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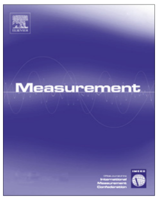

Preparation and characterization of poly (ethyl methacrylate) based polymer electrolytes doped with 1-butyl-3-methylimidazolium trifluoromethanesulfonate

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ABSTRACT

Solution casting technique is used to formulate the matrix of poly (ethyl methacrylate) (PEMA) and lithium trifluoromethanesulfonate (LiTf) with different 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([Bmim][TfO]) ionic liquid content. The increasing addition of [Bmim][TfO] in the PEMA: LiTf matrix increases the ionic conductivity by one order through the imposed plasticizing effect. The highest conductivity of 1.17×10^{-4} S cm^{-1} is achieved for the composition of PEMA: LiTf: [Bmim][TfO] (21 wt.%: 9 wt.%: 70 wt.%). The [Bmim][TfO]-plasticized matrix exhibits high ionic conductivity due to the interactions between the added constituents, confirmed by the FTIR spectrum, which gives rise to the presence of high concentration of amorphous phase. The increase in the structural disorderliness is seen from the decrease in the intensity of XRD diffraction peak, coherent length and glass transition temperature (T_g). The miscibility of [Bmim][TfO] also provides more presence of transit sites for the hopping of lithium conducting ions (Li^+), which ultimately results in high ionic conductivity. The increasing Li^+ ions kinetic energy with rise in temperature shows the thermally assisted conductivity mechanism that follows the Arrhenius rule. The dielectric behavior of the polymer electrolytes is also studied. The thermal profile of the matrix increases with increasing addition of [Bmim][TfO] content.

1. Introduction

In these recent years, polymers had grasped a great deal of attention among the scientists since its usage are widely spread in numerous industry applications such listed are electronic devices, plastics and pharmaceutical products [1]. In the application of electronic devices the polymers are used as a separator, functioning as a solid electrolyte membrane which has improved properties compared to the conventional liquid type. The development of solid polymer electrolytes (SPE) is also in compliment to invent slimmer phones.

In this research work, PEMA is used as the host polymer to build up the solid matrix. PEMA is another derivation of methyl acrylate polymers that are currently gaining its popularity in the development of polymer electrolytes membrane. The PEMA is found to be a better performing type of polymer compared to the poly (methyl methacrylate) (PMMA) owing to its large pendant group that makes the PEMA to be more flexible. Fig. 1 depicts the chemical structures of PEMA and PMMA. For the purpose of developing high conducting polymer electrolytes a flexible polymer backbone is needed. Since this requirement is

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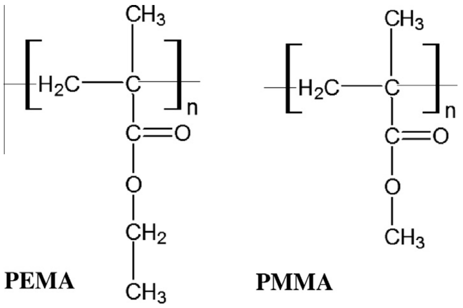

Fig. 1. Chemical structures of PEMA and PMMA.

attain by the PEMA backbone thus it is potential to exhibit high ionic conductivity upon doping with proper additives.

Previously, the insulating property of PEMA was tailored upon blending with different natured type of polymers such are poly (vinyl chloride) (PVC) and poly (vinylidene fluoride) (PVdF) in the presence of ionic salt [2,3]. Progressively, plasticizers and fillers were added into the PEMA matrix. And in recent years, greener development is carried out by incorporating with ionic liquid, which is a type of ionic solvent that has plasticizing effect. The ionic liquid is the newest eye-catching material that can effectively improves the properties of PEMA based polymer electrolytes in terms of the ionic conductivity, mechanical strength and thermal stability. This is due to its useful physical and electrochemical properties.

Almost all the characteristics possess by ionic liquid well suits for the application of polymer electrolytes. Ionic liquid from the name itself gives an idea on its physical state that present in liquid form. This liquid remains on its original state over a wide temperature ranging from room temperature to a higher temperature of 100 °C. Besides, the ionic liquid is also identified to be air and moisture stable, this characteristic separates it from other type of liquids. Apart from this, the presence of ionic liquid in liquid form makes it easier to be miscible with the added constituents without requiring any additional dissolving step.

Other appealing property of ionic liquid is the conducting nature. This liquid is made of 99.99% ions, which includes large sized cations and small sized anions either from the organic or inorganic type [4]. The bond connecting these two different charges is weak and thus makes the liquid to have low melting point. When the solution containing ionic liquid is being heated up at a low supply of heat, the ionic liquid will provide more availability of mobile ions in the solution and hence exhibit higher ionic conductivity.

From the literature study, it is been found that most of the utilized ionic liquid is consisting of large asymmetrical ions such as imidazolium salt. The choice of imidazolium salt has number of excellent properties: (1) low vapor pressure, (2) great ionic conductivity due to its high viscosity and (3) large electrochemical window. Apart from that, the imidazolium salts do not solidify easily at low temperatures, making it to possess low glass transition temperature and this eases its solubility in variety of organic solvents [1,4]. Besides this, ionic liquid also has an unusual solvent property. This property can suppress the degree of crystallinity in the polymer in a greater extent, allowing more presence of amorphous fraction that capable in enhancing the polymer electrolytes conducting nature.

Apart from the chemistry view point of ionic liquid, its good structural characteristics also make this material to be a promising additive to be incorporated in polymer insulating matrix. The structure of ionic liquid helps in assisting the transportation of mobile cations in polymer electrolytes which subsequently gives rise to an excellent ionic conductivity property. This is attributed to the high presence of polar groups in its structure which provides an additional transit sites for the hopping of mobile ions along the polymer backbone.

As concluding the above discussed point on the physical and electrochemical properties of ionic liquid, it is understood that these combination characteristic can tailor the insulating properties of PEMA matrix and allow it to be highly conductive. The incorporation of ionic liquid improves the ionic conductivity of the matrix in three ways: (1) increases the amorphous fraction in PEMA matrix, (2) increase the charge carrier mobility and (3) making more number of additional transit sites to be availability [5,6].

In this communication, the effect of the [Bmim][TfO], with the chemical structure as in Fig. 2, is studied by varying its content in PEMA: LiTf: [Bmim][TfO] matrix. This study is done by characterizing the developed matrix in terms of its electrical, structural and thermal properties.

2. Experimental

The materials used in this research work are saturated polymeric ester PEMA ($M_w = 515{,}000\ \mathrm{g\ mol^{-1}}$), LiTf, [Bmim][TfO] ($M_w = 288.29\ \mathrm{g\ mol^{-1}}$) and A.R. Grade tetrahydrofuran (THF) solvent, which each purchased from Sigma to Aldrich, Fluka, ACROS organics and J.T. Baker respectively. Prior preparing the polymer electrolytes, LiTf is dried at 100 °C for 1 h to eliminate all the traces of water in the material.

The polymer electrolytes were prepared by dissolving PEMA, LiTf and [Bmim][TfO] with the compositions shown in Table 1 in 15 ml of low volatile THF solvent. Then the mixture is stirred continuously for 24 h at room temperature. The homogeneous solution is then casted on a glass Petri dish in fume hood at room temperature to yield a mechanical free standing thin film.

The casted thin films were then characterized on its electrical, structural and thermal properties.

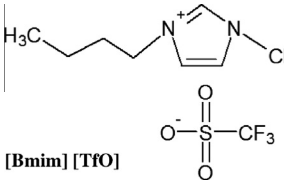

Fig. 2. Chemical structure of [Bmim][TfO].