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RESEARCH ARTICLE

Effect of Pyrazole as Nitrogenous Dopant on the Electrical Conduction of a New Polymer Blend Electrolyte System

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Abstract: New solvent-free polymer blend electrolyte thin film specimens consisting of poly (ethylene oxide) (PEO)/polyvinyl pyrrolidine (PVP) were obtained by means of addition of potassium iodide, KI and iodine, I_2 and incorporated with pyrazole as the dopant material using solution casting technique. The freshly-prepared films were structurally examined using x-ray diffraction (XRD) analysis 111as an enhanced ionic conductivity (σ) behavior was characterized by employing complex impedance analysis resulting in 8.46×10^{-6} Scm^{-1} at room temperature. The occurrence of complexation of the pyrazole with the chosen polymer blend has been confirmed by the Fourier transform infrared spectroscopy (FTIR) while differential scanning calorimetric (DSC) analysis has suggested the feasibility of complete miscibility of these polymeric systems.

Keywords: Solid polymer electrolytes, Nitrogenous compound, Pyrazole

Introduction

Fabrication of new materials suitable for various device applications such as batteries, sensors, fuel cells, solar cells, *etc*., has been gaining a lot of attention in recent years. In this context,one of the much progressed fields involves solid-state electrochemical devices based on polymer electrolytes, which efficiently over come many disadvantages that are present in those devices based on liquid electrolytes in terms of aspects dealing with safety, geometrical flexibility, ease of fabrication, cost-effectiveness, packaging, light weight and slimness[1]. Poly (ethylene oxide) (PEO) has been recognized as one of the versatile polymeric systems because of its arrangement for an effective interaction of the free electron pair on the oxygen with alkali metal cations however, PEO is known to exhibit high degree of crystallinity which reduces in turn the ionic conductivity that may considerably affect its practical application in pure form. To enhance the amorphous phase within PEO certain degree of disorder has to be introduced into the original structure and the same can be achieved by appropriate blending of two polymers[2]. In the present study PEO has been considered as the primary polymer and PVP as the secondary polymer which is highly amorphous in nature and contributes an easy processability. Further an attempt has also been made to study the detailed structural and thermal characteristics behavior of the chosen blended polymer on the addition of nitrogen-containing dopant material namely pyrazole as well.

Experimental

Polyethylene oxide (PEO) ($M_w=5\times10^6$g/mol) and poly vinyl pyrrolidone (PVP) (M_w=40,000 g/mol) purchased from Sigma Aldrich (USA) and potassium iodide (KI), iodine (I_2), acetonitrile, pyrazole procured from Merck (India) were used as the starting materials for the synthesis of blended polymeric systems during the course of the present endeavor.

Synthesis of blended polymer electrolyte

Initially 0.27 g of PEO and 0.03 g of PVP was dissolved in acetonitrile. Successively 0.1 M of KI, 0.05 M of I_2 and 0.03 M of pyrazole, were added to the blended polymer matrix and stirred at a temperature of 343 K for 3 h to form a homogenous liquid electrolyte The polymer electrolyte thus obtained is cast into thin films by casting them onto a glass petridish and vacuum dried in oven at 315 K for 19 h.

Characterization

To determine the ionic conductivity of the synthesized thin films at room temperature, complex impedance analysis was used. The samples are placed in between a pair of stainless steel electrodes and the impedance analysis was carried out at room temperature using a computer-controlled Hewlett-Packard model HP4284A Precision LCR Meter in the frequency range 1MHz-20 Hz. The room temperature X-ray diffraction pattern for each specimen was recorded using a Siefert Model SF60 X-ray diffraction with step size of 0.02°. The differential scanning calorimetric (DSC) analysis was performed by employing NETZSCH DSC 200F3 system under N_2 atmosphere at a heating and cooling rate of 10 °C/min. Fourier transform infrared (FTIR) spectra were recorded using a Bruker TENSOR 27 FTIR spectrometer at ambient condition.

Results and Discussion

Impedance analysis

The electrical conductivity data for the samples were determined using the complex impedance plots obtained in the form of Nyquistplot exhibiting a high frequency semi-circle and a low frequency spike. The conductivity of the sample has been evaluated using the formula,

$$\sigma = \frac{t}{R_{bA}} \tag{1}$$

Where‘t’ is the thickness of the film in (cm), ‘R_b’the bulk resistance of the film (Ω) and ‘A’ is the surface area in (cm^2) of contact of the film with the electrode. The thickness and area of the specimen are 0.6×10^{-3} cm and 1 cm^2 respectively. The value of bulk resistance R_b has been determined from the point of intercept of Nyquist plot on the real axis using the z-simsoftware. Figure 1 depicts the set of impedance plots observed for (a) PEO/PVP/KI/I_2 and (b) PEO/PVP/KI/I_2/0.03M pyrazole thin film specimens. The ionic conductivity (σ) value of pure PEO is found to be 1.3×10^{-8} Scm^{-1} at room temperature and for the pure blended PEO/PVP films σ value is observed to be 4.08×10^{-8} Scm^{-1} thus inferring that this trivial increase in the value of σ may be due to the presence of PVP which is acting as a plasticizer[3].

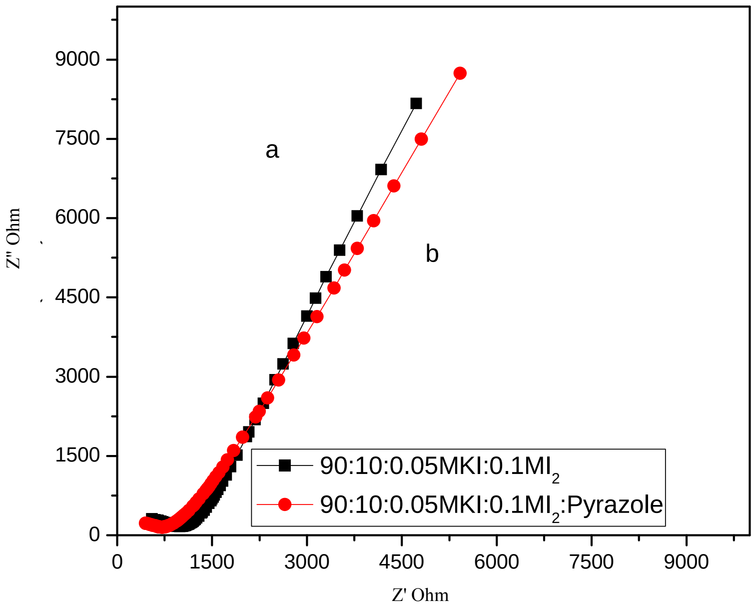

Figure 1. Impedance plots obtained for (**a**) PEO/PVP/KI/I_2 polymer and (**b**) PEO/PVP/KI/I_2/Pyrazole

The importance of adding a nitrogenous compound like pyrazole into the polymer matrix is to provide a charge transfer complex in conjunction with KI and I_2 and enhance the segmental motion of the polymer matrix[4]. During the present study the value of room temperature ionic conductivity has been found to be enhanced by two orders of magnitude to 8.46×10^{-6} Scm^{-1} with addition of pyrazole into the PEO/PVP/KI/I_2 matrix.

Differential scanning calorimentry(DSC) studies

The DSC curves for observed pure PEO/PVP blend and PEO/PVP/KI/I_2 complex and PEO/PVP/KI/I_2/0.03 M pyrazole polymer electrolyte systemare given in Figure 2. The degree crystallinity was calculated from the DSC result using the relation,

$$X_c = \frac{\Delta H_m}{\Delta H_m} \tag{2}$$

The melting temperature (T_m), melting enthalpy (ΔH_m) and degree of crystallinity (χ_c) values were determined from these plots and the values are listed in Table 1. ΔH_m is the pure melting temperature of PVP which is nearly[5] 179° Jg^{-1}. The DSC thermogram of PEO/PVP as shown in Figure 2(a) shows a sharp and intense curve and occurrence of the melting temperatureat 127 ◦C, there by exhibiting a considerable degree of crystallinity. The T_m value of PEO/PVP/KI/I_2 is found to be 96.1◦C which tends to support the conductivity result where PVP being an amorphous polymer considerably brings down the crystallinity of PEO phase. However, the melting temperature observed for the polymer electrolyte PEO/PVP/KI/I_2/pyrazole is apparently lowered to 67.8 °C which may be probably related to the most probable coordination of PEO/PVP with pyrazole that may eventually result in lowering of the degree of crystallinity for pure PEO/PVP from 32.9 to 22.7% for PEO/PVP/KI/I_2/pyrazole as revealed form Table 1.

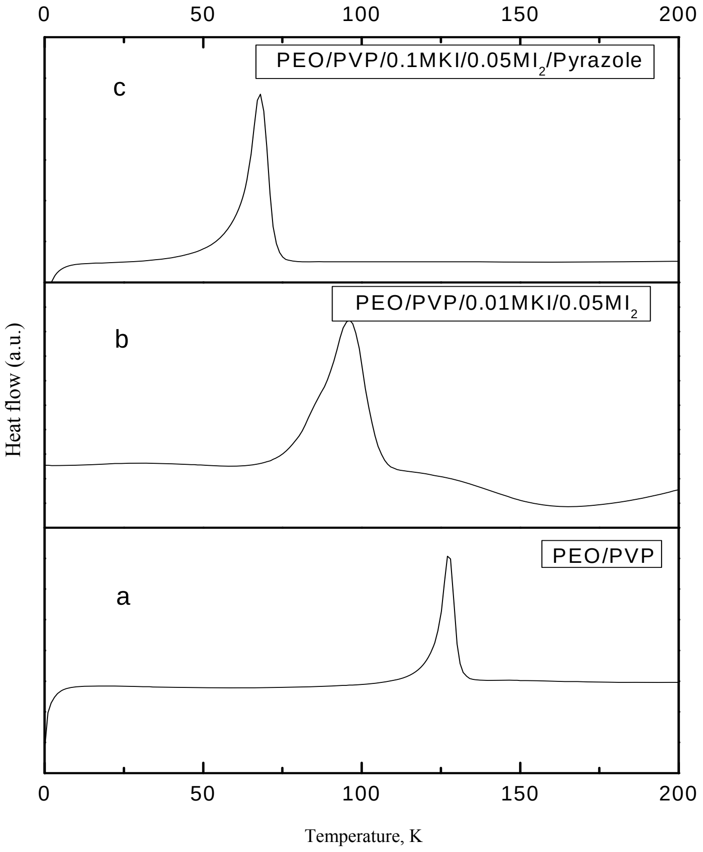

Figure 2. Differential scanning calorimetric curves of (**a**) PEO/PVP (**b)** PEO-PVP-KI-I_2 (**c**) PEO/PVP/KI/I_2/pyrazole

Table 1. Thermal parameters derived for PEO/PVP, PEO/PVP/KI/I_2 and PEO/PVP/KI/I_2/ pyrazolepolymer electrolytes

System	Melting temperature, T_m, °C	Melting enthalpy, ΔH_m, Jg^{-1}	Degree of crystallinity, χ_c %
PEO-PVP	127.5	58.94	32.9
PEO-PVP-0.05 M KI-0.1 M I_2	96.1	52.61	29.4
PEO-PVP-0.05 M KI-0.1 M I_2-0.03 M Pyrazole	67.8	40.7	22.7

X-ray diffraction (XRD) data

The X-ray diffraction results have been used to confirm the feasibility of complexation of polymer blend chosen with the dopant material namely pyrazole. From Figure 3 it is evident that characteristic peaks for PEO and PVP are observed at 2θ=19, 23° and 2θ=11, 20° respectively. The set of sharp peaks that are observed appear to support thecrystalline nature of PEO whereas those humps that are present would correspond to the amorphous nature of PVP polymer. The blended polymer matrix exhibits a reduction in intensity of the crystalline peaks of PEO which is evident in Figure 3(e) which may be due to the addition of pyrazole into the blended matrix. These results may be associated with Hodge *et al.,* principle which establishes acorelation between the height of the diffraction peak and extent of crystallinity[6]. The above results thus suggest that as the content of amorphous nature increases the ionic mobility is expected to increase as confirmed by the conductivity studies.

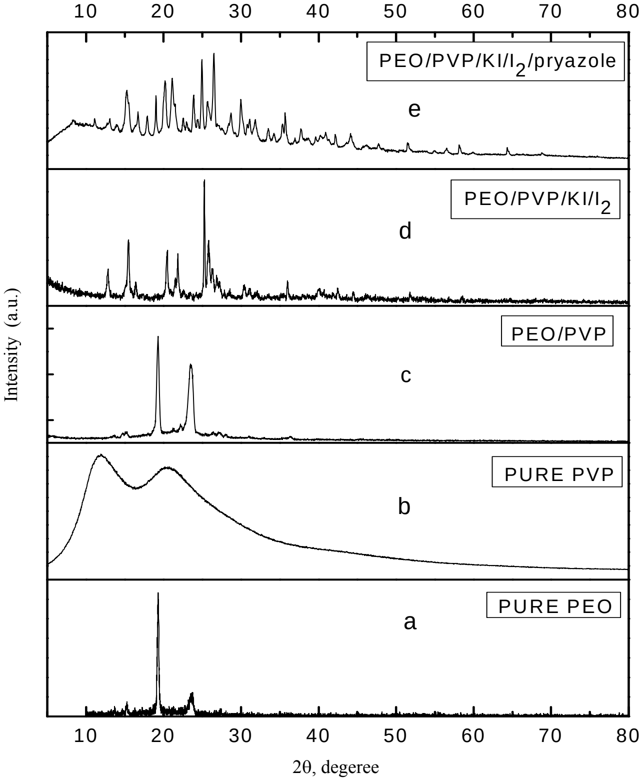

Figure 3. XRD patterns of (**a**) pure PEO (**b**) pure PVP (**c**) PEO/PVP (**d**) PEO/PVP/KI/I_2 (**e**) PEO/PVP/KI/I_2/pyrazolepolymer

Fourier tranform infrared spectroscopy (FTIR) results

The most frequently performed observations to confirm the complexation of the polymer host with dopant involve variation in intensity of the bands, shifting of the bands with respective to the dopant content and appearance of new bands due to the presence of salt content in the polymer host[6]. The FTIR spectrum for the specimen ofpristine PEO/PVP/KI/I_2/0.03 M pyrazole, recorded between 4000 and 400 cm^{-1} is shown in Figure 4.

PEO confirmation

The absorption band observed at 1349 cm^{-1}, corresponds to CH_2 bending of PEO, while the band at 935 cm^{-1}may be assigned to the CH_2 rocking vibrations of the ethylene group. Another band noticed at 832 cm^{-1}may be assigned to helical structure of PEO whereas the typical band at 1445 cm^{-1} is ascribed to the CH_2 scissoring mode of PEO matrix.

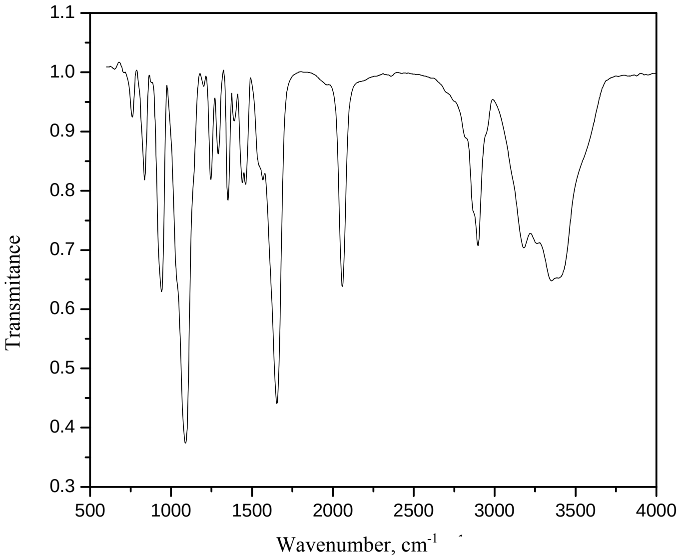

Figure 4. FTIR spectrum recorded for PEO/PVP/KI/I_2/pyrazole

PVP confirmation

The characteristic vibrational band observed at 2897 cm^{-1}may be attributed to the aliphatic CH stretching of PVP matrix whereas the typical band appearing in 3406 cm^{-1} confirms the presence of PVP polymer. It is interesting to note that the vibrational band appearing at 1243 cm^{-1} corresponds to the CH_2 twisting or wagging of both PEO and PVP chains. On the other hand stretching vibrations of C-N in PVP is present[7] at 1082 cm^{-1}.

Complexation of PEO/PVP/KI/I_2/pyrazole

The C–O–C stretching modes sen around the region 1111to 1115cm^{-1} may be ascribed as due to the complexation of ether oxygenwith K^+ ion. The Shift in band positions was also observed, which confirms the complexation when plasticizer was added to the PEO/PVP martrix. Further more the C–H bending of CH_2 in both PEO and PVP polymers appearing at 1483 cm^{-1} was shifted gradually towards 1441 cm^{-1} The characteristic vibration band at 1051 cm^{-1} of pure blend assigned to C–O stretching of PEO was also found to get shifted to 1088 cm^{-1}. These changes are in good agreement with the spectral behaviour of PEO/KI/I_2 complex and are associated with the increase in the number of gauche conformers along the PEO chain[8]

Conclusion

The PEO/PVP/KI/I_2 based soild polymer electrolyte system incorporated with 0.03M of nitrogenous dopant pyrazolewas prepared using solution casting technique. The room temprature ionic conductivity of PEO/PVP/KI/I_2 polymer electrolyte doped with pyrazole has witnessed two orders of magnitude enhancement compared to that of the undoped polymer. The present XRD studies have shown the disordered crystalline structure of PEO/PVP occuring due to the addition of dopant pyrazole as whereas the DSC studies of the polymer blend electrolyte with pyrazole have clearly demonstrated that because of the interaction between the pyrazole and blended polymes a depression of the melting temperature and melting enthalpy of the polymer blend take place. The FTIR studies of these blends have revealed the presence of strong interaction of pyrazole with PEO/PVP/KI/I_2 matrix which results in the miscibility of pyrazole with PEO/PVP. From the above results it is inferred that obtained the chosen polymer electrolyte may be suitable for an all solid-state electrochemical devices.

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