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Influence of lithium ions on structural and conductivity studies of composite electrolyte consisting of PVC and PMMA

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The general idea of dispersion of fine ceramic particles in moderate ionic conductors is not new. In 1973, Liang reported the enhancement of the Li^+ conductivity in LiI by addition of fine Al_2O_3 particles [1]. This is a two-phase system with coexistence of an insulating oxide and a moderate ion conductor. Recently, lithium ion conductive polymers and oxide heterogeneous composites have received much attention as the electrolyte in lithium secondary batteries and have been successfully employed to improve the mechanical and the interfacial [2] properties of complexes of a lithium salt with poly (ethylene oxide) (PEO). Furthermore, observations of conductivity enhancement following the addition of ceramic fillers have been reported [3]. Studies on the morphologies and the ionic conductivities of the plasticized polymer electrolyte and the effect of the morphology on the characteristics of the ionic conduction are reported [4]. The importance of PVC/PMMA blend polymer electrolytes and their electrochemical properties have been reported, in which PVC acts as a phase-separated mechanical rigid network that provides the desired mechanical strength to be polymer films.

In our study, ZrO_2 dispersed in the electrolyte has been introduced to improve both electrical and mechanical properties of electrolyte films. In fact a 5 wt% of ZrO_2 particle size 21.5 μm increases the conductivity of a PVC-PMMA-Li_2SO_4-DBP film by as much as three orders of magnitude.

All electrolytes were prepared by forming slurry with the appropriate amounts of polymers, plasticizer and salt in anhydrous tetrahydrofuran (THF) and casting as films using a casting technique method as reported earlier [5]. FTIR measurements were made in the range 4000–400 cm^{-1} using a Perkin-Elmer-Paragon 500 Grating IR spectrometer. The simultaneous thermal analysis systems of thermal analyser model STA 1500, PL Thermal Sciences, (UK), were used in the present study. The bulk electrical conductivities of the polymer complex were evaluated from the impedance plots in the temperature range 304–373 K using a Keithley 3330 LCZ meter. The plots were recorded in the frequency range 40 Hz–100 kHz with signal amplitude of 10 mV.

The FTIR spectra of the starting materials PVC, PMMA, Li_2SO_4, DBP, ZrO_2 and polymer complexes are shown in Fig. 1. It shows the bands more characteristic of the spectrum in the region of 600–700 cm^{-1}, corresponding to C—Cl stretching vibrations in Fig. 1a. These bands are of complex origin and depend on the conformational structure of the polymer and on the spatial position of the atoms surrounding the C—Cl bonds [6]. Two medium CH_2 deformation vibration bands are observed at 1489 and 1436 cm^{-1} in PVC. The 961 and 956 cm^{-1} bands are assigned to the weak trans CH wagging and the 669 and 660 cm^{-1} bands are assigned to the cis CH wag vibration in pure PVC. If a vinyl group is conjugated to a trans CH=CH group, the CH wag vibrations of the two groups can interact also. C=C stretching vibration at 1654 cm^{-1} of pure PVC, which is split up into 1681 and 1651 cm^{-1} (Fig. 1g) in the polymer complexes.

Fig. 1b, for pure PMMA contains a carbonyl group, yielding a υ (C=O) stretching mode at 1734 cm^{-1}. Hydrogen bonding of the C=O groups of PMMA, for example, would lead to a shift to lower frequencies of this mode. In PMMA, which is saturated polymeric ester, the C=O symmetrical stretching frequency gives rise to an intense, a very strong and a sharp peak at 1734 cm^{-1} [7]. Pure PMMA shows a strong absorption band at 1149 cm^{-1}, ascribed to the asymmetric stretching vibration of the C—O—C bond {υ_a (C—O—C)} whereas the latter arises due to υ (C—O) of the OCH_3 group. The FTIR spectrum of the plasticizer DBP (Fig. 1c) shows the typical doublet of the phthalates at 1560–1600 cm^{-1}. The bands corresponding to the aromatic and aliphatic C—H bonds can also be observed. The peak at 1599 cm^{-1} is assigned to C=C stretching vibration in DBP.

The region from 1600 to 2700 cm^{-1} has broadened (Fig. 1f, g and i), which is also an indication of complexation. The out-of-phase or asymmetric CH_3

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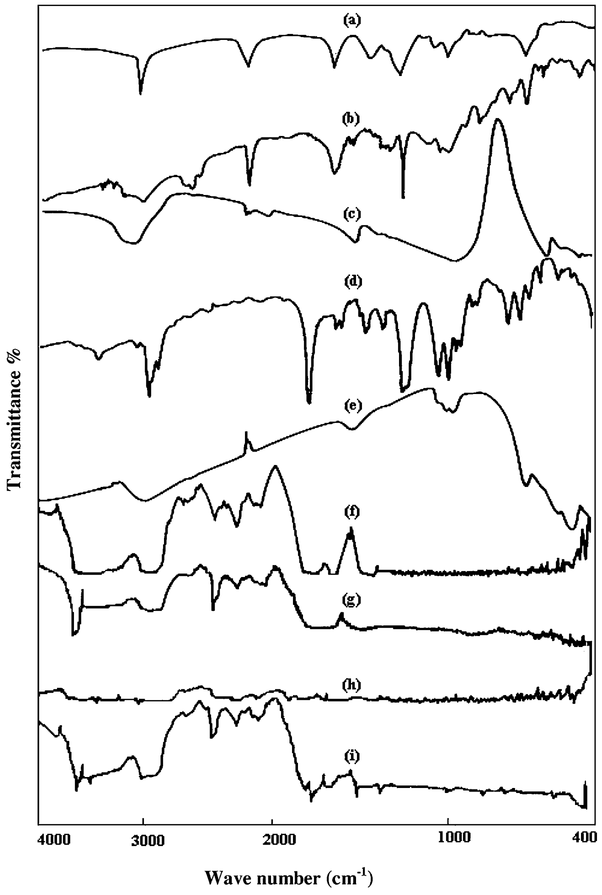

Figure 1 FTIR plots for PVC, PMMA, Li_2SO_4, DBP, ZrO_2 and the complexes: (a) PVC, (b) PMMA, (c) Li_2SO_4, (d) DBP, (e) ZrO_2 polymer complexes with (f) 0, (g) 5, (h) 10 and (i) 15 wt% of ZrO_2 to PVC-PMMA-Li_2SO_4-DBP.

stretching vibration in an aliphatic compound absorbs near 2960 ± 10 cm^{-1} and can be differentiated from the comparable CH_2 absorption near 2925 ± 10 cm^{-1} which has two or three times less intensity per group. The symmetrical, in phase CH_3 stretching vibration has a dipole moment change along the $C{-}CH_3$ bond, so this is not changed in orientation by CH_3 torsional rotation. The CH_3 group directly on an aromatic ring can rotate more easily about the $C{-}CH_3$ bond than it can in a $CH_2{-}CH_3$ group. The 2925–2865 cm^{-1} bands are not broadened and their peak heights are consistently prominent in methyl-substituted aromatics. The $C{=}C$ stretching frequency of PMMA appearing at 1654 cm^{-1} gets shifted to 1617 and 1681 cm^{-1} in the complex (Fig. 1f and g). From the above analysis, the complex formation has been confirmed.

DTA/TGA curves of PVC-PMMA-Li_2SO_4-DBP-ZrO_2 polymer complexes are shown in Fig. 2. An exothermic peak at ~42 °C is observed (Fig. 2a). In addition, an endothermic peak is also noted at ~90 °C, which may be attributed to the moisture. In addition an endothermic peaks has been noted at ~70 °C of 5% in Fig. 2b. A broad exothermic peak is observed from ~200 to ~406 °C, in the DTA curve of Fig. 2b. An endothermic peak is observed at ~105 and ~100 °C in Fig. 2c and d. In the TGA curve, the weight decreases gradually above around ~200 °C (Fig. 2b). This agrees with the DTA results. These results indicate that the sample is stable up to about ~200 °C before pyrolysis starts. One of the most stable liquid electrolytes is the EC/PC system [8], which decomposes at ~200 °C. This shows that there is no difference in the thermal stability between PVC-PMMA-Li_2SO_4-DBP-ZrO_2 polymer electrolytes and EC/PC liquid electrolytes.

Film S2 [5 weight ratio of ZrO_2 to PVC-PMMA-Li_2SO_4-DBP (7.5-17.5-8-67 mol%)] has the conductivity value of 2.47×10^{-7} S cm^{-1} at 304 K, which is found to be the maximum value (Table II). Weight losses are estimated as 1 and 2% at 100 and 140 °C respectively for the film S2 (Table I). This weight loss is found to be minimum among the five compositions

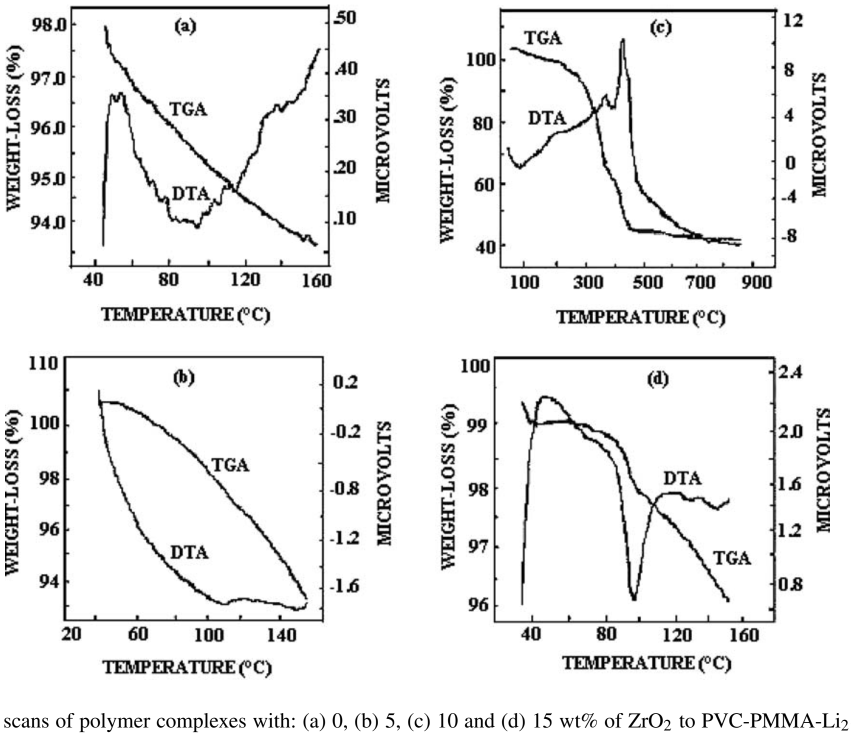

Figure 2 DTA and TGA scans of polymer complexes with: (a) 0, (b) 5, (c) 10 and (d) 15 wt% of ZrO_2 to PVC-PMMA-Li_2SO_4-DBP (7.5-17.5-8-67 mol%).

TABLE I Conductivity values of PVC-PMMA-Li_2SO_4-DBP-ZrO_2 polymer electrolytes

Sample	wt% of ZrO_2 to PVC-PMMA-Li_2SO_4-DBP	From TGA graph Weight loss% 100 °C	140 °C
S1	0	∼2.9	∼6
S2	5	∼4.75	∼5.5
S3	10	∼2.4	∼5
S4	15	∼1	∼2

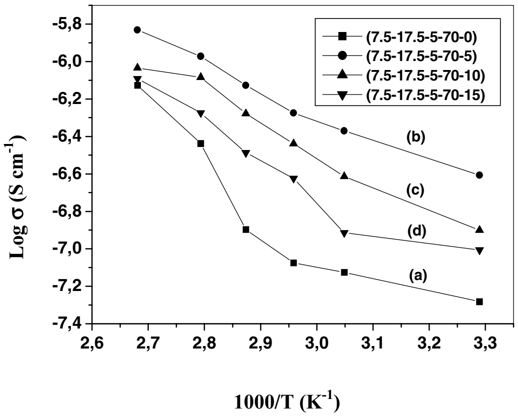

Figure 3 Arrhenius plot of log conductivity against reciprocal temperature for PVC-PMMA-Li_2SO_4-DBP-ZrO_2 polymer complexes: polymer complexes with (a) 0, (b) 5, (c) 10 and (d) 15 wt% of ZrO_2 to PVC-PMMA-Li_2SO_4-DBP.

studied. Hence the polymer electrolyte film S2 (5 wt% of ZrO_2 to PVC-PMMA-Li_2SO_4-DBP (7.5-17.5-8-67 mol%)) is found to be superior among the five films studied considering both the thermal stability and conductivity values.

The ionic conductivity for PVC-PMMA-Li_2SO_4-DBP complex films containing various compositions of ZrO_2 are obtained in the temperature range 304–373 K and are tabulated in Table II. The concentrations of ceramic filler are optimized through ionic conductivity measurements. The conductivity values for PVC-PMMA-Li_2SO_4-DBP-ZrO_2 systems are found in the range 10^{-8}–10^{-7} S cm^{-1} at 304 K which is comparable to the values reported [4] for various PVC/PMMA blends at 293 K.

The temperature dependences of electrical conductivity of the polymer blends are as shown in Fig. 3. The overall features of the Arrhenius plot are quite similar for the electrolyte systems in that no linear dependence could be obtained which seems to suggest that ion conduction follows the Williams-Landel-Ferry (WLF) mechanism [9]. In other words, the non-linearity indicates that ion transport in polymer electrolytes is dependent on polymer segmental motion [10]. Thus, the results may be more effectively represented by the empirical Vogel-Tamman-Fulcher (VTF) equation [11]:

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

where A and B are constants and T_g 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 ionic conductivity suggests that the ion moves through the plasticizer-rich phase. Because the conducting medium, i.e., plasticizer-rich phase, involves the plasticizer, the salt and PMMA, the characteristics of the viscous matrix are brought out.

The conductivity increases with the increase in concentration of ZrO_2 and shows a maximum value of 2.48×10^{-7} S cm^{-1}, corresponding to the sample with a 5 wt% of ZrO_2 to PVC-PMMA-Li_2SO_4-DBP polymer complex. The conductivity of the polymer electrolyte systems bereft of ZrO_2 is found to be 0.52×10^{-7} S cm^{-1} at 304 K. The initial rise in conductivity is due to the availability of conducting ions supplied by the PVC-PMMA-Li_2SO_4-DBP-ZrO_2 polymer complexes. In the region of high ZrO_2 concentration (10 wt%), it is found that the conductivity decreases.

A decrease in ionic conductivity was observed at high loadings of ceramic fillers. The appearance of a maximum in ionic conductivity for both the treated and untreated ZrO_2 indicates that there are two competing effects at play. At low ceramic filler loadings, the conductivity increases with ZrO_2 content and this may be due to the increase in the amount of conductive layers. At higher ceramic filler concentrations, phase discontinuities and dilution effects will predominate instead and result in low conductivities.

In conclusion, polymer electrolyte films consisting of PVC-PMMA-Li_2SO_4-DBP-ZrO_2 of different compositions have been prepared and subjected to a detailed structural characterization, thermal studies and ionic conductivity studies as follows:

FTIR studies suggest changes in the environment of functional groups complex formation. Frequency assignments for C═C stretching, CH_2 deformation, O─CH_3 stretching and C═O stretching vibrations are made for the polymer electrolyte systems. This analysis

TABLE II TGA results in PVC-PMMA-Li_2SO_4-DBP-ZrO_2 polymer complexes PVC-PMMA-Li_2SO_4-DBP (7.5-17.5-5-70 mol%)

Sample	wt% of ZrO_2 to PVC-PMMA-Li_2 SO_4-DBP	σ values (×10^{-7} S cm^{-1}) 304 K	328 K	338 K	348 K	358 K	373 K
S1	0	0.52	0.75	0.84	1.27	3.65	7.47
S2	5	2.48	4.26	5.32	7.47	10.65	14.77
S3	10	1.26	2.43	3.64	5.27	8.24	9.24
S4	15	0.99	1.22	2.38	3.26	5.32	8.12

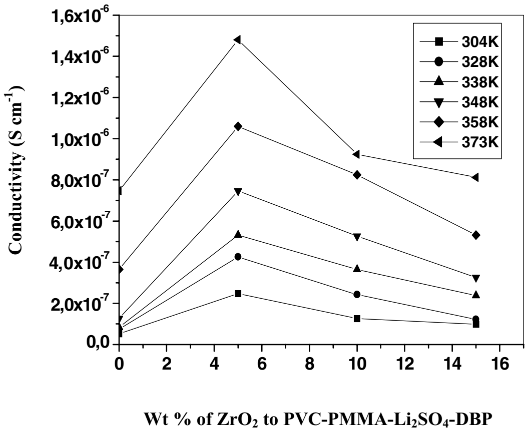

Figure 4 Variation of conductivity of PVC-PMMA-Li$_2$SO$_4$-DBP system as a function of ZrO$_2$ concentration at different temperatures.

show that the complex formation has been confirmed. The thermal stability was measured as a function of decomposition temperature and weight loss calculations. Also, it is understood that the addition of ZrO$_2$ has its impact over high temperature solid-state cells by the way of improving thermal stability and conductivity. The overall features of the Arrhenius plots are similar for the electrolyte systems that no linear dependence could be obtained seem to suggest that ion conduction follows the William-Landel-Ferry mechanism. The maximum value of room temperature conductivity is 2.48×10^{-7} S cm^{-1} for sample with a 5 wt% of ZrO$_2$ in the PVC-PMMA-Li$_2$SO$_4$-DBP (7.5-17.5-5-70 mol%) polymer electrolyte system. The effect of addition of ZrO$_2$ to the polymer complex on its conductivity value has been studied.

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