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Vibrational, thermal and ion transport properties of PVA-PVP-PEG-$MeSO_4Na$ based polymer blend electrolyte films

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ABSTRACT

Polyvinyl alcohol (PVA)-polyvinyl pyrrolidone (PVP)-polyethylene glycol (PEG) based polymer blend electrolyte films have been prepared by varying the Sodium methylsulfate ($MeSO_4Na$) salt, in different % ratio using solution cast technique. Various techniques i.e. ATR-FTIR, TGA, DSC and AC Impedance spectroscopy have been used to characterize the prepared samples. ATR-FTIR result shows the complexation of $MeSO_4Na$ salt with PVA-PVP polymer blend. TGA results show the thermal stability of polymeric blend electrolyte changes with $MeSO_4Na$ content in PVA-PVP based polymer blend and also formation of miscible blend. DSC analysis reveals that single glass transition temperature (T_g) and melting temperature (T_m) changes with increasing $MeSO_4Na$ content. The dielectric relaxation frequency, f_r has been found to increase with temperature in PVA-PVP-PEG-20$MeSO_4Na$. Ionic conductivity and dielectric relaxation frequency vs. 1/T plots for PVA-PVP-PEG-20$MeSO_4Na$ based polymeric films follows the Arrhenius behavior. The maximum conductivity of 1.67×10^{-5} S/cm has been found for sample PVA-PVP-PEG-20$MeSO_4Na$ at room temperature. AC conductivity vs. frequency (Hz) curves was obtained for different PVA-PVP based polymer blend with respect to salt concentrations and temperatures. Dielectric permittivity and electric modulus of the polymeric films have been studied for various frequencies. Scaling i.e. σ/σ_0 vs. ω/ω_o has been done for PVA-PVP-PEG-20$MeSO_4Na$ polymer blend electrolyte.

1. Introduction

The development of Lithium ion based ion conducting materials have drawn great attention from last two decade due to their potential applications in mobile phones, electric vehicles and energy storage devices. Limited availability of lithium is one of the important reasons to search another ion conducting materials such as sodium or magnesium based materials. Sodium is the most promising alternative to lithium for energy storage applications based on its high abundance, low cost, and suitable redox potential ($E^{o}_{Na^{+}/Na} = -2.71$ V vs. standard hydrogen electrode; 0.3 V above that of lithium) [1–3]. Though use of solid polymer electrolytes based on sodium ion has some limitations such as low ionic conductivity at room temperature, low thermal stability, chemical stability, etc. Several methods have been adopted for improving the ionic conductivity at room temperature such as use of polymer blending [4], use of ionic liquids [5–9] and addition of ceramic fillers [10]. The presence of plasticizing materials such as poly ethylene glycol (PEG), propylene carbonate (PC), ethylene carbonate (EC), etc. in the polymer matrix decreases the phase transition temperatures, softens the polymer i.e. enhances the segmental motion of polymer chain and thus increases the ionic conductivity [11–13]. Common method for obtaining polymer electrolyte is to use the alkali metal salts (like lithium perchlorate ($LiClO_4$), lithium hexaflouro phosphate ($LiPF_6$), lithium tetrafluoroborate ($LiBF_4$), sodium perchlorate ($NaClO_4$), etc.) with polymers/co-polymers (like poly (ethylene oxide) (PEO), poly (vinyl alcohol) (PVA), poly (vinyl pyrrolidone) (PVP), PVA-PVP polymer blend, poly(ethyl methacrylate)/poly(vinylidenefluoride-*co*-hexafluoropropylene) (PMMA/PVdF-HFP) [14–19], etc.). Polymer PVA (water soluble) has some unique properties such as high chemical stability, good charge storage capacity, easy processibility, good film making property, etc. PVP has also some important properties such as easy high dielectric strength, low scattering loss, good charge storage capacity, and dopant-dependent properties. Due to the presence of pyrrole group (C=O) with the side chain of PVP, it is more attractive to PVA (hydroxyl group (O–H) with the side chain) [20–23]. Miscible blending of two polymers is one of the suitable methods for the preparation of polymer electrolytes and to control the desirable physical properties within the compositional regime. Transport properties are controlled by amorphicity of the films, concentration of mobile ions, dielectric relaxation, etc. In the present investigation, the structural, thermal, dielectric and ion transport properties of prepared polymer blend electrolytes were analyzed using FTIR, TGA, DSC and AC

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impedance spectroscopic technique. Concentration and temperature dependent AC conductivity spectra and scaling are very useful method to understand the ion dynamics behavior in terms of transportation of charge carriers through the polymer matrix. The ion transport mechanism of polymer blend electrolytes are explored by studying the dielectric properties, AC conductivity formulation and scaling of PVA-PVP based polymer blend electrolyte containing different wt% of $MeSO_4Na$.

2. Experimental

2.1. Materials

PVA (average molecular weight ~ 125,000; purity > 98%), PVP (average molecular weight ~ 44,000; purity > 99%), PEG (liquid form having molecular weight 200) are purchased from Merck, Germany. Sodium methylsulfate ($MeSO_4Na$) with purity > 99% is procured from Sigma-Aldrich. Dimethyl sulfoxide (DMSO) used as solvent; purity > 98% procured from Merck.

2.2. Preparation of polymeric films

The polymeric films have been prepared using conventional solution casting method. In this method we have taken 50PVA-50PVP-10PEG with x wt%$MeSO_4Na$ (x = 0, 10, 15, 20) viz. PVA-PVP-PEG, PVA-PVP-PEG-10$MeSO_4Na$, PVA-PVP-PEG-15$MeSO_4Na$ and PVA-PVP-PEG-20$MeSO_4Na$, respectively. All the materials were dissolved in DMSO and then kept this mixture in oven at 50 °C for 24 h for swelling. The solution is stirred for 5 h in order to obtain the homogeneous viscous slurry and slurry was poured into poly propylene Petri-dishes. These Petri-dishes containing slurry were kept in oven to dry for the evaporation of solvent at 40 °C for 10 days, after that we select free standing films having uniform thickness of ~50 μm the films were stored in dried silica gel containing evacuated desiccators for further measurements.

2.3. Characterization techniques

The prepared polymeric films were characterized using vibrational spectroscopic, thermal and impedance spectroscopic techniques. Fourier Transform infrared (FTIR) in ATR mode technique (Perkin Elmer IR spectrometer with resolution of 1 cm^{-1}) has been used to know the interaction/complexation of polymer blend with the dopant $MeSO_4Na$ salt. Thermo-gravimetric analysis (TGA) using TGA/DSC-I (Mettler Toledo) having scan rate 10 K/min (accuracy of 0.01 K/min) in the presence of nitrogen inert atmosphere (30 ml/min) and differential scanning calorimetric (DSC) using DSC-I (Mettler Toledo) (scanning rate 10 K/min; in the presence of 30 ml/min nitrogen atmosphere with accuracy 0.01 K/min) were done for knowing the effect of dopant on the decomposition temperature, glass transition temperature and melting temperature of prepared samples. AC impedance spectroscopic technique (Wayne Kerr impedance analyzer (model 6500B; frequency range 20 Hz to 5 MHz with 100 mV)) is used for conductivity and dielectric measurements of the polymeric films. For proper electrode-electrolyte contact and temperature dependent electrical conductivity measurements (temperature range 30 °C to 90 °C) the circular polymeric films were sandwiched between two stainless steel electrodes with 0.5 cm radii in a homemade spring loaded sample holder. Linear sweep voltammetry (LSV) has been performed to know the electrochemical stability window (EWS) using Agilent Source unit (model No. B2901A) having resolution of 1 μV/1 pA.

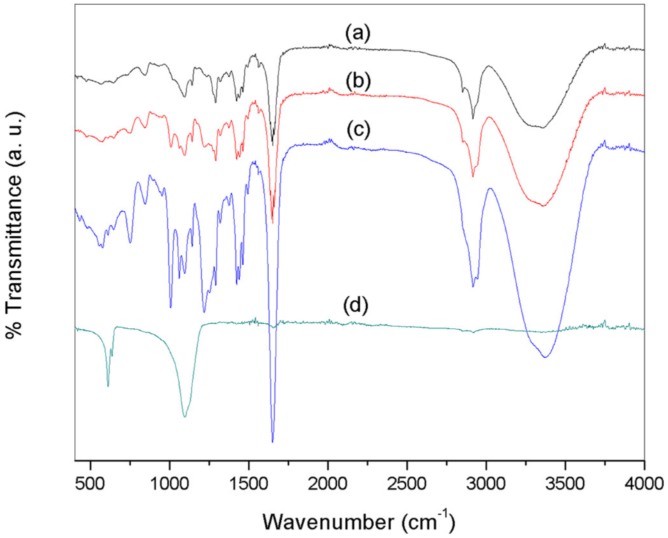

Fig. 1. (a–d) FT-IR spectra of PVA-PVP-PEG with x wt% $MeSO_4Na$ (x = 0, 10, 15, 20) polymer electrolyte films, respectively.

Table 1
Wave number and peak assignments for the blend and PVA-PVP-PEG complexed with $MeSO_4Na$.

IR vibrational band frequencies (1 cm^{-1}) of PVA-PVP-PEG with x wt%$MeSO_4Na$				
x = 0	x = 10	x = 15	x = 20	Band assignment
3247–3360	3257–3360	3284–3360	3340–3376	O—H stretch
2916	2916	2917	2918	CH_2 assy. stretch
2946	2944	2943	2940	ring CH_2 assy. stretch
1645	1645	1650	1654	C=C stretching
1290	1290	1290	1294	C—O—C stretching
1277	1275	1273	1274	C—N stretching
–	1226	1218	1216	CH_2 sym. twist
1141	1142	1142	1128	C—H wagging
1093	1093	1093	1095	C—H bending
1017	1007	1006	–	C=O stretching
845	846	846	842	CH_2 blending
–	750	750	–	CH_2 (rock)
576	567	567	604	N—C=O bending

3. Results and discussions

3.1. FTIR analysis

Fig. 1 (a-d) shows the FTIR spectra of PVA-PVP-PEG with x wt% $MeSO_4Na$ (x = 0, 10, 15, 20) based polymeric films. There is possibility to change in band frequencies of PVA (C—O stretching (842 cm^{-1}), O—H bending (1048 cm^{-1}), C—C stretching (1142 cm^{-1}), C=C stretching (1647 cm^{-1}), CH_2 assy. Stretching (2910 cm^{-1}) and O—H stretching (3455 cm^{-1})) [24,25], PVP (N—C=O bending (579 cm^{-1}), CH_2 bending (845 cm^{-1}), C—N stretching (1278 cm^{-1}), C=O stretching (1687 cm^{-1}), CH_2 assy. Stretching (2926 cm^{-1}), CH_2 ring sym. stretching (2958 cm^{-1})) [26] and CH_2 rock (777 cm^{-1}), C—O—O stretching (1064 cm^{-1}), CH_2 symmetric twist (1231 cm^{-1}) and C=O stretching (1639 cm^{-1}) of $MeSO_4Na$ [27] due to the complexation of salt with PVA-PVP polymer blend [28]. The ATR-FTIR data of PVA-PVP polymer blend and PVA-PVP polymer blend complexed with $MeSO_4Na$ are listed in Table 1 and possible interactions between the polymers and