

Short communication

Effect of salt concentration in poly(vinyl alcohol)-based solid polymer electrolytes

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Abstract

Polymer electrolytes comprising a blend of poly(vinyl alcohol) (PVA) and poly(methyl methacrylate) (PMMA) with different concentrations of LiBF_4 are prepared using a solvent-casting technique. The structure and complexation of the electrolytes are studied by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. The ionic conductivities of the electrolytes are measured in the temperature range 302–373 K. The maximum conductivity ($1.2886 \times 10^{-3} \text{ S cm}^{-1}$) is obtained for a polymer complex with 8 wt.% LiBF_4 . The thermal stability of this electrolyte is examined by thermogravimetric/differential thermal analysis (TG/DTA).

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Keywords: Polymer electrolytes; Poly(vinyl alcohol); Lithium tetrafluoroborate; Lithium-ion battery; Ionic conductivity; Thermal analysis

1. Introduction

Long-life, environmentally benign, low-cost and reliable batteries are required for many applications such as electric vehicles, computers, memory devices, sensors, reliable safe power sources, and portable electronic devices. Polymer electrolytes are promising candidates for rechargeable lithium batteries, fuel cells, electrochromic devices and sensors, due to their excellent thermal and mechanical stability, flexibility and processibility [1–3]. Indeed, the most recent development in lithium-ion battery technology is the replacement of the liquid electrolyte with a polymer membrane which is capable of operating both as a separator and as the electrolyte. The advantages of using solid polymer electrolytes (SPEs) are good compatibility with lithium metal, no leakage, low self-discharge, elastic relaxation under stress, easy processing, continuous production, and good electrical conductivity [4]. Investigations of polymer electrolytes have focused primarily on the enhancement of ionic conductivity at room temperature. Among the various methods to produce high ionic conduction, polymer blends are a valid and feasible approach. In this respect, studies have been conducted on the P(VdF-TrFE)/PMMA [5] and PVC/PMMA [6] systems (P(VdF-TrFE): poly(vinylidene

fluoride-co-trifluoroethylene); PVC: poly(vinyl chloride); PMMA: poly(methyl methacrylate)). In general, the miscibility of polymer blends requires a negative change in free energy.

Poly(vinyl alcohol) (PVA) is a polymer with a carbon chain backbone with hydroxyl groups attached to methane carbons. These OH-groups can be a source of hydrogen bonding and hence assist in the formation of polymer blends. Also, due to its high tensile strength and good abrasion resistance, the polymer is used as a binder, and in double-layer capacitors, electrochemical windows, etc. [7]. Kanbara et al. [8] studied the application of PVA in double-layer capacitors. Every et al. [9] reported that PVA complexed with lithium triflate system has a relatively high conductivity of about 10^{-8} to $10^{-4} \text{ S cm}^{-1}$. The conductivity can also be enhanced by blending PVA with another polymer.

Due to its good compatibility with other polymers, high resistance, non-tracking characteristics and surface resistance, PMMA is used in outdoor electrical and high-voltage applications [10]. Singh and Singh [11] studied the compatibility of PVA-PMMA polymer blends in solution by viscometric and ultrasonic techniques. In the present study, PVA-PMMA blend electrolytes have been prepared with four different concentrations of LiBF_4 . The salt LiBF_4 is chosen since it has a low lattice energy, viz. 699 kJ mol^{-1} [12]. Ethylene carbonate (EC) is used as a plasticizer due to its high dielectric constant (89.6 at 40°C) [13]. Plasticizers provide more mobile charge carriers and reduce the viscosity of the polymer matrix. The ionic conductivities

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of plasticised PVA–PMMA–LiBF₄ complexes are studied by means of the ac impedance technique. The influence of the salt concentration in the polymer blend complexes is investigated. The complexation and phase structure of the polymer complexes are studied by Fourier transform infrared (FTIR) and X-ray diffraction (XRD) analyses. The polymer electrolyte film with maximum conductivity is subjected to thermal studies and the results are discussed.

2. Experimental

Poly(vinyl alcohol) with an average molecular weight of 115 000 (BDH, England), PMMA with an average molecular weight of 120 000 (Aldrich, USA), LiBF₄ and ethylene carbonate (E-Merck, Germany) are used in the present study. The PVA, PMMA and LiBF₄ were dried before use in a Logitech DTC 5050 vacuum oven at 100, 90 and 80 °C, respectively, under 10⁻³ Torr pressure for 10 h. The plasticizer EC was used without further purification. When the melting temperature is close to the decomposition of the polymers, a solvent-casting technique is preferred for casting the films since this process reduces the energy for melting. In this study, PVA (15 wt.%)–PMMA (10 wt.%)–LiBF₄ (4, 6, 8, 10 wt.%)–EC (71, 69, 67, 65 wt.%) polymer electrolytes were prepared by means of solvent-casting.

The above compositions of lithium salt, EC, PVA and PMMA were dissolved in distilled DMF (dimethyl formamide) (Merck). The solution was stirred and heated continuously at 70 °C for several hours until the mixture became a homogeneous gel. The film was cast by spreading the suspension on a glass plate. The DMF was allowed to evaporate slowly. Finally, the film was dried at 85 °C in the vacuum oven under 10⁻³ Torr pressure for 4–5 h to remove any further traces of DMF. The resulting film was visually examined for its dryness and free-standing nature. Chemical storage, film-casting and cell assemblies were performed under a vacuum atmosphere.

The crystalline structure of the resultant electrolyte films was investigated by means of XRD (JDX 8030 X-ray diffractometer). The fundamental vibrations of the polymer complexes were studied by FTIR analysis in the range 4000–400 cm⁻¹ with a Perkin-Elmer 577 IR spectrometer.

The bulk electrical conductivity of the electrolyte was measured by sandwiching the electrolyte between stainless-steel electrodes. Conductivity measurements were performed under vacuum to avoid contamination of the film with moisture, and by means of ac impedance analysis to avoid electrode effects. The measurements were made with a Keithley LCZ meter Model 3330. The conductivity values were evaluated from complex impedance plots in the temperature range 302–373 K.

The thermal stability of the electrolyte with the highest conductivity was examined by thermogravimet-

ric/differential thermal analysis (TG/DTA) using a STA 1500 PL Thermal Sciences instrument. The sample was put in an aluminium pan and was heated at a rate of 10 °C min⁻¹ to 700 °C. The TG and DTA curves were recorded.

3. Results and discussion

3.1. XRD analysis

In order to investigate the influence of the concentration of Li salt, XRD studies were performed for PVA, PMMA, LiBF₄ and complexes (Fig. 1(a–g)). The following distinct features were observed.

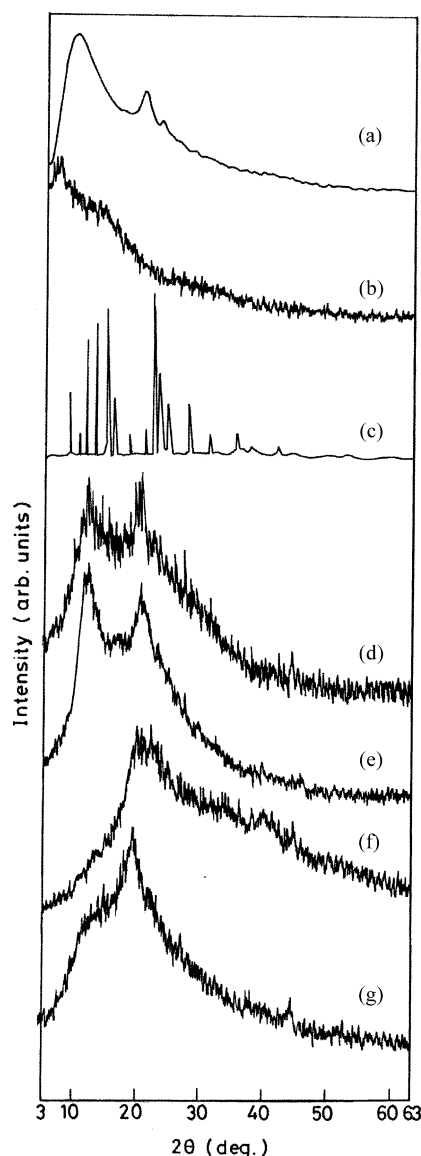


Fig. 1. X-ray diffraction patterns of (a) PVA, (b) PMMA, (c) LiBF₄, (d) PVA (15)–PMMA (10)–LiBF₄ (4)–EC (71), (e) PVA (15)–PMMA (10)–LiBF₄ (6)–EC (69), (f) PVA (15)–PMMA (10)–LiBF₄ (8)–EC (67), (g) PVA (15)–PMMA (10)–LiBF₄ (10)–EC (65).

- (i) There is a decrease in the relative intensity of the apparent peaks with increasing salt concentration up to 8 wt.%. These results can be interpreted in terms of the Hogde et al. [14] criterion which has established a correlation between the height of the peak and the degree of crystallinity.
- (ii) The diffraction peak at $2\theta = 28.3^\circ$ for LiBF_4 salt is shifted slightly in the complexes. All the remaining peaks for LiBF_4 are absent in the complexes. This indicates complete dissolution of the salt in the polymer matrix and hence complexation.
- (iii) The diffraction peak at $2\theta = 19.5^\circ$ for pure PVA is displaced in the complexes and the diffraction peak at $2\theta = 22^\circ$ for PVA is absent.

Thus, the X-ray diffraction studies reveal complex formation in the polymer matrices.

3.2. FTIR studies

Infrared spectral analysis monitors the vibrational energy levels in the region of different molecules. The IR spectra for PVA, PMMA, LiBF_4 , EC and the complexes, are shown in Fig. 2(a–h), respectively. The O–H stretching band in the IR spectrum is by far the most characteristic feature of alcohols and phenols, and appears at 3575 cm^{-1} in pure PVA. The hydroxyl band is displaced towards lower wave numbers in the complexes. This gives a clear indication of the specific interactions in the polymer matrices. The vibrational peak at 1452 cm^{-1} is assigned to a CH_2 scissor mode of pure PVA. The peak at 1726 cm^{-1} is assigned to C=O stretching in the acetate group of PVA, and is shifted to 1731 cm^{-1} in the complexes. The characteristic vibrational band at 1100 cm^{-1} is assigned to C–O stretching of secondary alcohols, and is shifted to 1095 cm^{-1} in the complexes. The characteristic peak attributed to PVA appears at 1663 cm^{-1} , and is shifted to lower wave numbers ($1651\text{--}1662\text{ cm}^{-1}$) in the complexes.

The CH_3 asymmetric stretching vibration of PMMA appears at 2954 cm^{-1} in all the complexes. The vibrational frequency at 1280 cm^{-1} is assigned to C–O stretching of PMMA, and is shifted to 1274 cm^{-1} in the complexes. The absorption peak at 625 cm^{-1} attributed to amorphous PMMA [15] is shifted to 615 cm^{-1} in the complexes. The peak at 3010 cm^{-1} is assigned to O– CH_2 asymmetric stretching of PMMA, and is shifted to 2996, 2997, 3000 and 2997 cm^{-1} in the complexes containing 4, 6, 8 and 10 wt.% LiBF_4 , respectively. The absorption peaks at 1483, 1173 and 750 cm^{-1} are assigned to CH_2 scissoring, twisting and rocking modes of PMMA and are at 1475, 1190 and 751 cm^{-1} , respectively, in the complexes. Characteristic peaks of PMMA at 840, 668 and 483 cm^{-1} are at 844, 665 and 481 cm^{-1} in the complexes.

The characteristic vibrational peak of LiBF_4 at 510 cm^{-1} is assigned to BF_4^- . This peak appears at 520 cm^{-1} in all the complexes, which is an evidence of polymer–salt interactions. Nyquist and Settineri [16] assigned the stretch-

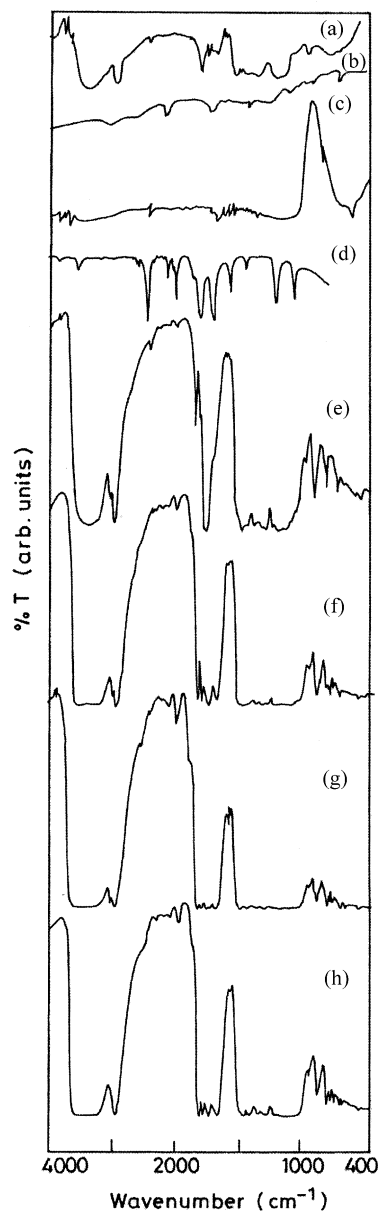


Fig. 2. FTIR spectra of (a) PVA, (b) PMMA, (c) LiBF_4 , (d) EC, (e) PVA (15)–PMMA (10)– LiBF_4 (4)–EC (71), (f) PVA (15)–PMMA (10)– LiBF_4 (6)–EC (69), (g) PVA (15)–PMMA (10)– LiBF_4 (8)–EC (67), (h) PVA (15)–PMMA (10)– LiBF_4 (10)–EC (65).

ing frequency corresponding to C=O ($\nu_{\text{C=O}}$) in the region 1810 cm^{-1} for EC; it occurs at 1805 cm^{-1} in the complexes. One of the significant bands in the $\nu_{\text{C=O}}$ region is due to Fermi resonance of skeletal breathing around 1788 cm^{-1} . The band shifts to 1770 cm^{-1} in the 8 wt.% LiBF_4 system and to 1774 cm^{-1} in the remaining complexes. Hence, this downward shift of $\nu_{\text{C=O}}$ to 1774 cm^{-1} indicates the interaction of the plasticizer with LiBF_4 on complexation. The characteristic vibrational frequency of EC at 1962 cm^{-1} is shifted to 1963, 1965, 1967 and 1969 cm^{-1} in the complexes. The vibrational peaks at 1551 and 2046 cm^{-1} attributed to EC are shifted to 1557 and 2057 cm^{-1} in the complexes.

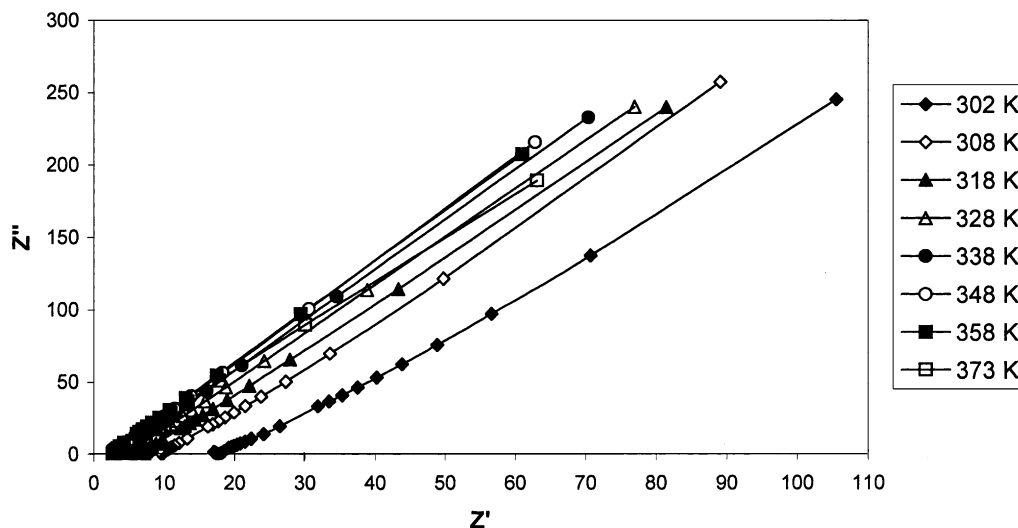


Fig. 3. Complex impedance plot of PVA (15)–PMMA (10)–LiBF₄ (8)–EC (67) system in temperature range 302–373 K.

The vibrational peaks at 3891, 3810, 3788, 3698, 3660, 3576, 2925 and 607 cm⁻¹ of PVA; 3446, 2927, 1559, 1542, 1508, 1384, 1149 and 990 cm⁻¹ of PMMA; 3563, 1305 and 1056 cm⁻¹ of LiBF₄; and 3566, 2775, 2659, 2550, 1073 and 719 cm⁻¹ of EC are absent in the complexes.

Thus, IR spectra confirms that complexation has occurred in the polymer–salt matrices.

3.3. Conductivity studies

The ionic conductivity of a polymer electrolyte depends on the concentration of the conducting species and on their mobility. The ionic conductivity values of the electrolytes are calculated by using the equation $\sigma = l/R_b A$, where l , A are the thickness and known area of the electrolyte film and R_b is the bulk resistance of the electrolyte film which is obtained from the intercept of real part of complex impedance plot. The plot for the PVA (15)–PMMA (10)–LiBF₄ (8)–EC (67) complex in the temperature range 302–373 K is shown in Fig. 3. In the impedance response curve, the absence of the high-frequency semicircular portion leads to the conclusion that the current carriers are ions and therefore the total conductivity is mainly the result of ion conduction [17]. The conductivity values of the four different concentrations of PVA–PMMA blend complexes are

given in Table 1. For all the complexes, conductivity increases with increase in temperature, as expected [18]. This can be rationalised by recognising the free-volume model [19].

The maximum conductivity value is observed for the 8 wt.% LiBF₄ complex and is $1.2886 \times 10^{-3} \text{ S cm}^{-1}$. This value is higher than that ($2.482 \times 10^{-5} \text{ S cm}^{-1}$) already reported by us [20] for the PVC–PMMA–LiBF₄–DBP system. It is also higher than the value 10^{-8} to 10^{-4} S/cm reported by Every et al. [9]. The effect of addition of salt concentration in the polymer matrices on the logarithm of conductivity is presented in Fig. 4. The initial increase in conductivity is presumably due to an increase in the number of charge carriers in the matrix. For a higher concentration of LiBF₄, the build-up of charge carriers is offset by the retarding effect of ion aggregates such as ion pairs and ion triplet formation, which cause constraints in ionic and polymer segmental mobility. Hence, the conductivity reaches the maximum value at 8 wt.% of LiBF₄ complex. This shows a balance between these two opposing forces: increasing the number of charge-carrier ions and decreasing ionic mobility. A further increment in salt concentration (10 wt.% LiBF₄) results a decrease in conductivity which may be due to the restricted ionic and polymer segmental mobility in a rigid matrix.

Table 1

Ionic conductivity values of PVA–PMMA–LiBF₄–EC systems for four different salt concentrations

Composition (wt.%)	Ionic conductivity ($\times 10^{-3} \text{ S cm}^{-1}$)							
	302 K	308 K	318 K	328 K	338 K	348 K	358 K	373 K
15–10–4–71	0.2388	0.4808	0.6268	0.8278	0.9918	1.3426	1.6837	2.2186
15–10–6–69	0.5069	0.5750	0.7553	1.4811	4.0178	5.0362	7.1471	8.0238
15–10–8–67	1.2886	2.3229	3.2850	4.5019	5.8933	7.5472	8.7892	9.0377
15–10–10–65	0.6214	0.7756	1.1001	2.0501	4.3967	5.2893	7.5731	8.2965

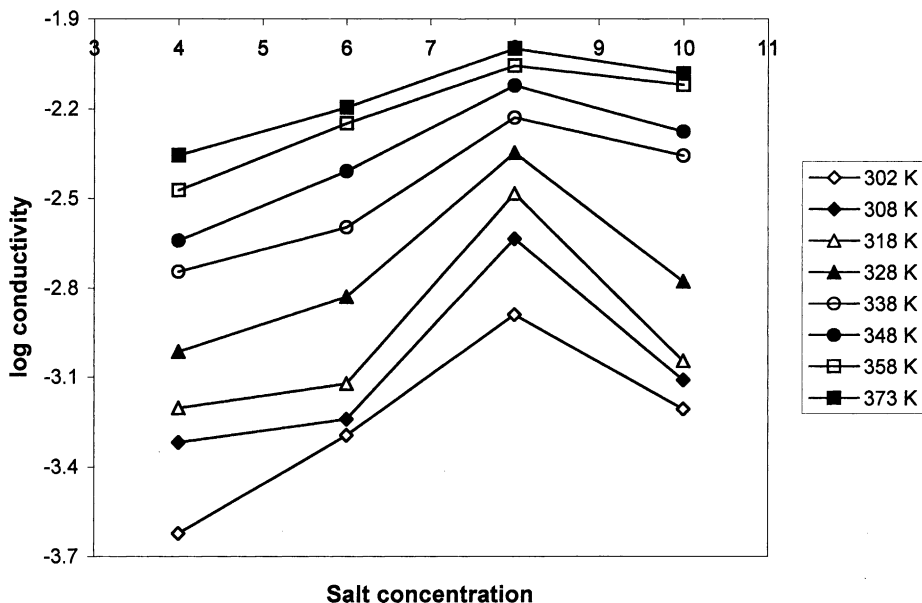


Fig. 4. Dependence of ionic conductivity on salt concentration for PVA-PMMA-LiBF₄-EC polymer complexes at different temperatures.

Arrhenius plots of $1000/T$ versus log conductivity of polymer complexes in the temperature range 302–373 K are given in Fig. 5. The non-linearity of the plots suggests that ion transport in polymer electrolytes is associated with polymer segmental motion [21].

3.4. TG/DTA analysis

The TG/DTA curve of the PVA (15)-PMMA (10)-LiBF₄ (8)-EC (67) complex is shown in Fig. 6. This is an effective tool for identification of the thermal stability and the transition behaviour of the electrolyte material. Mishra and Rao [22] reported that in pure PVA, decomposition occurs in two stages and the polymer is thermally stable up to 265 °C. In the present study, the TG curve shows that the first decomposition temperature occurs at 336 °C with a gradual weight

loss of 26%. There follows a rapid weight loss of 68% up to 435 °C. Complete decomposition of the film takes place between 600 and 618 °C with corresponding weight losses of 77 and 83%. The blended electrolyte has decomposition temperatures at 336, 435, 600 and 618 °C with corresponding weight losses of about 26, 68, 77 and 83%, respectively. No effort has been made to identify the decomposition products as it is well known that the decomposition leads to evolution of low molecular weight alkanes, alkenes, aldehydes, ketones, etc. and also acetaldehyde and acetic acid in case of pure PVA [23]. From the thermogram, it is found that there is a residue of about 17% and most of this could originate from the unhydrolysed acetate portions of PVA. In DTA curve, endothermic peaks are observed at 387, 404 and 510 °C and exothermic peaks at 32, 379, 421, 479, 540 and 612 °C. The first decomposition occurs in the range

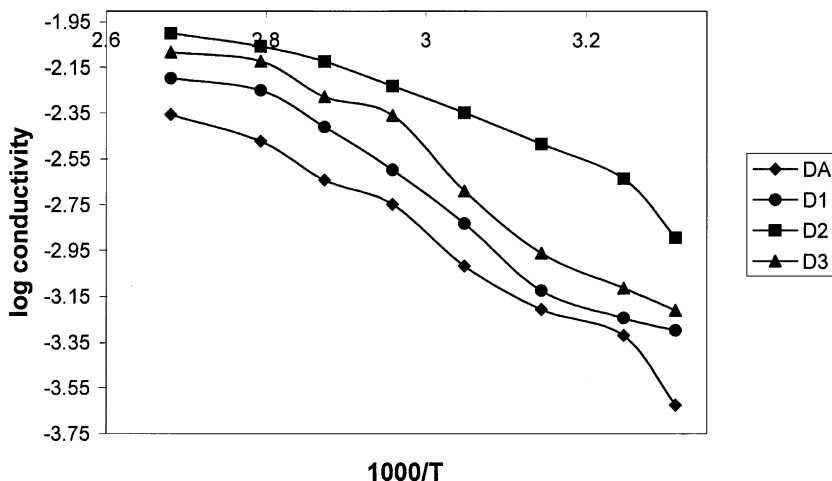


Fig. 5. Arrhenius plot of PVA-PMMA-LiBF₄-EC complexes for different salt concentrations.

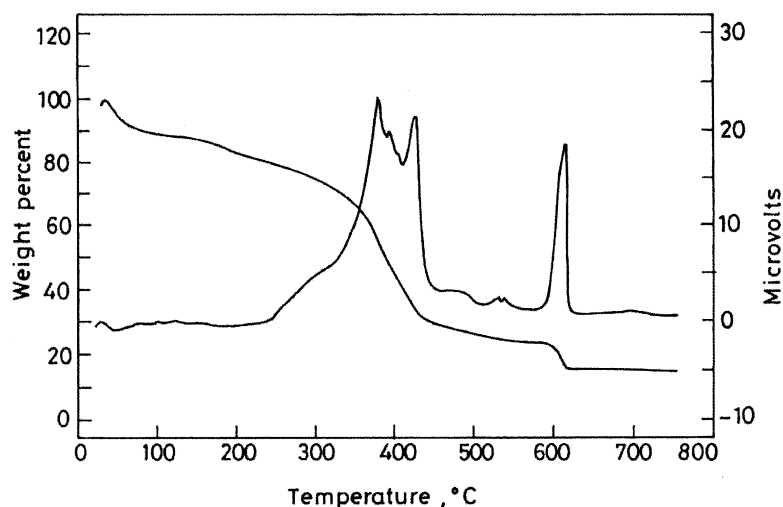


Fig. 6. TG/DTA curves for PVA (15)–PMMA (10)–LiBF₄ (8)–EC (67) complex.

336–435 °C and is accompanied by two large exothermic peaks at 379 and 421 °C. There is a sharp and large exothermic peak at 612 °C concurrent with an appreciable weight loss of about 82%. This indicates complete decomposition of the film, which is in agreement with the TG curve. From the above discussions, it is concluded that the thermal stability limit of the polymer electrolyte film is 336 °C.

4. Conclusions

- (i) The polymer electrolytes based on PVA–PMMA–LiBF₄–EC are prepared for different salt concentrations using a solvent-casting technique.
- (ii) The structural and complexation behaviour have been studied by XRD and FTIR analyses.
- (iii) The ionic conductivities of the electrolytes have been measured by an ac impedance technique at various temperatures. The influence of salt concentration in the polymer complexes is discussed. Arrhenius plots suggest that ion transport is due to polymer segmental motion. The maximum conductivity value ($1.2886 \times 10^{-3} \text{ S cm}^{-1}$) is obtained for a polymer complex with 8 wt.% LiBF₄.
- (iv) The thermal stability of the electrolyte with the maximum conductivity is ascertained by TG/DTA analysis.

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