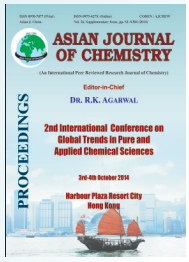
Asian Journal of Chemistry; Vol. 26, Supplementary Issue (2014), S262-S266

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.19061



Preparation and Characterization of Polymer Electrolyte Based on Glycidyl Methacrylate and 1-Butyl-3-methylimidazolium *bis*(Trifluoromethylsulfonyl)imide by *in situ* Photopolymerization

B.C.F. WONG, N.H. HASSAN*, A. AHMAD and S.A. HANIFAH

School of Chemical Sciences and Food Technology, Faculty of Sciences and Technology, University Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

*Corresponding author: E-mail: syareeda@ukm.edu.my

Published online: 24 December 2014; AJC-16486

Poly(glycidyl methacrylate) based solid polymer electrolytes were prepared *via in situ* photopolymerization. The effect of 1-butyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide (BmImTFSI) concentration on the chemical interaction, structure, thermal, morphology and conductivity of the electrolytes were investigated. The completion of polymerization and the chemical interaction between polymer film segments and BmImTFSI were confirmed by attenuated total reflectance-fourier transformation infra-red spectroscopy (ATR-FTIR). Based on thermagravimetric analysis result, the two-step weight loss process was observed for the BmImTFSI incorporated electrolyte films. X-ray diffraction analysis reveals that the semi-crystalline nature of poly(glycidyl methacrylate) were reduced to an amorphous state due to an increase of BmImTFSI content. Morphological studies by scanning electron microscopy shows the addition of BmImTFSI into the electrolyte films gave the homogenous and smoother surfaces. The highest ionic conductivity of the electrolyte film with 70 wt. % of BmImTFSI obtained at 3.08×10^{-6} and 6.37×10^{-3} S cm^{-1}, respectively at ambient temperature and 100 °C.

Keywords: *in situ* Photopolymerization, Room-temperature ionic liquids, Polymer electrolytes, Glycidyl methacrylate.

INTRODUCTION

Nowadays human society is facing a global energy crisis and environmental pollution problems. This has grabbed the attention of the scientific community towards the development of efficient electrochemical devices. Besides, the fast growing in the field of portable electronic devices does accelerate the research on the polymer containing charged species as solid electrolytes for next generation devices[1]. The reasons for choosing polymers as candidate materials are due to their flexibility, better safety and ease to fabrication at low cost[2]. Meanwhile the charged species are the ions of the salts that dissolved in the polymer system, it can be lithium salt, sodium salt[3], magnesium salt[4] *etc*. Recently, ionic liquids (ILs) as a liquid salts composing organic cations and couter ions have become an interest among the electrochemical researchers. The excellent physiochemical properties of ionic liquids, namely high ionic conductivity, good electrochemical and thermal stability and negligible vapor pressure, allow them to be suitable electrolytes[1,5-8].

At present, several processing methods have been developed to prepare the polymer electrolyte with the ionic liquids. One of the conventional methods is the solvent-casting method which the polymer and ionic liquid are dissolved in a volatile solvent, usually organic solvent and then evaporation of the latter. This method requires a long mixing and drying time[2]. The usage of solvents and the need of their evaporation are not friendly to the environment. Another preparation method is to soak the polymer film into the electrolyte. The disadvantage of this method is the amount of the electrolyte cannot be well defined. By comparing these methods, the direct polymerization of the homogenous mixture of monomer and ionic liquid is more promising, known as *in situ* polymerization. There are two types *in situ* polymerization, namely (a) *in situ* thermal polymerization and (b) *in situ* photopolymerization[9]. The former involves heating, based on the previous studies, the reaction had to be carried out at around 60- 80 °C and for a long time about 2 to 24 h[10-12]. The latter is the technique that requires UV light as an energy source to cure the monomer. This enables the polymerization to occur at room temperature and shorter time in minutes. Thus, it is low energy consumption, fast, environmentally friendly and low cost methods. However, this one pot photopolymerization process is limited to certain combinations of multifunctional monomers with ionic liquids and only a few researches were successful

reported. According to Andrzejewska and Stepniak[9], polyethylene glycol methacrylate, dipropyleneglycol diacrylate and aliphatic urethane acrylate with 5 types of ionic liquids and 2,2-dimethoxy-2-phenylacetophenone (DMPP) as photoinitiator, give a compatible and freestanding polymer films. Besides, incorporation of *N*-methoxyethyl-*N*-methylpyrrolidinum *bis*(trifluoromethanesulfonyl)imide and 1-ethyl-3-methy-limidazolium *bis*(perfluoroethylsulfonyl)imide into the dime-thacrylic monomer, bisphenol A ethoxylate (15 EO/phenol) dimethacrylate to obtain a homogenous polymer electrolyte film with high ionic conductivity[13,14].

In this work, a new combination of monomer glycidyl methacrylate (GMA) with different amount of BmImTFSI was explored. A single-step, *in situ* photopolymerization method will be applied in order to obtain free standing polymer electrolytes within a few minutes. Besides, as charge carrier, BmImTFSI also acts as a plasticizer to improve the structure and morphology of electrolyte films[11]. Photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPP) plays an important role to start the polymerization of glycidyl methacrylate by forming benzoyl radicals once it was radiated by UV light[15]. The chemical, physical and electrochemical properties of prepared polymer electrolytes were studied and reported.

EXPERIMENTAL

Monomer glycidyl methacrylate, photoinitiator 2,2-dimethoxy-2-phenylacetophenone, dichloromethane, silver nitrate and ionic liquid BmImTFSI were purchased from Sigma-Aldrich. All materials were used as received and no further purification was done except BmImTFSI.

Purification of BmImTFSI: The oily liquid BmImTFSI was further purified by liquid-liquid extraction method. BmImTFSI was added into dichloromethane and washed with deionized water. The washing process was repeated until the aqueous phase was free from halide which can be detected by $AgNO_3$ solution[16]. The solvent dichloromethane was removed on rotary evaporator and followed by drying process using vacuum line.

Preparation of polymer films: An appropriate amount of DMPP (2 wt. %) and BmImTFSI were added into GMA monomer and stirred until a homogenous mixture obtained. The homogenous mixture was then spread on the Teflon plate and cured under 196-5251 UV box (Rs Ltd) with four 60W UV lamp. While the samples were under curing of UV, a continuous flow of nitrogen gas was needed. The thickness of the films was controlled in between 300-600 µm. The completion of photopolymerization was ensured by curing the GMA and DMPP mixture with different irradiation times and followed by ATR-FTIR analysis.

Characterization of the polymer films: ATR-FTIR analysis was done using Spectrum 400 Perkin Elmer GX Spectrometer. The prepared film samples were cast on NaCl window and analyzed with the frequency in the range of 4000 to 650 cm^{-1}. This analysis was carried out to observe the changes of the vibrant energy of the covalent bond possessed by the polymer host before and after the addition of BmImTFSI.

Besides, thermal properties of the PGMA films were investigated by using the Shimadzu TGA-50 model. The heating rate was set at 20 ºC/min and the measurement temperature range was started from ambient temperature to 600 ºC.

Bruker D8-advance diffractometer were used to study the X-ray diffraction pattern of the prepared samples. The range of diffraction angle, 2θ from 10º to 50º were selected to study the structure of prepared PGMA films. The morphological studies of the PGMA films were carried out by using Model LEO VPSEM with 250x and 1000x magnification at 15 kV electron beam.

The ionic conductivity of the PGMA films were measured using HIOKI 3532-50LC HiTester impedance analyzer. The prepared films were sandwiched between two stainless steel electrodes and measured from 50 to 50000 Hz. Apart from that ionic conductivity was measured as the function of temperature in the range of 303 to 373 K. The ionic conductivity, σ was calculated using the formula $\sigma = l / R_b \cdot A$, where l represents the thickness of the film (cm), R_b is the bulk resistance of film and A is the effective contact area (cm^2) of the electrode.

RESULTS AND DISCUSSION

ATR-FTIR analysis: The polymer films, hereafter named PGIL-0 to PGIL-70, were prepared by *in situ* photopolymerization of the GMA mixture which consists of photoinitiator, DMPP and different wt. % of BmimTFSI. After UV curing, a transparent, freestanding and flexible film formed. However, the maximum loading of BmImTFSI is 70 wt. % in order to produce a freestanding film (PGIL-70). The further additional of BmImTFSI results in unstable film.

The FTIR spectra in Fig. 1(a) shows the vibrational peak at 1637 cm^{-1} which corresponds to stretching of sp^2 C=C double bond of GMA monomer. After the UV curing, the C=C peak disappeared, as shown in Fig. 1(b). Besides, FTIR spectra also shows the changes of polymer systems as in Fig. 1(c) when the BmImTFSI was added. This includes the changes of intensity, shapes and the shift of peaks and these may be able to show the occurrence of complexation and interaction between the ionic liquid and the polymer matrix. By comparing the PGIL-0 and PGIL-70, after the incorporating of BmImTFSI, six new peaks appeared as highlighted in Fig. 1(d). These peaks are corresponding to the C-S and S-N stretching mode at 788 cm^{-1}, C-H vibration mode of cyclic $BmIm^+$ at 1080 cm^{-1}, S-N-S asymmetric stretching mode at 1055 cm^{-1}, C-SO_2-N bending mode at 1351 cm^{-1}, C-C and C-N bending mode at 1573 cm^{-1} and cyclic BmIm CH_2 stretching mode at 3158 cm^{-1}. The intensity of these six peaks increases and more significant with the ascending of BmImTFSI content.

In order to prove the interaction between the BmImTFSI and polymer matrix, both of epoxy stretching peaks at 842 and 905 cm^{-1} decrease in the intensity and the peaks shift to 846 and 906 cm^{-1}, respectively after inclusion of 70 wt. % of BmImTFSI. Similar observation is shown in Fig. 2(a), the C-O-C ester peak of pristine PGMA (PGIL-0) with two shoulders at 1146 cm^{-1} changes in shape and shifts to 1131 cm^{-1} when the 70 wt. % BmImTFSI was incorporated. Besides, intensity of the peak of C-O-C symmetrical stretching mode at 1252 cm^{-1} (PGIL-0) decrease gradually and shifts upwards to 1272 cm^{-1} (PGIL-70). This indicates the interaction between

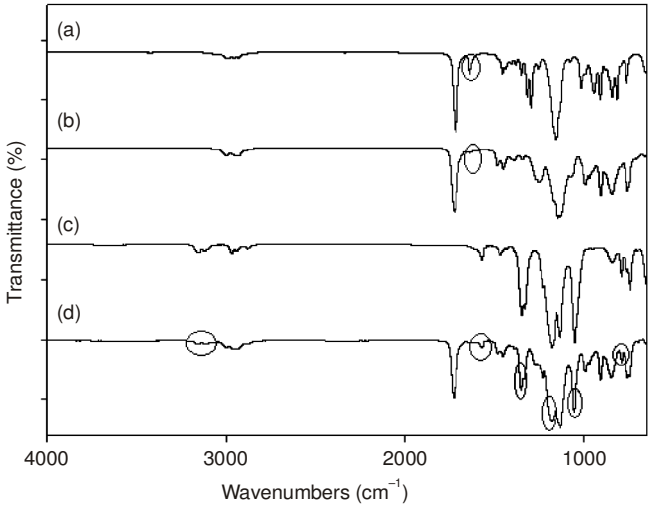


Fig. 1. FTIR spectra for (a) monomer GMA, (b) PGIL-0, (c) pure BmImTFSI and (d) PGIL-70

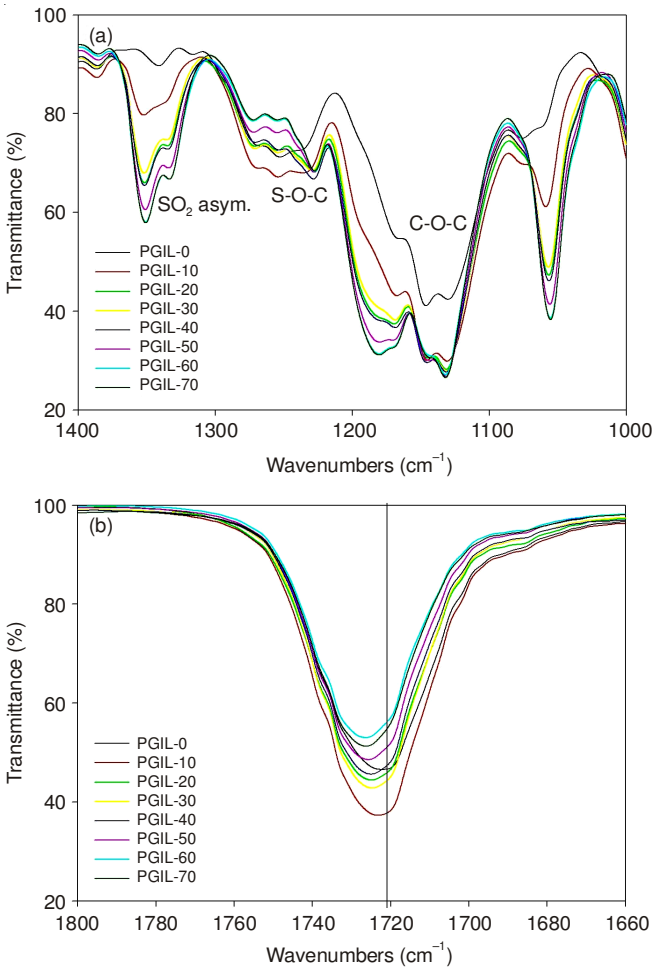


Fig. 2. FTIR spectra of PGILs films and BmImTFSI in the wavenumber region (a) 1400-1000 cm^{-1} and (b) 1800-1660 cm^{-1}

O^- and $BmIm^+$ which leads to the ion transportation by breaking and reforming the coordination bonds[17]. Another evidence for this interaction was shown by the C=O peak, shifts from 1722 to 1726 cm^{-1}. In Fig. 2(b) the intensity of the peak decreases with the higher BmImTFSI mass loading. This is because more O^- and $BmIm^+$ were formed when higher amount of BmImTFSI was added. The interaction between $BmIm^+$ and O^- may reduce the electronegativity differences between C and O atoms of the C=O bonds. This will then contribute to the less intense absorption and less intense peak was formed.

Thermal analysis: Fig. 3 shows the thermagravimetric analysis thermograms of the prepared PGIL films and pure BmImTFSI. The polymer matrix PGIL-0, undergoes a one-step weight loss process with a decomposed temperature of 261 ºC and ended at 350 ºC with the total mass loss of 99 %. This single step of degradation was due to random chain scission[18]. The BmImTFSI shows a single weight loss process which starts at 453 ºC and ended at 508 ºC with the total weight loss of 95 %. However, after the incorporation of BmImTFSI into the system, the thermogram shows two-steps weight loss process. The initial loss is corresponding to the degradation of the polymer matrix, PGMA and followed by the decomposition of the BmImTFSI in the system. It should be noted that the BmImTFSI incorporated films possess a higher onset of the weight loss process for PGMA than that of the pristine PGMA. Based on the thermogram, the initialization decomposed temperature of PGIL-70 was increased to 267 ºC and its total weight loss was 93.3 % after the temperature reaches 477 ºC. These evidences prove that high thermal stability of the prepared polymer films and the films are safe to be used at high temperature (up to 250 ºC).

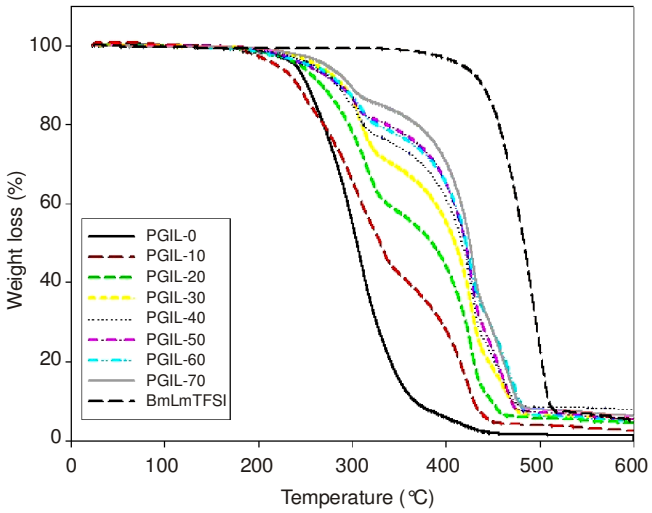


Fig. 3. Thermagravimetric analysis thermogram of the PGIL films and pure BmImTFSI with heating rate at 20 ºC/min from ambient temperature to 600 ºC

Structure and morphological analysis: XRD diffractogram (Fig. 4) shows the typical X-ray diffraction patterns of the PGIL films measured at room temperature. The diffractogram of PGIL-0 film shows 2 humps in the range between 15-25° and 25-35° meanwhile PGIL-10 to PGIL-70 show only one hump in range of 15-22°. The presence of the humps explained the PGIL films exist as amorphous. As the amount of BmImTFSI increases, the diffraction peaks become broader and less intense. This result could be due to the disruption of the PGMA crystallinity by incorporating of the BmImTFSI as a plasticizer[19,20]. The decreasing of the crystallinity of the films results in the softer films formed. Apart from that, the increases of the amorphousity results in the reduction of the energy barrier to the segmental motion of the polymer . In other words,

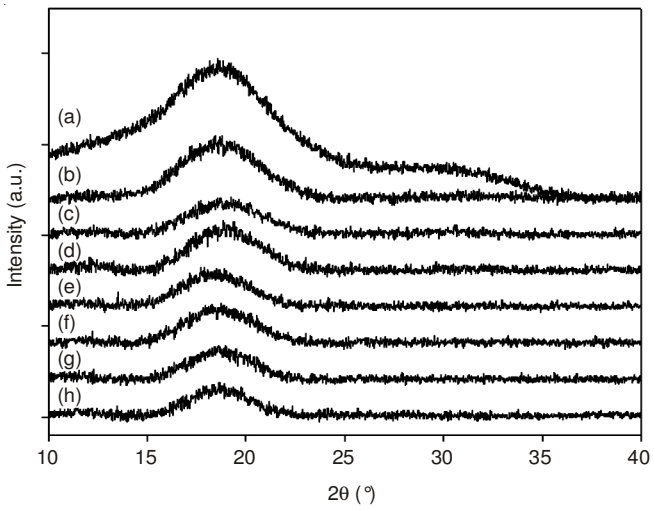


Fig. 4. X-ray diffractogram for PGIL- (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, (f) 50, (g) 60 and (h) 70

these may enhance the ionic mobility in the polymeric system and therefore improve the ionic conductivity of polymer at room temperature[21].

Moreover, by observing the cross-sectional morphology through SEM micrograph (Fig. 5), the PGIL samples show a homogenous surface without any phase separation. The PGIL-0 shows an uneven and rough cross sectional surface because of its brittle properties. This property causes the sample to crack and split easily[22,23]. However, the roughness of the surface and the cracking effect reduces accordingly as the content of BmImTFSI increases. A smooth and uniform surface can be observed on PGIL-70 film and it also shows a very good adhesion properties of glass and steel[19].

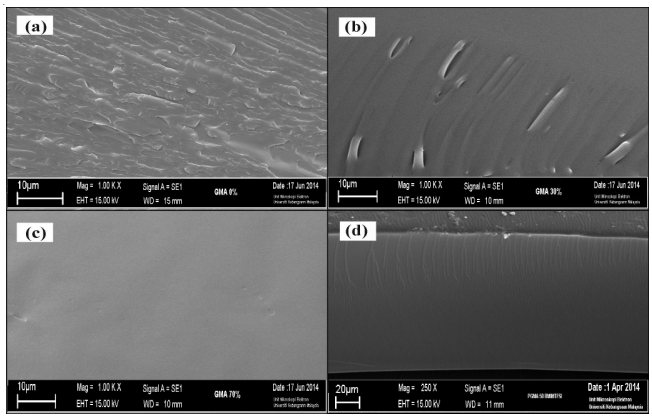


Fig. 5. Micrograph SEM of (a) PGIL-0, (b) PGIL-30 (c) PGIL-70 at 1000x magnification and (d) PGIL-50 at 250x magnification

Ionic conductivity analysis: The conductivity studies were done at room temperature and the results were shown in Fig. 6. For the PGIL-0, a PGMA without BmImTFSI shows the conductivity of 1.82×10^{-9} Scm^{-1}. By increasing the BmImTFSI content from 10 to 40 wt. %, the conductivity shows a slight increment. The PGIL-40 films have the conductivity of 3.19×10^{-9} S cm^{-1}. However, a drastic increase can be observed upon the addition of 50 to 70 wt. % of BmImTFSI. The addition of 70 wt. % of BmImTFSI achieved the highest ionic conductivity of 3.08×10^{-6} S cm^{-1}.

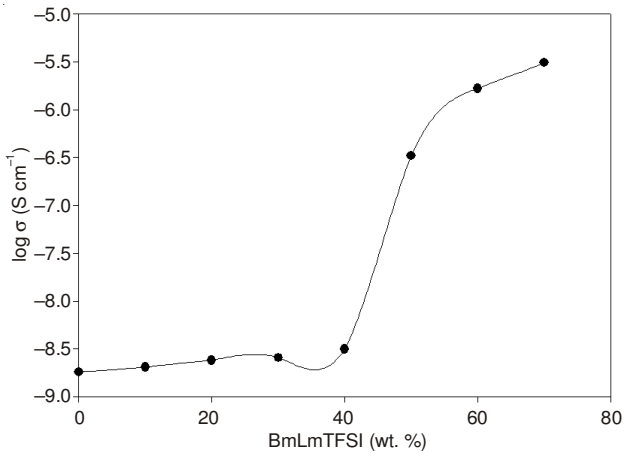


Fig. 6. Conductivity of the PGILs with different composition of BmImTFSI in wt. % at ambient temperature

The increases in ionic conductivity are due to the increases of the charge carriers in the PGMA-BmImTFSI complex system as provided by the following equation: $\sigma = c\Lambda$, where Λ is molar conductivity and c is salt concentration[24]. The strong plasticizing effect of BmImTFSI, softened the polymer backbone and increased the flexibility of polymer segment[25]. This enhances the segmental mobility and initiates the ionic hopping mechanism[17].

Fig. 7 is the Arrhenius plot of PGIL-70 film from 303 to 373 K. At 373 K, the ionic conductivity value is 6.37×10^{-3} S cm^{-1} which shows the increases of the ionic conductivity by four orders of magnitude. A linear plot was found in between conductivity and the temperature with the regression line in 0.9991. This indicates the PGIL films perform Arrhenius-like behaviour based on Arrhenius equation: $\sigma = \sigma_o e^{(-Ea/kT)}$, where the σ_o is pre-exponential factor, E_a is activation energy, k is Boltzmann constant and T is temperature in unit K. From the plot, the σ_o is 1×10^{11} S cm^{-1} and E_a is 0.98 eV. The BmImTFSI in the PGIL films provides $BmIm^+$ and $TFSI^-$ ions that exhibit the highest self-dissociating and ionic hopping properties[26]. As the heat was supplied to the system, the ions gain the kinetic energy and this enhances the mobility of the charge carriers in the films.

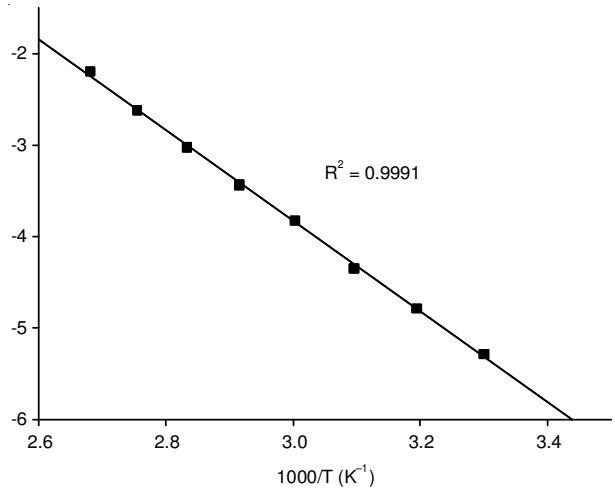


Fig. 7. Temperature dependance of ionic conductivity of PGIL-70 film from 303 to 373 K

Conclusion

The BmImTFSI based-polymer films were prepared by *in situ* photopolymerization methods. The changes in shapes, intensity and shifts of the vibrational peaks of ATR-FTIR spectra proved the completion of the polymerization of GMA and also the interaction between PGMA and BmImTFSI. BmImTFSI is dissolved and compatible with the PGMA, homogenous and transparent films were obtained and proved by SEM micrograph. To obtain a freestanding film, the maximum loading of BmImTFSI into the PGMA polymeric system is 70 wt. % and it shows the ionic conductivity of 3.08×10^{-6} S cm^{-1} at ambient temperature. The films exhibited Arrhenious behaviour. Finally, BmImTFSI incorporated in the films provides charge carriers and acts as a plasticizer to enhance the ionic conductivity.

ACKNOWLEDGEMENTS

The authors sincerely gratitude to Centre for Research and Istrumentation Management (CRIM, UKM) for giving the analytical study supports and Universiti Kebangsaan Malaysia for giving the grant codes ERGS/1/2013/TK07/UKM/02/4 and ETP-2013-027 in order to complete the research.

REFERENCES

1. M.J. Park, I. Choi, J. Hong and O. Kim, *J. Appl. Polym. Sci*., **129**, 2363 (2013).
2. J.R. Nair, C. Gerbaldi, G. Meligrana, R. Bongiovanni, S. Bodoardo, N. Penazzi, P. Reale and V. Gentili, *J. Power Sources*, **178**, 751 (2008).
3. K.B.M. Isa, L. Othman, N.H. Zainol, S.M. Samin, W.G. Chong, Z. Osman and A.K.M. Arof, *Key Eng. Mater*., **594-595**, 786 (2013).
4. N.H. Zainol, S.M. Samin, L. Othman and K.B. Md Isa, *Int. J. Electrochem. Soc*., **8**, 3602 (2013).
5. A. Noda, K. Hayamizu and M. Watanabe, *J. Phys. Chem. B*, **105**, 4603 (2001).
6. J. Jiang, D. Gao, Z. Li and G. Su, *React. Funct. Polym*., **66**, 1141 (2006).
7. H. Cheng, C. Zhu, B. Huang, M. Lu and Y. Yang, *Electrochim. Acta*, **52**, 5798 (2007).
8. A. Hofmann, M. Schulz and T. Hanemann, *Electrochim. Acta*, **89**, 823 (2013).
9. E. Andrzejewska and I. Belastepniak, *Polymer*, **51**, 11 (2006).
10. A. Noda and M. Watanabe, *Electrochim. Acta*, **45**, 1265 (2000).
11. M.A.B.H. Susan, T. Kaneko, A. Noda and M. Watanabe, *J. Am. Chem. Soc*., **127**, 4976 (2005).
12. H. Guan, F. Lian, K. Xi, Y. Ren, J. Sun and V. Kumar, *J. Power Sources*, **245**, 95 (2014).
13. C. Gerbaldi, J.R. Nair, S. Ahmad, G. Meligrana, R. Bongiovanni, S. Bodoardo and N. Penazzi, *J. Power Sources*, **195**, 1706 (2010).
14. C. Gerbaldi, J.R. Nair, S. Ferrari, A. Chiappone, G. Meligrana, S. Zanarini, P. Mustarelli, N. Penazzi and R. Bongiovanni, *J. Membr. Sci*., **423-424**, 459 (2012).
15. V. Mucci and C. Vallo, *J. Appl. Polym. Sci*., **123**, 418 (2012).
16. L. Li, J. Wang, P. Yang, S. Guo, H. Wang, X. Yang, X. Ma, S. Yang and B. Wu, *Electrochim. Acta*, **88**, 147 (2013).
17. C.W. Liew, S. Ramesh and R. Durairaj, *J. Mater. Res*., **27**, 2996 (2012).
18. T. Caykara, F. Cakar and S. Demirci, *Polym. Bull*., **61**, 311 (2008).
19. R. Leones, F. Sentanin, L.C. Rodrigues, I.M. Marrucho, J.M.S.S. Esperance, A. Pawlicka and M.M. Silva, *Express Polym. Lett*., **6**, 1007 (2012).
20. M. Imperiyka, A. Ahmad, S.A. Hanifah and M.Y.A. Rahman, *Int. J. Electrochem. Sci*., **8**, 10932 (2013).
21. M. Imperiyka, A. Ahmad, S. A. Hanifah and M. Y. A. Rahman, *Int. J. Polym. Sci.*, Article ID 638279 (2014).
22. M.S. Su'ait, A. Ahmad and M.Y.A. Rahman, *Ionics*, **15**, 497 (2009).
23. M.S. Su'ait, S.A.M. Noor, A. Ahmad, H. Hamzah and M.Y.A. Rahman, *J. Solid State Electrochem*., **16**, 2275 (2012).
24. A. Manuel Stephan and K.S. Nahm, *Polymer*, **47**, 5952 (2006).
25. S.S. Sekhon, P. Krishnan, B. Singh, K. Yamada and C.S. Kim, *Electrochim. Acta*, **52**, 1639 (2006).
26. S. Ramesh, C.W. Liew and K. Ramesh, *Non-Cryst. Solids*, **357**, 2132 (2011).