreversible decomposition began around 120°C. The weight loss at 100°C and 150°C are indicated in Table 5 for EC/PC and DEP. From Table 5, it seems that the films containing 186% EC/PC are preferred in terms of thermal stability. However, the films containing 279% EC/PC show better ionic conductivity and are also quite stable thermally, (see data weight loss at 100°C and 150°C). Generally, two peaks appear in the DTG curves for different plasticizer contents. The first peak may be due to slight moisture as discussed earlier and the second peak may be due to the stability of the films containing required lithium salts. Thus, these synthesized films are stable up to 120°C which is fairly high when compared to the operating temperature of lithium polymer cell viz. 50–60°C.

In the case of DEP, the thermal stability of the films comprising 0.894 g is superior when compared to film containing 0.447 g. In the case of films containing DEP as plasticizer, decomposition occurs at 55°C and 160°C. Fig. 9 shows the thermal stability of DEP alone (without LiClO₄) in PVC/PMMA polymer blend. As such DEP tries to decompose at 105°C and when salt is added it is advanced to 55°C as indicated in Fig. 8 which is not preferred in the lithium polymer batteries as its operating

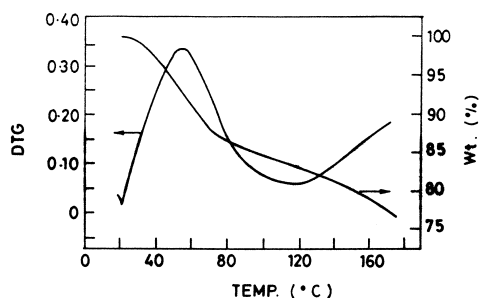


Fig. 8. TG and DTG data for plasticizer DEP contents 226%.

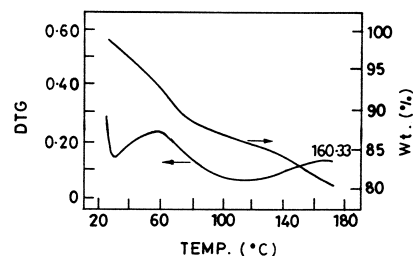


Fig. 9. TG and DTG data for plasticizer DEP alone without salt.

temperature is in the range of 40–70°C. Thus, the use of DEP as plasticizer is not preferred if LiClO₄ is used as salt in view of its poor conductivity and low thermal stability.

To corroborate these observations, the molecular interactions of the plasticizer with host polymer matrix has also been evaluated by FTIR analysis.

Fig. 10a shows the FTIR data for the polymer PVC/PMMA containing the plasticizer EC/PC without lithium salt while Fig. 10b and c indicate the effect of lithium salt (0.5 g) in PVC/PMMA (1:1), PVC/PMMA (1:2.25), respectively. These data were analysed only from the angle of symmetric ring deformation region of PC, C–O stretching and CH₂ rocking region of PC and C=O stretching region of PC when it acts as plasticizer containing LiClO₄ as salt.

Fig. 11 displays the symmetric ring deformation region of PC, the band at 712 cm⁻¹ in Fig. 11c. This band is shifted in PVC polymer alone containing LiClO₄ (0.5 g) with EC/PC as plasticizer (Fig. 11a, 705 cm⁻¹) and also PVC/PMMA of 1:2.25 containing LiClO₄ (0.5 g) with EC/PC a plasticizer (Fig. 11b, 705 cm⁻¹). This shift may be due to the addition of lithium perchlorate and this is consistent with the observation reported [9].

Fig. 12c shows the spectral region of another ring deformation for PC which occurs at the band 777 cm⁻¹. This band is shifted to 750 cm⁻¹ in the polymer PVC

Table 5
Weight loss and peak temperature data from TG and DTG curves

Plasticizer content	Weight loss (g)		Peak temperature (K)	
	at 373 K	at 423 K		
<i>EC/PC</i>				
140	0.39	0.74	310	390
186	0.15	0.26	302	374
233	0.37	0.17	312	404
279	0.20	0.30	–	–
326	0.21	0.90	–	493
<i>DEP</i>				
0.223	0.18	0.25	311	418
0.447	0.10	0.10	312	425
0.670	0.26	0.35	331	433
0.894	0.12	0.21	339	–
1.118	0.56	0.72	328	–

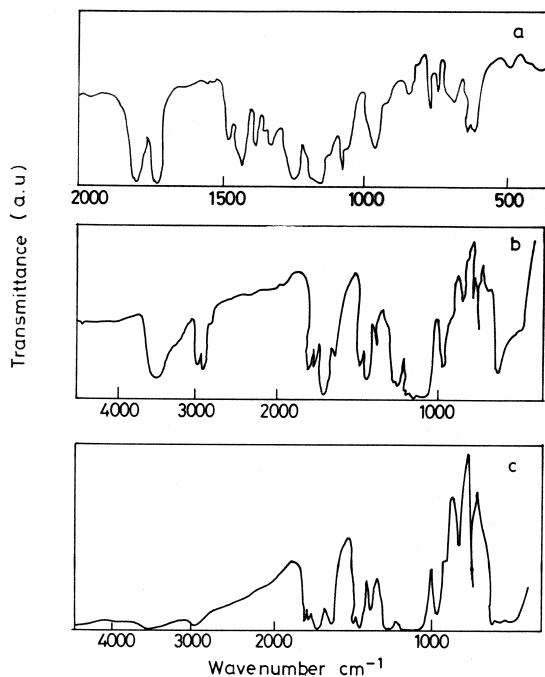


Fig. 10. (a) The FTIR data for PVC/PMMA polymer blend without salt for the plasticizer EC/PC, (b) PVC/PMMA equal ratio, (c) PVC/PMMA (1:2.25) ratio containing 0.5 g LiClO_4 .

alone in the presence of EC/PC as plasticizer and LiClO_4 salt. A slight shift occurs at 755 cm^{-1} in the case of polymer blend PVC/PMMA of 1:2.25. When the ratio for PVC/PMMA is equal (1:1) with the same plasticizer and LiClO_4 , the band occurs nearer to 778 cm^{-1} as in the case of pure PC alone. This may be due to the ionic association through the redistribution of charge accompanying the formation of ionic pairs and aggregation [10,11].

Fig. 13c shows the spectra in C–O stretching and CH_2 rocking region of PC (bands at 945 cm^{-1} and 956 cm^{-1}) in the plasticizer PC alone. Fig. 13a indicates the same stretching behaviour in the polymer PVC alone containing

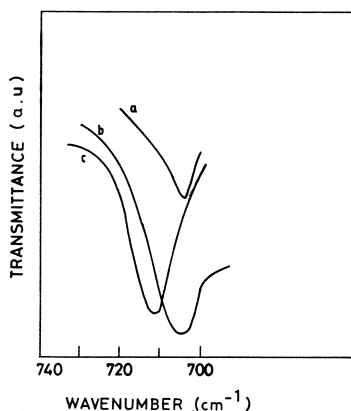


Fig. 11. Symmetric ring deformation region in (a) PVC alone with LiClO_4 (b) PVC/PMMA (1:2.25) ratio/ LiClO_4 /EC/PC (c) PC alone.

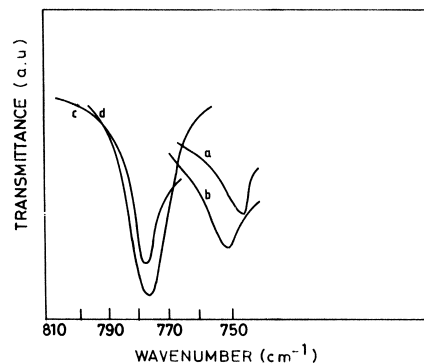


Fig. 12. The spectral region of another ring deformation: (a) PVC alone with LiClO_4 , (b) PMMA/PVC unequal ratio/ LiClO_4 /EC/PC, (c) PC alone, (d) PVC/PMMA equal ratio/EC/PC/ LiClO_4 .

LiClO_4 salt (bands at 965 cm^{-1}). In the case of polymer blend containing PVC/PMMA (1:2.25), the two bands narrowed at 965 cm^{-1} (Fig. 13b), whereas in the PVC/PMMA (1:1) the two bands merged at 968 cm^{-1} (Fig. 13d).

Fig. 14c shows the spectra in C=O stretching region of PC alone which is broadened at 1800 cm^{-1} . For the polymer containing PVC alone with EC/PC as plasticizer and LiClO_4 as salt, a narrow peak is observed at 1800 cm^{-1} (Fig. 14a). In the case of polymer blend PVC/PMMA (1:2.25) with EC/PC as plasticizer a slightly broader peak occurs at 1800 cm^{-1} (Fig. 14b). The observation that broadened peak shortens by the addition of lithium salt is also consistent with the data reported [12].

Fig. 15a and b show the spectra for PVC/PMMA (1:1) and PVC/PMMA (1:2.25) containing lithium perchlorate in the presence of EC/PC as plasticizer the band at 624 cm^{-1} is attributed to ClO_4^- anion related solvent ion interactions.

It is reported [13] by the use of band fitting method that four species: (1) free perchlorate ions [ClO_4^- at 930 cm^{-1}], (2) solvent shared ions [Li^+ + solvent ClO_4^- at 939 cm^{-1}], (3) contact ions pairs $\text{Li}^+ \text{ClO}_4^-$ at 948 cm^{-1} , and (4) multiple ion aggregates [$\text{Li}^+ \text{ClO}_4^-$] $_4$ at 955 cm^{-1} are

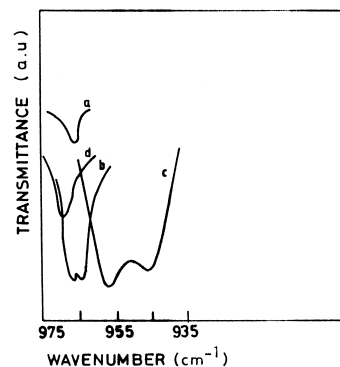


Fig. 13. The spectra of C–O stretching and CH_2 rocking region: (a) PVC alone with LiClO_4 , (b) PMMA/PVC unequal ratio/ LiClO_4 /EC/PC, (c) PC alone, (d) PVC/PMMA equal ratio/EC/PC/ LiClO_4 .

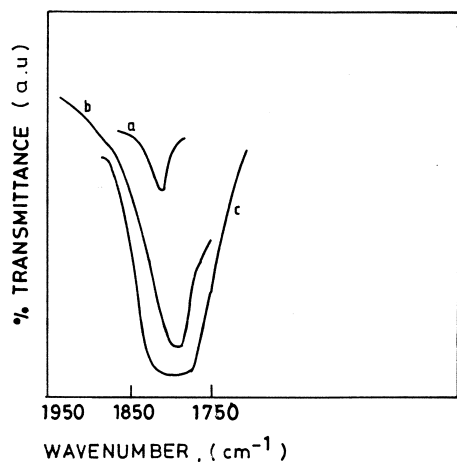


Fig. 14. The C=O stretching region: (a) PVC alone with EC/PC LiClO_4 , (b) PMMA/PVC unequal ratio LiClO_4 /EC/PC, (c) PC alone.

identified in the Raman spectra for the ion solvent interaction. Similar types of interactions can be expected in the present case as is evident from Fig. 13.

All these data demonstrate the importance of understanding the interactions between plasticizer and the host

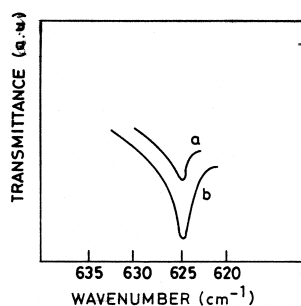


Fig. 15. IR spectra of PVC/PMMA in the presence of EC/PC as plasticizers: (a) PVC/PMMA equal ratio EC/PC/ LiClO_4 , (b) PVC/PMMA unequal/EC/PC/ LiClO_4 .

polymer matrix in evolving a pre-defined polymer electrolyte.

4. Conclusion

The influence of plasticizer in optimising polymer electrolyte design for PMMA/PVC blend has been proved through AC impedance analysis. TG and DTG and FTIR studies show a preference for LiBF_4 as a complexing ion along with EC/PC as plasticizer when compared to LiClO_4 /DEP.

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