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# Preparation and characterization of lithium ion conducting polymer electrolytes based on a blend of poly(vinylidene fluoride-co-hexafluoropropylene) and poly(methyl methacrylate)

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## Abstract

Ion conducting polymer electrolytes composed of poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP), poly(methyl methacrylate) (PMMA) and lithium triflate (LiTf) were prepared using the solution casting method. Structural change and complex formation in the blend electrolyte systems were confirmed from the X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) studies. Thermal properties of the samples were investigated by the differential scanning calorimetry (DSC) technique. The ionic conductivity of these polymer electrolytes was studied by impedance spectroscopy at various temperatures ranging from 303–393 K. The results reveal that the ionic conductivity of the polymer blend electrolytes depends on the PVdF-HFP:PMMA composition as well as the temperature. Maximum room temperature conductivity of  $7.4 \times 10^{-5} \text{ S cm}^{-1}$  was achieved with 22.5 wt.%

PMMA. The blending of PVdF-HFP with PMMA improved the thermal stability and ionic conductivity of the polymer electrolyte. Estimated transference numbers suggest the charge transport is predominantly ionic.

Keywords: Materials science

## 1. Introduction

Polymer electrolytes have been extensively researched due to the possibility of their commercial use in a variety of electrochemical devices such as electrochemical cells, rechargeable batteries, sensors and supercapacitors [1, 2, 3, 4, 5, 6, 7]. However, in order polymer electrolytes to be used in lithium ion batteries, further work is still needed to improve their physical and electrical properties. In their efforts to find polymer electrolytes with adequate ionic conductivity and thermal stability at ambient and sub-ambient temperatures, researchers have synthesized and characterized different polymer-salt complexes [8, 9, 10, 11, 12, 13, 14, 15]. Of all the polymer systems investigated, poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO), complexed with various suitable salts such as  $\text{LiPF}_4$ ,  $\text{LiClO}_4$  and  $\text{LiBF}_4$  are the most widely employed systems. Other polymer hosts under extensive investigations include poly(methyl methacrylate) (PMMA), poly(acrylonitrile) (PAN), poly(vinyl chloride) (PVC), poly(vinyl alcohol) (PVA), poly(vinyl acetate) (PVAc) poly(vinylidene fluoride) (PVdF) and, most recently, poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP).

In recent years, polymer blending has attracted a great deal of interest due to its simplicity of preparation and ease of control of its properties [16]. The possibility of using polymer blend electrolytes for rechargeable lithium batteries was explored by some researchers [17, 18, 19, 20]. Reports on lithium ion conducting PVdF-HFP based blend electrolytes have indicated that blending not only results in enhanced conductivity but it also improves the mechanical property of the electrolytes. Among the blend systems studied are PVDF-HFP/PVC/ $\text{LiClO}_4$  [17], PVDF-HFP/PMMA/ $\text{LiClO}_4$  [18], PVDF-HFP/hydroxypropyl methyl cellulose (HPMC)/ $\text{LiMn}_2\text{O}_4$  [19] and PVDF-HFP/PVAc/ $\text{LiClO}_4$  [21].

In the present study, ion conducting PVdF-HFP:PMMA blends consisting of lithium triflate ( $\text{LiTf}$ ) as dopant salt were prepared to investigate the effect of PMMA concentration on structural, thermal and electrical properties of the polymer electrolyte. Polymer electrolytes composed of PVdF-HFP are expected to have good electrochemical stability and non-combustibility owing to the strong electron-withdrawing functional groups, (-C-F-), in the VdF units [22] and plasticity due to steric hindrance provided by  $-\text{CF}_3-$  pendant group in the HFP monomers [23]. That is, it has both a crystalline phase due to its VdF units and an amorphous phase due to its HFP monomers. The amorphous phase of PVdF-HFP

facilitates the trapping of a large amount of liquid electrolyte providing mobile cations more free volume and hence helping in enhancing ionic conductivity, whereas the crystalline phase acts as a structural support for the formation of free-standing polymer electrolyte film. Also, PVdF-HFP possesses advantageous inherent properties such as high dielectric constant ( $\epsilon = 8.4$ ) and low glass transition temperature. The high dielectric constant facilitates dissociation of salts, giving rise to a high concentration of charge carriers in the electrolyte and thus higher ionic conductivity. Therefore, PVdF-HFP is chosen as the host polymer in preparing the polymer blend systems in the present study.

PMMA is a methacrylic ester polymer which has a very high amorphicity and good transparency. PMMA was chosen as the blending agent by taking into consideration that the presence of amorphous phase is very important for improving conductivity at low temperatures. Its sufficient mechanical strength and compatibility with PVdF-HFP is also another advantage to consider it as a suitable blending agent.

The blend films were characterized using XRD, FTIR, SEM and DSC. Conductivity and ionic transference number measurements were carried out for the blend films of varying PVdF-HFP:PMMA compositions.

## 2. Experimental

PVdF-HFP (Average molecular weight  $4 \times 10^5$  g/mol, Aldrich, USA) and PMMA (Average molecular weight  $1.2 \times 10^5$  g/mol, Aldrich, USA) were dried at  $70^\circ\text{C}$  and LiTf (Aldrich, USA) was dried at  $100^\circ\text{C}$  under vacuum for about 10 h before use with the aim of eliminating any moisture. The solvent anhydrous tetrahydrofuran (THF) was used as received. All polymer electrolyte films were prepared by the solution casting technique. The mixture of the appropriate quantities of the polymers and the salt was dissolved in THF by continuous magnetic stirring for several hours. The resulting homogenous solution was then cast as film onto a clean petri dish to allow THF to evaporate slowly at room temperature. Then mechanically stable and free-standing films were formed. The films were further dried in a temperature-controlled hot-air oven at  $60^\circ\text{C}$  for 5 h to remove any traces of THF. The weight percentage of the salt was maintained at a fixed amount of 25 wt.%. The PVdF-HFP:PMMA:LiTf compositions used during the film preparation are presented in Table 1.

X-ray diffraction (XRD) studies of the electrolyte films were carried out using PHILIPS X'Pert diffractometer, operating at 40 kV, in the glancing angles ranging from  $2\theta = 10^\circ$  to  $80^\circ$ . The FTIR spectra were recorded using IRPrestige-21 (Shimadzu) spectrophotometer over the wavenumber range of  $4000\text{--}400\text{ cm}^{-1}$ . The films were examined under scanning electron microscope (SEM) (ZEISS EVO18) for their morphological properties. Thermal analysis was carried out for

**Table 1.** Composition of PVdF-HFP:PMMA:LiTf complexes.

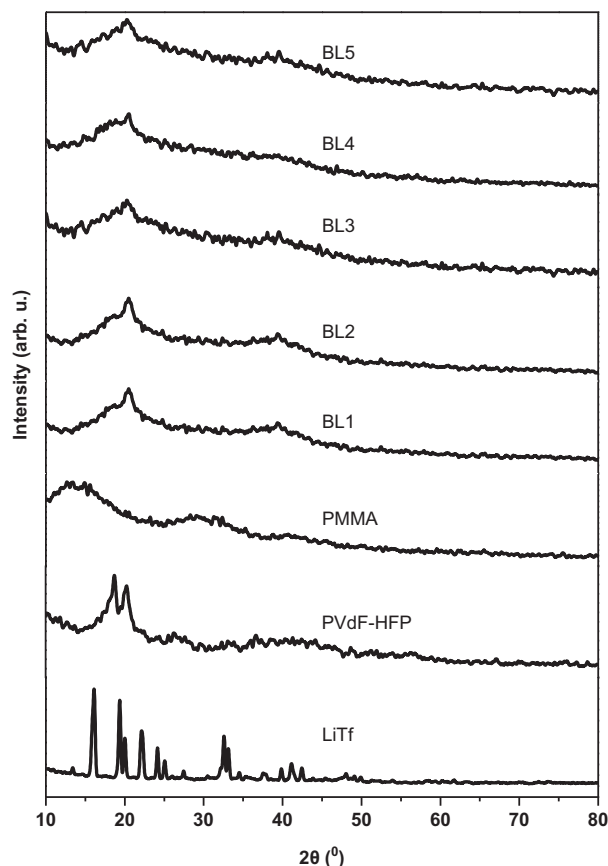
Sample code	PVdF-HFP (wt.%)	PMMA (wt.%)	LiTf (wt.%)
BL1	67.5	7.5	25
BL2	60	15	25
BL3	52.5	22.5	25
BL4	45	30	25
BL5	37.5	37.5	25

the samples using Q20 differential scanning calorimeter at a heating rate of 10 °C/min. Conductivity analysis of the various electrolyte samples was carried out using Hioki 3532 LCR HiTester in the frequency range 42Hz to 1 MHz. The ionic conductivity ( $\sigma$ ) of each sample, at various temperatures between 303 and 393 K, was calculated from bulk resistance measurements obtained from impedance plots. Lithium ion transference number of the polymer blend electrolytes was determined by DC polarization technique [24]. The electrolyte film was coated on both faces with conductive silver paste so that it makes good contact with the stainless steel (SS) electrodes. A small DC potential ( $\sim 1$  V) was applied across the SS/Electrolyte/SS configuration to initiate flowing of current through the system. Consequently, the DC current passing through the electrode-electrolyte system was monitored as a function of time until saturation was reached. Transference number was determined at room temperature (303 K).

### 3. Results and discussion

#### 3.1. XRD analysis

In order to investigate the phase nature of the blend films, XRD analysis was performed. The XRD patterns of pure LiTf, PVdF-HFP, PMMA and PVdF-HFP:PMMA:LiTf complexes are presented in Fig. 1. The figure shows that high diffraction intensity, sharp peaks of pure LiTf are observed at several values of  $2\theta$ . It can be noted from the XRD patterns of the samples in Fig. 1 (BL1–BL5) that the sharp crystalline peaks corresponding to LiTf are absent in all the polymeric blends, confirming that no separate phase of the lithium salt exists in the blends. This indicates a complete complexation has occurred between the polymer blend and the lithium salt. The diffractogram of pure PVdF-HFP (Fig. 1) reveals two well distinguished peaks at  $2\theta = 18.7^\circ$  and  $20.2^\circ$ . These peaks indicate the semicrystalline nature of pure PVdF-HFP [24]. Moreover, the predominantly amorphous nature of PMMA can be observed from the XRD pattern of pure PMMA in Fig. 1. However, it is observed that upon blending of both polymers and complexing them with LiTf, the two Bragg peaks of PVdF-HFP disappear and a

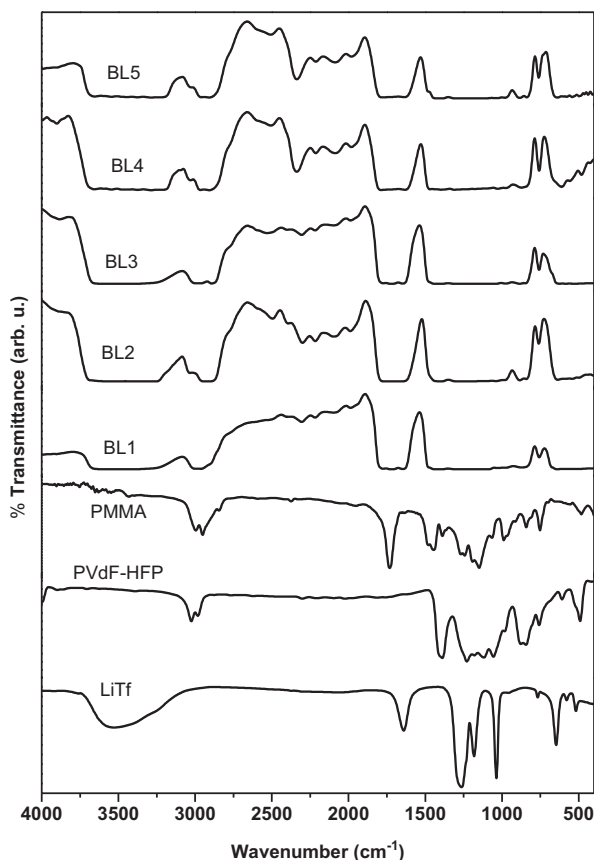


**Fig. 1.** XRD patterns of LiTf, PVdF-HFP, PMMA and PVdF-HFP:PMMA:LiTf complexes.

new broadened peak with lowered intensity is observed in the blend system. This suggests an increase of amorphicity of the polymeric blend films by addition of PMMA and LiTf and the occurrence of complexation between PVdF-HFP, PMMA and LiTf.

### 3.2. FTIR spectral analysis

Fig. 2 shows the FTIR spectra of pure PVdF-HFP film, pure LiTf powder, pure PMMA powder and blend polymer electrolyte films containing different concentrations of PMMA in the wave number range  $4000$  to  $400$   $\text{cm}^{-1}$ . The absence of the absorption bands  $976$ ,  $796$ ,  $760$  and  $530$   $\text{cm}^{-1}$ , which are all associated to the  $\alpha$ -phase crystals of the VdF units [25, 26, 27, 28], in the PVdF-HFP:PMMA blends indicates that the addition of PMMA to PVdF-HFP results in reduction of crystallinity of PVdF-HFP. The absorption bands of PVdF-HFP detected at  $1383$  and  $490$   $\text{cm}^{-1}$  are assigned to the wagging vibrations of  $\text{CH}_2$  and  $\text{CF}_2$  groups [29, 30], respectively. These peaks were observed to shift to  $1398$  and  $482$   $\text{cm}^{-1}$ , respectively, in the blend polymer electrolytes.



**Fig. 2.** FTIR spectra of LiTf, PVdF-HFP, PMMA and PVdF-HFP:PMMA:LiTf complexes.

The strong peaks of PMMA detected at 1445, 1244, 1150 and 989  $\text{cm}^{-1}$ , which are assigned to O-CH<sub>3</sub> bending, C-C-O bending, C-O-C asymmetric stretching and CH<sub>2</sub> wagging [18], respectively, were all absent in the blends. The IR absorption peaks for PMMA at 2951 (CH symmetric stretching), 1732 (C=O asymmetric stretching [31]), 843 (C-O-C stretching) and 751  $\text{cm}^{-1}$  (CH<sub>2</sub> rocking [18]) shifted to 2918, 1718, 873 and 758  $\text{cm}^{-1}$ , respectively, due to the interaction between PVdF-HFP, PMMA and LiTf in the blend complexes. Moreover, new peaks were identified around 2500, 2305, 2214, 2090 and 1985  $\text{cm}^{-1}$  in the blends.

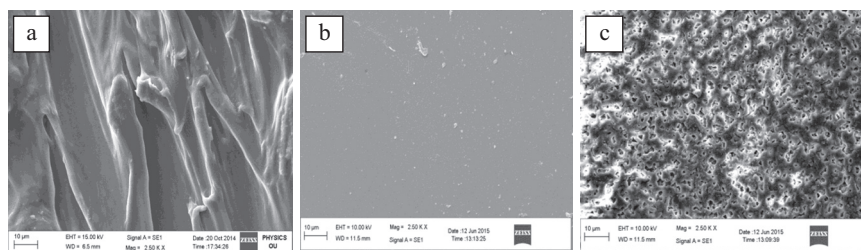
The absorption peak of LiTf at 1640  $\text{cm}^{-1}$ , corresponding to the characteristic peak of Tf<sup>-1</sup> [32], got shifted to 1635  $\text{cm}^{-1}$  in the polymer blend electrolytes. Most of the other peaks detected for LiTf at various frequencies were absent in the blend systems. The shifting and absence of IR bands of the pure polymers or the salt, as well as the appearance of new peaks in the PVdF-HFP:PMMA:LiTf blend systems suggest that the two polymers are compatibly mixed with each other and strongly interact with the dopant lithium salt.

### 3.3. Morphological studies

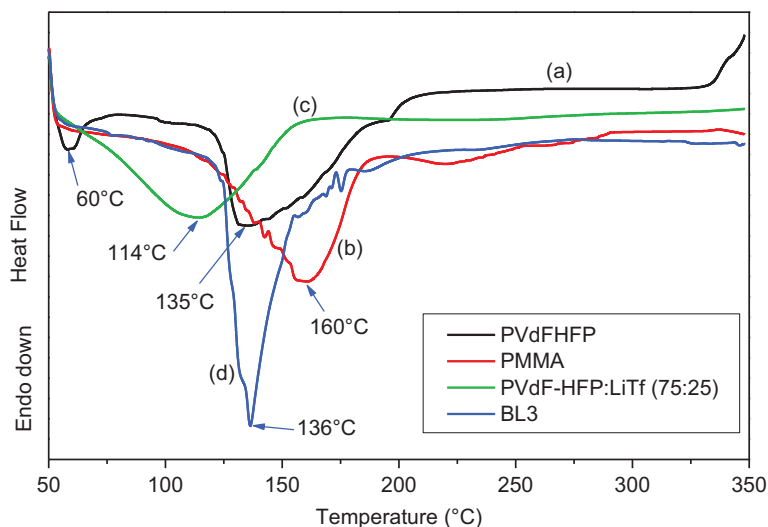
The morphological study of the blend which exhibited maximum conductivity has been carried out using the SEM. Fig. 3 shows the SEM images of PVdF-HFP, PMMA and PVdF-HFP:PMMA:LiTf (52.5:22.5:25 wt. %). As evident from the images, the surface morphology of PVdF-HFP is significantly modified due to the addition of PMMA and LiTf. Thus, no separate phases exist in the blend system indicating that PMMA can compatibly be blended with PVdF-HFP. It can also be seen from the SEM micrographs in Fig. 3(c) that the surface of PVdF-HFP:PMMA:LiTf film has numerous network of interconnecting microstructures as compared to that of pure PVdF-HFP and PMMA films in Fig. 3(a) and Fig. 3(b). It is, therefore, evident that the blending results in a completely different morphological structure. These interconnecting structures are formed as a result of phase separation between the polymers and the solvent during evaporation. The microstructures can help the lithium ions hop easily in the blend system and the electrolyte absorb more liquid, and hence they are responsible for improving ionic conductivity of the polymer blend electrolyte.

### 3.4. DSC studies

Thermal property of the polymer blend electrolyte with the highest conductivity was analyzed using DSC measurements. Fig. 4 shows the DSC curves of pure PVdF-HFP, pure PMMA, PVdF-HFP:LiTf (75:25 wt.%) and the highest-conducting PVdF-HFP:PMMA:LiTf film (BL3). PVdF-HFP exhibits a sharp endothermic peak at 135 °C [Fig. 4(a)], which is ascribed to its melting point. The endothermic peak of the curve in Fig. 4(b) at 160 °C corresponds to the melting point of PMMA. The melting temperature of PVdF-HFP was observed to shift to a lower temperature (114 °C) [Fig. 4(c)] by the addition of 25 wt.% LiTf. However, when the PVdF-HFP:LiTf complex is blended with PMMA, the endothermic peak obtained at 114 °C before blending is observed to re-shift towards a higher temperature of 136 °C. This can be observed from the DSC curve for BL3 in Fig. 4(d). This implies that the thermal stability of the salted PVdF-HFP electrolyte is improved significantly by blending it with PMMA. In addition, no exothermic



**Fig. 3.** SEM micrographs of (a) PVdF-HFP, (b) PMMA and (c) PVdF-HFP:PMMA:LiTf (52.5:22.5:25) (at 2500 × magnification).



**Fig. 4.** DSC curves of PVdF-HFP, PMMA, PVdF-HFP:LiTf (75:25) and PVdF-HFP:PMMA:LiTf (52.5:22.5:25) complex.

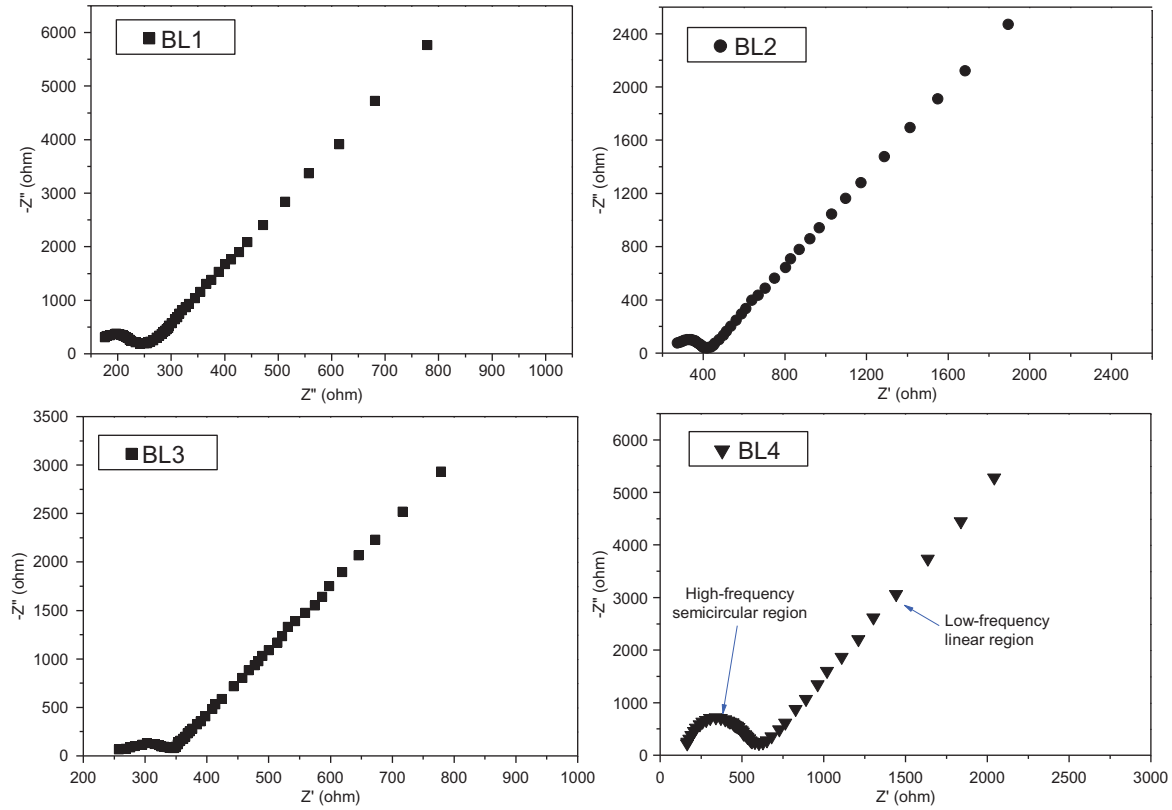
peaks were detected for the investigated polymer blend electrolyte, indicating that no decomposition takes place up to at least 350 °C. These results are interesting from device application point of view because wider thermal stability is desirable in polymer electrolytes for battery and fuel applications. The second small endothermic peak observed around 165–174 °C for the blend [Fig. 4(d)] is attributed to the melting point of the crystalline phase PVdF [33].

### 3.5. Conductivity studies

The electrical conductivity of blends of PVdF-HFP and PMMA complexed with LiTf was investigated in order to determine the optimal blend composition for maximum conductivity. The conductivity values were calculated using the equation  $\sigma = \frac{t}{AR_b}$ ,

where  $t$  is the thickness,  $A$  is the area, and  $R_b$  is the bulk resistance of the polymer electrolyte disc obtained from impedance plots. The electrolyte resistance was determined from the real axis intercept of the low frequency spur in the Nyquist plot for the polymer electrolytes. The impedance plots for the PVdFHFP:PMMA:LiTf blend films containing different PVdF-HFP:PMMA compositions (at room temperature) are shown in Fig. 5. The plots show two well-defined regions - semicircular region at high frequency range and linear region at low frequency range. The semicircular region in the high-frequency range is related to conduction process in the bulk of the blend complex and the linear region in the low-frequency range is attributed to the effect of blocking electrodes [34, 35].





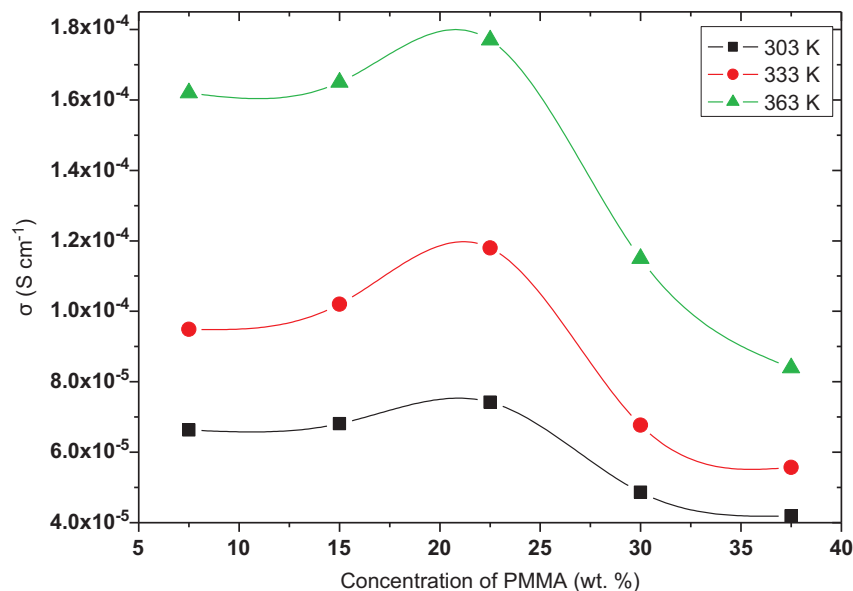
**Fig. 5.** Impedance spectra of PVdF-HFP:PMMA:LiTf complexes containing different PMMA concentrations at room temperature.

The room temperature conductivity data of the polymer blend electrolytes as a function of PMMA concentration are presented in Table 2. It is observed that the ionic conductivity initially increases with PMMA content up to its maximum value at 22.5 wt.% of PMMA. The maximum room temperature (303 K) ionic conductivity achieved for the polymer blend electrolyte comprising 22.5 wt.% of PMMA is  $7.4 \times 10^{-5} \text{ S cm}^{-1}$ . The increase in conductivity with PMMA content could be due to increase in amorphicity of the blend film during complexation (as witnessed by the XRD results). However, upon further increase of the concentration of the PMMA over 22.5 wt.%, the conductivity falls down. The ionic conductivity of PVdF-HFP:PMMA:LiTf blend electrolytes as a function of PMMA concentration at various temperatures is shown in Fig. 6.

The temperature dependence of conductivity was also investigated at various temperatures ranging from 303–393 K in order to understand the conductivity-temperature relationship of the polymer blend. Fig. 7 shows variation of ionic conductivity (in terms of  $\log \sigma$ ) versus reciprocal temperature of the polymer blends for 7.5, 15, 22.5, 30 and 37.5 wt.% of PMMA. The conductivity of all the blend systems is observed to increase with temperature. The logarithm of conductivity versus reciprocal temperature plots of the samples studied show nonlinearity, suggesting that the temperature-dependent ionic conductivity of the polymer blend electrolytes obeys the Vogel-Tamman-Fulcher (VTF) rule. Similar behaviour has been observed in other earlier reports on conductivity property of various polymer blend systems [16, 18, 23]. The observed increase in conductivity with temperature could be due to increased segmental motion of the polymer chains and mobility of ions in amorphous environment. This behaviour may be explained with the help of the free volume theory in polymers [36, 37]. With an increase of temperature, the rate of dissociation of the ionic salt and the thermal movement of the polymer chains increase, leading to higher ionic conductivity in the polymer blend complex.

**Table 2.** Ionic conductivity and transference number of PVdF-HFP:PMMA:LiTf complexes at room temperature (303 K).

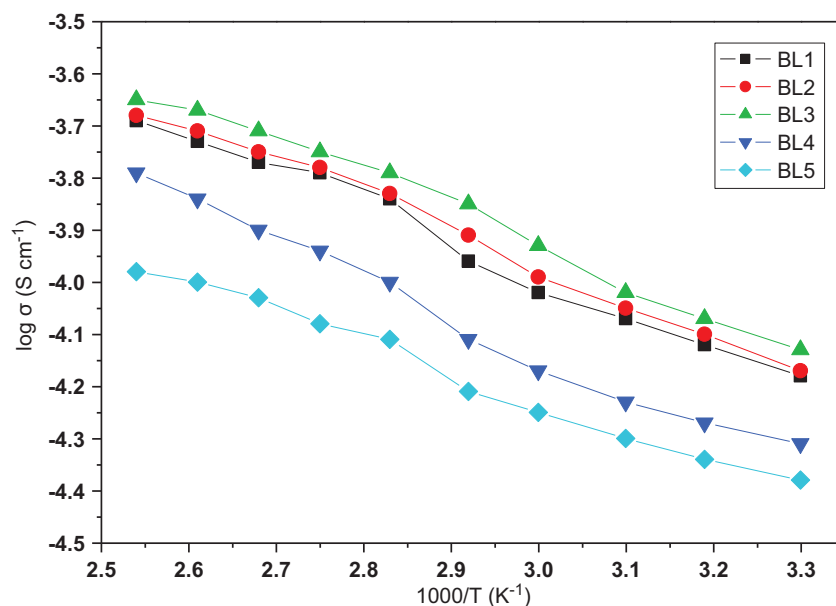
Sample code	Conductivity ( $\times 10^{-5} \text{ S cm}^{-1}$ )	$t_i$
BL1	6.6	0.84
BL2	6.8	0.88
BL3	7.4	0.86
BL4	4.9	0.86
BL5	4.2	0.85



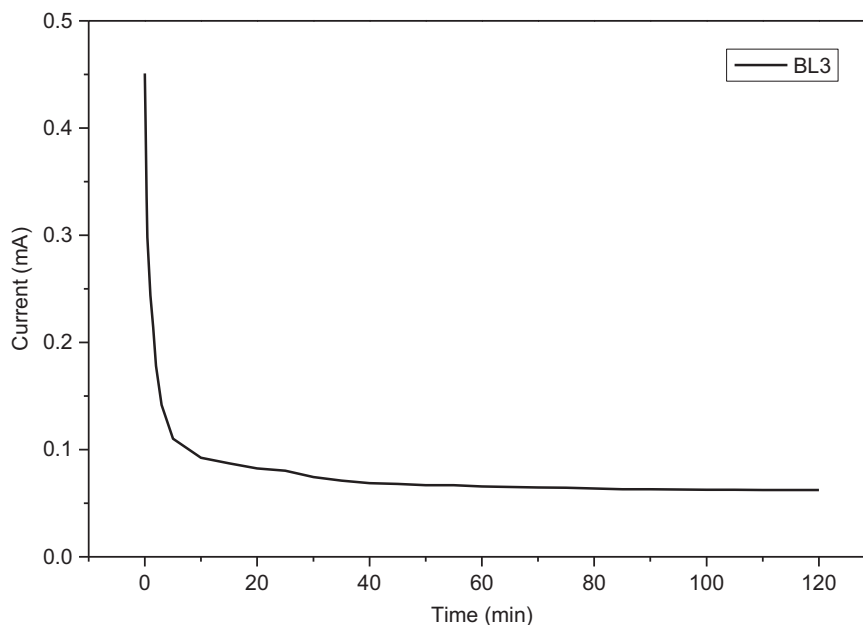
**Fig. 6.** Conductivity of PVdF-HFP:PMMA:LiTf complexes containing different PMMA concentrations at various temperatures.

### 3.6. Ionic transference number

The variation of DC electric current as a function of time was recorded over a time range of 120 min. Fig. 8 depicts the current versus time variation for the highest-conducting polymer blend electrolyte at room temperature (303 K). Using the



**Fig. 7.** Temperature dependence of ionic conductivity of PVdF-HFP:PMMA:LiTf polymer blend electrolytes containing different PMMA concentrations.



**Fig. 8.** Variation of DC current with time for PVdF-HFP:PMMA:LiTf (52.5:22.5:25).

initial total current  $I$  and final stabilized current  $I_e$  after polarization, the lithium ion transference number  $t_i$  of the various polymer blend electrolyte systems was estimated from the relationship,

$$t_i = \frac{I - I_e}{I}$$

The ionic transference number data for the blend polymer electrolytes are displayed in Table 2. The lithium ion transference numbers obtained are high (0.84–0.88) means that the charge contribution comes predominantly from the ions dissociated in the blends.

#### 4. Conclusions

Self-standing polymer blend electrolytes based on PVdF-HFP, PMMA and LiTf were successfully synthesized using the solution casting method. XRD, FTIR, SEM and DSC studies confirm that significant structural and morphological changes take place in the polymer blend electrolyte films upon addition of PMMA and LiTf to PVdF-HFP. The studies also suggest that interaction and complete complexation between the constituents occurred. The conductivity of the polymer blend electrolytes is observed to be dependent on the relative percentage of PMMA. Furthermore, the conductivity-temperature dependence of the blend films seems to exhibit the VTF behaviour. For all compositions, the ionic conductivity of the polymer electrolyte increases with temperature, which can be attributed to the expansion of the polymer matrices to produce free volume for enhanced segmental

movement of polymer chains and better mobility of carrier ions. Estimated ionic transference number measurements suggest that the conductivity in the blend systems is predominantly ionic.

## Declarations

### Author contribution statement

Merhawi A. Gebreyesus: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Y. Purushotham: Contributed reagents, materials, analysis tools or data.

J. Siva Kumar: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

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### Competing interest statement

The authors declare no conflict of interest.

### Additional information

No additional information is available for this paper.

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