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Short communication

Characterization and electrical properties of polyvinyl alcohol based polymer electrolyte films doped with ammonium thiocyanate

N. Kulshrestha, B. Chatterjee, P.N. Gupta*

Department of Physics, Banaras Hindu University, Varanasi - 221005, India

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ABSTRACT

In this communication, films of polyvinyl alcohol (PVA) polymer complexed with ammonium thiocyanate (NH_4SCN) salt were studied. XRD (X-ray diffraction) was used to study the complexation of salt with the polymer matrix and amorphicity in the films. DSC (differential scanning calorimetry) studies showed that the glass transition temperatures (T_g) of the PVA:NH_4SCN complexed films were less than pristine PVA. Raman analysis was analyzed in order to study the change in the vibrational bands due to the complexation of salt with PVA. Optical micrographs confirm the fractal formation in 75:25 and 70:30 PVA:NH_4SCN films. Ionic transference number was estimated by Wagner's polarization method and its large value indicates that conduction takes place mainly due to mobile ionic species. Maximum conductivity $\sim 10^{-3}$ S/cm at room temperature was obtained for 70:30 ratio of PVA: NH_4SCN polymer electrolyte films.

1. Introduction

Ion conducting solid polymer electrolytes (SPEs) are preferred over the conventional ionic solids because of their light weight, flexibility, durability, mechanical stability, corrosion free properties, etc. [1]. SPEs are of great importance due to their wide applications in solid state electrochemical devices like batteries, fuel cells, super capacitors, sensors, etc. [1–6]. Interest in the field of polymer electrolyte started after detailed study of polyethylene oxide (PEO) films complexed with sodium and potassium thiocyanates salts [7–10]. However, PEO films have the drawback of liquid-solid phase co-existence and mechanical instability at high temperatures [11]. Therefore, a large number of alternative polymers like PVA, polymethyl methacrylate (PMMA), polyvinylpyrrole (PVP), etc. have been used to prepare the electrolytes and characterized for electrochemical devices [12–14].

PVA is a non-toxic, water soluble polymer having strong film forming ability with very high dielectric strength, good charge storage capacity, high mechanical tensile strength and dopant dependent electrical and optical properties [15]. To obtain a polymer electrolyte film, a suitable salt is added to the polymer matrix. Survey of accessible literature shows that ammonium salts are very good proton donors [16,17]. Earlier studies on PVA-NH_4SCN systems having low molecular weight PVA were showing low order of conductivity at room temperature [15–22] and thus not suitable for electrochemical devices. However, high molecular weight PVA, NH_4SCN salt and DMSO as a solvent were used for the preparation of polymer gel electrolytes [21,22].

In the present work, PVA of high molecular weight ~125,000, NH_4SCN as the dopant salt and water as the solvent have been used. This system of solid polymer electrolyte (SPE) has larger conductivity in ambient conditions than earlier reports on PVA-NH_4SCN SPE films. SPE films of PVA with different weight percentage of NH_4SCN have been characterized by various techniques such as XRD, DSC and Raman spectroscopy. Fractal patterns have been observed in the PVA complexed electrolyte films for higher concentration of NH_4SCN salt. Variation of conductivity and dielectric properties for different compositions of PVA:NH_4SCN polymer electrolyte films have been studied.

2. Experimental techniques

PVA (S.D. Fine-Chem Ltd, M.W. 125,000 LR) and NH_4SCN (Sigma-Aldrich NH_4SCN 97.5 + %ACS reagent) were used in the synthesis of PVA:NH_4SCN polymer electrolyte films. These films were prepared by solution cast technique with 5, 10, 15, 20, 25 and 30 weight% (wt%) of NH_4SCN in PVA matrix. PVA was dissolved in triply distilled water at 70 °C. After complete dissolution of PVA, known amount of NH_4SCN salt was added. The polymer salt solution was stirred for several hours until a viscous homogenous solution was formed. The resulting viscous solution was poured into a glass Petri dish and

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* Corresponding author. Tel.: +91 9839460194.
E-mail addresses: niharikakul@gmail.com (N. Kulshrestha), guptapn07@yahoo.co.in (P.N. Gupta).

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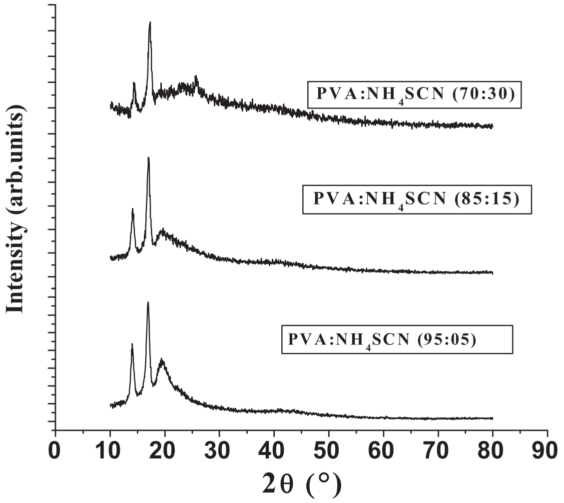

Fig. 1. XRD pattern of PVA:NH$_4$SCN polymer electrolytes: (A) 95:05, (B) 85:15 and (C) 70:30.

left to dry at room temperature. Finally the films obtained were vacuum dried thoroughly at the pressure of 10^{-3} Torr for 7–8 h. Films of uniform thickness ranging from 0.2 to 0.5 mm were taken for various experimental studies.

X-ray diffraction (XRD) patterns of the polymer electrolyte films were recorded at room temperature with a PANalytical XPert-PRO Diffractometer System using Cu-Kα radiation in the Bragg angle (2θ) in the range of 10–80°. Differential scanning calorimetry (DSC) thermograms were obtained at a heating rate of 10 °C/min under nitrogen atmosphere using DSC 131 Evo in the temperature range of 27–300 °C. Raman spectra of the polymer electrolyte films were recorded by Renishaw Raman Spectrometer using laser beam of 514.5 nm from Argon ion source in the wave number range 200–3500 cm^{-1}. Optical micrographs of the fractals were taken using Nikon ECLIPSE E600 optical microscope. Ionic transference number was estimated from Wagner's Polarization Technique. The impedance measurements were performed using WAYNE KERR Impedance Analyser 6500B Series in the frequency range from 100 Hz to 5 MHz at room temperature (28 °C). Ionic conductivity can be obtained from the complex impedance plot drawn using impedance data.

3. Results and discussion

3.1. X-ray diffraction studies

Table 1
Degree of crystallinity for different weight percent ratio of PVA:NH$_4$SCN films.

PVA:NH$_4$SCN weight percent ratio	Degree of crystallinity
95:05	11.4
85:15	6.1
70:30	3.2

XRD patterns for films with different PVA:NH$_4$SCN composition are shown in Fig. 1. Characteristic peaks of pure PVA are reported to occur at 14°, 17° and 20° [23,24]. In PVA:NH$_4$SCN films, decrease in intensity of the characteristic peaks of PVA with salt is a signature of increasing amorphicity [25]. Degree of crystallinity (χ_c) obtained from the XRD pattern can be estimated by the relation [24]

$$\chi_c = \frac{A_C}{A_T} \times 100 \tag{1}$$

where A_C is the total area of all crystalline peaks and A_T is the total area under the diffractogram.

It is observed that degree of crystallinity decreases with salt concentration and its values are listed in Table 1. Absence of peaks corresponding to NH$_4$SCN salt in the XRD patterns of 95:05 and 85:15 PVA:NH$_4$SCN films indicate the complete dissolution of salt in these compositions. However, the XRD pattern of the PVA:NH$_4$SCN (70:30) polymer electrolyte film shows a low intensity peak at 25.75°. This corresponds to the presence of NH$_4$SCN salt as confirmed by the JCPDS database (file No 23-0029).

3.2. DSC studies

DSC thermograms of PVA films complexed with different contents of NH$_4$SCN salt is shown in Fig. 2. Films of PVA:NH$_4$SCN show different melting temperatures, i.e. T_{m1} corresponds to the amorphous part of PVA, T_{m2} crystalline part of PVA, T_{m3} complex crystalline part of PVA, and T_{m4} uncomplexed salt in PVA [19,26]. Glass transition temperatures and melting temperatures for different compositions of PVA:NH$_4$SCN films are marked with arrows as shown in Fig. 2. Variation of T_g and melting temperatures are listed in Table 2. Glass transition temperature (T_g) of pure PVA comes out to be about 84 °C which is in good agreement with the earlier report [27]. For 85:15 PVA:NH$_4$SCN film, melting point of amorphous part of PVA is observed at 124 °C. The absence of T_{m2} in this composition may be attributed to different stabilization time taken by amorphous and crystalline phases in complexed PVA:NH$_4$SCN polymer electrolytes. In XRD, large crystallite size and longer range order are required whereas DSC is due to change in the thermodynamic heat of fusion of small crystallites account for the difference in the degree of crystallinity [28]. From the DSC curves, it can be observed that the glass transition temperature is reduced with the increasing salt content in the film. Reduction in glass transition temperature is a sign of increased flexibility of the polymer backbone which results in the enhancement of conductivity [17]. As shown in Table 2, melting temperatures corresponding to the NH$_4$SCN salt were observed in 75:25 and 70:30 PVA:NH$_4$SCN films.

3.3. Raman analysis

Raman spectra of pure PVA and complexed PVA-NH$_4$SCN films are shown in Fig. 3 in the region 200–3500 cm^{-1}. Raman band

Table 2
DSC data for PVA:NH$_4$SCN polymer electrolyte films with varying composition.

PVA:NH$_4$SCN weight percent ratio	T_g (°C)	T_{m1}	T_{m2}	T_{m3}	T_{m4}
100:0	84	–	199	–	–
95:05	64	164	190 & 198	249	–
85:15	65	124	–	251	–
75:25	55	–	174	255	164
70:30	51	–	221	240	157

T_g (glass transition temperature) in °C, T_{m1} (melting temperature of the amorphous part of PVA) in °C, T_{m2} (melting temperature of the crystalline part of PVA) in °C, T_{m3} (melting temperature of complex crystalline part) in °C, and T_{m4} (melting temperature of the uncomplexed salt in the polymer electrolyte) in °C.