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An investigation ofpolymer electrolyte based on poly(glycidylmethacrylate) doped with imidazolium ionic liquid

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Abstract

PGMAdoped with ionic liquid of bmimTFSI was prepared by using solution casting technique. Chemical interactions, structure and ionic conductivities were studied by infrared analysis, x-ray diffraction, differential scanning calorimetry, electrochemical impedance spectroscopy and scanning electron microscopy. BmimTFSI spread homogenously between the polymer chain and interact with the oxygen atom from the polymer matrix. The result showed that the addition of bmimTFSI has reduced the crystalline region in the solid polymer electrolyte with the restructuring of the polymer chain. Ionic conductivity shows optimum conductivity at the addition of 70 wt. %bmimTFSI with the value of 1.86×10^{-6} S cm^{-1} at room temperature. Temperature dependence of ionic conductivity for solid polymer electrolytes showed PGMA-bmimTFSI obeyed Arrhenius equation and the activation energy decreases with increasing weight percent bmimTFSI.

Keywords: Ionic Liquids; Poly(glycidyl methacrylate); Solid polymer electrolyte; Ionicconductivities

1. Introduction

Solid polymer electrolytes are more convenient because they have better shape, easy to be handled, and possibilities for electrolytes leaking are none.PEOis a polymer matrix that widely studied and it functions as a role model for the selection of a suitable matrix characteristics. Based on the theory, the functional groups that exist in the matrix will improve the dissociation of salt. Therefore, the selection of matrix such as PEO, PVdF and PMMA are also for the same purposes[1-3]. Conventional polymer electrolytes are the solution of salt in polymers. Nowadays, the aeroplanes international regulations limit the carrying of lithium batteries on board because of the safety issues since it consist of lithium electrolytes that may cause the flammability hazards. Thus, to enhance the safety of batterysystem is the type of flammable salt based electrolytes may reduce or replace to the safer electrolytes system. The ideal electrolytes are ionic liquids or also known as molten salts which consist of positive and negative ions.

Ionic liquids are organic salts with melting point below 100°C. Dielectric constant, electrochemical window and ionic conductivitiesare the important physical properties to determine the suitability of the ionic liquids to use in polymer electrolytes. As organic salts, ionic liquids have negligible vapour pressure as such as non-volatile and also non-flammable. Previous study was focused on the ability of the ionic liquids to use as electrolytes based on several factors which are the length of the alkyl chain and the molecular size of the cations and anions [4]. Ionic liquids with large molecule of anions have a greater charge distribution and have least tendency to form hydrogen bonds with cations. Consequently, the ionic mobility is higher and increases the ionic conductivities.

The previous studies reported on the use of ionic liquids as plasticizers [5-6]. This is due to the small diameter of ionic salts haveencouragescoordination to occur on functional groups in the polymer, henceaffect the ionic conductivitiesbecause of limited ionic movement. However, few studies indicate that the increasing of the ionic conductivities is due to the increasing number of charge carriers contribute by the ionic liquids [6].Therefore,ionic liquids have the potential to replace the using of salt as a dopant in the solid polymer electrolytes. Besides, the replacement of salt with ionic liquids inpolymer electrolytesshowed better value which is approximately near to pure ionic liquids by using in situ preparation method [7]. However, an understanding of the effects of the use of ionic liquids in the solid polymer electrolytes has yet to be achieved.

To the best of our knowledge, solid polymer electrolyte based on poly(glycidyl methacrylate) (PGMA) doped 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (bmimTFSI) has not been reported yet. The ionic liquid chosen for this work is air stable and less hydrophilic thus allowing the preparation at room temperature without electrolytesdegradation.This paper discusses the effect of bmimTFSIionic liquid into a series of PGMA from the view of possible interaction between the matrix and ions, structure of polymer, and its ionic conductivity.

2. Experimental

2.1 Materials

Glycidyl methacrylate (GMA), 2,2-dimethoxy-2-phenylacetophenone (DMPP), and bmimTFSI were purchased from Aldrich. Ethanol (95% purity) was obtained from Systerm, while tetrahydrofuron was purchased from J.T. Baker. All chemicals were used without further purification, except for bmimTFSIthat was purified prior to use [8].

2.2 Preparation of samples

PGMA with molecular weight of 45, 200 g/mol was prepared following the procedure described in the reference [9]. PGMA-bmimTFSI films were prepared by solution casting technique. PGMA (3 g) was dissolved in 30 mL of tetrahydrofuran for 24 h. An amount of 10wt.%, 20wt.%, 30wt.%, 40wt.%, 50wt.%, 60wt.% and 70wt.% of bmimTFSI was added into the polymer solutions, followed by stirring for another 3 h. The solutions were then casted into a Teflon mould, and allowed to evaporate slowly at ambient temperature. Further drying was performed at 50^{o}C in a vacuum oven for 24 h.

2.3 Instrumentation

FTIR analysis was carried out using Perkin Elmer Spectrum with frequency ranging from 4000 cm^{-1} to 650 cm^{-1}, while the scan resolution was about 4 cm^{-1}. X-ray diffraction pattern was studied using a Bruker D8-Advance diffractometer. Data were collected from the range of diffraction angle 2θ from 10° to40°. Glass transition temperature,T_g was measured using differential scanning calorimeter brand Mettler Toledounder nitrogen environment with a scanning rate of 10°C/minand at temperature range of -15°C to 120°C. Ionic conductivity was measured by electrochemical impedance spectroscopy model HIOKI 3532-50 LCR HiTESTER. The polymer film was sandwiched between stainless steel electrodes with frequency range of 50-5 MHz at ambient temperature and at the range of 30°C-100°C for temperature dependence. The ionic conductivity was calculated using the equation of $\sigma = [t/(A.R_b)]$, where t is thickness of the film, A is the surface area, and R_b is the bulk resistivity calculated from cole-cole plot.Cross-sectional morphology was obtained using scanning electron microscopy model LEO VPSEM with 2000x magnification. The samples were coated with gold using sputtering machine for 1 minute at 20 mA current before the analysis.

3. Results and discussion

3.1 FTIR

Figure 1 and 2 showed infrared spectrum that was used to study the changes of wavenumbers for functional groups attached to pure PGMA which is stretching mode for carbonyl, unsymmetry stretching mode of ether (C-O-C), weak stretching of epoxy ring, deformation mode of epoxy ring (unsymmetry) and deformation of epoxy and ether (symmetry). Molecular structure of PGMA and bmimTFSI was shown in Figure3. From Figure1(b)-(e) and Figure 2(a)-(c), there are new bands that shows the appearance of functional groups for pure bmimTFSI (Figure 2(d)) that is two unsymmetry bands of SO_2 at 1346 cm^{-1} and 1326 cm^{-1}, stretching of SO_2 at 1060 cm^{-1} and CF band at 1243 cm^{-1}. No significant changes of wavenumber observed in SPE at 10wt.% until 70wt.% bmimTFSI. Uma et al. suggested that there is a significant change on wavenumber of functional groups if the coordination occurred between polymer and ions [10]. Coordination occurred in functional groups mayweaken the bond between the atoms, in turn, will increase the frequency of vibration and obtained lower wavenumber values. FTIR spectra show that there is some interactions occur between the oxygen atoms with the ionic liquids. This can be seen from the intensity changes of the C-O-C from the epoxy and ether groups and C=O of the polymer chain. The similar results have been reported by Singh et al. using the ionic liquid 1-ethyl-3-methylimidazolium dicyanamida (EMImDCN) in the polymer electrolytes based onPEO [6]. Imidazoliumcation is a bulky molecule with low charge density and tends to provide less probability to form coordination with the oxygen atoms in the polymer as compared to the smaller size of the Li^+ ion.

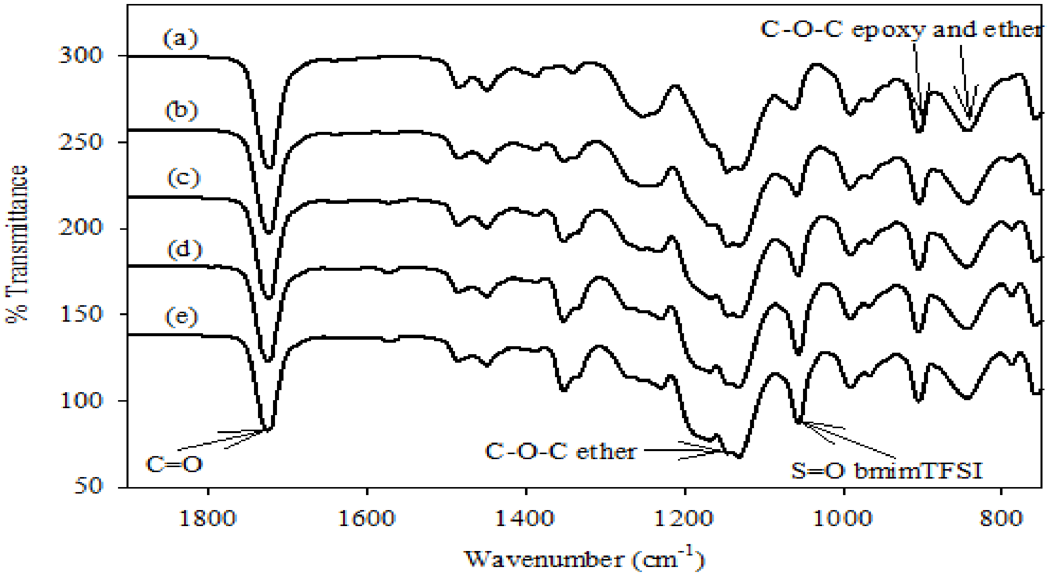

Figure 1:FTIR spectra of (a) PGMA; SPE at; (b) 10wt.%; (c) 20wt.%.; (d) 30wt.% and (e) 40wt.% mimTFSI.

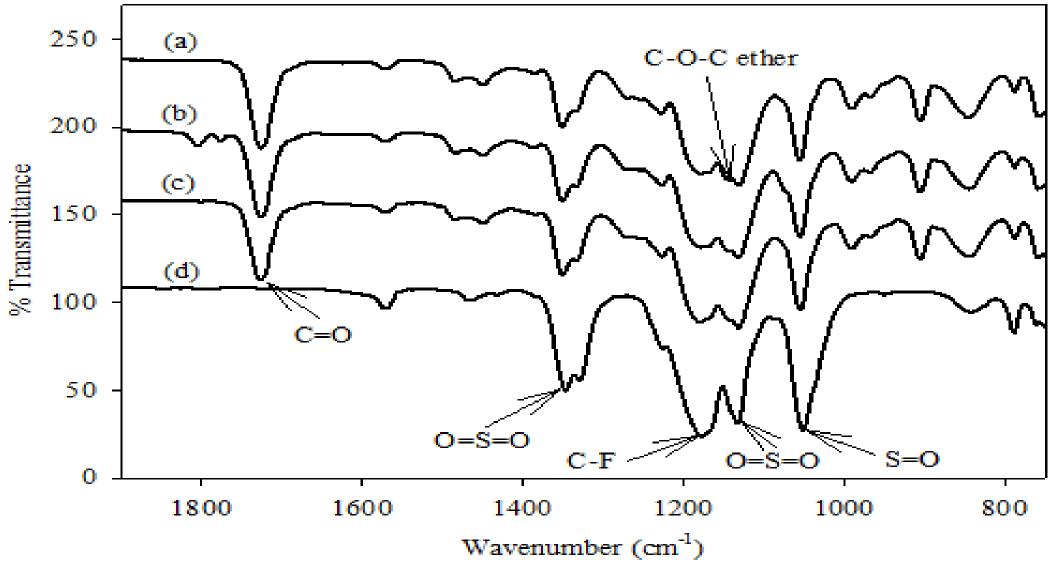

Figure2: FTIR spectra of SPE at; (a) 50wt.%; (b) 60wt.%; (c) 70wt.%bmimTFSIand (d) pure bmimTFSI.

3.2 XRD diffractogram

The determination of polymer structure in the solid polymer electrolytes were studied using X-ray diffraction techniques. PGMA diffractogram showed semi-crystalline peak in 2theta = 13° -24°, as shown in Figure 4 (a). In Figures 4 (b)-(h), the peak intensity of PGMA was found to decrease with increasing weight percent of bmimTFSI. This is in agreement with Singh et al. whom describes that doping of ionic liquid reduces crystallinity of polymer matrix [11]. It is interesting to notice that, no additional peak obtained from Figure 4(b)-(h) and proved that this type of ionic liquid is stable in ionic forms compared to other ionic liquid such as 1-butyl-3-methylimidazolium chloride and a few type of metal salt (NaCl, LiClO$_4$ and LiOTf). Previous study has reported that, the maximum amount of dopant that can be loaded into such polymer matrix are around 25wt.% to 40wt.% only, otherwise salt associations might occur and this can affect the ionic conductivity enhancement[9,12-13].

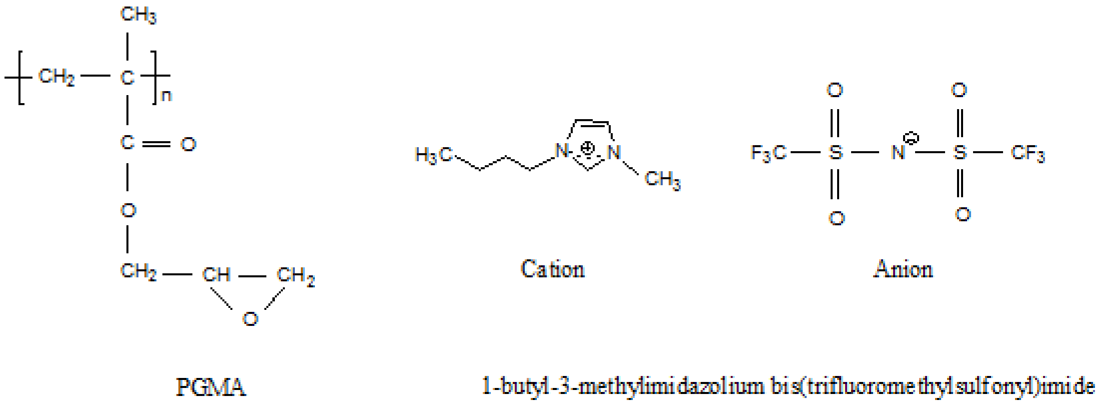

Figure3:Molecular structure

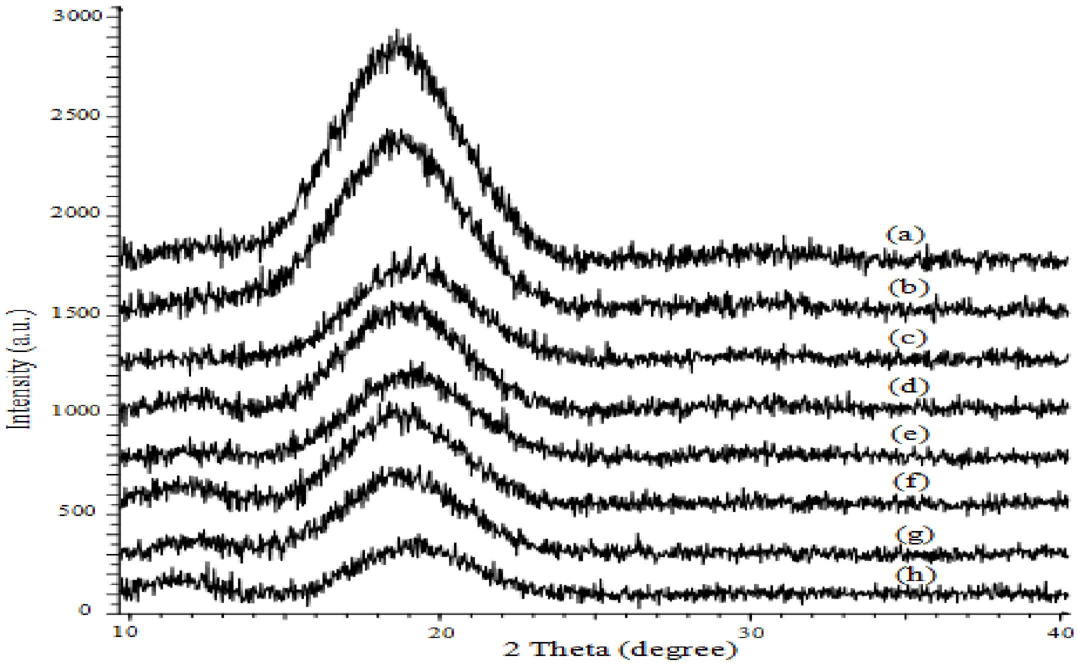

Figure 4: X-ray diffractogram for (a) PGMA; SPE at (b) 10wt.%; (c) 20wt.%; (d) 30wt.%; (e) 40wt.%; (f) 50wt.%; (g) 60wt.% and (h) 70wt.% ofbmimTFSI.

3.3 DSCthermograms

Glass transition temperature, T$_g$, describes the changes in properties from glass to amorphous of a polymer [14]. Figure 5 shows that T$_g$ decrease from 45°C (PGMA) to 42°C, 36°C, 24°C and 5°C for bmimTFSI amount of 10wt.%, 30wt.%, 50wt.% and 70wt.%. In this case, the effect of doping ionic liquid in lowering the T$_g$ of polymer is the same with previously reported [15].The presence of ionic liquid molecules between polymer networks encourages restructuring of polymer chains and possibly has resulted disordered chain arrangement[16-19]. For that reason, the prepared polymer electrolytes are flexible than pure PGMA. According to Chew and Tan, an increase in the amorphous regions caused by the disordered polymer chains in polymer electrolytes system may provide more routes and spaces for the ions to mobile [13]. However, melting point, T_m was not observed in these DSC thermograms.

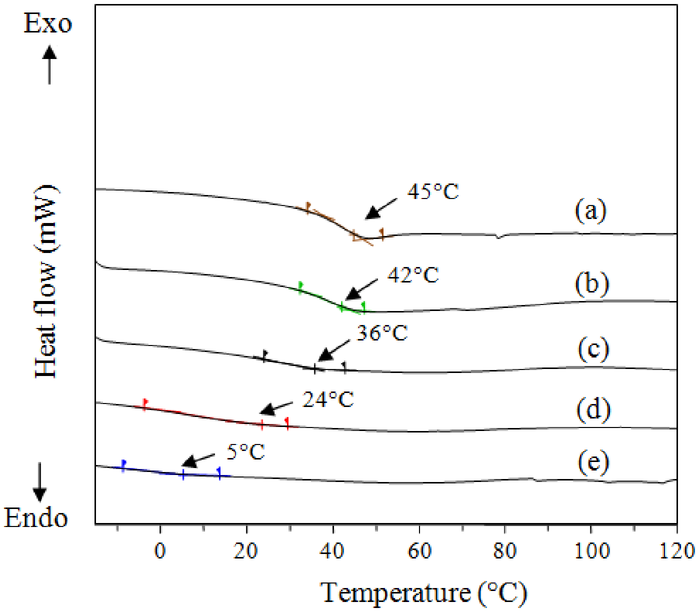

Figure 5: DSC thermograms for (a) PGMA; SPE at (b) 10wt.%; (c) 30wt.%; (d) 50wt.% and (e) 70wt.% of bmimTFSI.

3.4Ionic conductivity

Figure6 shows a plot of ionic conductivity (σ) for PGMA-bmimTFSI films at different bmimTFSI weight percent. Conductivity value for the polymer is 3.09×10^{-10} S cm^{-1} and σ was found to increase with increasing weight percent bmimTFSI. The highest σ of 1.86×10^{-6} S cm^{-1}, was observed at addition of 70wt. %bmimTFSI and this value is the maximum value for this electrolytes system. Addition of bmimTFSI at a higher weight percent hastransformed the physical properties of the solid polymer electrolyte to fully gel. The increasing in σis due to the increasing number of ionic species of $bmim^+$ and $TFSI^-$ [5]. The presence of these two ions providedcharge carriers for ionic conduction to occur. At the same time, the existence of more amorphous regions in the solid polymer electrolytes as indicated by the diffraction pattern in Figure 4 (b)-(h) and reduction of T_g values has facilitated the movement of molecules and ions. However, this σ value is lower than the σ of polymer-based solid electrolyte salt and reliable due to the large size of the ionic molecules, which cause more loads for the molecules. Leys et al. in their study reported that the use of ionic liquid with large size of cations caused a difficult to mobile through the system [4]. However, for the purpose of use in lithium batteries, lithium ions may be added to the electrolytes and the ionic conductivity should be higher than this.

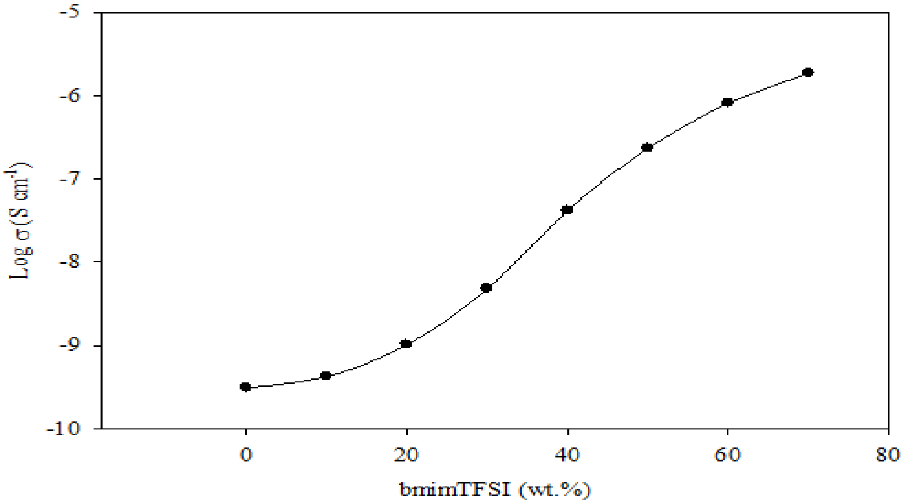

Figure6: Ionic conductivity for PGMA-bmimTFSI films

In order to examine the temperature dependence of the samples, the temperature dependent ionic conductivity measurement have also been carried out from temperature of 303 K until 373 K for the samples with 30 wt.%, 50 wt.% and 70 wt.% bmimTFSI. The relationship between these two variables was shown in Figure7 and it is almost linear with the regression value, r^2 of 0.9956, 0.9931 and 0.9975 for the solid polymer electrolytes samples at 30 wt.%, 50 wt.% and 70 wt.% bmimTFSI respectively. These linear lines obeyed Arrhenius equation of;

$$\sigma=\sigma_o e\ (-E_a/kT) \qquad (1)$$

where σ is ionic conductivity, σ_o is pre-exponential factor,E_a is activation energy, k is Boltzmann constant, and T is temperature. It has been proved that the system is sensitive to temperature increment. The pre-exponential factor, σ_o and activation energies, E_a calculated from the Arrhenius plots are shown in Table 1. In Arrhenius theory, activation energies play an important role in determining the ability of the ions to hop in the system in order to create ionic conductivities [20]. Table 1 shows a decrease of E_a with increasing weight percent bmimTFSI. Changes of more crystalline region into amorphous region wereincreasing the free volumes in the samples system as has been discussed in previous section, Figure 4 and Figure 5.

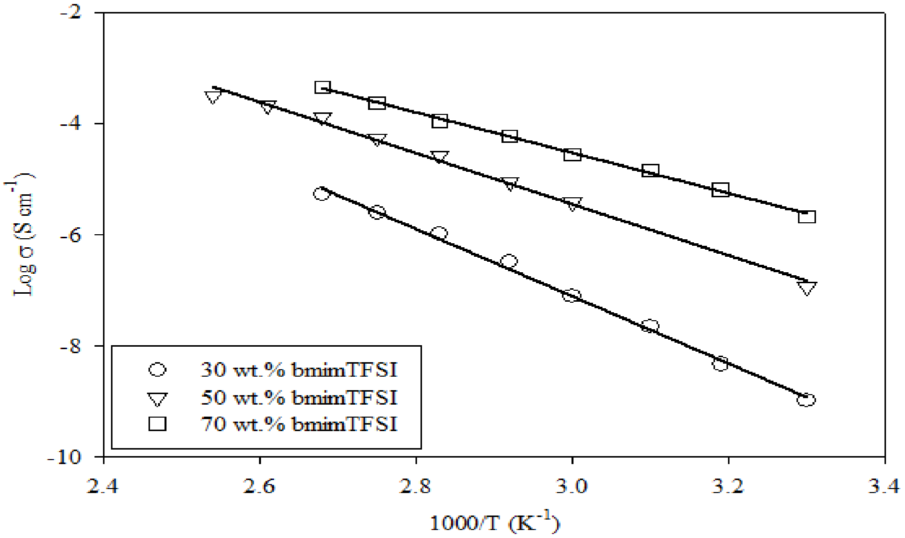

Figure7: Arrhenius plots

Table 1: Pre-exponential factor σ_o, activation energy E_a and regression r^2 for PGMA-bmimTFSI films

bmimTFSI (wt.%)	**σ_o(S cm^{-1})**	**E_a (eV)**	**r^2**
30	3.73×10^{-4}	1.200	0.9956
50	2.03×10^{-3}	0.913	0.9931
70	4.64×10^{-3}	0.728	0.9975

The heat supplied to the samples therefore facilitates fast ions motion between the polymer networks causes E_a value to decrease. In addition, the E_a values also was influencing by the viscosity of the ionic liquid. Thermal energy obtained by heating has indirectly reduced its viscosity and therefore E_a [21]. Pre-exponential factor, σ_o represents the number of free ions involved in ionic conduction [22]. σ_o values increase from 3.73×10^{-4} S cm^{-1} to 4.64×10^{-3} S cm^{-1} where samples contains 70 wt.% of bmimTFSI have the highest pre-exponential value. This showed that the number of free ions are most numerous in this system and has been proven by the highest ionic conductivities.

*3.5 SEM micrograph*s

A cross-sectional morphology of polymer electrolytes system is shown in Figures 8 (a)-(c). The rough surface, as depicted in Figure 8 (d) is contributed by the brittle properties of PGMA. Incorporation of bmimTFSI into the polymer network was found to reduce the surface roughness of the pristine polymer. On the other hand, no phase separation was observed at all for the bmimTFSI loadings and therefore, confirmed the homogeneity of PGMA-bmimTFSI polymer electrolyte system. The improvement in surface morphology provides a good contact between the electrode and the electrolyte in the application of these films [23].

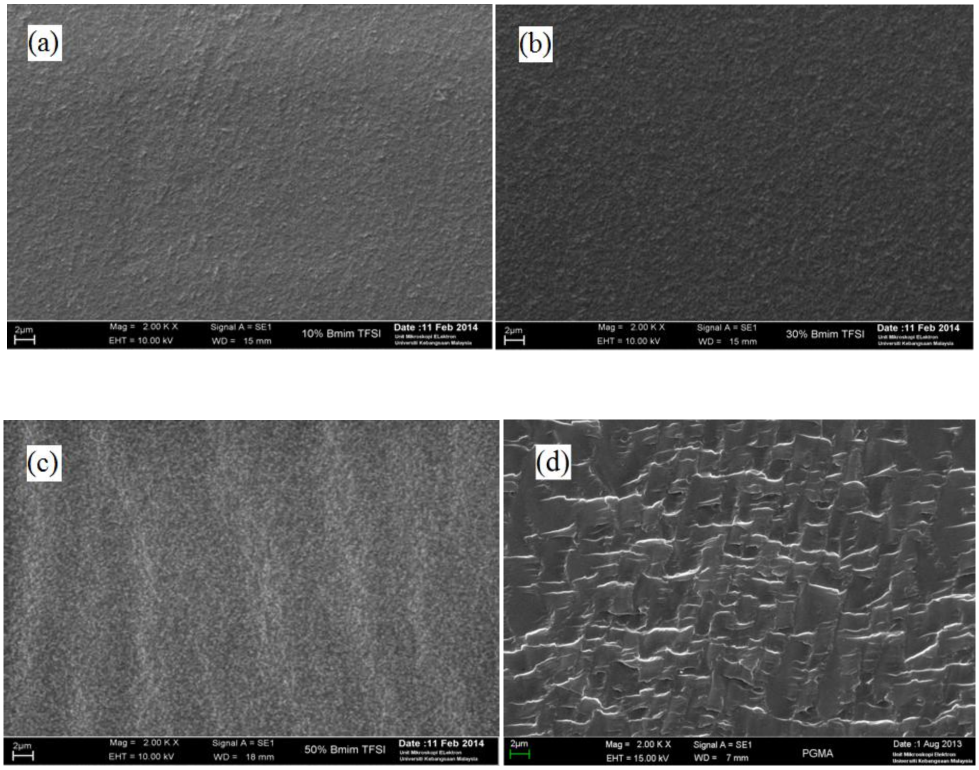

Figure 8: SEM micrograph at magnification of 2000x for (a) 10 wt.%; (b) 30 wt.%; (c) 50 wt.% of bmimTFSIand (d) PGMA

Conclusion

PGMA solid polymer electrolyte films doped with ionic liquids of bmimTFSI successfully prepared using solution casting technique. The highest ionic conductivity is at the addition of 70wt. %bmimTFSI with the ionic conductivity of 1.86×10^{-6} S cm^{-1}. No interaction occurs at functional groups in the polymer structure shows that the ionic liquid is dispersed among the polymer network. XRD diffraction pattern showed a decrease of semi-crystalline peak of PGMA at high amount of bmimTFSI while DSC thermograms determined that the doping of ionic liquid into polymer matrix has lowered T_g values of the system. Solid polymer electrolytes of PGMA-bmimTFSI comply Arrhenius equation which shows that the ionic conductivities mainlyoccur through ion hopping method. SEM cross-section morphology confirmed that ionic liquid spread homogenously among the polymer matrix. The electrolyte films can be used as safer separator in electrochemical devices.

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