Int. J. Electrochem. Sci., 9 **(2014)** 821 - 829

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Structural and Electrical Properties of Plasticized Radiation Induced Chitosan Grafted Poly(methylmethacrylate) Polymer Electrolytes

N.K. Jaafar[1], *A. Lepit*[1], *N.A. Aini*[1], *A.M.M. Ali*[1,2], *A. Saat*[2], *M.Z.A. Yahya*[3,*]

[1]Faculty of Applied Sciences, Universiti Teknologi MARA 40450 Shah Alam, Malaysia.
[2]Institute of Science, Universiti Teknologi MARA 40450 Shah Alam, Malaysia.
[3]Faculty of Science & Defence Technology, Universiti Pertahanan Nasional Malaysia, 57000 Kuala Lumpur, Malaysia.
[*]E-mail: mzay@upnm.edu.my

Received: 15 May 2013 / *Accepted:* 3 June 2013 / *Published:* 8 December 2013

Plasticized grafted polymer electrolytes composed of chitosan-grafted-poly(methylmethacrylate) (Ch-g-PMMA), ethylene carbonate (EC) plasticizer and lithium triflate (LiTf) salt were prepared by the solution cast technique. Impedance spectroscopy was performed in the temperature range of 303-373 K. The highest conductivity of 1.63 x 10^{-4} Scm^{-1} was obtained for the salted grafted polymer with 50 wt% LiTf and enhanced to 2.23 x 10^{-4} Scm^{-1} with the addition of 30 wt.% EC. The temperature dependence conductivity data obeys Arrhenius relationship. Dielectric behavior was analyzed using complex permittivity (ε) and electrical modulus formalism (M) for the highest conducting unplasticized and plasticized samples at various temperatures. The structure and complexation of the electrolyte were studied by Fourier transform infrared (FTIR) spectroscopy.

Keywords: Grafted, Chitosan, Poly(methylmethacrylate), Ionic conductivity, Plasticizer

1. INTRODUCTION

Solid polymer electrolytes (SPEs) are a class of materials that is attracting ever-increasing interest in the industry and academe due to their applicability for a variety of solid-state and electrochemical device applications including batteries, fuel cells, supercapacitors and chemical sensors [1]. However, most SPEs have lower conductivity compared to the liquid solutions thus limit for commercially use in electrochemical devices [2]. Therefore, various approaches such as blending, copolymerization, plasticization and composite fabrication techniques have been introduced to enhance the ionic conductivity of the SPEs [3-4].

The techniques of graft copolymerization include chemical, radiation, photochemical, plasma-induced techniques and enzymatic grafting. Among all the methods, radiation-induced graft copolymerization is well known for its merits and potential in modifying the chemical and the physical properties of pre-existing polymeric materials without altering their inherent properties [5]. The properties of polymer electrolytes can be improved by graft copolymerization technique as follows: increase of electrolyte uptake, reduce the crystallinity as well as generating amorphous domain structure of the polymer and improve mechanical strength and thermal stability. Moreover, it is be noted that there are several reports [6-7] on the use of radiation-induced graft copolymerization to prepare polymer electrolytes that suitable for electrochemical applications such as fuel cell, batteries and sensor.

In recent years [8], chitosan (an N-deacetylated derivative of chitin) has been extensively studied due to its biodegradable, biocompatible and non-toxic polymer. A work [9] concentrated on chitosan modification through copolymerization of chitosan and vinyl monomers for preparation of new materials, which can endow chitosan with special properties and hence allowing versatile applications.

In this work, the modification of chitosan-g-PMMA by plasticization is presented. Our previous work [10] revealed that PMMA could be grafted onto chitosan backbone by gamma radiation. The results also showed that the crystallinity of chitosan was reduced and the thermal stability improved. The focus is attributed to investigate on the structural and electrical properties of salted and plasticized chitosan-g-PMMA that perhaps to be a promising candidate in lithium conducting polymer electrolytes.

2. EXPERIMENTAL

2.1 Materials

Materials comprise of chitosan, MMA and LiTf were purchased from Sigma-Aldrich INC, USA. Acetone and acetic acid were purchased from Mallinclerod Baker INC, USA. All of reagents were used without further purification. Doubly distilled water was used throughout the experiments.

2.2 Preparation of plasticized Ch-g-PMMA Based Electrolytes

The grafted polymer electrolytes were prepared using two-steps procedure. The first step involved the preparation of grafted polymer by graft copolymerization of MMA onto chitosan using simultaneous irradiation technique. 0.5 g chitosan was dissolved in 50 ml 1% acetic acid solution and then 0.5 g of MMA solution was added accordingly. After complete dissolution being obtained, the solutions were irradiated in a ^{60}Co–γ-ray field. The facility of ^{60}Co–γ-ray source was carried out using One Stop Gamma Sterilizing Center, SINAGAMA, Malaysian Nuclear Agency (NUCLEAR MALAYSIA).Upon irradiation, the grafted sample solutions were cast into petri dishes and left to form a grafted chitosan film. The homopolymer formed in the reaction was removed via Soxhlet extraction using acetone for 8 h. The grafted copolymer was then dried in a vacuum oven at 40 ^{o} C until a constant weight was obtained. Different concentrations (10-50 wt%) of EC plasticizer was then separately doped into the optimum of Ch-g- PMMA –LiTf solution which provides the highest conducting salted sample. Each sample was prepared using solution cast technique.

2.3 Characterization

In order to investigate the occurrence of complexation between Ch-g-PMMA polymer, LiTf salt and EC plasticizer, FTIR study was performed. The FTIR spectroscopy was carried out using VARIAN 3100 FTIR, Excalibur series at the Institute of Science, UiTM, Shah Alam. The spectra of the samples were measured in the transmittance mode at a wave number of 4000 to 400 cm^{-1} with resolution of 4.0 cm^{-1}.

The conductivity of the grafted polymer electrolytes was measured using a Won A Tech, WEIS510, Multichannel electrochemical impedance spectroscopy (EIS) System that has been interfaced to a computer. The impedance spectroscopy measurement was carried out in the frequency range between 100 Hz and 1 MHz. The sample was sandwiched between two stainless steel blocking electrodes. The conductivity–temperature study was conducted in the temperature range of 303-373 K in a Temperature Chamber (ESPEC-SH 221).

3. RESULTS AND DISCUSSION

3.1 FTIR analysis

The FTIR spectra of pure chitosan, PMMA, LiTf and their grafted complexes are depicted in Fig. 1. The vibration peak at 1637 cm^{-1} and 1543 cm^{-1} wavenumbers are due to the carbonyl, C=O-NHR and amine, NH_2 band [11-14] of pure chitosan respectively. The band at 1543 cm^{-1}, which is the characteristic peak of the primary amine N–H vibration in chitosan, disappeared in the spectra of the grafted polymer. This indicates deformation of the primary amine in the graft copolymer. This also implies that grafting occurred at the $–NH_2$ groups [15]. The carbonyl band which appears at 1631 cm^{-1} in the spectrum of Ch-g-PMMA has shifted to 1643 in the spectra of Ch-g-PMMA- salt. The shift in Ch-g-PMMA spectrum indicates the occurrence of the grafted polymer -salt interaction. The peak observed at 1728 cm^{-1} which is due to the C=O asymmetric stretching of the carbonyl group in pure PMMA. Other band observed at 1485 cm^{-1}, 1365 cm^{-1} and 1431 cm $^{-1}$ are due to CH_2 scissoring, CH_2 twisting, and O-CH_3 asymmetric bending, respectively. The presence of new bands at 1726 cm^{-1} and 1431 cm^{-1} on the grafted polymer indicate that PMMA was successfully grafted onto the chitosan backbone [10]. The C=O stretching band of grafted polymer at 1724 cm^{-1} has shifted to 1730 cm^{-1}. This indicates that there is an interaction between carbonyl group and lithium salt via a coordinate bond and hence complexation has occurred. The FTIR spectrum of pure LiTf as shown in Fig. 1(d) are observed to make justify of the coordination of the lithium salt. The band of $LiCF_3SO_3$ at 1247 cm^{-1} and 1039 cm^{-1} are assigned to asymmetric SO_3 and symmetric SO_3 vibration of $LiCF_3SO_3$, respectively.

In the spectrum of salted grafted polymer complexes (Fig. 1(f)) it can obviously be seen that there are existence of this ‘free triflate’. The band of $LiCF_3SO_3$ at 1247 and 1039 cm^{-1} is shifted to 1238 and 1026 cm^{-1} in the salted grafted polymer complexes respectively. This happens may be due to the change in environment for the $F_3SO_3^{-1}$ ion in the complexes. Moreover, the appearance of new peak along with changes in the FTIR spectra confirms the complexation has occurred between grafted polymer and lithium salt at carbonyl site of chitosan and PMMA of the grafted polymer [16-18]. Fig. 1(g) represents the spectrum of Ch-g-PMMA-LiTf-EC, There is hardly any noticeable shift in peaks in the plasticized film. The C=O band in plasticized Ch-g-PMMA-LiTf with EC (1782 cm^{-1}) seems to have broadened and overlapped implying that the plasticizer just interacts physically with the grafted polymer and salt. Hence, it can be said that there is no apparent chemical interaction between grafted polymer with EC or between the plasticizer and the salt [18-19].

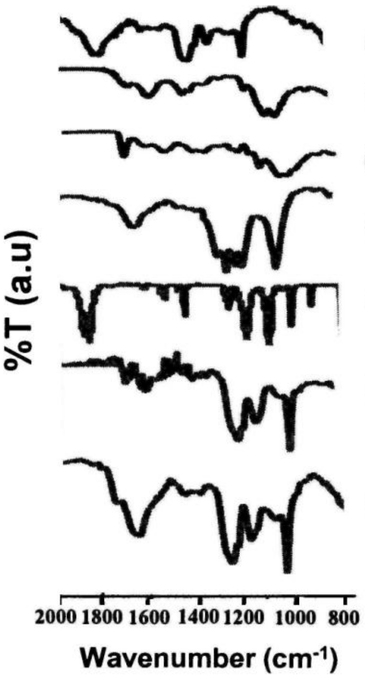

Figure 1. FTIR spectrum of (a) pure PMMA, (b) pure Chitosan (c) Chitosan-g-PMMA (d) pure LiTf (e) pure EC (f) Chitosan-g-PMMA -50 wt% LiTf (g) Chitosan-g-PMMA-50 wt% LiTf – 30 % EC

3.2. Ionic conductivity

The explanation pertaining to the increase and decrease of ionic conductivity of Ch-g-PMMA-LiTf electrolytes can be ascribed in terms of the phenomenon of ion dissociation and ion association respectively. The variation of conductivity as a function of weigh percent (wt %) lithium salt at room temperature is shown in Fig. 2. The highest electrical conductivity achieved is 1.63 x 10^{-4} Scm^{-1}. The increase in conductivity with the increase in salt concentration up to 50 wt % LiTf could be attributed to the increase of mobile ions number which is attributed to ion dissociation. However, at the high salt concentration (>50 wt %), the decrease in conductivity could be attributed in the decrease of free mobile ions number as a result of ions association has taken place. This occurs probably due to the decrease in the mean distance between the ions, which become more significant because the ions become closer to one another and tend to associate [20].

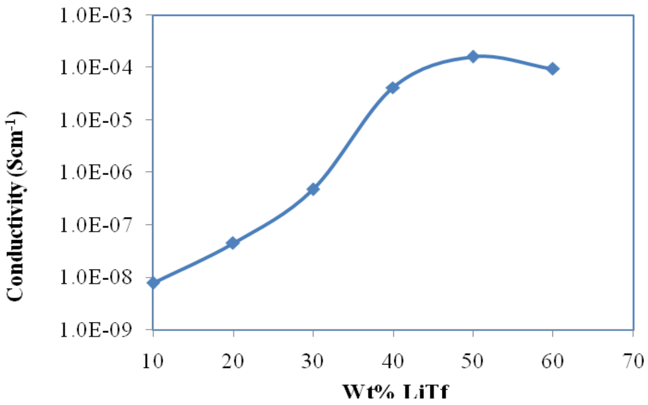

Figure 2. The dependence of ionic conductivity of salted system at room temperature (30 °C).

The variation of conductivity as a function of weight percent (wt%) of plasticizer in a Ch-g-PMMA-50% LiTf system at room temperature is shown in Fig. 3. It can be observed that the room conductivity of the plasticized Ch-g-PMMA-50% LiTf system increases to the maximum value of 2.23 x 10^{-4} Scm^{-1} when 30 wt% EC was added. The addition of EC plasticizer to grafted polymer electrolytes can establish attractive forces between EC molecules and grafted polymer chain segments. These attractive forces reduce the cohesive forces between the grafted polymer chains and increase the segmental mobility and can result in facilitating greater ion dissociation which allows greater numbers of charge carriers for ionic transport, thus enhancing the ionic conductivity. However, the decrease in conductivity upon the addition of higher than that of 30 wt % EC could be ascribed to the occurrence of ions association and thus decrease the number of free mobile ions available in the system.

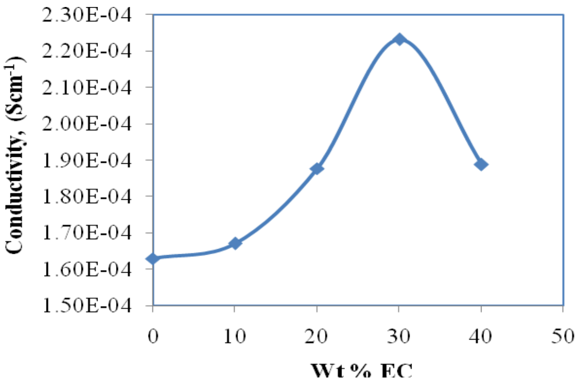

Figure 3. The dependence of ionic conductivity of plasticized system at room temperature (30 °C).

The temperature dependence ionic conductivity measurement has also been carried out within the temperature 303K to 363 K. The ionic conductivity results as a function of temperature for the highest conducting unplasticized (Ch-g-PMMA-50 % LiTf) and plasticized (Ch-g-PMMA - 50% LiTf - 30 % EC) samples are shown in Fig. 4. The relationship between log σ and 1000/T is almost linear. Hence, it can be concluded that the conductivity mechanism is thermally assisted.

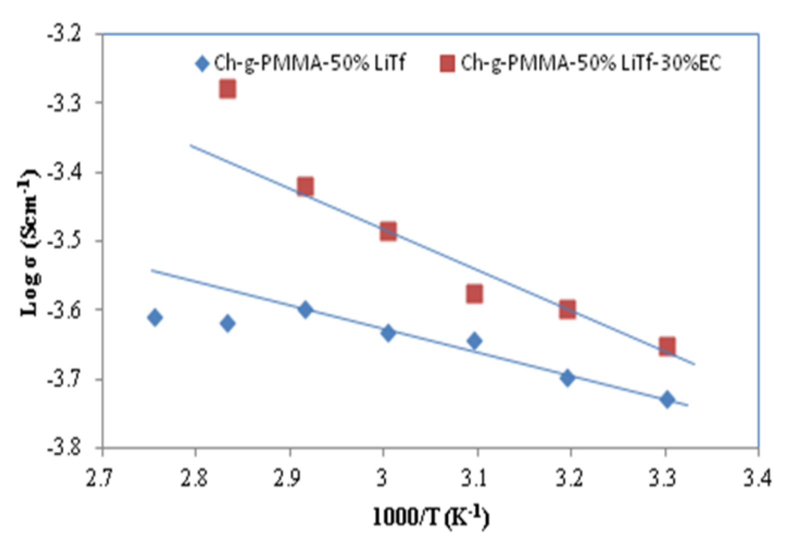

Figure 4. The relationship between log σ and 1000/T for the highest conductivity unplasticized (Ch-g-PMMA-50 % LiTf) and plasticized (Ch-g-PMMA-50 % LiTf -30 % EC) samples

3.3 Dielectric relaxation studies

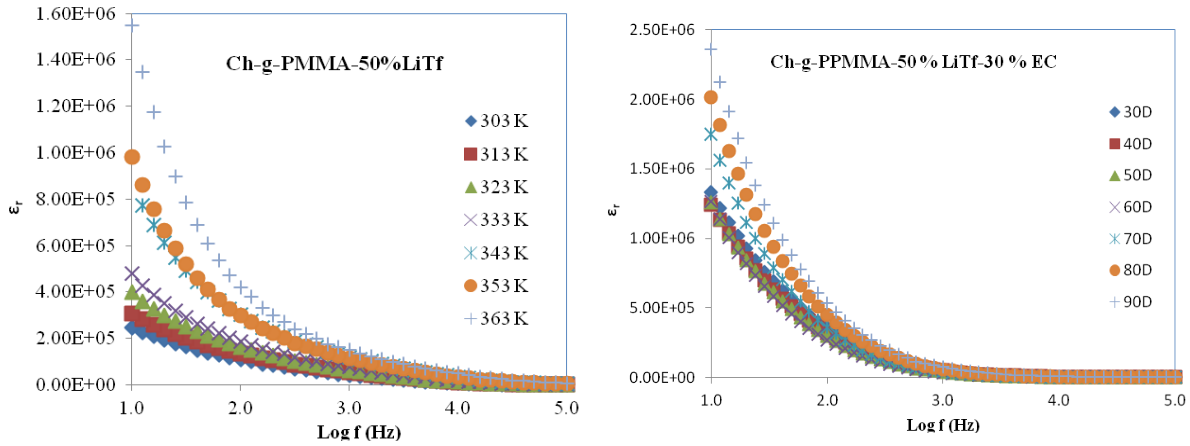

Figure 5. Variation of real part of the electric constant (ε_r) as a function of frequency at various temperature for the unplasticized (Ch-g-PMMA-50 % LiTf) and plasticized (Ch-g-PMMA-50 % LiTf -30 % EC) samples with highest conductivity.

The variation of the real (ε_r) and imaginary part (ε_i) parts of the electric constant as a function of frequency for the highest conducting unplasticized (Ch-g-PMMA-50 % LiTf) and plasticizer (Ch-g-

PMMA-50 % LiTf -30 % EC) samples are shown in Fig. 5 and 6 respectively. Both (ε_r) and (ε_i) rise sharply towards low frequency due to the electrode polarization effect [21]. At high frequencies, the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field. The polarization is due to the charge accumulation decrease, leading to the decrease in the value of (ε_r) and (ε_i) [22].

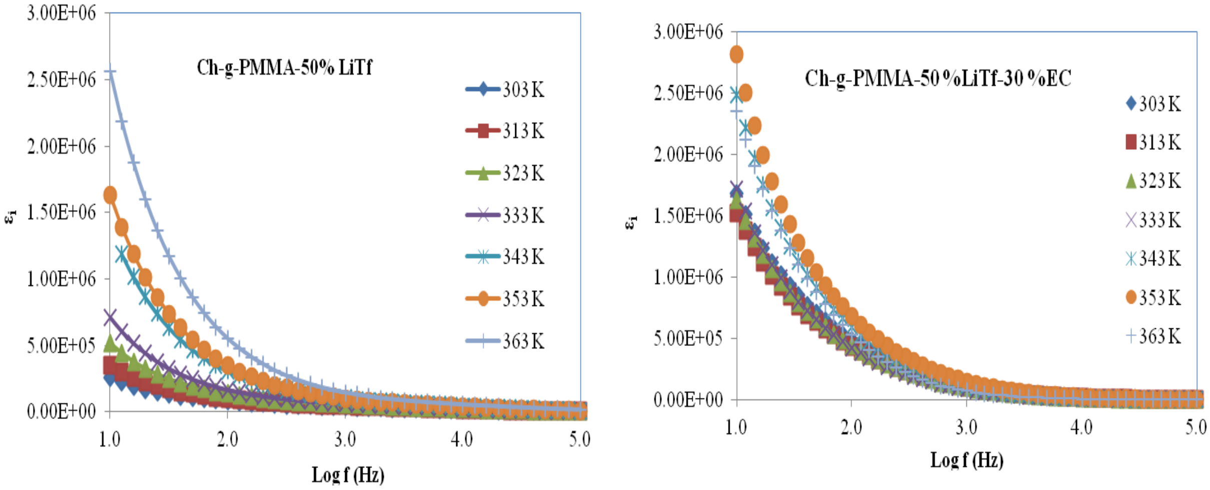

Figure 6. Variation of imagine part of the electric constant (ε_i) as a function of frequency at various temperature for the unplasticized (Ch-g-PMMA-50 % LiTf) and plasticized (Ch-g-PMMA-50 % LiTf -30 % EC) samples with highest conductivity.

3.4 Dielectric modulus formalism study

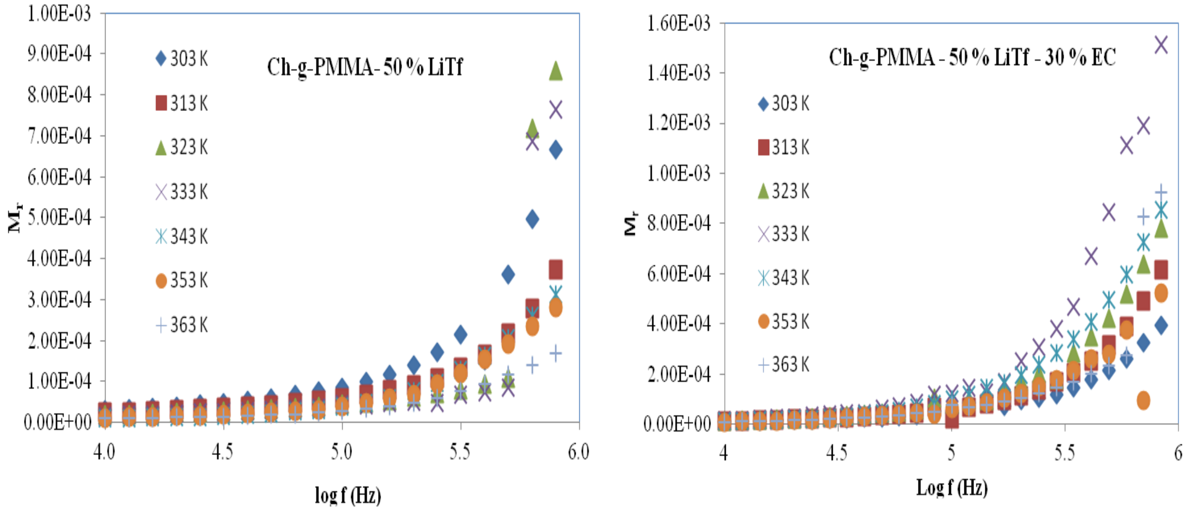

Figure 7. Variation of real part of the electric constant (M_r) as a function of frequency at various temperature for the unplasticized (Ch-g-PMMA-50 % LiTf) and plasticized (Ch-g-PMMA-50 % LiTf -30 % EC) samples with highest conductivity.

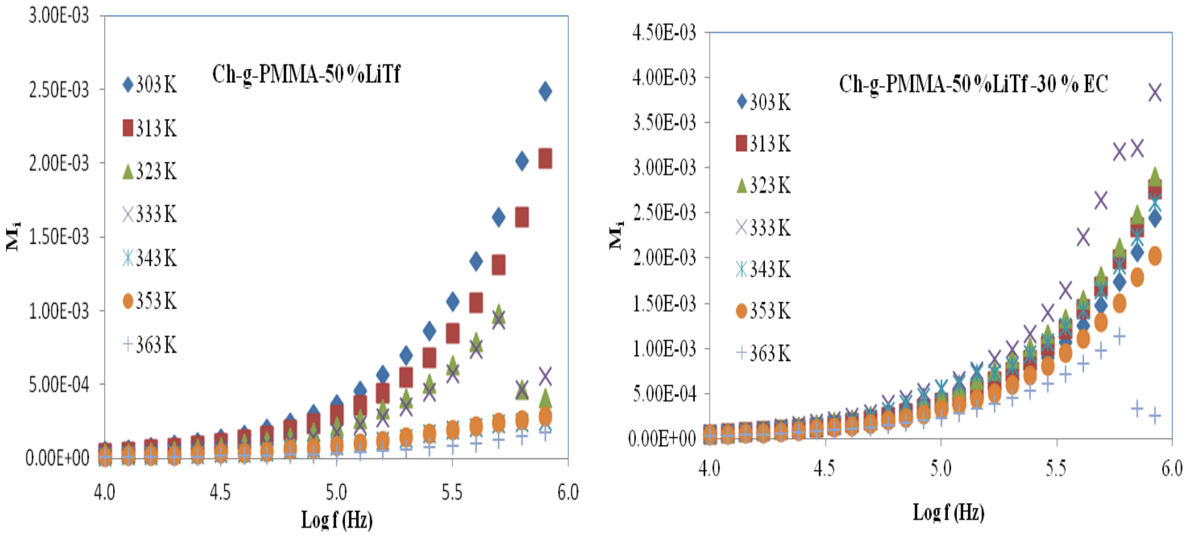

Figure 8. Variation of imagine part of the electric constant (M_i) as a function of frequency at various temperature for the unplasticized (Ch-g-PMMA-50% LiTf) and plasticized (Ch-g-PMMA-50 % LiTf -30 % EC) samples with highest conductivity.

Variation of the real part (M_r) and imaginary part (M_i) parts of the modulus constant as a function of frequency for the highest conducting unplasticized (Ch-g-PMMA-50 % LiTf) and plasticized (Ch-g-PMMA-50 % LiTf -30 % EC) samples are shown in Fig. 7 and 8 respectively. M_r and M_i shown an increase at higher frequency end, but well defined dispersion peaks are not observed. At low frequencies, it is observed that the value M_r and M_i is decrease showing of electrode polarization is negligible. The long tail is probably the result of the large capacitance associated with the electrode [23].

4. CONCLUSION

Grafted polymer electrolyte flm containing Ch-g-PMMA-LiTf-EC were prepared using solvent casting technique. The change in position (shifting) of the peak confirmed the complexation between Chitosan-g-PMMA and LiTf. Ionic conductivity increases as salt concentration increased and reached 1.63 x 10^{-4} Scm^{-1} with 50 wt% salt concentration. The conductivity of Ch-g-PMMA-LiTf increased to the highest value, 2.23 x 10^{-4} Scm^{-1} with employing 30 wt% of EC plastisizer. The conductivity value that has been obtained by adding LiTf and EC into the grafted chitosan could make this grafted polymer complexes as a potential material in some electrochemical devices.

ACKNOWLEDGEMENT

This work is supported by the Fundamental Research Grant Scheme (FRGS) awarded by the Ministry of Higher Education Malaysia (MOHE).

References

1. J.Y. Song, Y.Y. Wang and C.C. Wan: *J. Power Sources*, 77 (1999), p. 183-197.

2. A.N. Alias, T.I.T. Kudin, Z.M. Zabidi, M.K. Harun and M.Z.A. Yahya: *Adv. Mater. Res.*, 501 (2012), p. 39-43.
3. S.Z.Z. Abidin, A.M.M. Ali, O.H. Hassan and M.Z.A. Yahya: *Int. J. Electrochem. Sci.*, 8 (2013), p. 7320- 7326.
4. M. Z. A. Yahya, A.M.M. Ali, M.F. Mohammat, M.A.K.M. Hanafiah, M. Mustaffa, S.C. Ibrahim, Z.M. Darus and M.K. Harun: *J. Appl. Sci.*, 6 (2006), p. 1287- 1291.
5. A. Lepit, N.A. Aini, N.K. Jaafar, N. Hashim, A.M.M. Ali, K.Z.M. Dahlan and M.Z.A. Yahya: *Int. J. Electrochem. Sci.*, 7 (2012), p. 8560-8577.
6. A. Lepit, M.Z.A. Yahya, N.A. Aini, N.K. Jaafar, A.M.M. Ali and K.Z. M. Dahlan: *Int. J. Electrochem. Sci.*, 7 (2012), p. 7712-7719.
7. A. Lepit, N.A. Aini, A.M.M. Ali, K.Z.M. Dahlan, M.Z.A. Yahya: *Adv. Mater. Res.*, 476-478 (2012), p. 636-641.
8. R.A.A. Muzzarelli and C. Muzzarelli: *Adv. Polym. Sci.*, 186 (2005), p. 151-209.
9. Y. Zhou, B. Lieberg, N.A. Gorochovceva, R. Makuska, A. Dedinaite and P.M. Claesson: *J. Colloid Interf. Sci.*, 305 (2007), p. 62-71.
10. N. K. Jaafar, A. Lepit, N. A. Aini, A. Saat, A. M. M. Ali and M. Z. A. Yahya: *Mater. Res. Innov.*, 15 (2011), p. S202-S204.
11. C. Peniche, C. Elvira and, J. San Roman: *Polymer*, 39 (1998), p. 6549-6554.
12. M.Z.A. Yahya and A.K.Arof: *Eur. Polym. J.*, 39 (2003), p. 897-902.
13. H.Y. Kweon, I.C. Um and Y.H. Park: *Polymer*, 42 (2001), p. 6651-6656.
14. X. Qu, A. Wirsen and A.C. Albertsson: *Polymer*, 41 (2000), p. 4841-4847.
15. J.P. Wang, Y.Z. Chen, X.W. Ge and H.Q. Yu: *Chemosphere*, 66 (2007) p. 1752-1757.
16. S. Rajendran, R. Kannan and O. Mahendran: *J. Power Sources*, 96 (2000), p. 406-410.
17. S. Ramesh, Kaoy Leen, K. Kumutha and A.K.Arof: *Spectrochim. Acta Part A*, 669 (2007), p. 1237-1242.
18. Z. Osman and A.K. Arof: *Electrochim. Acta*, 48 (2003), p. 993-999.
19. A.M.M. Ali, M.Z.A. Yahya, H. Bahron, R.H.Y. Subban, M.K. Harun and I. Atan: *Mater. Lett.*, 61 (2007), p. 2026-2029.
20. A.M.M. Ali, R.H.Y. Subban, H. Bahron, T. Winie, F. Latif and M.Z.A. Yahya: *Ionics*, 14 (2008), p. 491- 500.
21. N.I. Harun, R.M. Ali, A.M.M. Ali and M.Z.A. Yahya: *Ionics*, 18 (2012), p. 599- 606.
22. F. Latif, M. Aziz, N. Katun, M. Ali and M.Z.A. Yahya: *J. Power Sources*, 159 (2006), p. 1401-1404.
23. R. Mishra and K.J. Rao: *Solid State Ionics*, 106 (1998) p. 113-127.