

Electrochemical analysis on poly(ethyl methacrylate)-based electrolyte membranes

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MS received 24 March 2014; revised 13 May 2014

Abstract. Polymer blend composed of poly(vinyl chloride) and poly(ethyl methacrylate) with lithium perchlorate (LiClO_4) and the plasticizer ethylene carbonate (EC) mixture with propylene carbonate, γ -butyrolactone (GBL), dibutyl phthalate and diethyl carbonate have been synthesized using the solution casting technique. Structural changes and thermal stability of the films were resolved using X-ray diffraction analysis and thermogravimetric/differential thermal analysis, respectively. The membrane that contains EC+ GBL exhibits maximum ionic conductivity of the order of $1.208 \times 10^{-3} \text{ S cm}^{-1}$ at 303 K. The temperature-dependent ionic conductivity of the polymer membranes has been estimated using AC impedance analysis.

Keywords. Gel polymer electrolyte; electrochemical analysis; structural properties; thermogravimetry.

1. Introduction

In recent years, solid-state Li-ion batteries have been successfully used in various applications such as hybrid electric vehicle (HEV), portable electronic devices, sensors and in energy storage applications. In a secondary battery, a polymer electrolyte will function as a separator as well as an electrolyte.¹ The realization that the Li^+ ion has a low mobility in solid polymer electrolyte (SPE) matrices has led numerous research groups to develop different approaches that have improved the ambient conductivity. Some of the approaches include crosslinking two polymers,^{2,3} addition of plasticizers to polymer electrolytes,^{4–6} addition of fillers to make composite polymer electrolytes⁷ and blending of two polymers.^{8–10} Polymer blending is a good approach to improve ionic conductivity and mechanical properties. However, the enhancement of room temperature ionic conductivity further has been improved by the addition of plasticizers.

Adding plasticizer is an important criterion for improving the ambient conductivity of the polymer electrolyte system. While adding the plasticizer, the amorphous region, which helps for easy ionic movement, is greatly being enhanced, hence the overall conductivity of the system is improved; it will also improve the flexible nature of the blend electrolytes. For the same salt concentrations, the ionic conductivity value of the polymer electrolyte depends upon the viscosity and dielectric constant value of the organic solvent used and as a result, conductivity varies with the change of solvent.

The addition of the plasticizer in polymer blend results not only in altering the viscosity and the thermal stability, but also tensile strength, flexural strength and modulus. These cases suggest that the plasticizer may function as a compatibilizer of the polymer blend.¹¹ As a higher value of dielectric constant and a low value of viscosity should result in higher conductivity, this study deals to find the combined effect of both these parameters by incorporating double plasticizers. However, it apparently reduces the mechanical stability of the electrolyte system and has a poor interfacial stability with the electrodes. Although it has several advantages and disadvantages, we have aimed to improve the room temperature ionic conductivity using different kind of plasticizers that help in enhancing the room temperature conductivity.

In most polymer electrolytes, the polymer host is doped with some inorganic salts and one or more plasticizers, which are often added for conductivity enhancement. Among the polymer electrolytes that are currently studied, polyvinylchloride (PVC)-based electrolyte has a special significance.^{12–14} The use of poly(ethyl methacrylate) (PEMA) as a host polymer was first reported by Fahmy and Ahmed.¹⁵ Proof of the blend concept was demonstrated with a PVC/PEMA gel electrolyte by Han *et al.*¹⁶ The effect of organic solvents on the structural and electrical properties of PVC/PEMA-based polymer complex was studied by Rajendran and Ramesh Prabhu.¹⁷ The use of plasticizer in the design of polymer electrolyte has a greater preference as compared to virgin polyblending process, as its approach provides several advantages to the polymer electrolyte laminate for electrochemical application. To understand this approach we have studied here the influence of organic solvents in the PVC/PEMA/ LiClO_4 blend electrolyte.

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2. Experimental

2.1 Preparation of SPE

Polymer electrolytes were prepared using the solution cast technique with tetrahydrofuran (THF) from SRL, Mumbai, as the solvent for high-molecular-weight PVC, PEMA with an average molecular weight of 515,000 and the salt lithium perchlorate (LiClO_4) from Aldrich, USA. The plasticizer propylene carbonate (PC), ethylene carbonate (EC), gamma butyrolactone (GBL), diethyl carbonate (DEC) and dibutyl phthalate (DBP) are obtained from Aldrich, USA. We set the total weight of polymers PVC, PEMA, lithium salt LiClO_4 and plasticizer combination to be identical (100%) when preparing the films of various combination of plasticizers. The polymer solution was cast as film and THF was allowed to evaporate at room temperature. After the evaporation of THF, mechanically stable films (free standing) were obtained. The films were further dried in the temperature-controlled oven at 50°C for 12 h to remove the traces of THF, if any. The electrolytes were prepared for different compositions as PVC (5 wt%), PEMA (20 wt%), LiClO_4 (8 wt%) and EC + X [X = PC, DEC, DBP and GBL] (67 wt%). The weight ratio between EC and PC/GBL/DBP/DEC is maintained as 50:50, i.e., 33.5 wt% + 33.5 wt%.

2.2 Characterizations

The X-ray diffraction (XRD) patterns of the samples were recorded using a computer-controlled X'pert PRO PANalytical diffractometer using $\text{Cu-K}\alpha$ (wavelength, $\lambda = 1.541 \text{ \AA}$) radiation as source and operated at 40 kV with the scanning range between 10° and 80° . Fourier transform infrared (FT-IR) spectroscopy studies are carried out using JASCO-plus 460, Japan. FT-IR spectrophotometer was in the range $400\text{--}4000 \text{ cm}^{-1}$. The impedance measurements were carried out on the polymer electrolyte films with stainless-steel blocking electrodes by using a computer controlled μ -AUTOLAB Type-III Potentiostat/Galvanostat in the frequency range 40 Hz–300 kHz and the measurements were taken between room temperature and 90°C (302–363 K). TG/DTA thermal analysis of polymer electrolyte samples was studied using Perkin Elmer Pyris-6 TG/DTA with the scan rate of $10^\circ\text{C min}^{-1}$.

3. Results and discussion

3.1 X-ray diffraction analysis

XRD patterns of the constituents and the blend electrolytes based on PVC/PEMA blend are shown in figure 1. The XRD pattern of LiClO_4 shows high intense peaks at $2\theta = 21^\circ$, 23° , 31° and 36° . This shows the crystalline nature of lithium salt. The broad humps observed in figure 1b and c confirmed the amorphous nature of the polymers PVC and PEMA. It is noted from figure 1d–g that the addition of plasticizers in

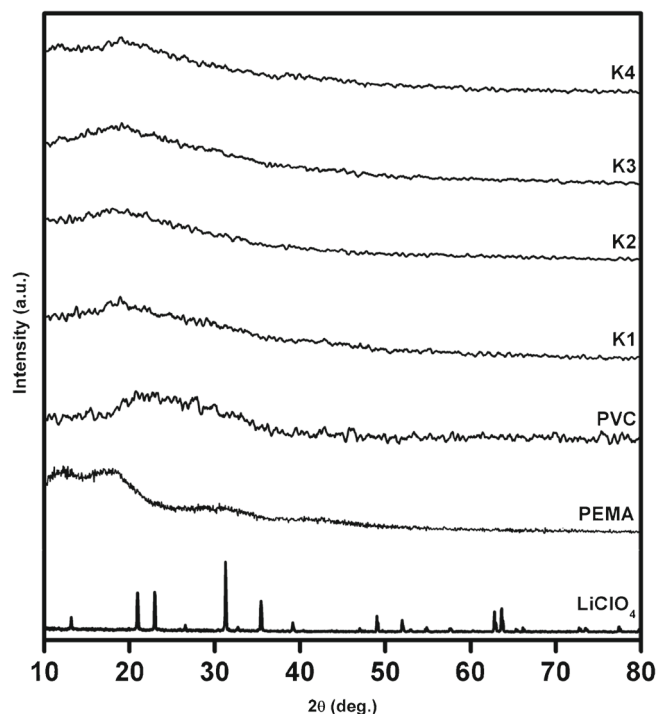


Figure 1. XRD plots of LiClO_4 , PEMA, PVC and their complexes: PVC/PEMA/EC+X/ LiClO_4 [X = PC(K1), GBL(K2), DEC(K3), DBP(K4)].

the polymer–salt complex further enhanced the amorphous regions of the matrix. It can be observed that the characteristic peaks corresponding to the lithium salt in their respective electrolyte systems were absent, which indicates that the lithium salt is not crystallized in the film, but rather molecularly dispersed in the PVC/PEMA blend. This may be due to the complete dissolution of the salts in the complex matrix, which implies that, the salt do not have any separate phase in the electrolytes. From the result, it is concluded that the polymers undergo significant structural reorganization while adding plasticizers and salt. The ionic conduction in the polymer electrolytes mainly occurs in the amorphous region and it has been achieved by the addition of low-molecular-weight plasticizer molecules.¹⁸ The structural changes on the addition of plasticizer reveal the enhancement of amorphous nature of polymer blend. Thus, the miscibility of these two polymers PVC and PEMA in the presence of different plasticizers and lithium salt was confirmed from this study.

3.2 FT-IR analysis

FT-IR spectroscopy has been used to analyse the interactions between the atoms or ions in the electrolyte system. FT-IR spectra of polymer complexes are shown in figure 2. The asymmetric C–H methylene group vibration, *trans*-CH rocking, *cis*-CH wagging and in-plane –CH deformation of PVC were observed at 2963 , 954 , 630 and 1329 cm^{-1} , respectively.

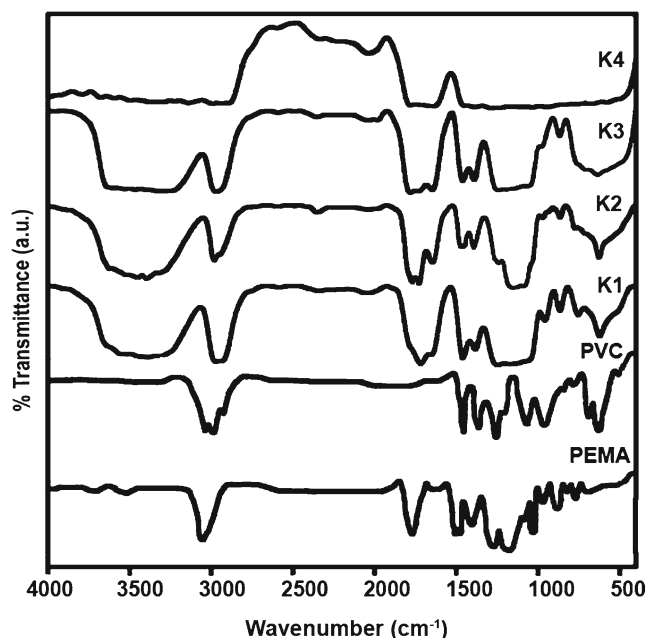


Figure 2. FT-IR spectra of PEMA, PVC and their complexes: PVC/PEMA/EC+X/LiClO₄ [X = PC(K1), GBL(K2), DEC(K3), DBP(K4)].

The absorption peaks at 1730 cm^{-1} were responsible for C=O carbonyl group vibration of PEMA. The vibrational frequencies at 1485 , 947 and 756 cm^{-1} are due to $-\text{CH}_2$ scissoring, $-\text{CH}_2$ wagging and $-\text{CH}_2$ rocking vibrations in PEMA, respectively. The sharp vibrational peak at 1774 cm^{-1} represents the C=O stretching vibration of the EC, which can be observed in all polymer complexes. The shift observed in the perchlorate (ClO_4^-) anion at 925 cm^{-1} in the complexes has been used as an indicator for the dissociation of LiClO_4 . The Li^+ ions are associated with the oxygen atoms of the C=O group, as the oxygen is a strong electron dopant. The characteristic frequencies of PC at 1483 and 1400 cm^{-1} correspond to $-\text{CH}_3$ asymmetric bending and C–O stretching vibrations. However, in the electrolytes, these bands are found changed in complexes on the addition of organic solvents, which is due to the structural reorganization of the polymer. By comparing the band spectra of pure polymers and polymer–salt complex, it is clear that the band assignments of FT-IR spectra of polymer–salt complex are shifted from their pure spectra. In addition, some new peaks are present and some of them disappeared in the complex. Thus, the spectral analysis confirms the complexation.

3.3 TG–DTA analysis

As a qualitative tool, TG can be used to identify the thermal stability and decomposition of polymers and its constituents based on their volatility. Volatile components such as organic solvents and water evaporate at low temperatures (say 100 – 120°C), at intermediate temperatures, plasticizers are removed and at high temperatures only

non-volatile components such as inorganic fillers remain as residue.

TG and DTA curves of polymer complexes are presented in figure 3. All the electrolytes show weight loss of about 10 – 16% at 100°C , which is mainly due to the presence of moisture. The melting of the plasticizer EC may start in complexes because the melting point of the plasticizer EC is 36°C .^{19,20} As the melting point of the PVC is 100 – 260°C , the vinyl chloride unit in the electrolyte also starts degrading slowly in this temperature range. This weight loss is also confirmed by the presence of small endothermic peaks observed in the DTA curves of the samples around 60 – 100°C . The second decomposition of PVC/PEMA/EC+X/LiClO₄ [X = PC, GBL, DEC, DBP] samples occurs around 250 , 240 , 250 and 210°C , respectively, beyond which all the films are found to lose their weight drastically indicating the decomposition of polymer electrolyte. About 240°C , the observed significant change in the polymer's structure indicates the breakage of $-\text{CH}_2$ bonds in the polymer chain and the elongation of the carbon–halogen bonds, which leads to the elimination of the halogen atoms at sites along the polymer chain. It is found that there is no appreciable weight loss of all the polymer electrolytes beyond 300°C . The presence of sharp exothermic peaks in DTA results confirms the decomposition temperature of complexes. The loss of approximately half of the chlorine atoms from the polymer chain also results in significant changes in the stability of polymer electrolyte.²¹ It is obvious from the observation that all the films could be operated until 200°C . Even though the polymer PVC has poor thermal stability, the gel polymer electrolyte resulting on blending with PEMA and plasticizer has enhanced thermal stability. It is found that the film containing EC + GBL combination exhibited maximum ionic conductivity and thermal stability up to 240°C . The thermal stability is also satisfactory for this composition, even though maximum thermal stability is obtained for the film with plasticizer combination EC + PC and EC + DEC.

3.4 Impedance spectroscopy

The electrochemical impedance spectroscopy is an excellent tool to characterize many of the electrical properties of materials and their interfaces with the electronically conducting electrodes. The ionic conductivity of all the electrolyte systems is calculated using the equation $\sigma = t/(AR)$, where A is the area of electrode, t the thickness of the film and R the bulk resistance from AC impedance. In the present study, the impedance of the polymer electrolyte membranes based on PVC/PEMA blend were measured. The room temperature complex impedance plot of PVC/PEMA/EC+X/LiClO₄ (where X = PC, GBL, DEC, DBP) based electrolytes are shown in figure 4. The estimated conductivity values are given in table 1. From the table, it is identified that among the various compositions of the plasticizers, EC+GBL (sample K2)-based system shows higher ionic conductivity than the other films at room temperature. Similar studies were

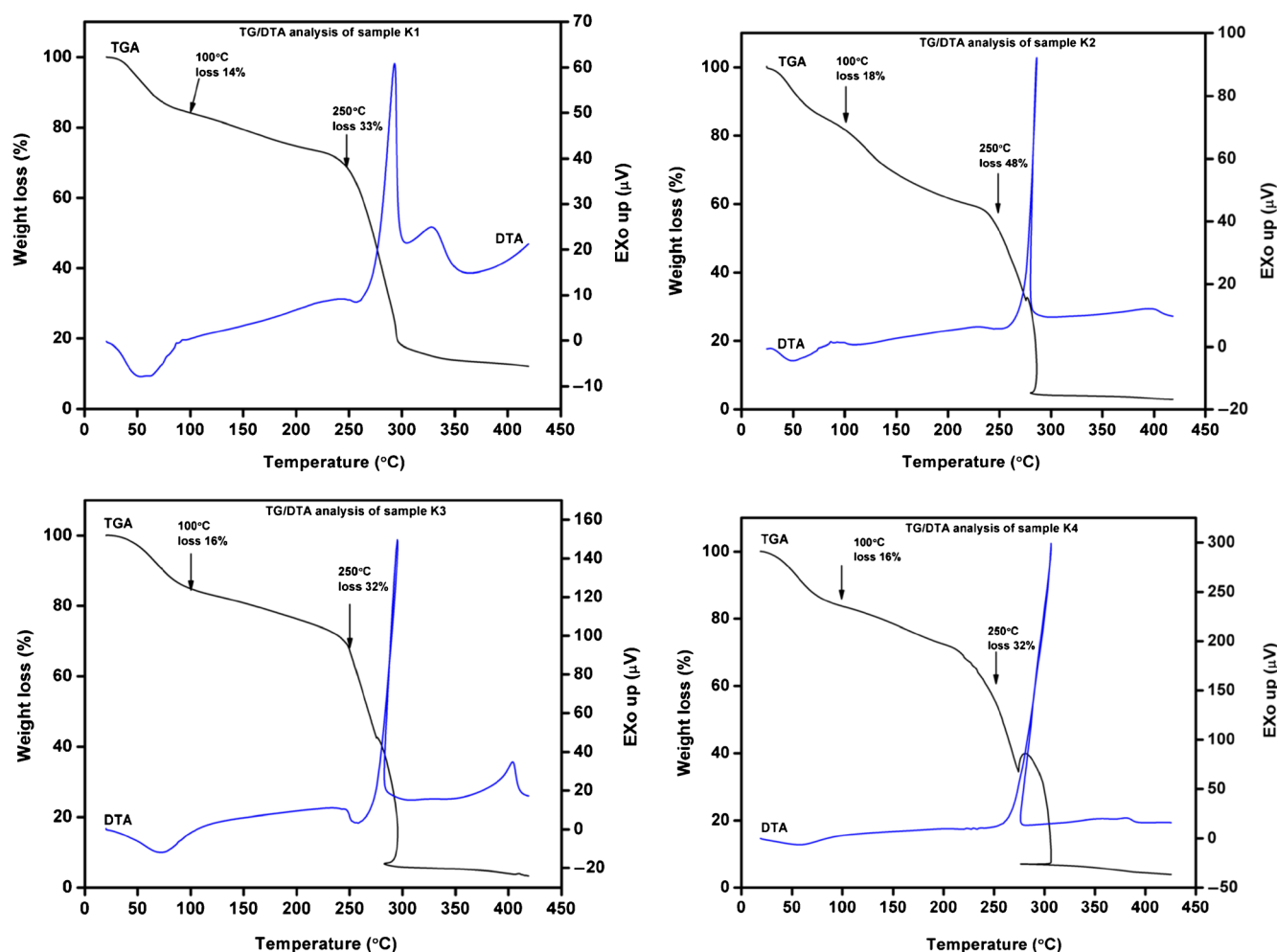


Figure 3. TG/DTA curves of prepared samples: PVC/PEMA/EC+X/LiClO₄ [X = PC(K1), GBL(K2), DEC(K3), DBP(K4)].

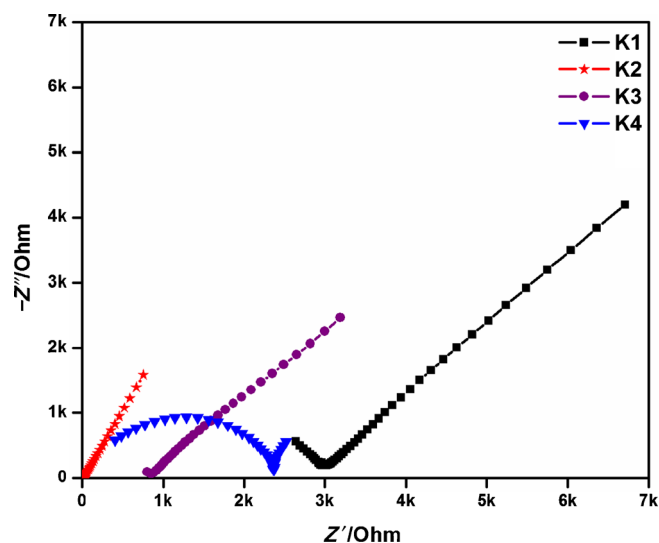


Figure 4. Room temperature complex impedance plot of PVC/PEMA/EC+X/LiClO₄ [X = PC(K1), GBL(K2), DEC(K3), DBP(K4)].

carried out by Ulaganathan and Rajendran.²² The variation in the conductivity is mainly due to the specific properties

of the plasticizers such as viscosity as well as dielectric nature. It is a well-accepted fact that the conductivity is fully controlled by the viscosity of the medium, likewise higher dielectric nature would enhance more charge carrier dissolutions. In the present work, among various plasticizers, EC has maximum dielectric constant and minimum viscosity.^{23–26} When a plasticizer is used with the polymers, the viscosity of the blend is reduced through the replacement of polymer–polymer hydrogen bonding by polymer–plasticizer hydrogen bonding. Free volume theory holds that the presence of a plasticizer lowers the glass transition temperature (T_g) of the polymer. When small molecules such as plasticizers are added, the free volume available to polymer chain segments increases and therefore the glass transition temperature lowers.²⁷ GBL has lower viscosity, which favours for easy ionic movement when it is combined with other plasticizer. The viscosity and dielectric constant values of plasticizers are given in table 2.

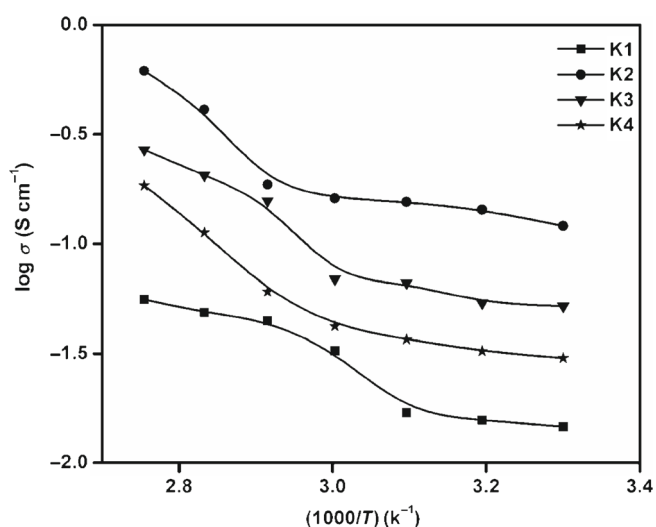
The plot of $1000/T$ vs. $\log \sigma$ is shown in figure 5. To analyse the mechanism of ionic conduction in polymer electrolytes, ionic conductivity measurements were carried out at different temperatures. From the plot $1000/T$ vs. $\log \sigma$, it is observed that the increase of temperature increases the

Table 1. Conductivity values of polymer complex at different temperatures.

Sample code	PVC/PEMA/LiClO ₄ /EC+X	Conductivity, $\sigma \times 10^{-3} \text{ S cm}^{-1}$						
		303 K	313 K	323 K	333 K	343 K	353 K	363 K
K1	X = PC	0.146	0.156	0.169	0.325	0.446	0.487	0.557
K2	X = GBL	1.208	1.432	1.552	1.611	1.861	4.102	6.154
K3	X = DEC	0.520	0.536	0.663	0.690	1.566	2.050	2.688
K4	X = DBP	0.301	0.324	0.366	0.421	0.605	1.126	1.184

Table 2. Dielectric constant and viscosity values of plasticizers.

	EC	PC	GBL	DEC	DBP
Viscosity at 25°C (cP)	1.85	2.5	1.7	0.75	0.66
Dielectric constant	89.6	64.4	39.1	2.82	5.8

**Figure 5.** Temperature dependence of ionic conductivity for the prepared samples PVC/PEMA/EC+X/LiClO₄ [X = PC(K1), GBL(K2), DEC(K3), DBP(K4)].

ionic conductivity for all the compositions over the studied temperature range. Moreover, it is clear that increasing temperature results in the expansion of the polymer membrane, which produced the local empty space and expands the free volume, and it promoted the motion of polymer segments and ionic carriers. As both macroscopic flow of polymer and local segmental motion are permitted for viscous solutions, it is suggested that the local segmental motion plays an important role in the ionic migration in the polymer electrolytes. Hence, as the temperature is increased, the R_b decreases.²⁸ However, the nonlinear behaviour of the plot indicates that the ion transport in polymer electrolyte depends on polymer segmental motion. The result seems to obey the Vogel–Tamman–Fulcher (VTF) equation. The Arrhenius behaviour is typical for crystalline materials, whereas the VTF behaviour is more appropriate for amorphous materials. The enhanced amorphous nature was due to the addition of plasticizer already observed from XRD analysis.

4. Conclusions

The present work is concerned with PVC-based polymer blend electrolytes, in which XRD analysis revealed the amorphous nature of all the polymer blend electrolytes, which helps for ionic conduction. The interaction of the cation (Li) and anion (ClO₄[−]) with the polymer host and the plasticizers have been confirmed by FT-IR spectroscopic analysis. The miscibility of PVC and PEMA is due to a specific interaction of hydrogen from (CH–Cl) groups of PVC and hydrogen bonding type between carbonyl groups (C=O) of PEMA, as proved by FT-IR spectroscopy. Thermal stability of the polymer electrolytes has also been ascertained using TG/DTA analysis.

The ionic conductivity is further enhanced by the addition plasticizers into PVC:PEMA:LiClO₄ complex. It is noted that the combination of EC and GBL system showed the higher ionic conductivity value ($1.208 \times 10^{-3} \text{ S cm}^{-1}$) than the other complexes, which is mainly due to higher dielectric nature of the plasticizer. The higher dielectric nature increases the dissolution of the charge carriers and the amorphous region of the polymer matrix. Hence, the ionic conductivity is improved. Although the complex based on EC and GBL exhibits maximum ionic conductivity, it has thermal stability up to 210°C. Ionic conductivity value has also been increased by the incorporation of combination of plasticizers, and the estimated conductivity value is $0.146 \times 10^{-3} \text{ S cm}^{-1}$ for EC- and PC-based polymer electrolyte system.

To conclude, polymer blend electrolyte for possible application as in high-energy density batteries has been identified in terms of parameters such as conductivity, thermal stability and dimensional stability.

Acknowledgement

We acknowledge the Union Grants Commission (UGC), Government of India, for the financial support [F. No. 40-459/2011(SR)].

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