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ORIGINAL PAPER

Investigation of dibutyl phthalate as plasticizer on poly (methyl methacrylate)–lithium tetraborate based polymer electrolytes

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Abstract Polymer electrolyte membranes, comprising of poly(methyl methacrylate) (PMMA), lithium tetraborate ($Li_2B_4O_7$) as salt and dibutyl phthalate (DBP) as plasticizer were prepared using a solution casting method. The incorporation of DBP enhanced the ionic conductivity of the polymer electrolyte. The polymer electrolyte containing 70 wt.% of poly(methyl methacrylate)–lithium tetraborate and 30 wt.% of DBP presents the highest ionic conductivity of 1.58×10^{-7} S/cm. The temperature dependence of ionic conductivity study showed that these polymer electrolytes obey Vogel–Tamman–Fulcher (VTF) type behaviour. Thermogravimetric analysis (TGA) was employed to analyse the thermal stability of the polymer electrolytes. Fourier transform infrared (FTIR) studies confirmed the complexation between poly(methyl methacrylate), lithium tetraborate and DBP.

Keywords PMMA · Polymer electrolyte · Impedance · Conductivity

Introduction

Interest in polymer electrolytes has been sustained since the development of complexes of alkali metal ions with poly (ethylene oxide) (PEO) by Fenton et al. [1]. Solid polymer electrolytes have been extensively studied for applications in high-energy density batteries, gas sensors, electrochemical devices, electrochromic displays, fuel cells, supercapacitors, etc. A polymer electrolyte can be used as both electrolyte and the separator between the electrodes in solid state rechargeable lithium batteries [2–5].

Polymer electrolytes must fulfill numerous requirements such as ionic conductivity, electrochemical stability, compatibility, thermal stability, mechanical stability and availability in order to function as both a separator and electrolyte [6]. The main aim of most research is focused on the enhancement of ionic conductivity. Various investigations have been performed, by blending of polymers, cross-linking, insertion of ceramic fillers and plasticization in order to enhance the ionic conductivity [7–10]. Plasticization was an effective way to improve the ionic conductivity [11]. In order for a plasticizer to enhance ionic conductivity, high dielectric constant to dissociate ions and low viscosity to facilitate the ion transport are essential. Examples of plasticizers that exhibit these properties are dibuthyl phthalate (DBP), propylene carbonate (PC), ethylene carbonate (EC) and diocthyl adipate (DOA) [12].

The crystallinity of PMMA is low compared with other polymers like PEO and PVC. In addition, PMMA-based polymer electrolytes have better interfacial properties towards the lithium electrodes [13]. Pure PMMA is an insulator with a conductivity range from 10^{-10} to 10^{-12} S/cm. Adding plasticizers to PMMA will affect the overall ionic conductivity through crystalline complex formation, intramolecular cross-linking of the polymer chains and the degree of salt dissociation [14–16].

In this study, plasticized polymer electrolytes composed of PMMA as the host polymer, $Li_2B_4O_7$ as the salt and DBP, as the plasticizer were prepared. The high molecular

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weight polymer and the range of plasticizer concentrations were selected to produce a polymer–salt–plasticizer system. The conductivity of polymer salt complexes exhibits a maximum at a given concentration, which depends on several factors. Among the most discussed factors is the effect on simultaneously increasing the plasticizer concentration on the conductivity and reduced mobility of the ions in the amorphous phase [17]. The properties and characteristics of the polymer complexes are studied by Fourier transform infrared (FTIR), Impedance spectroscopy and thermogravimetric analysis (TGA).

Experimental

PMMA with an average molecular weight of 35,000, was obtained from Acros Organic, lithium tetraborate ($Li_2B_4O_7$), dibutyl phthalate (DBP) was obtained from Aldrich and tetrahyrofuran (THF) was obtained from J.T. Baker.

Prior to the preparation of the polymer electrolytes, $Li_2B_4O_7$ was dried at 120 °C for 24 h to eliminate any trace amounts of water in the material. Different ratio compositions of polymer thin film were prepared by solution casting method. The designations of polymer electrolytes are as listed in Table 1. The PMMA, $Li_2B_4O_7$ and DBP were dissolved in THF and stirred for 24 h to make a homogeneous solution. The solution was cast in a Petri dish and allowed to evaporate slowly inside a dessicator. This procedure yields free standing and mechanically stable films. The thickness of the films was then measured with a micrometer screw gauge.

FTIR studies were carried out using Perkin-Elmer FTIR Spectrophotometer Spectrum RX1. It was recorded in the range of 4,000 and 400 cm^{-1}, with a resolution of 4 cm^{-1}. Two stainless steel electrodes with a surface area of 2.50 cm^2 were used for conductivity measurements. A thin layer of a sample film was inserted between them. A HIOKI 3532-50 LCR Hi-Tester was used for impedance spectra measurements between the frequency ranges of 50 Hz and 1 MHz. The conductivity dependent temperature was obtained at temperature range of 303–373 K. Thermal stability of polymer films was determined by using a Mettler Toledo analyzer that consisted of TGA/SDTA851^e main unit and STARe software. The temperature profile carried out was in the range of 30–400 °C with a 10 °C/min heating rate. Inert nitrogen gas was used in the analysis with a rate of 10 ml/min.

Table 1 Designations of PMMA–$Li_2B_4O_7$–DBP polymer electrolyte thin films

Designation	Composition (PMMA/$Li_2B_4O_7$/DBP (wt.%))
SPE1	70.0:30.0:0.0
SPE2	66.5:28.5:5.0
SPE3	63.0:27.0:10.0
SPE4	59.5:25.5:15.0
SPE5	56.0:24.0:20.0
SPE6	52.5:22.5:25.0
SPE7	49.0:21.0:30.0
SPE8	45.5:19.5:35.0
SPE9	42.0:18.0:40.0

Results and discussion

Impedance studies

Conductivity studies

The graph of logarithmic conductivity against various percentage of plasticizer content is shown in Fig. 1. The conductivity of PMMA–$Li_2B_4O_7$ solid polymer electrolyte is found to increase as DBP is added until a conductivity of 1.58×10^{-7} S cm^{-1} is obtained at 30 wt.% DBP. This is the highest conductivity achieved. Further addition of DBP reduces the conductivity.

The ionic conductivity enhancement of the plasticized polymer electrolyte is explained as follows: a fraction of Li^+ ions detaches itself from the PMMA and attaches to DBP which results in the weakening of the dipole–ion interaction. This structural change in the electrolyte causes a substantial decoupling of the Li^+ motion from that of the polymer chain. These electrolytes are believed to have structures in which the lithium salt is complexed to both the polymer, through its electron donor group, and the plasticizer solvent [18].

The ionic conductivity value depends upon the viscosity value of the plasticizer used. The low viscosity of DBP (η= 16.45 cP) causes a greater mobility to the ions. The mobility of the system increases with the increase in

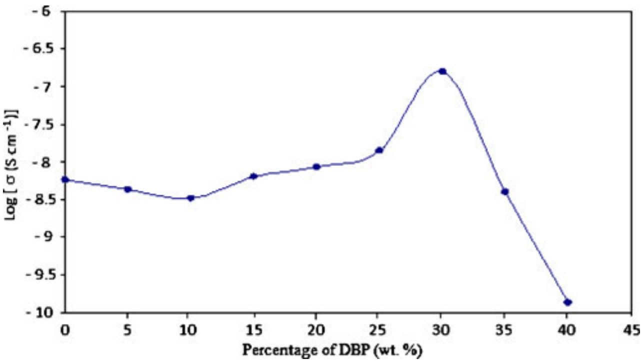


Fig. 1 Variation of ionic conductivity of various DBP concentrations in the polymer films

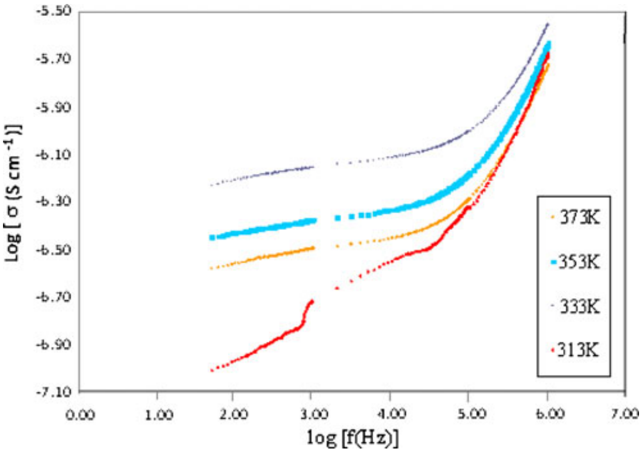


Fig. 2 Logarithmic conductivity against logarithmic frequency for SPE7 at various temperatures

plasticizer content, which in turn increases the conductivity of the polymer electrolyte. However, the conductivity values were found to decrease after SPE7. This phenomenon was due to the formation of linkages between the plasticizer itself, thus causing it to crystallize, resulting in the decrease in conductivity [19–21].

Conductivity–frequency dependence

The conductivity of the PMMA–$Li_2B_4O_7$–DBP salt polymer electrolytes was analysed with respect to the frequency. The logarithmic conductivity against logarithmic frequency for SPE7 between 303 K and 373 K is shown in Fig. 2. The figure shows that the conductivity of the samples increase with increasing frequency and temperature. The low frequency dispersion may be due to the interfacial impedance or space charge polarization [22]. As the frequency decreases, more and more charge accumulation occurs at the electrode and electrolyte interface, which leads to a decrease in the number of mobile ions and eventually to a drop in conductivity at low frequency. In the high frequency region, the mobility of charge carriers is high and hence the conductivity increases with frequency [7].

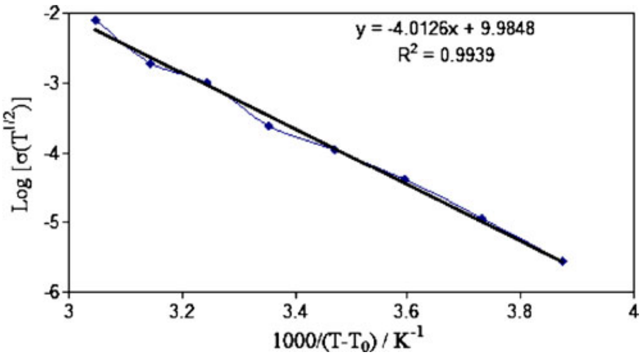


Fig. 3 Temperature dependence of ionic conductivity for sample SPE7

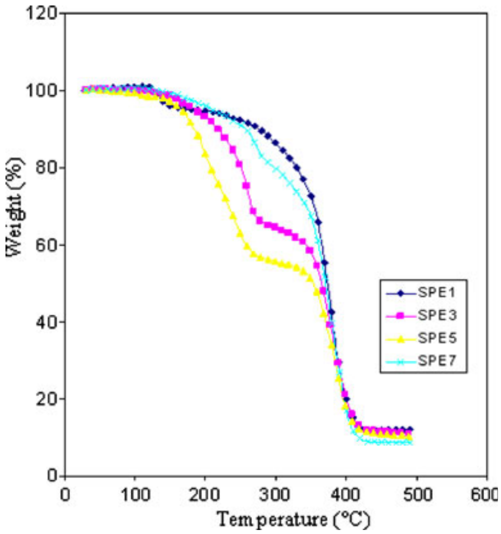


Fig. 4 TGA thermograms for SPE1, SPE3, SPE5 andSPE7

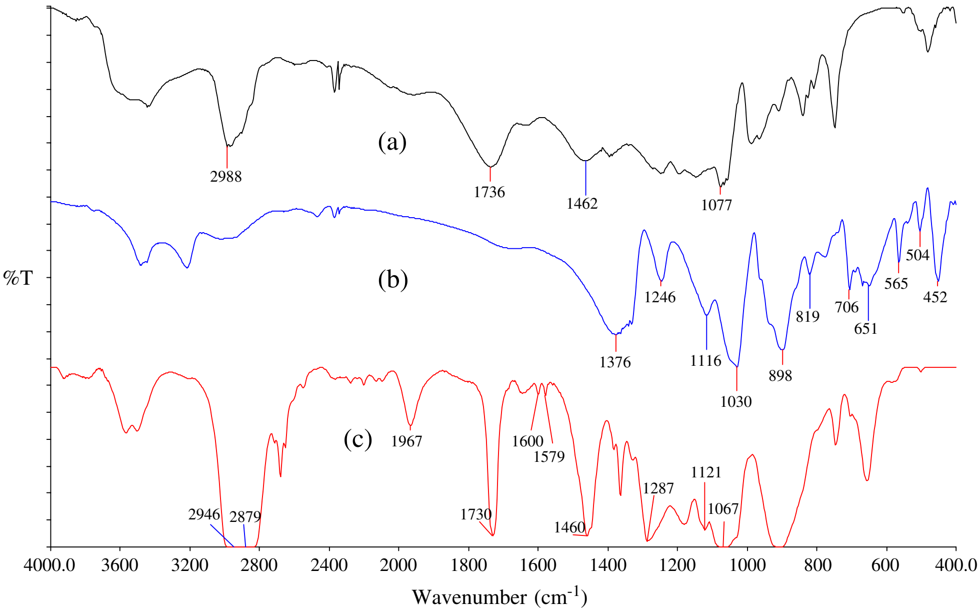
Temperature-dependent conductivity studies

The temperature dependent conductivity of SPE7 was investigated at the temperature range of 303–373 K. The conductivity of the plasticized polymer electrolyte increased gradually with temperature due to the increase of ionic mobility in the polymer electrolyte as shown in Fig. 3. This is because when the temperature increases, small spaces are created by pushing the polymer segment against the hydrostatic pressure applied by the neighboring atoms as the result of vibrational energy. Hence, free volume is produced and enables the ions, solvated molecules, or polymer segments to move through the resulting conductivity. The overall mobility of ion and polymer is influenced by the free volume around the polymer chain. Thus, increase in free volume due to the increase in temperature causes the increase in conductivity since it also increases the ion mobility and segmental mobility [7].

Table 2 Temperature and total weight loss percentage of first and second decomposition of various composition polymer films

Sample	First decomposition temperature (°C)	Second decomposition temperature (°C)	Weight loss at first decomposition (%)
SPE3	270.13	370.10	34.54
SPE5	230.37	370.29	42.48
SPE7	228.93	378.62	48.31
SPE9	218.99	378.91	41.52

Fig. 5 FTIR spectra for **a** pure PMMA, **b** $Li_2B_4O_7$, **c** pure DBP



When the ion transport is dominated by the mobility of the solvent molecules the conductivity will correlate with Vogel–Tamman–Fulcher (VTF) equation:

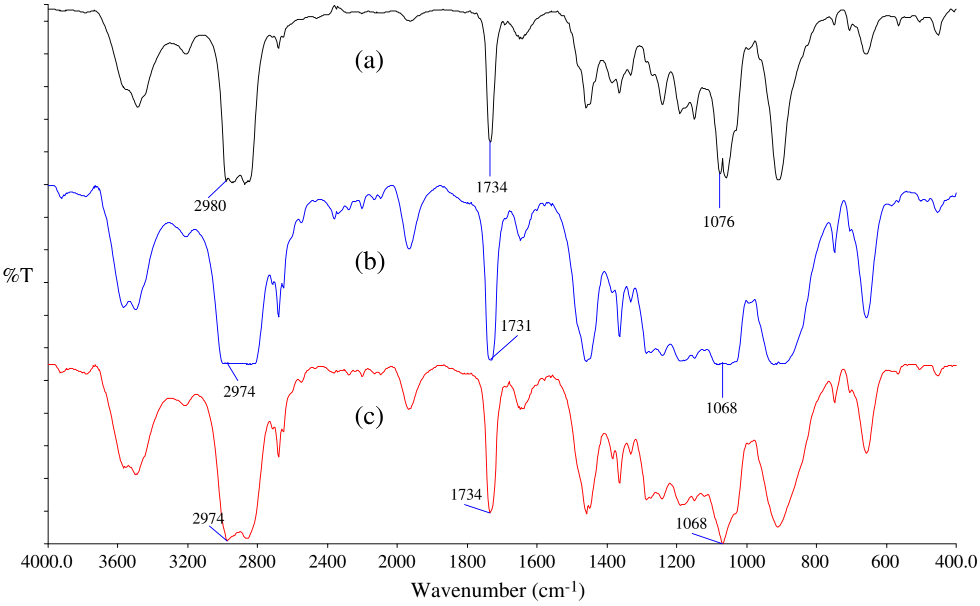
$$\sigma(T) = A/T^{1/2} \exp[-B/k(T - T_0)]$$

where A is the pre-exponential factor, B is the pseudo-activation energy for conduction, k is the Boltzmann constant and T_0 is the equilibrium glass transition. The temperature-dependent conductivity can be fitted with VTF equation very well as shown in Fig. 3. The VTF equation describes transport properties in a viscous matrix. It suggests that the ion moves through the plasticizer-rich phase [23]. In conclusion, the increase in temperature will affect the ion mobility and segmental mobility in the system. This assists ion transport and virtually compensates for the retarding effect of the ion cloud and causes a higher conductivity [24].

TGA analysis

The significant weight loss which begins at temperature above 100 °C is due to crystallization [25] (Fig. 4). The second weight loss is caused by the decomposition of the

Fig. 6 FTIR spectra for **a** SPE1, **b** SPE5, **c** SPE7



polymer electrolyte. The first and second decomposition temperature and the weight loss at the first decomposition temperature for SPE3, SPE5, SPE7 and SPE9 are listed in Table 2.

The results indicate that as plasticizer content increases, the weight loss at first decomposition temperature of the polymer films also increases. The stability of the polymer films with higher plasticizer content decreases due to the decline of T_g. This, as a result, softens the polymer backbone and causes increase in its segmental motion which allows easier flow for ions through the material when there is an applied electric field [26, 27]. High thermal stability of the polymer films will restrict the movement of ions, hence when plasticizer content of the polymer films increases, the thermal stability of the polymer films decreases.

From TGA analyses, the least stable polymer film is found to be SPE7 with a weight loss at first decomposition of 48.31%. The ionic conductivity is maximum for SPE7 as evident from the fact that in the least stable polymer film, there is no restriction for ion movement, hence giving rise to high ionic conductivity [24].

FTIR studies

FTIR spectroscopy is a powerful tool for identifying the nature bonding and different functional groups present in a sample by monitoring the vibrational energy levels of molecules, which are essentially the fingerprint of different molecules [28]. The FTIR spectra of pure PMMA, lithium tetraborate ($Li_2B_4O_7$) and DBP are shown in Fig. 5a, b and c, respectively.

From FTIR spectra in Fig. 5a, C–H stretching mode can be observed at 2,988 cm^{-1}, C=O asymmetric stretching mode at 1,736 cm^{-1}, and CH_3 stretching mode at 1,462 and 1,077 cm^{-1} are assigned to O–CH_3 stretching vibrations in pure PMMA [29]. Figure 5b shows that the absorption peaks at 1,376 and 1,246 cm^{-1} are allocated to B–O (B) stretching vibration of BO_3 triangle in $Li_2B_4O_7$. The absorption peaks at 1,116, 1,030, 898, 819 and 706 cm^{-1} are given to B–O (B) stretching vibration of BO_4 tetrahedral and the absorption peaks at 651, 565, 503 and 447 cm^{-1} are assigned to O-B-O deforming vibration of BO_4 tetrahedral in $Li_2B_4O_7$ [29]. Figure 5c illustrates the spectrum of DBP. C–H stretching mode can be observed at 2,946 and 2879 cm^{-1}, C=O asymmetric stretching mode at 1730 cm^{-1}, C=C stretching mode at 1600 cm^{-1}, CH_3 stretching mode at 1,462, 1,121 and 1,067 cm^{-1} are assigned to O–CH_3 stretching vibrations in pure DBP.

Complexation may shift the polymer cage peak frequencies. FTIR would be sensitive both in situations where complexation has occurred in crystalline or amorphous phase [30]. The characteristic peaks of pure PMMA at 2,988, 1,736 and 1,077 cm^{-1} are shifted to 2,980, 1,734 and 1,076 cm^{-1} for SPE1, 2,974, 1,732 and 1,068 cm^{-1} for SPE5 and 2,974, 1,734 and 1,068 cm^{-1} for SPE7, respectively, in Fig. 6. The cause of these peaks shifting is due to the complexation occurring between PMMA and $Li_2B_4O_7$.

In addition, some new peaks at 2,201 and 1,967 cm^{-1} are also observed which are not present in the pure PMMA and $Li_2B_4O_7$ spectrum. The changes in position of some PMMA-related peaks along with the appearance of some new peaks show that complexation had taken place [28].

The FTIR spectra of the samples containing DBP (SPE5 and SPE7) in the polymer–salt complexes are similar to that of the unplasticized polymer–salt complexes (SPE1). However, the C=O bands in DBP (1,730 cm^{-1}) seem to have overlapped and broadened. The broadening of the C=O band in the plasticized polymer salt complexes indicated that the plasticizer just interacts physically with the polymer and salt. No chemical reaction occurred between the plasticizer and polymer or between the plasticizer and the salt [28].

Conclusion

The composition and temperature dependence of conductivity and electrical relaxation behaviour of the films have been examined. The highest conducting sample was SPE7 with a conductivity of 1.58×10^{-7} Scm^{-1}. The plasticizer acts as a conductivity enhancer by reducing the T_g of the polymer complexes and increasing the segmental motion of the polymer chain. Temperature dependence studies indicate that the ion conduction follows the VTF rule in which the ion transport in polymer electrolytes is correlated with polymer segmental motion. In addition, FTIR studies confirm the interaction between pure PMMA, $Li_2B_4O_7$ and DBP. TGA studies showed that sample SPE7 is the most unstable polymer film with a weight loss of 48.31%. The stability of the polymer films will influence the conductivity of the polymer films by affecting the movement of ions.

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