

AC-Impedance, Dynamic mechanical analysis and DSC investigations on poly(methyl methacrylate)–LiTf polymer electrolyte systems

A. M. Soliman

Physics Department, Faculty of Science, Cairo University, 12613 Giza, Egypt

e-mail : ars1995@hotmail.com

M. M. GHANNAM

Physics Department, Faculty of Science, King Saud University, Riyadh, Saudi Arabia

Abdullah S. Al-Arifi

Chemistry Department, Faculty of Science, King Saud University, Riyadh, Saudi Arabia

E. El. Shafee

Chemistry Department, Faculty of Science, Cairo University, 12613 Giza, Egypt

e-mail : ezeldain@sci.cu.edu.eg

ABSTRACT

Gel polymer electrolytes synthesized from Poly(methylmethacrylate) (PMMA) as the host, ethylene carbonate (EC)/propylene carbonate (PC) as plasticizer and LiCF_3SO_3 (LiTf) as a salt has been prepared using solution casting technique. X-ray characterization confirms the complete dissociation of the LiTf salt in the gel polymer. The effect of LiTf salt on ionic conductivity, ionic transference number (t_{ion}) and mechanical characteristics were investigated. The ac impedance has been studied to evaluate the ionic conductivity. It was observed that the ionic conductivity of the prepared gel reached the highest value of 6.60×10^{-5} S/cm at 10.2 wt.% (1M) of LiTf salt. The temperature dependence studies showed that the samples were ionic conductors and seemed to obey the Vogel–Tamman–Fulcher (VTF) rule. Dynamic mechanical analysis (DMA) indicates that the LiTf salt induces a remarkable increase in the storage modulus of the matrix at temperatures above the glass transition (rubbery plateau region).

Keywords

gel polymer electrolyte, PMMA, ionic conductivity, Dynamic mechanical analysis

Academic Discipline And Sub-Disciplines

Science

SUBJECT CLASSIFICATION

Material Science

1. INTRODUCTION

Nowadays, lithium ion batteries (LIBs), which have become one of the most important energy storage technologies, play a crucial role in the modern world and have become an indispensable part of our daily life. They were invented in the early 1990s, and now are widely used to power many portable devices such as cellular phones, laptops and digital cameras [1–5].

Gel polymer electrolytes (GPEs) have recently received much attention again, owing to their high ionic conductivity at ambient temperature and reduction of risk of leakage of electrolyte solution [6–8]. A number of polymer networks including poly(ethylene oxide) (PEO), poly(methacrylate) (PMMA), poly(vinylidene fluoride) (PVDF), poly(acrylonitrile) (PAN), or poly(vinyl alcohol) (PVA) have been studied as the polymer matrix for the gel polymer electrolytes [9–18].

In particular, PMMA based gel electrolytes have been found to be most preferred potential candidates as electrolytes in electrochromic windows due to their high transparency as well as good gelatinizing and solvent retention ability [19,20]. The absence of potential harmful subunits in PMMA was credited as an added advantage. In addition, the presence of amorphous regions and a polar functional group in its polymer chain contributes to a high affinity for lithium ions and plasticizing solvents [21]. This initial awareness on the integrity of PMMA was created by Iijima et al. [22] and Bohnke et al. [23] that contributed to a preliminary invention by utilizing this type of host polymer. Agnihotry et al. [24] was involved in an effort to investigate the transport properties of lithium electrolytes gelled with PMMA. Ghosh et al. [25] was also engaged in the utilization of PMMA in the production of polymer complexes but in this invention the enhancement in room temperature ionic conductivity was done by blending with poly(ethylene oxide) (PEO) in the presence of ionic salt. A similar method was employed by Rajendran et al. [26] to enhance the ionic conductivity of polymer complexes composed of PMMA but superseded with poly(vinyl alcohol) (PVA). Appetecchi et al. [27] examined PMMA-based electrolytes, prepared as thin films, which were plasticized by (ethylene carbonate) EC/PC–LiX ($X = \text{ClO}_4, \text{AsF}_6 \text{ or } \text{N}(\text{CF}_3\text{SO}_2)_2$). It was found that PMMA-based electrolytes exhibit similar conductivity behavior with only a slight difference in the activation energy. Holland and Hay [28] studied the kinetics and mechanisms of the thermal degradation of poly(methyl methacrylate) by thermal analysis and Fourier transform infrared (FT-IR) spectroscopy. Vondrak et al. [29] examined gel polymer electrolytes based on PMMA. The conductivity of gels containing cations of smaller ionic radii (Li and Mg) is lower than that of the others.



Based on previous studies, it can be seen that PMMA-based polymer complex will grant an appreciable ionic conductivity depending on the type of additives incorporated. The ideal additive is one that can exert greater amorphocity in polymer matrix since the ion conduction will occur predominantly in this region. Ion conduction takes place in this specific region due to the ease of free ions movement within the matrix that contributes to the enhancement in the ionic conductivity. Hence, there is a dire need to convert most of the crystalline phase in PMMA to amorphous phase for better ion conduction.

In this study we focus on gel electrolytes based on PMMA gel polymer electrolyte (GPE) samples consisting of PMMA, EC, PC and various concentrations of LiCF_3SO_3 were prepared. The ionic conductivity and ionic transport properties of the samples were studied by impedance spectroscopy and transference number measurements. The effects of different concentrations of LiCF_3SO_3 on mechanical properties were also investigated and discussed.

2. EXPERIMENTAL

2.1. Materials

Poly (methyl methacrylate), (PMMA, Mw. = 996,000, Sigma-Aldrich), anhydrous propylene carbonate (PC- 99.7 %) and anhydrous ethylene carbonate (EC- 99%), and Lithium Trifluoromethanesulfonate (LiTf, LiCF_3SO_3 , 99.995%) were all Aldrich products. Tetrahydrofuran (THF, E-Merck, Germany) was used as received. All other reagents were of analytical reagent grade and used without purification.

2.2. Preparation of Gel Electrolyte Films

All preparations were performed in a nitrogen atmosphere in a LABCONCO glove box. Polymeric gel electrolytes films were prepared by the solution casting technique. This procedure yields mechanically stable and free-standing films.

Liquid electrolytes were prepared by dissolving different concentrations of LiTf-salt in binary solvent mixtures of EC : PC (1 : 1) weight ratio and stirred mechanically at room temperature. Poly (methyl methacrylate) (PMMA) (15 wt %) was dissolved in tetrahydrofuran (THF) in another flask. These two solutions were then mixed for 24 h with continuous stirring to obtain a homogeneous mixture. The mixture was cast into a petri dish and the solvent was allowed to evaporate in a glove box at room temperature. Residual THF was then removed in a vacuum oven for 24 h at 60 °C.

2.3. Characterization

2.3.1. Conductivity measurements

Ionic conductivity was determined using the complex impedance method in the temperature range from ambient temperature until 80 °C. The impedance measurements were carried out using a WAYNE KERR precision component analyzer, model 6440 B (UK), with an applied voltage of (10 mV), over the frequency range of 20 Hz to 3 MHz.

2.3.2. XRD Analysis

The XRD patterns were analysed using Ultrima 4 X-Ray Diffractometer (Rigaku) using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 40 mA. The diffraction pattern was recorded at room temperature for the Bragg angles (2θ) varying from 10° to 85° with a scan rate of 0.5 deg./min.

2.3.3. DSC studies

DSC data were obtained between (-100 and 150 °C) using a differential scanning calorimeter (DSC-60) Shimadzu, Japan, with a low temperature measuring head and liquid-nitrogen cooled heating element. The samples in aluminium pans were stabilized by slow cooling to (-100°C) and then heated at (20 °C/min) to (150 °C). An empty aluminium pan was used as a reference.

2.3.4. Dynamic mechanical property measurements

For the measurement of the dynamic mechanical properties of the nanocomposite gel polymer electrolytes, a dynamic mechanical analyzer (DMA) 7e [Perkin Elmer (USA)] was utilized. The tension-torsion mode was used under the test temperature range from (-30 °C to 120 °C) and the heating rate was 5 °C/min. For each sample, Storage modulus (E'), loss modulus (E'') and loss tangent ($\tan \delta$) were recorded at frequency (1 Hz).

3. RESULTS AND DISCUSSION

3.1. Ionic Conductivity

Fig. 1 shows the Cole–Cole plots for the gel PMMA electrolyte samples containing 7, 10.2 and 12.5 wt.% of LiTf. The inset figure shows the Cole–Cole plot for a gel PMMA sample without salt. The bulk resistance R_b of the samples were calculated from the Cole–Cole plots from the intercept of the higher frequency region on the Z' axis and were used to calculate the dc-conductivities, σ , from $\sigma = IR_b / A$ where l is the thickness of the gel electrolyte film and A its area. The Cole–Cole plot for the gel PMMA sample without salt exhibits a semicircle at the high frequency region while in the Cole–Cole plots for the gel PMMA electrolyte samples containing salt the semicircle at the high frequency region apparently disappeared. This is due to the increase in the salt concentration, and the consequence increase in ionic conductivity.

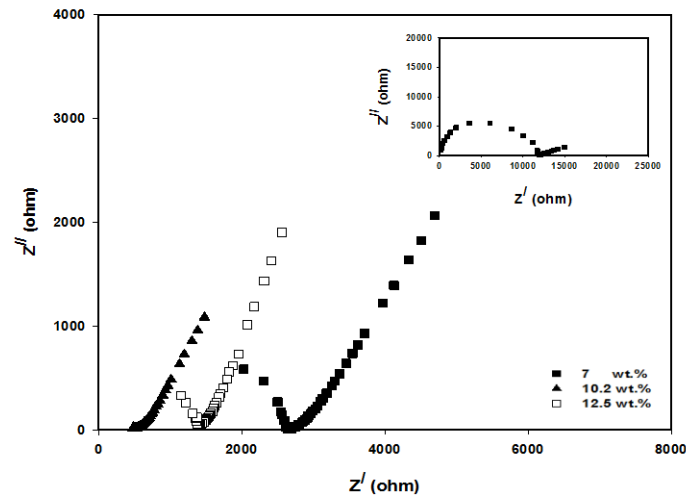


Fig. 1: Cole–Cole plots for the gel PMMA electrolyte samples
The inset figure shows the Cole–Cole plot for a gel PMMA sample without salt

Fig. 2 shows the plot of conductivity versus the weight percentage of LiTf in the gel polymer electrolytes. It can be observed that the conductivity of the gel polymer electrolyte samples increases with increasing the weight percent LiTf salt. The conductivity continued to increase until it reached the highest value of 6.60×10^{-5} S/cm at 10.2 wt.% of LiTf salt, thereafter it slightly decrease when the weight percent LiTf salt is higher than 12 wt.% of LiTf salt. Therefore, 10.2 wt.% LiTf salt is the conductivity optimizing concentration.

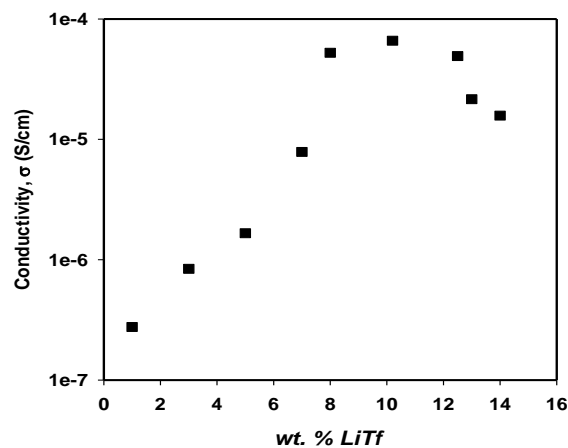


Fig. 2: Variation of ionic conductivity of the the gel polymer Electrolytes as a function of LiTf content at 298 K

It is well known that the conductivity of polymer electrolytes can be described by the relationship [30]:

$$\sigma = \sum u_i n_i q_i$$

where μ_i , n_i , and q_i represent the mobility of the i species, the concentration of carriers of the i species and the charge of the i species, respectively. Hence, the increase in the conductivity with increasing salt concentration could be attributed to the increase in the number of charge carriers and the mobility of the charge carriers. When the amount of LiTf salt added is higher than 12 wt.%, a saturation in the gel polymer electrolytes samples occurs and this leads to the reduction of free space in the samples; thus the ionic conductivity is decreased [31]. This is probably due to the formation of ion aggregates; and thus the number of charge carriers is decreased [32]. Morita et al. [33] also confirmed the formation of ion aggregates using Raman spectroscopy for the system PEO-PMMA/LiCF₃SO₃-LaCF₃SO₃. They reported a decrease in ionic conductivity for the higher concentrations of LaCF₃SO₃ due to the formation of aggregates when added to the system PEO-PMMA/LiCF₃SO₃.

Fig. 3 represents the variation of ac conductivity at room temperature with frequency for different salt concentrations in the gel polymer electrolytes. A general pattern in the frequency dependence of conductivity is observed for all gel PMMA electrolytes. The plots consist of two distinct regions: at the lower frequencies, <1 kHz, the conductivity is found to increase with increasing frequency, describing the electrodes polarization phenomena [34], and is followed by the frequency independent plateau region at higher frequencies, > 1 kHz.

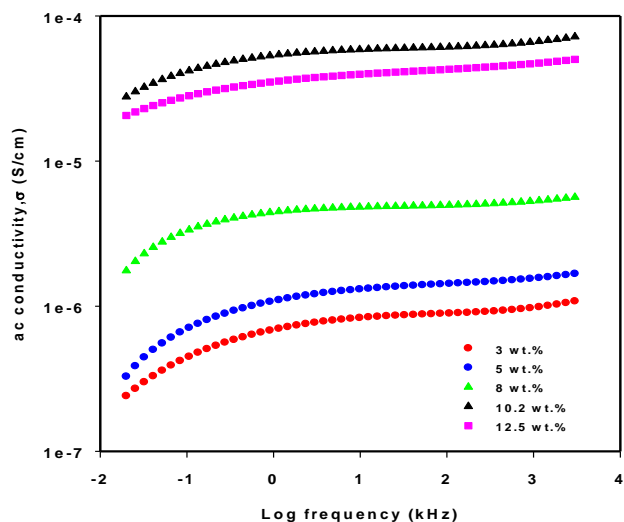


Fig. 3: Conductivity vs. Frequency for different salt concentrations in the gel polymer electrolytes at 298 K

The frequency independent conductivity is correlated with the dc conductivity, σ_{dc} [35]. The σ_{dc} of the prepared gel PMMA electrolyte samples has been determined by extrapolating the plateau region on the x-axis. The calculated σ_{dc} values from the conductivity–frequency dependence plots are in good agreement with those obtained from the Cole–Cole plot. The pattern of conductivity–frequency dependence obtained in this study is very similar to the one reported from previous work that focused on ionically conducting polymers, glasses and doped crystalline solids [36–38]. This is believed to be reflected in the mechanism of charge transport behavior of charge carriers.

Conductivity–temperature dependence studies

Fig. 4 depicts the Arrhenius plot of ionic conductivity for gel PMMA electrolytes containing various content of LiTf salt. There are two very clear features in the figure and they are, (i) Conductivity increases with increasing temperature. This is attributed to the expansion of polymer matrix. The polymer matrix expands with increase in temperature thereby weakens the interaction within the polymer matrix, promoting the decoupling of Li cations from the polymer complex. This assists the mobility of ions. The polymeric chain also acquires faster internal vibrational modes (i.e. decreasing viscosity) with increasing the temperature, which in turn to increase in mobility of polymer segments by initiating the bond rotation within the polymer matrix. Therefore, it favors the ionic transportation and hence increases the ionic conductivity [39]. (ii) Conductivity–temperature behavior can be explained by Vogel–Tamman–Fulcher (VTF) equation.

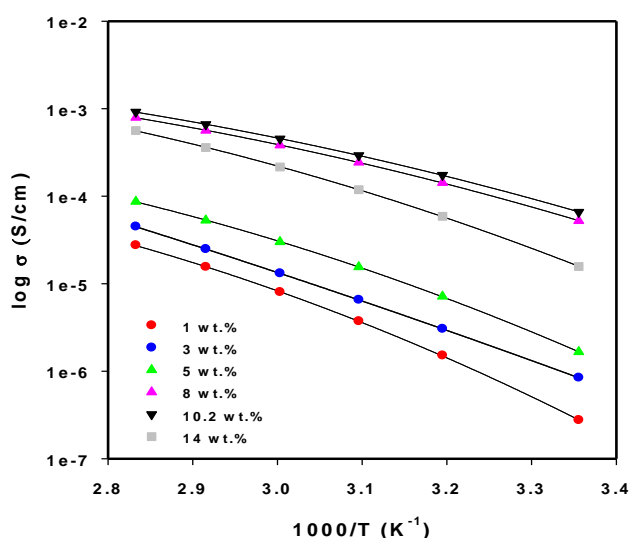


Fig. 4: dependence of ionic conductivity on temperature for gel PMMA electrolytes containing various content of LiTf salt

When conductivity is correlated by VTF, it is said to be depending on free volume theory. That is, the mobility of charge carriers is governed by polymer segmental motion by providing sufficient free space. As per the observation in **Fig. 4**, it can be suggested that polymer segmental motion imparts a considerable effect on conductivity of the gel polymer electrolytes.

The variation of ionic conductivity with temperature were fitted to VTF expression according to the equation [40]:

$$\sigma = AT^{-1/2} \exp\left[\frac{-B}{R(T-T_o)}\right]$$

where σ is conductivity, A is pre-exponential factor, which is proportional to the number of charge carriers, B is estimated apparent activation energy for conduction, R is gas constant, T is absolute temperature, and T_o is normally called the equilibrium glass-transition temperature, which is usually 50 K lower than that of the glass transition temperature (T_g). **Fig. 5** shows the VTF plots of PMMA-based gel polymer electrolytes.

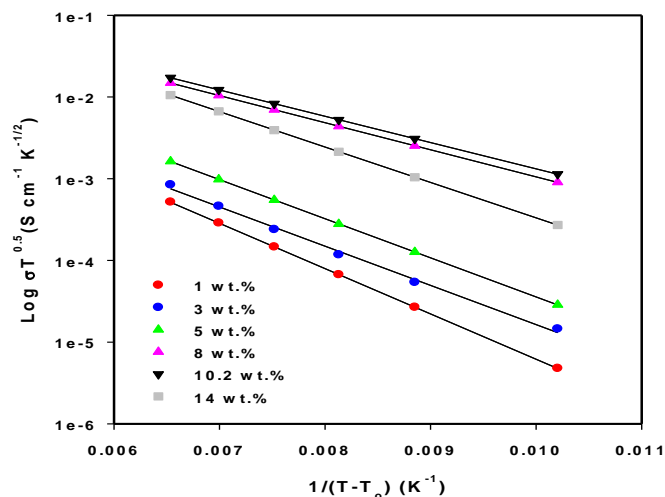


Fig. 5: VTF plots of PMMA-based gel polymer electrolytes containing various content of LiTf salt

The linear relationship in the Figure 5 confirms that the variation in conductivity with temperature follows a VTF relationship. The parameter A and B determined from the linear plots of $\ln \sigma T^{1/2}$ versus $1/(T - T_o)$ are listed in **Table 1**.

Table 1: Transference numbers and The parameters A and B for the gel polymer electrolytes

wt % LiTf	A (S K ^{1/2} cm ⁻¹)	B (kJ mol ⁻¹)	t_{ion}
1 wt. %	8.86	10.60	90.7
3 wt. %	10.30	9.16	92.8
5 wt. %	21.73	9.13	95.6
8 wt. %	44.36	6.33	96.1
10.2 wt.%	71.44	6.14	97.2
14 wt. %	41.09	8.27	96.5

It is seen that the parameter A increases as the lithium salt concentration increases. This result indicates that the number of charge carriers such as anions and a cations in PMMA-based gel polymer electrolytes increase with increasing the lithium salt concentration.

The parameter B of PMMA-based gel polymer electrolytes is in the range of 6.1 to 10.6 kJ mol⁻¹. The values are almost equal to or higher than those of the reported gel polymer electrolytes, such as PVDF-HFP-based gel polymer electrolyte (7.72 kJ mol⁻¹ to 9.85 kJ mol⁻¹) [41], PMMA-based gel polymer electrolyte (3.33 kJ mol⁻¹ to 9.86 kJ mol⁻¹) [42], PAN-based gel polymer electrolyte (10.6 kJ mol⁻¹ to 14.0 kJ mol⁻¹) [43], poly(oxetane) with cyanoethoxy group in the side chain-based gel polymer electrolyte (5.80 kJ mol⁻¹ to 9.39 kJ mol⁻¹) [44].

Transference number measurements

The ionic transference numbers (t_{ion}) for the gel PMMA electrolytes containing different percentage of the lithium salt were estimated using the dc polarization technique, and the results are cited in **Table 1**. A representative DC polarization data is depicted in **Fig. 6** can be used to estimate the contribution of lithium ions to the overall ionic conductivity of the electrolyte sample.

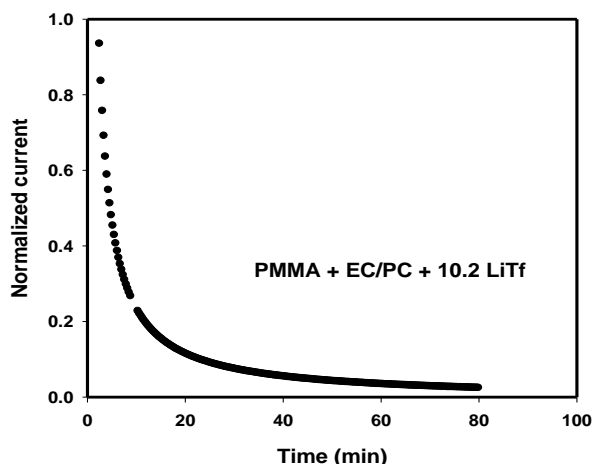


Fig. 6: DC-Polarization curves for the gel PMMA electrolytes containing 10.2 % of LiTf salt

For all compositions of the PMMA/ LiTf salt gel electrolyte systems, the values of the ionic transference number (t_{ion}) are in the range of 0.96–0.98. This suggests that charge transport in these polymer electrolyte films is predominantly due to ions; only a negligible contribution comes from electron

3.2. X-ray diffraction

Fig. 7 shows the X-ray diffraction patterns of pure PMMA, the LiTf salt and the PMMA gel electrolytes doped with various content of the LiTf salt.

The following points are observed while comparing pure XRD spectra with those of the complex gel electrolytes.

1. The XRD pattern of the LiTf salt shows Sharp diffraction peaks at $2\theta = 16.3^\circ, 19.8^\circ, 20.6^\circ, 22.9^\circ, 24.7^\circ, 32.9^\circ, 33.6^\circ, 40.1^\circ$ and 41.8° reveal the crystalline nature of pure LiCF_3SO_3 .
2. Most of the peaks pertaining to the LiTf salt disappeared in the gel electrolyte complexes. This indicates the complete dissolution of the salt in the polymeric matrix. It is evident from Fig. 7 that the amorphous nature is predominant in the complex gel electrolyte.
3. The diffractogram of PMMA shows a very broad peak at ($2\theta = 17.07^\circ$), which reveals the amorphous phase of PMMA. The intensity of this peak decreases with increasing salt content.

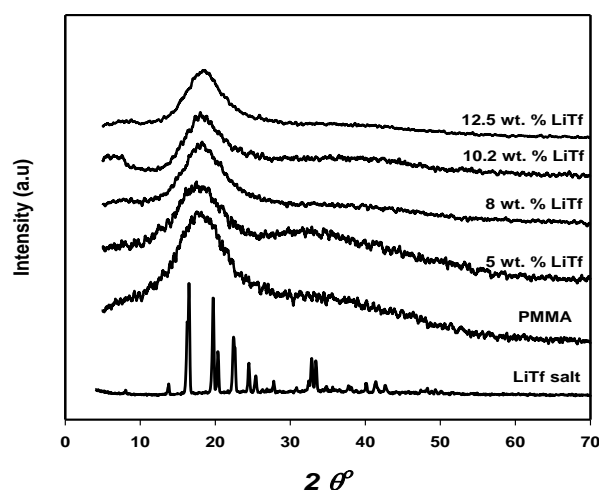


Fig. 7: XRD patterns of LiTf salt, pure PMMA and PMMA gel electrolytes doped with various content of the LiTf salt

These observations apparently revealed that the polymer undergoes significant structural reorganization while adding plasticizers and salt. The plasticizers may have induced significant disorder into the original polymer, and this is attributed to the interactions between the polymer and the solvents which resulted in polymer electrolytes with much lower crystallinity.

3.3. DSC analysis

Thermal analysis using differential scanning calorimeter (DSC) has been performed in order to observe the change in transition temperature that is caused by addition of salt. DSC thermograms of pure PMMA, PMMA gel, and PMMA gel electrolytes with different contents of the LiTf salt are depicted in **Fig. 8**. The glass transition temperatures (T_g) of pure PMMA and PMMA gel electrolytes obtained from the DSC measurements are tabulated in **Table 2**.

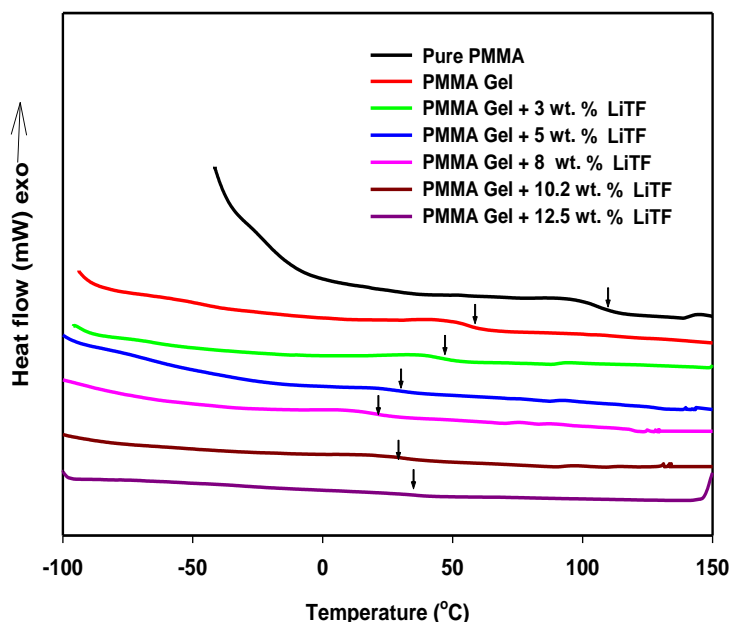


Fig. 8: DSC curves of pure PMMA, PMMA gel, and PMMA gel electrolytes with different contents of the LiTf salt

Pure PMMA shows a T_g value of 106 °C which decreases to 56 °C upon the addition of the EC/PC plasticizers. All the PMMA gel electrolytes show single T_g 's indicating the compatibility of gel PMMA/LiTf salt samples and the electrolytes are still remains amorphous structure with the addition of LiTf, consistent with the XRD results.

Table 2 : The glass transition temperatures (T_g) of pure PMMA and PMMA gel electrolytes

	T_g °C (DSC)
Pure PMMA	106
PMMA gel (PMMA + EC/PC)	56
3 % LiTf	48
5 % LiTf	31
8 % LiTf	22
10.2 % LiTf	29
12.5 % LiTf	35

In the PMMA gel electrolytes, initially the T_g values decrease with increasing the LiTf content up to 8 wt.% and then increase with further addition of the LiTf salt. This type of behavior may be related to the interaction between the salt and the PMMA segments. This interaction may induce the structure modification of polymer chains and break the polymer segment-segment interactions, thereby increasing the free volume and consequently decreases the T_g . But with the further increase of LiTf amount, interaction of Li^+ cations with the C=O and C–O–C of PMMA predominate thereby hindering the movement of the polymer chains and hence slightly increases the T_g values. Similar results have also been previously reported by Silva M.M. et al. and Chiodelli G. et al. for the poly(trimethylenecarbonate) with $LiBF_4$ and PEO– $LiBF_4$ polymer electrolytes, respectively [45,46]. This is suggestive of enhanced segmental motions, resulting in higher conductivity.

3.4. Dynamic mechanical analysis

Fig. 9a and **b** shows the dynamic mechanical properties of PMMA gel electrolytes. A significant dependence exists for the storage modulus (E') and $\tan \delta$ of the gel electrolytes on the temperature and the presence of LiTf salt. The E' values

in the glassy plateau region of the PMMA gel electrolytes decreases slightly with increasing the LiTf content, probably due to the losing of interchain interactions of PMMA and decreased stiffness of the polymer. However, E' decreased slowly with increasing the temperature, showing a very strong decay in the temperature range between 0 and 30 °C, which corresponds to the glass transition of the material. The decrease in the modulus is attributed to the energy dissipation phenomenon involving the cooperative motions of the polymer chains [47]. Incorporating of the LiTf salt induces a remarkable increase in the storage modulus of the matrix at temperatures above the glass transition (rubbery plateau region). This reflects the increased complexation of the added LiTf salt with the C=O and C–O–C functional groups of PMMA in the jelly (rubbery state).

The $\tan \delta$ plots shown in **Fig. 9b** exhibit a clear maximum for all samples, that typically represents the T_g of the gel electrolyte samples. The T_g values (the maximum values in the $\tan \delta$ vs. temperature plots) decreases with increasing the LiTf content up to 8 wt.% and then increase slightly with further addition of the LiTf salt. This type of behavior is consistent with the DSC results and again may be related to the interaction between the salt and the PMMA segments. This interaction may induce the structure modification of polymer chains and break the polymer segment-segment interactions, thereby increasing the free volume and consequently decreases the T_g . But with the further increase of LiTf amount, interaction of Li^+ cations with the C=O and C–O–C of PMMA predominate thereby hindering the movement of the polymer chains and hence slightly increases the T_g values.

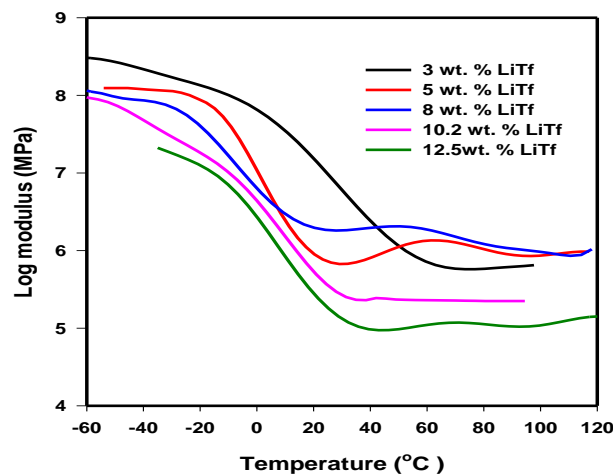


Fig. 9a: DMA Storage Modulus (E') versus Temperature for gel PMMA electrolytes containing various content of LiTf salt

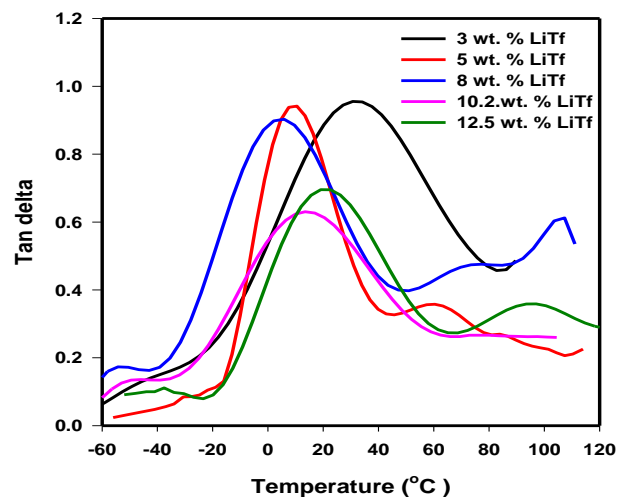


Fig. 9b: Tan Delta profile of gel PMMA electrolytes containing various content of LiTf salt

4. CONCLUSION

A gel polymer electrolytes synthesized from Poly(methylmethacrylate) (PMMA) as the host, ethylene carbonate (EC)/propylene carbonate (PC) as plasticizer and LiCF_3SO_3 (LiTf) as a salt were investigated. X-ray characterization confirms the complete dissociation of the LiTf salt in the polymeric matrix. AC impedance spectroscopy revealed that the ionic conductivity of gel polymer electrolyte continued to increase until it reached the highest value of 6.60×10^{-5} S/cm at 10.2 wt.% of LiTf salt, thereafter it slightly decrease when the weight percent LiTf salt is higher than 12 wt.% of LiTf salt.



For all compositions of the PMMA/ LiTf salt gel electrolyte systems, the values of the ionic transference number (t_{ion}) are in the range of 0.96–0.98. This suggests that charge transport in these polymer electrolyte films is predominantly due to ions; only a negligible contribution comes from electrons. The storage modulus E' values in the glassy plateau region of the PMMA gel electrolytes decreases slightly with increasing the LiTf content. However, E' decreased slowly with increasing the temperature. Incorporating of the LiTf salt induces a remarkable increase in the storage modulus of the matrix at temperatures above the glass transition (rubbery plateau region). The T_g values decreases with increasing the LiTf content up to 8 wt.% and then increase slightly with further addition of the LiTf salt.

5. REFERENCES

- [1] Simon P., and Gogotsi Y., *Nat. Mater.* (2008); 7, 845–854.
- [2] Wu Y. P., Dai X. B., Ma J. Q., and Cheng Y. J., *Lithium Ion Batteries: Practice and Applications*, Chemical Industry Press, Beijing, (2004).
- [3] Zuo X., Liu X. M., Cai F., Yang H., Shen X. D., and Liu G., *J. Mater. Chem.* (2012); 22, 22265–22271.
- [4] Tarascon J.M., Armand M., *Nature* (2001);414, 359–367.
- [5] Wang F. X., Xiao S. Y., Shi Y., Liu L. L., Zhu Y. S., Wu Y. P., and Holze R., *Electrochim. Acta* (2013); 93, 301–306.
- [6] Zhai W., Zhu H. J., Wang L., Liu X. M., and Yang H., *Electrochim. Acta* (2014);133, 623–630.
- [7] Rao M. M., Liu J. S., Li W. S., Liang Y., and Zhou D. Y., *J. Membr. Sci.* (2008);322, 314–319;.
- [8] Kim J. K., Manuel J., Lee M. H., Scheers J., Lim D. H., Johansson P., Ahn J. H., Matic A., and Jacobsson P., *J. Mater. Chem.* (2012); 22, 15045–15049.
- [9] Zhu Y., Wang F., Liu L., Xiao S., Chang Z., Wu Y., *Energy Environ. Sci.* (2013); 6 (2), 618.
- [10] Costa C.M., Silva M.M., Lanceros-Mendez S., *RSC Adv.* (2013); 3 (29),11404;.
- [11] Zhang P., Yang L.C., Li L.L., Ding M.L., Wu Y.P., and Holze R., *J. Membr. Sci.* (2011); 379 (1–2); 80.
- [12] B. Kurc, *Electrochim. Acta* (2014); 125, 415-420.
- [13] Sun P., Liao Y., Xie H., Chen T., Rao M., and Li W., *J. Power Sources* (2014); 269, 299.
- [14] Sun J., Stone G.M., Balsara N.P., and Zuckermann R.N., *Macromolecules* (2012); 45 (12), 5151.
- [15] Tsutsumi H., and Suzuki A., *Solid State Ionics* (2014); 262, 761.
- [16] Song J.Y., Wang Y.Y., and Wan C.C., *J. Power Sources* (1999);77 (2), 183.
- [17] Manuel Stephan A., and Nahm K.S., *Polymer* (2006); 47 (16), 5952.
- [18] Scrosati B., *Chem. Rec.* (2005); 5 (5), 286.
- [19] Deepa M., Agnihotry S.A., Gupta D., and Chandra R., *Electrochim. Acta* (2004); 49,373-83.
- [20] Agnihotry S.A., Ahmad S., Gupta D., and Ahmad S., *Electrochim. Acta* (2004); 49, 2343-9.
- [21] Ramesh S., and Lu S.-C., *J. Power Sources* (2008); 185, 1439-1443.
- [22] Ijima T., Toyoguchi Y., and Eda N., *Denki Kagaku* (1985);53, 619.
- [23] Bohnke O., Frand G., Rezzazi M., Rousselot C., and Truche C., *Solid State Ionics* (1993); 66, 97.
- [24] Agnihotry S.A., Ahmad S., Gupta D., and Ahmad S., *Electrochim. Acta* (2004); 49, 2343-2349.
- [25] Ghosh A., Kofinas P., *ECS Trans.* (2008); 11, 131-137.
- [26] Rajendran S., Sivakumar M., and Subadevi R., *J. Power Sources* (2003); 124, 225-230.
- [27] Appetecchi G.P., Croce F., and Scrosati B., *Electrochim. Acta* (1995); 40, 991.
- [28] Holland B.J., and Hay J.N., *Polymer* 42 (2001); 4825.
- [29] Vondrak J., Sedlarikova M., Velicka J., Klapste B., Novak V., and Reiter J., *Electrochim. Acta* (2001); 46, 2047.
- [30] Gray F.M., *Solid Polymer Electrolytes: Fundamentals of Technological Applications*, Wiley-VCH, United Kingdom, (1991); 1–30.
- [31] Othman L., Chew K.W., and Osman Z., *Ionics* (2007);13, 337-42.
- [32] Ramya C.S., Selvasekarapandian S., Savitha T., Hirankumar G., and Angelo P.C., *Physica B* (2007);393, 11-7.
- [33] Morita M., Araki F., Yoshimoto N., Ishikawa M., and Tsutsumi H., *Solid State Ionics* (2000); 136–137, 1167.
- [34] Siekierski M., Wiczorek W., and Przulski J., *Electrochim Acta* (1998); 43, 1339-42.
- [35] Jonsher A.K., *Dielectric Relaxation in Solids*, London, Chelsea Dielectric Press; (1983).



- [36] Elliott S.R., *Solid State Ionics* (1988); 27, 131-49.
- [37] Leon C., Lucia M.L., and Santamaria J., *Phy Rev B: Condens Matter* (1997); 55, 882-7.
- [38] Leon C., Lucia M.L., Santamaria J., Parsi M.A., Sanz J., and Varez A., *Phy Rev B: Condens. Matter* (1996); 54, 184-9.
- [39] Baskaran R., Selvasekarapandian S., Kuwata N., Kawamura J., and Hattori T., *Solid State Ionics*, (2006b); 177, 2679-2682.
- [40] Fulcher G.S., *J. Am. Ceram. Soc.* (1925); 8, 339.
- [41] Isa K.B.M., Osman Z., Arof A.K., Othman L., Zainol N.H., Samin S.M., Chong W.G., and Kamarulzaman N., *Solid State Ionics* (2014); 268 (Part B), 288.
- [42] Bohnke O., Frand G., Rezrazi M., Rousselot C., and Truche C., *Solid State Ionics* (1993); 66 (1–2), 97.
- [43] Park U.-S., Hong Y.-J., and Oh S.M., *Electrochim. Acta* (1996); 41 (6), 849.
- [44] Tsutsumi H., and Suzuki A., *Solid State Ionics* (2014); 262, 761.
- [45] Silva M.M., Barros S.C., Smith M.J., and MacCallum J.R., *Electrochimca Acta* (2004); 49, 1887.
- [46] Chiodelli G., Ferloni P., Magistris A., and Sanesi M., *Solid State Ionics* (1988); 28–30, 1009.
- [47] Menard K. P., in “*Dynamic Mechanical Analysis: A Practical Introduction*”, edited by K. P. Menard, CRC Press, (1999); 17-37.