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Investigations on poly(methyl methacrylate)-poly(ethylene oxide) hybrid polymer electrolytes with dioctyl phthalate, dimethyl phthalate and diethyl phthalate as plasticizers

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Abstract Plasticizers can be used to change the mechanical and electrical properties of polymer electrolytes by reducing the degree of crystallinity and lowering the glass transition temperature. The transport properties of gel-type ionic conducting membranes consisting of poly(ethylene oxide) (PEO), poly(methyl methacrylate) (PMMA), LiClO₄ and dioctyl phthalate, diethyl phthalate or dimethyl phthalate (DMP) are studied. The polymer films are characterized by X-ray diffraction, Fourier transform infrared and impedance spectroscopic studies. It is found that the addition of DMP as the plasticizer in the PEO-PMMA-LiClO₄ polymer complex favours an enhancement in ionic conductivity. The maximum conductivity value obtained for the solid polymer electrolyte film at 305 K is 3.529×10^{-4} S cm⁻¹.

Keywords Polymer blend electrolyte · Plasticizers · X-ray diffraction · Fourier transform infrared spectroscopy · Impedance studies

Introduction

The properties of polymer electrolytes such as their high compliance, good adherence to electrodes and the possibility of fabricating the polymers into thin films are attractive for advanced applications such as high energy density rechargeable batteries [1, 2]. Polymer complexes consisting of poly(ethylene oxide) (PEO) and alkali metal salts are ionic conductors of considerable technical interest owing to the ready availability of PEO at various molecular weights and the wide range of their possible applications in various devices [3]. The forma-

tion of crystallites in PEO systems has prevented their use as electrolytes at room temperature. The most straightforward approach to overcome this problem is to modify the solvating polymer in order to decrease the crystallinity and glass transition temperature of the polymer electrolyte while retaining the solvating properties of the ethylene oxide chain. Several methods such as copolymerization [4], plasticization [5], blending [6] and addition of a ceramic filler additive [7] are in use to modulate the conductivity of the polymer electrolytes. Blending of polymers is a useful method to develop new polymeric materials with improved mechanical stability. The problem in choosing the polymer blends is the miscibility of the components. Combinations of proton donating and accepting polymers can form intermolecular complexes in aqueous or organic media. Poly(methyl methacrylate) (PMMA) and PEO form one such couple [1, 8]. The crystallization and miscibility behaviour of PMMA-PEO blends have been studied on the basis of techniques such as differential scanning calorimetry (DSC) [9] and dynamical mechanical analysis (DMA) [10].

The plasticizers are low molecular weight non-volatile substances which when added to a polymer improve the flexibility, processability and hence utility. Plasticizers such as an aprotic solvent with a high dielectric constant, which would dissolve enough charge carriers, provide a more mobile medium for the resultant films. The major drawbacks of plasticized electrolytes are solvent volatility, poor mechanical properties due to a high degree of plasticization and reactivity of polar plasticizer with the lithium electrodes. Among the host polymers used for such plasticized polymer electrolytes are PMMA [11], poly(vinylidene fluoride) (PVdF) [12], poly(vinyl chloride) (PVC) [13] and blend-based systems based on PEO [14, 15]. Appetecchi et al. [16] studied the kinetics and stability of a lithium electrode in PMMA-based gel electrolytes. PEO-PMMA blend-based polymer electrolyte systems plasticized with ethylene carbonate and propylene carbonate have been reported to be applicable to lithium and lithium ion secondary batteries [17].

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In the present study, solid polymer electrolyte thin films consisting of PEO, PMMA, LiClO₄ and esters of dibenzoic acids, such as dioctyl phthalate (DOP), diethyl phthalate (DEP) and dimethyl phthalate (DMP), as plasticizers are prepared and characterized by XRD, FTIR and a.c. impedance spectroscopic studies. It has been found that the addition of DMP as the plasticizer favours an enhancement in the ionic conductivity compared to the values due to the addition of other plasticizers (DOP, DEP).

Experimental

The polymer electrolytes were prepared by the solvent casting technique using distilled tetrahydrofuran (THF) as the solvent. PEO, PMMA and LiClO₄ were commercially purchased from Aldrich. Prior to their use, the starting materials PEO, PMMA and LiClO₄ were dried under vacuum at 50, 100 and 110 °C, respectively, for 5 h. Appropriate quantities of polymer and the salt were dissolved in THF and stirred magnetically for 10 h at room temperature; then the plasticizer was added to the above solution, which was stirred further for about 5 h. Thin films of polymer electrolytes were prepared by casting the gelatinous polymer solution into Teflon pushes/glass plate. Solvent was then allowed to evaporate slowly and films of the polymer samples were obtained. The prepared films were then dried under vacuum conditions and stored in a desiccator.

X-ray diffraction (XRD) studies of the films were performed using a JEOL JDX 8030 X-ray diffractometer with 2θ values between 7° and 80°. IR measurements were made with a Perkin-Elmer 577 IR spectrophotometer in the range 200–4000 cm⁻¹. The bulk electrical conductivities of the polymer complex were evaluated from the impedance plots using a Keithley 3330 LCZ meter. The plots were recorded in the frequency range from 40 Hz to 100 kHz with a signal amplitude of 10 mV. The polymer film was sandwiched between stainless steel electrodes for conductivity studies.

Results and discussion

XRD studies

XRD measurements have been carried out for the polymeric electrolyte films in order to examine the nature of the crystallinity. XRD patterns of the polymer complexes are shown in Fig. 1. It is found that there is a decrease in the relative intensity of the peak corresponding to PEO in the polymer complex, which may be due to the reduction in crystallinity of PEO after the addition of PMMA, LiClO₄ and plasticizer. These results can be interpreted by considering the Hodge et al. [18] criterion, which establishes a correlation between the height of the peak and the degree of crystallinity.

As most of the LiClO₄ peaks disappear in the polymer complex, it is concluded that the LiClO₄ salt is completely mixed with the polymer host.

FTIR studies

The IR plots of pure PEO, PMMA, LiClO₄ and the polymer films are shown in Fig. 2. The two peaks in the

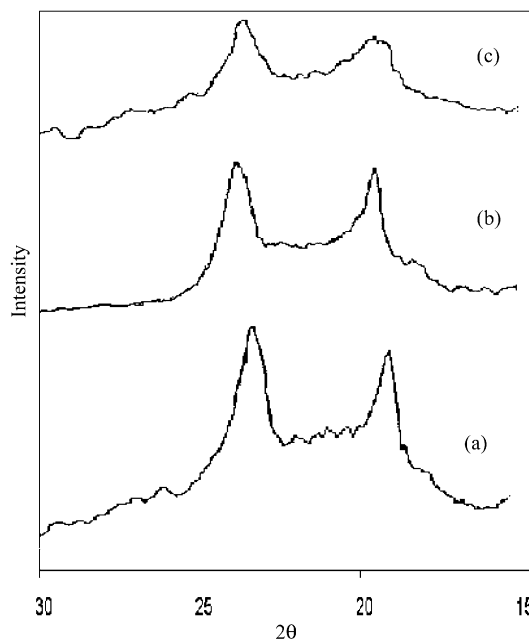


Fig. 1. XRD patterns for (a) PEO-PMMA-LiClO₄-DOP (79:10:10:1), (b) PEO-PMMA-LiClO₄-DEP (79:10:10:1), (c) PEO-PMMA-LiClO₄-DMP (79:10:10:1)

800–1000 cm⁻¹ region are assigned to CH₂ rocking vibrations and may be attributed to the *gauche* form. The region from 1060 to 1150 cm⁻¹ has been assigned to contributions from C-C stretching and C-O-C stretching modes in the mutual couplings. If the alkali metal cation were coordinated to the ether oxygens, one would expect to see large changes in this region. This is observed in the present study: the broad peak at 1130 cm⁻¹ in the pure PEO shifts to 1160 cm⁻¹ in the polymer complex. The peak at 1105 cm⁻¹ is shifted to 1115 cm⁻¹. The shift in the C-O-C stretching band is due to the association of Li⁺ with the ether oxygen. If we take the band at 470 cm⁻¹ for pure LiClO₄, it may be assumed to have been replaced by two bands at 475 and 450 cm⁻¹ in the complex, indicating the presence of two kinds of environment for the ClO₄⁻ ion in the complex. Peaks for pure LiClO₄ (1070 and 1610 cm⁻¹) disappear in the polymer complex, which indicates that no excess salt is present in the complex. Thus complex formation has been confirmed by the above analysis.

Conductivity measurements

The typical impedance plot (Z' and Z'') for the composition PEO-PMMA-LiClO₄-DMP is shown in Fig. 3. In the impedance response behaviour, the disappearance of the high-frequency semicircular portion in the complex impedance plot leads to a conclusion that the current carriers are ions and this leads one to further conclude that the total conductivity is mainly the result of ion conduction [19]. From the complex impedance plot, the intercept at the higher frequency side on the Z' axis gives the resistance

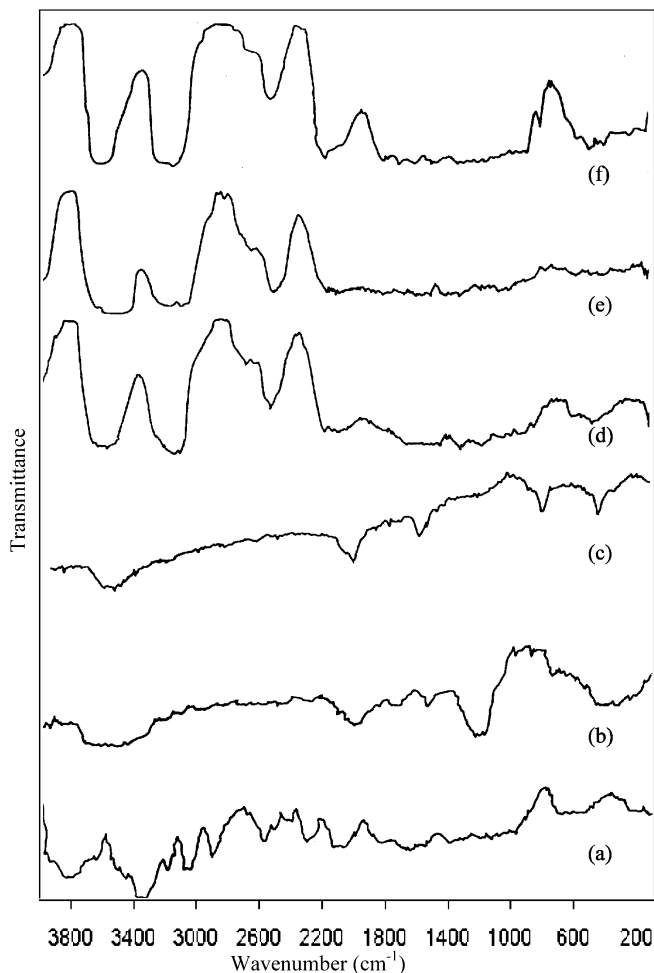


Fig. 2. IR plots for polymer complexes: (a) pure PEO, (b) LiClO_4 , (c) PMMA, (d) PEO-PMMA- LiClO_4 -DEP (79:10:10:1), (e) PEO-PMMA- LiClO_4 -DMP (79:10:10:1), (f) PEO-PMMA- LiClO_4 -DOP (79:10:10:1)

of the bulk electrolyte. The conductivity of the electrolyte was calculated from the measured resistance for the known area and thickness of the polymer film.

The ionic conductivities of the polymer electrolyte PEO-PMMA- LiClO_4 with plasticizers are summarized in Table 1. It is found that addition of DMP as the plasticizer favours the enhancement in ionic conductivity of the polymer complex. The composition of 1 mol% of DMP in PEO-PMMA- LiClO_4 gives a conductivity of $3.529 \times 10^{-4} \text{ S cm}^{-1}$ at 305 K, which is indeed a higher value than the $6 \times 10^{-5} \text{ S cm}^{-1}$ reported by Borkowska et al. [20] for a thermally polymerized PEO-PMMA blend at room temperature. This value is also in close agreement with the value of $10^{-4} \text{ S cm}^{-1}$ reported by Morita et al. [21] for a PEO-PMMA complex with lithium salts and ethylene carbonate (EC) as the plasticizer, and the value of $5.1 \times 10^{-4} \text{ S cm}^{-1}$ reported by Peled et al. [22] for a PEO-PMMA-Li-EC (2.5:0.25:1:1) complex.

All the plasticized polymer electrolyte samples showed a conductivity enhancement in comparison to

the electrolyte without the plasticizer [23]. The increased conductivity by the addition of plasticizers may be due to the existence of separate ionic pathways for the migration of free lithium ions through the plasticizer [1, 24]. Li ions may prefer to conduct through these new paths because the medium is less viscous, thus enhancing the mobility of the ions. The plasticizer introduces more free volume to the polymer, which lowers the glass transition temperature. This effect is due to the reduction in the cohesive force of attraction between polymer chains. Plasticizer molecules, being relatively small in size compared with polymer molecules, penetrate into the polymer matrix and establish an attractive force between the plasticizer molecule and chain segments. These attractive forces reduce the cohesive forces between the polymer chains and increase the segmental mobility, thus enhancing the conductivity, i.e. the plasticizer can interrupt polymer-polymer interactions by occupying the inter- and intra-chain free volume. The decrease in polymer-polymer interactions and the increase in polymer-plasticizer interactions influence the glass transition behaviour.

A slight drop in the conductivity values has been obtained for polymer electrolytes with the plasticizers DOP and DEP compared to DMP. The effect of the plasticizers on the polymer mobility and conductivity depends on the specific nature of the plasticizer, including viscosity, dielectric constant, polymer-plasticizer interaction and ion-plasticizer coordination. The molecular weight of the plasticizer will also influence the degree of mixing and the polymer-polymer or polymer-plasticizer interactions and hence it has an inverse effect, i.e. an increasing molecular weight decreases the system's conductivity [25]. The observed increase in conductivity for the addition of DMP as plasticizer may be due to the low molecular weight of DMP compared to the other two plasticizers [26].

From Table 1 it is observed that as the temperature increases the conductivity values also increase for all the compositions. This is in agreement with the theory [27]. As the temperature increases, the polymer can expand easily and produce a free volume. Thus ions, solvated molecules or polymer segments can move into the free volume. The resulting conductivity is represented by an overall mobility of ion and polymer, which is determined by the free volume and leads to the increase in ionic mobility and segmental mobility that will assist ion transport and practically compensate the retarding effect of the ion clouds. The temperature dependence of the electrical conductivities of the polymer films is shown in Fig. 4. The overall features of the Arrhenius plot are quite similar for the electrolyte systems and no linear dependence could be obtained, which seems to suggest that ion conduction follows the Williams-Landel-Ferry (WLF) mechanism [28]. In other words, the non-linearity indicates that ion transport in polymer electrolytes is dependent on the polymer segmental motion [29]. Thus, the result may be more effectively represented by the empirical Vogel-Tamman-Fulcher (VTF) equation [30, 31, 32]:

Fig. 3. Typical impedance plot of PEO-PMMA-LiClO₄-DMP at 305 K

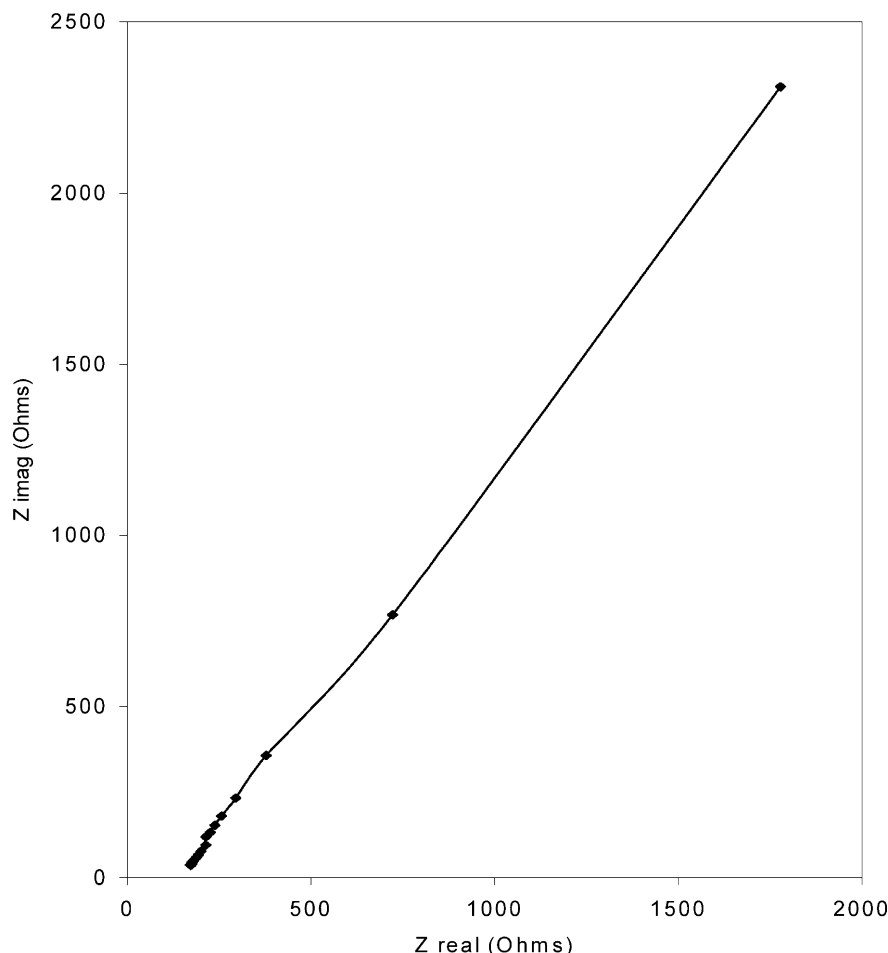


Table 1. Conductivity values of the polymer complexes

Film	Polymer complex	σ values ($\times 10^{-3}$ S cm ⁻¹)					
		305 K	328 K	338 K	348 K	358 K	373 K
F1	PEO-PMMA-LiClO ₄ -DOP (79:10:10:1)	0.031	0.226	0.584	1.654	2.535	2.810
F2	PEO-PMMA-LiClO ₄ -DEP (79:10:10:1)	0.178	0.403	1.299	2.533	2.805	3.412
F3	PEO-PMMA-LiClO ₄ -DMP (79:10:10:1)	0.352	0.532	2.067	3.217	4.107	4.927

$$\sigma = AT^{-1/2} \exp[-B/T - T_g] \quad (1)$$

where A and B are constants and T_g is the reference temperature taken as the glass transition temperature here. Constant A in the VTF equation is related to the number of charge carriers in the electrolyte system and constant B is related to the activation energy of ion transport associated with the configurational entropy of the polymer chains. The temperature dependence of the ionic conductivity suggests that the ion moves through the plasticizer-rich phase. Because the conducting medium, i.e. the plasticizer-rich phase, involves the plasticizer, the salt and polymers, the characteristics of the viscous matrix are brought out.

Conclusion

The performance of PEO-PMMA-LiClO₄ systems was studied using three (DOP, DEP, DMP) plasticizers. The complexation has been confirmed from XRD and FTIR studies. Using impedance spectroscopy the bulk electrical conductivity has been determined. It was found that the addition of DMP as plasticizer in the PEO-PMMA-LiClO₄ polymer complex favours an enhancement in ionic conductivity. The temperature dependence of the conductivity of the polymer films seems to obey the VTF relation.

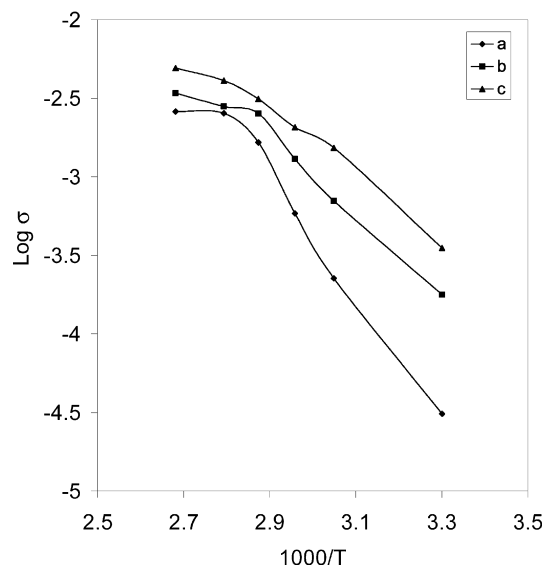


Fig. 4. Temperature dependence of ionic conductivity for (a) PEO-PMMA-LiClO₄-DOP, (b) PEO-PMMA-LiClO₄-DEP, (c) PEO-PMMA-LiClO₄-DMP

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