Comparative Studies on Plasticized and Unplasticized PVA Polymer Electrolytes Containing NaF Salt

Mohammed Irfan[1,a)], A. Manjunath[1,b)] and S.S. Mahesh[2]

[1]*Department of P.G. Studies in Physics, Government Science College (VTU-RRC), Chitradurga-577501, Karnataka, India.*
2Department of Physics, Acharya Institute of Technology, Soladevanahalli, Bangalore-560107, Karnataka, India
[a)]Corresponding author: irfan.bse@gmail.com,
[b)]manjugsc@yahoo.com

Abstract. Solid Polymer electrolyte films based on Poly (vinyl alcohol) (PVA) containing Sodium fluoride (NaF) and PEG (Polyethylene Glycol) as plasticizer are prepared by solution casting method and characterized by XRD and FTIR techniques. The X-ray diffraction (XRD) spectra shows a characteristic peak of PVA indicating its semi-crystalline nature. By the addition of NaF, PEG and NaF into the polymer blend matrix, the intensity of peak decreases gradually, suggesting a decrease in the degree of crystallinity of the samples. FTIR study confirmed the complexation and functional group occurred by the addition of NaF and plasticizer PEG in the polymer blend. Dielectric and a.c. conductivity studies were carried out to the as prepared films at room temperature. Dielectric Constant (ε′) is maximum and found to decrease with increase in frequency and electrical conductivity of the complexed polymer blends increases by the addition of NaF with PEG. Literature reveals that these films found applications in energy storage devices.

Keywords: Polymer Electrolytes, Plasticizer, XRD, FTIR, Dielectric constant, AC conductivity.

INTRODUCTION

Polymers have relatively poor mechanical, thermal and electrical properties as compared to metals and ceramics [1]. Polymers when doped with metal salts give complexes which are useful for development of the advanced high energy electrochemical devices such as high energy density rechargeable batteries, fuel cells, electrochromic displays, sensors and solar cells [2, 3]. PVA is recognized as one of the very few water soluble vinyl polymers containing carbon backbone with hydroxyl groups which can be used as a source of hydrogen bonding and assist in the formation of polymer composites [4, 5]. Polymer electrolytes are promising host candidates for many applications because of their excellent properties such as high transparency, low cost and easy fabrication [6]. Literature reveals that by the addition of plasticizers into the host polymer matrix will increase the ionic conductivity of polymer electrolytes in addition to polymerization, ceramic fillers and blending [7]. Present work is aimed to synthesize PVA-NaF & PVA-PEG-NaF solid polymer electrolyte films and to investigate the effect of plasticizer (PEG) and NaF salt on the conductivity, complexation and structural properties of other polymer electrolyte films [8]. Plasticizer based film is suitable and can be used for the fabrication of batteries and solar cells [9].

EXPERIMENTAL

Solid polymer electrolyte films of PVA polymer containing NaF as alkali salt and PEG as plasticizer were prepared by standard solution casting technique for complexation. Appropriate measured quantities of PVA and NaF salt were dissolved separately in deionized water using magnetic stirrer for about 24 hour at room temperature to form standard solution respectively [10]. Required amount of PEG is added to this solution which acts as plasticizer and stirred for about 4 hour to get homogeneous solution. The homogeneous solution is casted in a glass dish.

Solvent is evaporated in an open air at room temperature in dust free chamber. The thickness of the film obtained is in the range of 0.49 mm and 0.59 mm [11]. The structural analysis of PVA-NaF and PVA-PEG-NaF solid polymer blend electrolyte films were undertaken by XRD analysis using Bruker (Model: Microstar Proteum 8) 2θ values ranging from $2\theta = 10^0$ to 80^0. FT-IR spectroscopy studies were carried out using Bruker ALPHA FTIR spectrometer (4000-600 cm^{-1}) at a resolution of 4 cm^{-1}. Dielectric and a.c. conductivity measurements on the as prepared films were carried out in the frequency range from 50 Hz to 5 MHz at room temperature using HIOKI 3532-50 LCR HITESTER and the results are reported.

RESULTS AND DISCUSSIONS

Consolidated XRD pattern of Pure PVA, PVA-NaF and PVA-PEG-NaF solid polymer blend electrolyte films is shown in figure 1. The X-ray diffractogram of these films exhibits broad peak at $2\theta = 19.49^0$ which is characteristic of the PVA crystalline phase. On the inclusion of NaF salt and PEG plasticizer into the polymer, the intensity of peak decreases gradually which suggests that there is a decrease in the degree of crystallinity of the polymer complex and creation of salt-polymer complexes. This could be due to the disturbance of the PVA crystalline structure by NaF salt. Hodge et al. [12] established an interaction between the intensity of the peak and the degree of crystallinity. This indicates that PEG most likely blends with PVA at the molecular levels and functions as both blend polymer as well as plasticizer. This feature is essential as the ion conduction takes place in amorphous region [13].

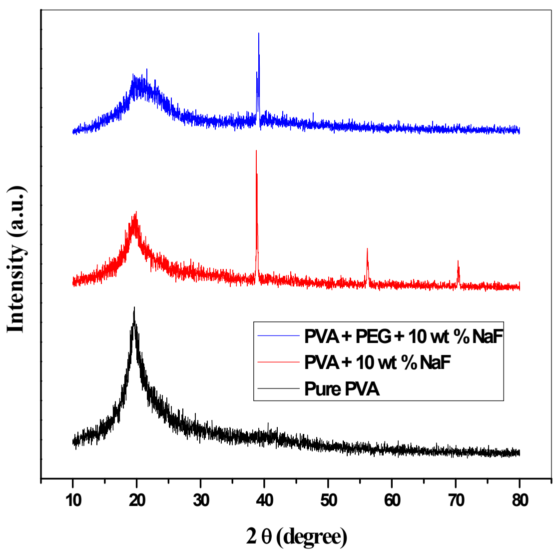

FIGURE 1. XRD spectra of pure PVA, PVA-NaF and PVA-PEG-NaF solid polymer blend electrolyte films.

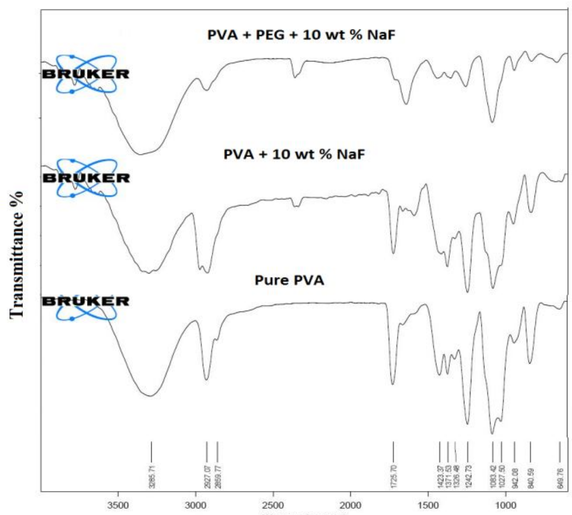

FIGURE 2. FTIR Spectra of pure PVA, PVA-NaF and PVA-PEG-NaF solid polymer blend electrolyte films.

The chemical structure of PVA, PVA-NaF and PVA-PEG-NaF solid polymer blend electrolyte films were studied using FT-IR analysis as shown in figure 2. The FT-IR spectrum exhibits absorption peaks. Broad absorption band observed at 3373.13 cm-1 is ascribed to intermolecular hydrogen bonding and –OH stretching vibration which is further shifted to 3287.72 cm-1 after addition of PEG. Vibrational band noticed at 2909.61 cm-1is related to CH stretching from alkyl groups. Further, band at 1646.11 cm-1 is attributed to H-O-H bending mode. Noticed band at 1349.17 cm-1 is due to bending vibration of the ionic C-H. The band appearing around 1086.27 cm-1 is due to stretching of C-O. All these changes in the FT-IR spectra are clear sign of the complexation and functional groups of PVA-NaF and PVA-PEG-NaF solid polymer blend electrolyte films [14].

The dielectric constant (ε′) is calculated from CP for different frequencies using the following relation,

$$\varepsilon' = \frac{C_P d}{\varepsilon_0 A} \qquad (1)$$

Where, C_P is the capacitance and $\boldsymbol{\varepsilon_o}$ is permittivity of free space.

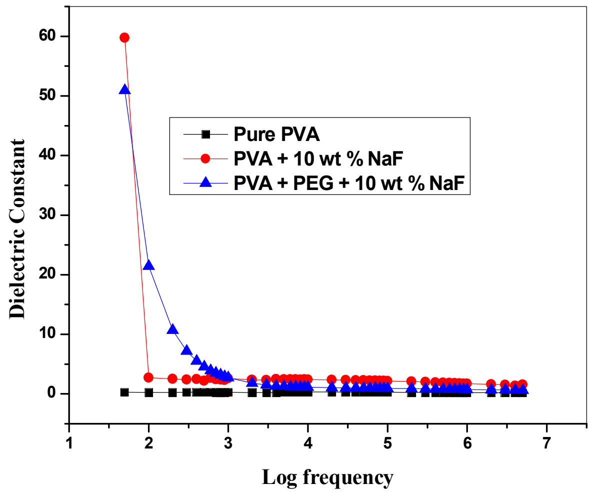

FIGURE 3. Variation of ε′ with frequency for pure PVA, PVA-NaF and PVA-PEG-NaF solid polymer blend electrolyte films.

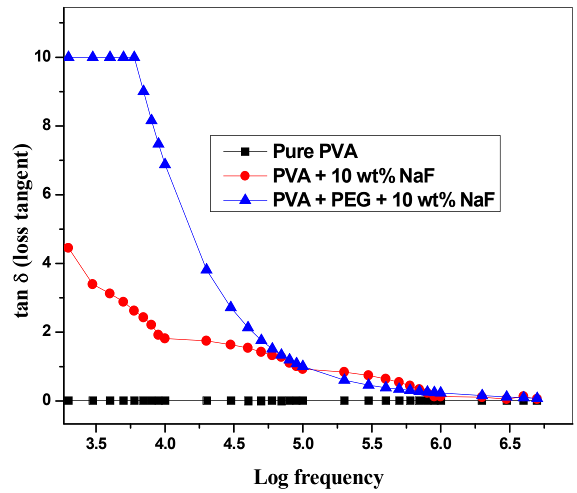

FIGURE 4. Variation of dielectric loss tangent (tan δ) with frequency for pure PVA, PVA-NaF and PVA-PEG NaF solid polymer blend electrolyte films.

Variation of ε′ with frequency for pre PVA, PVA-NaF and PVA-PEG-NaF solid polymer blend electrolyte films is shown in figure 3. The ε′ is found to decrease with increase in frequency. By the addition of PEG with NaF, dielectric constant is maximum and found to decrease with increase in frequency. Similar behavior has been observed in other polymer electrolyte films [15]. Observed higher values of ε′ in these samples are due to the Debye-type relaxation mechanism [16]. Figure 4 shows the variation of dielectric loss tangent with frequency for the as prepared films. Dielectric loss tangent (tan δ) measures the loss in the applied electrical energy into samples at different frequencies. From figure 4, it is clear that, the tan δ decreased with increase in frequency, reached minimum value and thereafter decreased. The loss peaks and shifts suggest a dielectric relaxation process.

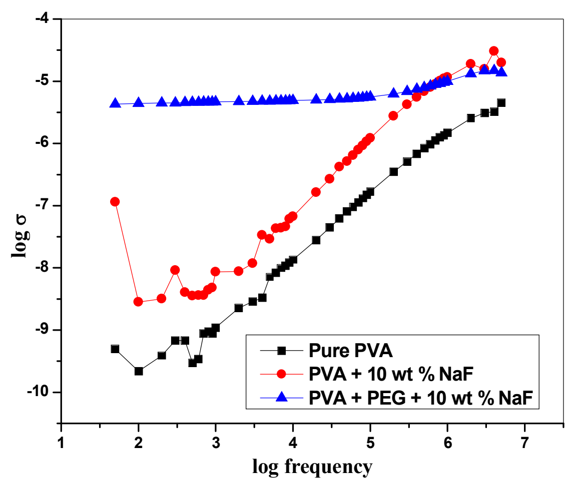

FIGURE 5. Variation of a. c. conductivity with frequency for pure PVA, PVA-NaFand PVA-PEG-NaF solid polymer blend electrolyte films.

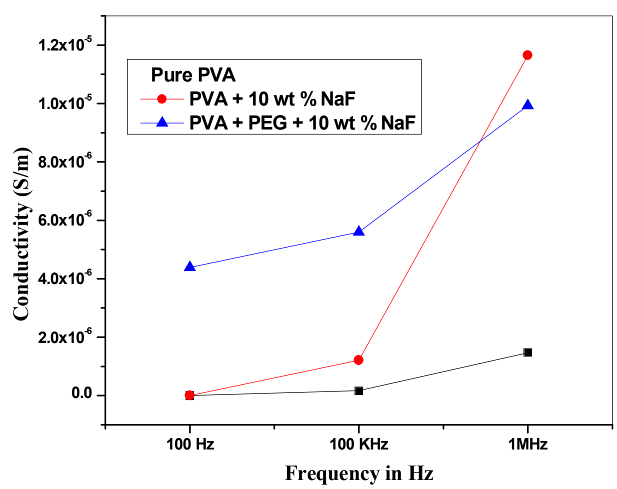

FIGURE 6. Variation of a.c. conductivity with different frequency of pure PVA, PVA-NaF and PVA-PEG-NaF solid polymer electrolyte films at different wt %.

Figure 5 shows the variation of a.c. conductivity with frequency for pure PVA, PVA-NaF and PVA-PEG-NaF solid polymer blend electrolyte films. We see that at room temperature a.c. conductivity is found to increase with increasing frequency range. On addition of plasticizer to the salted-PVA films, the conductivity is further increased. This indicates that the plasticizer has helped to dissociate the salt into mobile ions so that the conductivity of films can be enhanced. This behavior is characteristic of disordered materials at higher frequencies. Thus, the increase in conductivity with the frequency is according to hopping model of charge transport in disordered materials [17]. Figure 6 shows the variation of a.c. conductivity with different wt % of PVA-NaF and PVA-PEG-NaF solid polymer blend electrolyte films at different frequencies.

CONCLUSION

Plasticized and Unplasticized PVA based solid polymer blend electrolyte films were prepared and characterized by XRD, FTIR, Dielectric constant and a.c. conductivity studies. XRD analysis showed the crystalline phase of the samples. FTIR analysis revealed the presence of functional groups like –OH, CH, H-O-H and C-O in the synthesized films. Dielectric constant was found to decrease with increase in frequency by the addition of PEG with NaF. The a.c. conductivity was found to increase with increase in frequency. The plasticized film containing PVA+PEG+10 wt % of NaF had higher conductivity. The plasticizer PEG helps to dissociate the salt thereby increasing the number of mobile ions and lead to enhancement in conductivity. Electrical conduction mechanism was understood on the basis of electron-hopping model. All these study clearly shows that PEG is a good plasticizing agent and it increases conductivity of the samples. Present PVA-PEG-NaF solid polymer blend electrolyte films may find applications in the electronic energy storage devices as reported in literature.

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