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Structural, thermal and electrical transport behaviour of polymer electrolytes based on PVA and imidazolium based ionic liquid

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ABSTRACT

A series of polymer electrolyte films based on Poly(vinyl alcohol) (PVA) and ionic liquid, 1-Butyl-2, 3-dimethylimidazolium tetraflouroborate [BDMITFB], PVA-BDMITFB-1 to PVA-BDMITFB-5, has been prepared by varying the concentration of BDMITFB viz. 5, 10, 15, 20, 25 wt%, respectively using solution cast technique. These samples were characterized using Attenuated Total Reflection-Fourier transform infrared spectroscopy (ATR-FTIR), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Thermo gravimetric Analysis (TGA), Differential Scanning Calorimetric (DSC) and AC impedance spectroscopic techniques. The ATR-FTIR analysis shows the interaction of cationic ionic liquid, BDMITFB with hydroxyl group of PVA. TGA results show that thermal stability of PVA-BDMITFB films decreases with increasing content of BDMITFB. DSC results reveal that glass transition temperature (T_g), melting temperature (T_m) and percentage degree of crystallinity (%X_c) decreased with increasing BDMITFB content in PVA films except in PVA-BDMITFB-3. Similar results were also observed from XRD analysis. The changes in film morphology were examined by SEM which reveals the aggregation of PVA/BDMITFB. The fractional area% for decomposition peak, $T_{d2,\ peak}$ of PVA-BDMITFB complex estimated from 1st derivative of TGA (DTGA) curves exhibit the aggregation of polymer. Ionic conductivity, log σ vs. 1/T plots for PVA-BDMITFB films show Arrhenius type behaviour. Loss tangent, tan δ shifts to the higher frequency region with increasing temperature.

1. Introduction

In last two decades ionic liquid based polymer electrolytes attracted much attention due to their potential application in electrochemical devices [1]. Solid polymer electrolytes, based on polar polymers such as poly ethylene oxide (PEO), poly(vinyl pyrrolidone) (PVP), PVA with alkali metal salts like $LiClO_4$, $LiBF_4$, $NaClO_4$, $LiCF_3SO_3$, NH_4X (X = Cl, Br, I) have been traditionally employed but these materials have certain limitations such as low ionic conductivity at room temperature, poor chemical stability and thermal stability [2–6]. Several techniques have been adopted to enhance the ionic conductivity at room temperature such as co-polymerization, polymer blending, addition of low molecular weight plasticizers viz. ethylene carbonate (EC), propylene carbonate (PC), polyethylene glycol (PEG) and ionic liquids [7–10]. The ionic liquids are room temperature molten salts and consist of ions of small molecules. Use of imidazolium based ionic liquids to enhance ionic conductivity is the radical approach due to its unique properties viz. wide electrochemical stability window, wide usable temperature range, low volatility and flammability, low vapor pressure and high ionic conductivity, etc. [11–13]. Due to these properties of ionic liquids, they play significant role in the field of renewable energy [14], as electrolytes for solar cells [15], fuel cells [16], etc. Several hydrophilic and hydrophobic ionic liquids are used as plasticizers and ion suppliers in different host polymer matrices such as PVA, PVP, poly(ethylene oxide) (PEO), poly(vinylidene fluoride)–hexafluoropropylene (PVdF(HFP)) and biodegradable corn starch [17–22] etc. to facilitate the relative movement of polymeric chains and increase the long range migration of ions and collectively improve the ionic conductivity. PVA is a polar polymer having carbon chain backbone attached with hydroxyl group, excellent film making property, chemical stability, high dielectric strength, good charge storage capacity, dopant-dependent electric and optical properties and abrasion resistance [23]. Recent studies have shown that the polymer electrolytes containing ionic liquids, having ethyl group with imidazolium ring limits their performance due to the presence of acidic proton attached to C(2) of the ring which is highly reactive with electrodes when such electrolytes are used in rechargeable batteries. Therefore, attempts have been made to replace the reactive proton at C(2) position of the imidazolium ring by butyl group or

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with another imidazolium ring [24–26]. In the present investigation, 1-Butyl-2, 3-dimethylimidazolium tetraflouroborate [BDMITFB] has been chosen in which methyl group attached at C(2) position (besides C(3) position) can overcome the above mentioned difficulty. To see the effect of BDMITFB on PVA (i.e. semi-crystalline in nature), prepared films (PVA-BDMITFB) were characterized using ATR-FTIR, XRD, SEM, TGA, DSC and AC impedance spectroscopic techniques. The temperature dependence conductivity and dielectric relaxation frequency have also been studied for PVA-BDMITFB based polymeric films.

2. Experimental

Poly(vinyl) alcohol (PVA) (molecular weight ~125,000, purity > 99.99%) and dimethyl sulphoxide (DMSO) (purity > 99%, water content < 0.2%) were obtained from Merck, Germany. 1-Butyl-2, 3-dimethylimidazolium tetraflouroborate, BDMITFB (purity > 98%) was purchased from Sigma Aldrich. These chemicals were used for the preparation of PVA and PVA-BDMITFB based polymeric films. PVA and BDMITFB was vacuum dried before use.

To obtain the homogeneous films, the appropriate quantities of PVA and PVA with x wt% BDMITFB (x = 0, 5, 10, 15, 20, 25) were mixed with DMSO used as solvent (beyond 25 wt% BDMITFB the films were found to be sticky) and in order to swell the resulting solution, it was kept in oven at 40 °C for 24 h. The solution was stirred at 40 °C for 5 h to obtain a viscous solution. The viscous slurry was poured into the polypropylene Petri dishes and dried for 10 days at 40 °C to obtain free standing films. These films were further vacuum dried at 10^{-3} Torr for 2 days to evaporate the solvent. The films having thickness around 0.1 mm were obtained and stored in evacuated desiccators for further measurements.

The TGA and DSC measurements were carried out using TGA/DSC-I (Mettler Toledo) and DSC-I (Mettler Toledo) systems at a heating rate 10 °C/min in presence of nitrogen atmosphere with the accuracy of ± 0.3 K and ± 0.02 K, respectively. XRD patterns of PVA and PVA-BDMITFB based films were recorded with the help of Philips X-ray diffractometer (PW 1710) at a scan rate 1°/min with the step width 0.02°. The ATR-FTIR spectra of films of different compositions were recorded in the transmission mode using spectrometer (Model RX 1) in the range 700–4000 cm^{-1} with the resolution of 1 cm^{-1}. The conductivity and dielectric measurements of PVA and PVA-BDMITFB based polymer electrolyte films were carried out using Wayne Kerr impedance analyzer (model 6500 B) in the frequency range 100 Hz to 5 MHz at 100 mV. For electrical contact and temperature dependent conductivity measurements the samples were sandwiched between two stainless steel electrodes (1 cm radii) embedded in a spring loaded sample holder in temperature range 30 °C to 200 °C.

3. Results and discussion

3.1. ATR-FTIR analysis

The ATR-FTIR data of PVA, BDMITFB and PVA-BDMITFB is reported in Tables 1 & 2 and the plausible interactions between PVA and BDMITFB are shown in Scheme 1. The cationic BDMITFB can form intermolecular hydrogen bonding through the nitrogen site of tertiary amine in it and with the hydroxyl hydrogen of PVA. It was confirmed through the shifting of stretching frequencies of hydroxyl group of PVA and C=N of BDMITFB, toward lower region.

Fig. 1(a–g) presents the ATR-FTIR spectra of the polymer electrolyte films. The bands related to sym. CH stretching, C=O stretching, CH_2 bending, C−H deformation and O−H bending, C−C stretching and C−O stretching of PVA [27,28] were observed at 2930, 1732, 1430, 1048, 1142 and 842 cm^{-1}, respectively (Fig. 1(a)). The vibrational bands related to PVA were found to be shifted due to the incorporation of BDMITFB in polymer (Table 1). The band frequencies related to BDMITFB and PVA-BDMITFB complex are shown in Table 2. The change in band frequencies of BDMITFB and PVA clearly gives the signature of complexation of BDMITFB with PVA back bone.

Table 1
Vibrational band frequencies of PVA and PVA-BDMITFB complex polymer electrolyte films.

IR vibrational band frequencies (± 1) (cm^{-1})						
PVA	PVA-BDMITFB					Band assignment
	1	2	3	4	5	
2930	2942	2938	2941	2939	2942	Sym C−H stretch
1732	1727	1726	–	1722	1726	C=O stretch
1430	1426	1429	1426	1429	1426	CH_2 bend
1048	–	1048	1049	1049	1049	C−H def. & O−H bend.
1142	1141	1138	1137	1137	1136	C−C stretch
842	841	844	845	846	846	C−O stretch

3.2. XRD studies

Fig. 2(a–f) shows the X-ray diffraction patterns of PVA and PVA-BDMITFB-1 to PVA-BDMITFB-5 complexes, respectively. In XRD measurement, 2θ (angle of diffraction) was varied from 10°–80° to identify the changes in the crystal structure due to the interaction of BDMITFB with PVA. The XRD pattern of PVA (Fig. 2(a)) reveals two characteristic peaks at 2θ ~ 20° and 42° riding over haloes [29,30] shows semi-crystalline nature. The intensity of the peak at 2θ ~ 20° PVA decreases on the addition of BDMITFB. The haloes associated with both the peaks (at 2θ ~ 20° and 42°) increase with increasing BDMITFB content in PVA (with the exception for PVA-BDMITFB-3). The decrease in intensity and broadening of halo indicate that there is a reduction in % degree of crystallinity due to enhancement in amorphous phase at higher loading of BDMITFB.

From XRD patterns of semi-crystalline material (PVA is semi-crystalline in nature) the % degree of crystallinity/or amorphocity was calculated by estimating the areas of crystalline peaks and broad halo under the crystalline peaks. The % degree of crystallinity (X_c) can be calculated using XRD pattern of the samples by using the equation:

$$X_c = \left(\frac{S}{S_o}\right)\cdot 100\%$$

where 'S' is the area under the crystalline peak and 'S_o' is the total area under the diffractrogram (area under the crystalline peaks + area of the broad halo). The results of variation of % degree of crystallinity with BDMITFB content are shown in Fig. 3 (with ± 3% error bars).

From Fig. 3 it was observed that the % degree of crystallinity decreases with BDMITFB concentration in PVA except for sample PVA-BDMITFB-3.

3.3. SEM analysis

SEM characterization is frequently used to explore the compatibility between salt/ionic liquid and polymer of the polymer electrolytes through the perception of phase separation/aggregation [31,32]. Fig. 4(a–d) shows the SEM images of PVA, PVA-BDMITFB-1, PVA-BDMITFB-3 and PVA-BDMITFB-4, respectively. In case of PVA-BDMITFB-1 and PVA-BDMITFB-4, SEM images (Fig. 4b & d) show fibriller form having 3–4 μm size. Whereas PVA-BDMITFB-3 (Fig. 4c) shows bigger particles having 24 μm size. This is clearly indicating that PVA-BDMITFB-3 has higher aggregation of polymer/BDMITFB, which also evidence from XRD results. On further increase in the amount of BDMITFB in PVA the matrix of PVA-BDMITFB becomes flexible i.e. enhancement in amorphous.