Structural and Electrical Studies on PVP - Pan Blend Polymer System for Energy Storage Devices

R. Daniel^{1,2}, S. Janet Priscilla^{1,2}, S. Karthikeyan²,
S. Selvasekarapandian³, S. Madeswaran⁴, K. Sivaji^{1*}

¹Department of Nuclear Physics, University of Madras, Chennai-600025, Tamil Nadu, India; ²Department of Physics, Madras Christian College, Chennai-600059, Tamil Nadu, India; ³Materials Science Research Center, Coimbatore, India; ⁴Department of Physics, School of Advanced Sciences, VIT, Vellore-632014, Tamil Nadu, India.

ABSTRACT

Research on Polymeric materials have special interest in the recent years due to its high stability and hazardous free nature that are useful for the development of sensors, photovoltaic cells, high energy electrochemical devices, fuel cell etc. Solid blend polymer films have been prepared with the polymers polyvinylpyrrolidone (PVP) & polyacrylonitrile (PAN) by solution casting technique. The prepared films were investigated by different techniques. The XRD results confirms that the variation in the amorphous nature of the blend polymer with different blend-ratio. AC impedance spectroscopy has been used to examine the ionic conductivity and dielectric behavior of all the prepared blend polymer films was investigated in the frequency range 20 Hz to 4 MHz. The maximum conductivity has been found to be $4.45 \times 10^{-8} \text{ S cm}^{-1}$ at room temperature. The conductivity has been increased to $1.68 \times 10^{-5} \text{ S cm}^{-1}$ as the temperature is increased to 373 K. The activation energy of all the concentration of blend polymer was calculated using the Arrhenius plot and it is found to be 0.91 eV to 1.41 eV.

Key Words: Blend Polymer, PVP, PAN, Impedance spectroscopy analysis

INTRODUCTION

In recent years, the interest in the study of polymer electrolyte system is rapidly growing, because of the application of these materials in a great variety of electrochemical devices such as high energy density batteries¹, Supercapacitors², fuel cells^{3,4}, sensors^{5,6} etc. The development of polymer system with high ionic conductivity is one of the main objectives in polymer research. Therefore, it becomes essential to extend research on obtaining higher conductivity and mechanically stable polymer for polymer electrolytes. Many techniques have been introduced to modify the structure of polymer electrolytes in order to improve their electrical, mechanical and electrochemical properties⁷. These approaches include: synthesizing new polymers⁸; cross linking two polymers⁹; blending of two polymers^{10,11}; adding plasticizers to polymer electrolytes¹²; adding inorganic inert fillers to make composite polymer electrolytes^{13,14}. Among these approaches, polymer blending is a useful technique for designing materials with a wide variety of properties by changing the composition of blend ratio. (PVP)

is a synthetic bio-degradable polymer and it has a unique attention among the conjugated polymers due to its easy process ability, moderate electrical conductivity and rich in charge transport mechanism. In the present work, the effect of various PVP - PAN blend ratio on the ionic conductivity has been studied.

MATERIALS AND METHODS

Polyvinylpyrrolidone (PVP) (average mol wt 40,000) and Polyacrylonitrile (PAN)(average mol wt 150,000) bought from Sigma – Aldrich were used to prepare the blend polymer films. Dimethyl formamide (DMF) has been used as a solvent.

Preparation of blend polymer films

Blend polymer (PVP: PAN) film preparation

Blend polymer films were prepared using solution casting technique. Initially PVP was added to the solvent at room

Corresponding Author:

K. Sivaji, Department of Nuclear Physics, University of Madras, Chennai-600025, Tamil Nadu, India;
E-mail: sivaji@unom.ac.in

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temperature and stirred continuously until the complete dissolution of the polymer. PAN was added separately into solvent and heated at 60°C in order to dissolve PAN and stirred for 24 hours. Then PAN was mixed to the solution and allowed to stir continuously to obtain homogenous mixture. The resulting solution was then poured into a Petri dish and kept in a vacuum oven at 70°C for 48 hrs to remove the presence of solvent in the sample. This procedure yields mechanically stable and free standing membranes with 3 different molar ratios (85PVP:15PAN, 80PVP:20PAN, and 75PVP:25PAN).

Characterization of the blend polymer films

X-ray diffraction patterns of the prepared blend polymer samples have been recorded at room temperature on a Bruker D8 Advanced X-ray diffractometer using Cu K α radiation. Dielectric and conductivity measurements are made using HIOKI 3536 impedance analyzer in the range of 20 Hz– 4 MHz and the temperature of 305 K–373 K. The conductivity value depends on the bulk resistance¹⁵; the impedance accuracy is $\pm 0.97\%$.

RESULTS

Structural analysis: X-Ray diffraction

X-ray diffraction is a non-destructive technique and versatile which unveils the information about the structure of the materials. XRD measurements were performed on different concentration of PVP: PAN. The crystallinity and the amorphous nature of the films are examined. The X-ray diffraction patterns of the PVP blend with PAN with different concentrations are shown in figure 1.

Figure 1: XRD pattern of PVP – PAN blend polymer for different concentration.

AC Impedance spectroscopy analysis

The ac impedance technique is a constructive method for characterizing the electrical properties of materials. Figure 2. Shows the Cole - Cole plot for PVP –PAN blend polymer films of different compositions at room temperature.

Figure 2: Cole - Cole plot for PVP –PAN blend polymer of different concentrations at room temperature.

The frequency dependent conductivity for 80PVP:20PAN blend polymer film as a function of different temperatures as shown in figure 3.

Figure 3: Conductance spectra for high conductivity blend polymer concentration at different temperatures.

The dc ionic conductivity values for all the compositions of PVP: PAN blend polymer at different temperatures has been tabulated in Table 1.

Table 1: Conductivity for different concentrations of PVP and PAN blend polymer at different temperatures

Temperature (K)	Conductivity σ (S cm ⁻¹)		
	75PVP:25PAN	80PVP:20PAN	85PVP:15PAN
305	3.39×10^{-10}	4.45×10^{-8}	3.19×10^{-10}
313	8.61×10^{-10}	4.91×10^{-8}	5.01×10^{-10}
323	3.54×10^{-9}	9.32×10^{-8}	3.63×10^{-9}
333	4.55×10^{-8}	2.64×10^{-7}	2.55×10^{-8}
343	1.10×10^{-7}	1.04×10^{-6}	7.97×10^{-8}
353	4.71×10^{-7}	2.90×10^{-6}	3.13×10^{-7}
363	1.53×10^{-6}	5.61×10^{-6}	1.54×10^{-6}
373	2.99×10^{-6}	1.68×10^{-5}	3.14×10^{-6}

The variation of conductivity at room temperature and activation energy as a function of different PVP: PAN blend polymer with different concentration is shown in figure. 4. As the conductivity of the sample increases it can be noticed that E_a decreases.

Figure 4: Blend polymer concentration dependent conductivity and activation energy

Figure 5 shows the temperature dependence conductivity for all the prepared PVP: PAN blend polymer over the temperature range 305 K–373 K. The activation energy calculated for all the blended polymer films has been tabulated in table 1.

Dielectric spectra analysis

Figure 6 (a), (b) shows that the values of ϵ' and ϵ'' are very high at low frequency and high temperature and this is due to the effect of 'blocking electrodes'¹⁶ ionic conductivity and thermal properties have been measured for the gel polymer electrolyte system poly(acrylonitrile).

Figure 5: Log σ vs. $1000/T$ for different concentrations of PVP–PAN blend polymer. **Figure 6a:** Variation of real dielectric constant of high conductivity blend polymer with frequency. **Figure 6b:** Variation of imaginary dielectric constant of high conductivity blend polymer with frequency.

Figure 7: Tangent loss spectra of high conductivity blend polymer 80PVP:20PAN at different temperatures.

DISCUSSION

From the XRD pattern as shown in figure 1, the peak intensity was observed to be minimum for the blend polymer 80PVP:20PAN showing high degree of amorphicity which is in good agreement with the conductivity result¹⁷. The highest amorphous sample is the blend of 80% PVP and 20% PAN. The peak at $2\theta=29.54^\circ$ is small and broad. The decrease in the degree of crystallinity causes a reduction in the energy barrier to the segmental motion of the blend polymer film thus resulting in high ionic conductivity¹⁸.

Figure 2. shows the complex impedance plot of 75PVP:25PAN, 80PVP:20PAN and 85PVP:15PAN blend polymer films at 305 K. The figure shows a high frequency semicircle and a low frequency spike for PVP: PAN blend polymer films. The bulk resistance for all samples has been calculated from the low frequency intercept of the semicircle or high frequency intercept of the spike on the real axis. The bulk resistance R_b decreases with increase in blend polymer ratio. The ionic conductivity increases with increase in blend ratio and attain a maximum value of $4.4 \times 10^{-8} \text{ Scm}^{-1}$ at room temperature for 80PVP:20PAN, which has greater ionic conductivity than that of 75PVP:25PAN ($3.39 \times 10^{-10} \text{ Scm}^{-1}$) and 85PVP:15PAN ($3.19 \times 10^{-10} \text{ Scm}^{-1}$).

The ionic conductivity is calculated using the relation, $\sigma = L/R_b A$

Where

L is the thickness of the film

R_b is the bulk resistance of the film

A is the contact area of the film

Figure 3 shows the conduction spectra consist of two regions of importance, a low frequency dispersive region due to the

electrode polarization effect and at high frequency region, the plateau representing the dc conductivity where the ac conductivity is generally taken to assume the frequency independent value, which is equal to the dc conduction¹⁶ionic conductivity and thermal properties have been measured for the gel polymer electrolyte system poly(acrylonitrile). The extrapolation of the dc plateau on the $\log \sigma$ axis or zero frequency gives the values of dc ionic conductivity and it has been calculated to be $4.4 \times 10^{-8} \text{ Scm}^{-1}$ at room temperature for the blend polymer 80PVP:20PAN. Also it has been found that the dc conductivity increases with increase in temperature. The values of dc conductivity are tabulated in Table 1 and this suggests that the free volume around the polymer chain causes the mobility of ions and polymer segments.

Figure 4 shows that when the conductivity of sample increases, it can be noticed that activation energy decreases indicating that the ions in highly conducting samples require lower energy for migration. The high conductivity with low activation energy is observed for 80PVP:20PAN concentration. The activation energy is found to be low of the order of 0.91 eV for the high conductivity sample.

Figure 5 shows that the conductivity increases linearly with increase in temperature for all the polymer blend of PVP: PAN. The highest conductivity exhibits in the blend ratio of 80PVP:20PAN concentration and the temperature dependent ionic conductivity for all the concentration obey Arrhenius relation.

$$\sigma = \sigma_o \exp\left(\frac{E_a}{KT}\right)$$

Where

σ_o is the number of charge carriers in the film

E_a is the activation energy

K is the Boltzmann constant

Based on the least squares analysis of the data, a straight line fit has been obtained for all the PVP with PAN concentration. The experimental data indicates that the ionic conductivity has increases with increase in temperature. The activation energy E_a is calculated for all the composition of the blend polymer films by linear fit of the Arrhenius plot. The calculated activation energy values have been tabulated in Table 2.

Table 2: Activation energy for different concentration of blend polymer (from Arrhenius plot)

PVP: PAN	Activation energy EA (eV)	Conductivity at room temperature σ (Scm ⁻¹)
75:25	1.38	3.39×10^{-10}
80:20	0.91	4.45×10^{-8}
85:25	1.41	3.19×10^{-10}

From table 2 the activation energy is low (0.91 eV) for the 80PVP:20PAN concentration and this is due to the amorphous nature of the blend polymer film that facilitates the ionic motion in the polymer system. The increase of activation energy with the increase of PAN concentration may be due to the increase in the crystallinity¹⁹.

The dielectric property specifies the amount of charge that can be stored by a material. If dielectric property of the material increases, the amount of charge stored by the material will also increase²⁰. The dielectric response is usually described by the complex permittivity

$$\epsilon^* = \epsilon' - i\epsilon'',$$

Where

ϵ' is the real part of dielectric constant

ϵ'' is the imaginary part of dielectric constant

Figure 6 (a), (b) shows that the values of ϵ' and ϵ'' are very high at low frequency and high temperature and this is due to the effect of blocking electrodes. In Figure 6a, it is clearly seen that at low frequency and high temperature, the dielectric constant (ϵ') is very large approximately in the order of 10^6 at 373K, indicates the existence of “space charge polarization”. In Figure 6b, the dielectric loss is inferred to be very large approximately in the order of 10^6 at low frequency and high temperature, which is due to the free charge motion at the interface between the material and the electrodes. For very low frequencies there is a time for the charges to build up at this interface before the field changes its direction, giving a very large value of ϵ' . With increasing frequency there is no time for the buildup of the charges at the interface and this is due to high periodic reversal of the field at the interface, the contribution of charge carriers towards the dielectric constant decreases with increasing frequency. This phenomenon is called “conductivity relaxation”²¹.

The expression for the dielectric loss tangent is given as

$$\tan \delta = \frac{\epsilon''(\omega)}{\epsilon'(\omega)}$$

The dependence of the dielectric loss tangent ($\tan \delta$) on frequency under different temperature for high conducting blend polymer concentration 80PVP: 20PAN is shown in Figure 7. All the curves show a peak corresponding to the relaxation of dipoles leading to the dielectric loss²². The frequency, ω corresponding to the peak is related to the relaxation time, τ by the expression $\omega\tau = 1$. The relaxation time for the high conductivity blend polymer at different temperature is calculated and tabulated in Table 3.

Table 3: Relaxation time for the high conductivity blend polymer at different temperatures

Temperature (K)	Relaxation time τ (ms)
313	19.2
323	13.1
333	10.3
343	3.78
353	1.93
363	1.26
373	0.64

The height of the peak increases and shifted to the right with the increasing frequency at different temperatures is due to the increment in the number of charge carriers for conduction. The low relaxation time has been observed at high temperature for the highest conducting blend polymer 80PVP:20PAN.

CONCLUSION

PVP–PAN polymer blend film has been prepared by solution casting technique. The increase in amorphous nature of the PVP–PAN polymer blend films has been confirmed by XRD analysis. The dielectric permittivity (ϵ^*) and relaxation time are calculated from the ac impedance spectroscopy in the frequency range 40 Hz – 4 MHz and the temperature range 305–373 K. The maximum conductivity has been found to be $4.45 \times 10^{-8} \text{ Scm}^{-1}$ at room temperature for 80PVP:20PAN concentration. The conductivity is increased to $1.68 \times 10^{-5} \text{ Scm}^{-1}$ as the temperature increases to 373 K. The values of ϵ' and ϵ'' are very high at low frequency and high temperature but at high frequency these are constant with frequency. The activation energy of all the concentration of blend polymer was calculated using the Arrhenius plot and it is found to be 0.91 eV to 1.41 eV.

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