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Synthesis, Characterization and Spectroscopically Studies of PVP and PVDF-blended Systems for Energy Storage Applications

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ABSTRACT

Blend polymer electrolytes have been produced with the use of poly (vinylidene fluoride) (PVDF)and Poly (vinylpyrrolidone) (PVP) mixed with $NaClO_4$ by the method of solution cast technique. Characteristics of the Fourier transform infrared spectroscopy(FTIR), X-ray diffraction (XRD), and scanning electron microscopy are studied to authorize the complexation of sodium perchlorate salt with blend systems. AC and DC conductivity studies are carried out for all blend systems by changing PVP wt%, and PVDF wt% at fixed 4 weight percentage of $NaClO_4$. Impedance spectroscopy has been used to examine the nonconducting (Dielectric) properties, and electric modulus (M*) from 10Hz to 30 MHz between 298 K and 343 K for all the systems. The maximum ionic conductivity is noticed for PVDF: PVP-$NaClO_4$ (20:80-4) system at room temperature, that could be due to decrease in the crystalline nature and enlargement of amorphous region. The variation of ionic conductivity of the blend polymer electrolyte systems with temperature followed Arrhenius behaviour and the maximum ionic conductivity 4.332×10^{-5} S cm^{-1} was observed for PP-4 System at room temperature.

Keywords: Solution cast method, Blend polymer electrolyte, SEM, FTIR, XRD, Impedance analysis, Nyquist plots.

INTRODUCTION

SPEs, or solid polymer electrolytes, play a key technical function in the fabrication of energy storage devices, hydrogen fuel cells, cells, mobile phones and smartphones and sensor applications[1-2].

SPE membranes have extremely excellent durability throughout the thermoelectric, dynamic, electrical, and flexible domains. In order to produce this SPEs, an alkali metal and even its compounds should always be immersed in a polymer host[3-5]. These solid polymer electrolytes (SPEs) have several benefits over liquid electrolytes, the most notable of which are their safer operation, longer equipment life, avoidance of electrolyte leaks, wider windows of electrochemical stability, and wider working temperature range[6-7]. Lithium, sodium, potassium, and silver ion (Li^+, Na^+, K^+, Ag^+) based on solid electrolyte solutions have seen much research[8]. Electrochromic displays, highly dense fuel cells, sensors, and rechargeable batteries are just a few of the cutting-edge technologies that have sparked a flurry of interest in this area recently[9]. Due to the existence of polar strands with a considerable cation co-ordination and a low rotational barrier, polymer is used as a host polymer in these electrolytes[10]. PVP is most studied polymer from an economic and commercial standpoint due to PVP polymer is reasonably priced, excellent more dimensional accuracy, greater mechanical stability and higher ionic conductivity.

Numerous research teams are actively working to achieve an increase in conductivity while maintaining the same temperature using a variety of techniques, Cross-linking[11,12], mixing polymers[13,14], adding low-molecular-weight plasticizers, and adding inorganic nano particles[15-19]. The term "blend" refers to a mixing of more than one polymer there at matrix level[20]. At room temperature, Koduru observed a maximum conductivity of 1.56×10^{-7} S/cm on a mixture of PEO & PVP polymers forms a complex with 10 wt.% of Sodium periodate[21]. Dave and Kanchan identified the greatest conductivity in polymers PEO & PAM at ambient temperature was 2.81×10^{-7} S/cm when they were complexed with 17.5 weight percent of the ionic compound Sodium trifluoromethanesulfonate[22].

In order to achieve good mechanical strength, thermal stability and high electrical conductivity, polymer blend selection is crucial. Because of its large value of dielectric constant, superior mechanical toughness and great stability of temperature. PVdF is an excellent material for use in electrospinning. As a semi-crystal of PVDF has a very long zigzag chain and it has been shown that it can improve the mechanical & electrochemical performance of solid polymer electrolyte systems[23]. Mahboube Mohamad[24] highlighted the possibility that PEO and PVDF may mix together without causing any problems. PVDF-based SPEs have a large number of functional groups that attract a large number of electrons, a relatively low dissipation factor, and a high dielectric constant[25], it is anticipated that these materials will be stable anodic materials.

Within the scope of this work, Polymer electrolyte systems are made with the help of solution casting with PVP, PVdF and $NaClO_4$. Pure form of blend polymers has a very poor conductivity at ambient temperature, hence a constant 4 wt% of $NaClO_4$ is added and all the samples are prepared in accordance with (100-x) wt% PVDF: x wt% PVP-4 wt% $NaClO_4$ (x=20, 40, 60 and 80). This research work aims to analyse the dielectric and conductivity studies by using impedance analysis using FTIR and XRD data, look into how the structure of blended polymer electrolytes changes.

Methodology for Experiments

Sodium perchlorate ($NaClO_4$, AR≥98%) poly (vinylpyrrolidone) (PVP, MW=3,60,000), poly (vinylidene fluoride) (PVDF, MW=2,70,000) & Dimethyl formamide (DMF, AR grade) are procured from Sigma Aldrich, India. Solution cast technique has been used to prepare the blend polymer electrolyte systems by varying the wt% of PVP and PVdF with a fixed 4wt% of $NaClO_4$. 50 mL of DMF is used to dissolve PVP, PVdF and $NaClO_4$ by keeping a 1-h break between every occurrence of chemical dissolution on a magnetic stirrer. After two hours at 60°C, the entire solution is heated before being stirred constantly for another 30 h to ensure a uniform consistency. The solution is dried at 60°C in a vacuum oven for 40 h after being blown out into a Petri dish. All electrolyte systems have been prepared in accordance to (100-x) wt% PVDF–x wt% PVP-4 wt% $NaClO_4$ (here x=20, 40, 60 and 80). All the samples are examined to the electrical and structural properties after seven days. XRD and FTIR were utilised to identify the complex formation of $NaClO_4$ salt with a PVP & PVDF blend matrix. DSC is used to find out the melting temperatures. For study the surface morphology Scanning electron microscopy (SEM) is used. Electrical impedance spectroscopy (EIS) is used to study of dielectric characteristics, ionic conductivity and electrical modulus.

RESULTS AND DISCUSSION

XRD studies

Figure 1 depicts the XRD diffractogram of pure form of PVDF, $NaClO_4$ and varying PVP concentrations relative to PVDF at a fixed 4 wt% of $NaClO_4$. The noticeable peaks in the XRD form of pure PVDF observed at 20.1° and 38.9° indicate and phases respectively indicating semi crystalline nature[26]. The peaks observed at 24.8°, 32.1° and 36.2° indicate the crystalline nature of $NaClO_4$. No crystalline peaks related to $NaClO_4$ observed in complexed polymer films, which demonstrate that $NaClO_4$ is complexed in PVP and PVDF polymer matrix[27]. It has been observed that the peak at 20° related to beta phase of PVDF broadened, decrease in intensity and shifted slightly towards lower angle as the PVP concentration increases. This could be due to reduction in crystalline nature and rise in amorphous nature from PP-1 to PP-4 systems.

The detailed compositions of blended polymer electrolytes, at 298 K were listed in Table 1.

Table 1: The blend system compositions of the prepared samples are listed below

Sample code	PVP(wt%)	PVDF(wt%)	$NaClO_4$(wt%)
PP-1	20	80	4
PP-2	40	60	4
PP-3	60	40	4
PP-4	80	20	4

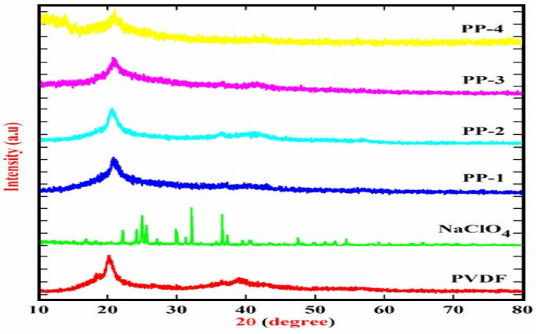

Fig. 1. XRD diffractogram of pure PVDF, $NaClO_4$, PP-1, PP-2, PP-3 and PP-4 systems

SEM studies

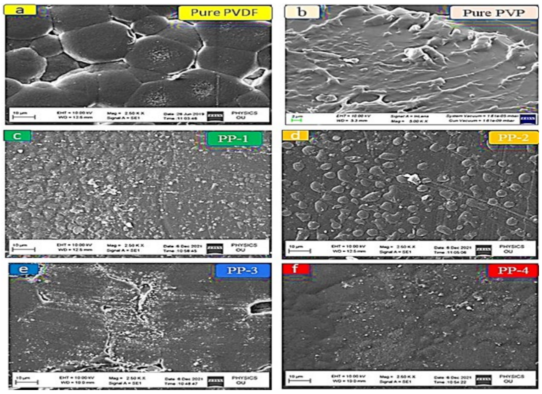

Fig. 2. SEM Images of (a) Pure PVDF (b) Pure PVP (c) PP-1 (d) PP-2 (e) PP-3 (f) PP-4

Figure 2(a) & 2(b) depict the pure form of PVDF and PVP respectively. The complexed polymer mix electrolyte films are depicted in Figs. 2(c) to (f). As PVP concentration rises, spherulite formations are observed to diminish. Fig. 2(f) clearly indicates that the PP-4 sample exhibits smoother surface compare to all other films showing decrease in crystallinity and increase in amorphous behaviour[28-30].

Impedance spectroscopic studies

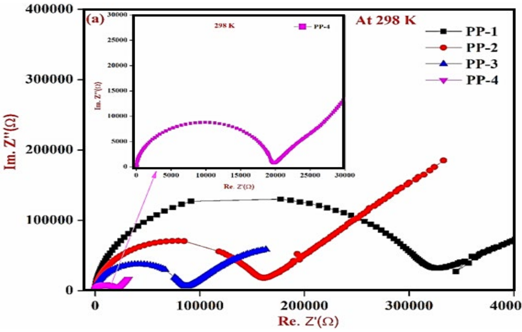

Fig. 3(a). Impedance plots of PP-1 to PP-4 systems at 298 K

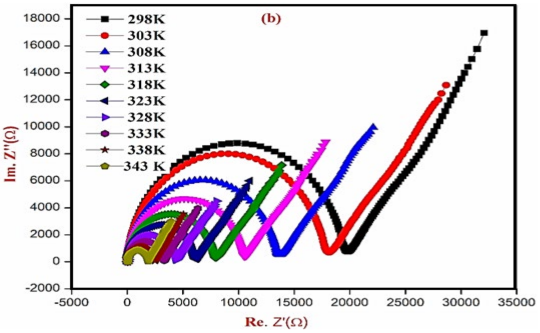

Fig. 3(b). Impedance plot for PP-4 system at various temperatures

In order to have a better understanding of the effects of combining PVP and PVDF complexed with Sodium perchlorate, the complex impedance spectra at a range of temperatures are collected. Fig. 3(a) illustrates the complex impedance curves for a number of different systems at a temperature of 298K. The figure in the inset shows the cole-cole plot of PP-4 system. The PP-4system has least possible bulk resistance (R_b) thus, it has maximum ionic conductivity which is chosen for further studies. Fig 3(b) represents the impedance spectrum of PP-4 system at different temperatures. The semicircles and associated spikes observed for all the systems at various temperatures reveal that the systems are partially capacitive and partially resistive[31]. As the temperature increases, the bulk resistance of the sample seems to decrease which could be due to thermally activated process.

AC conductivity

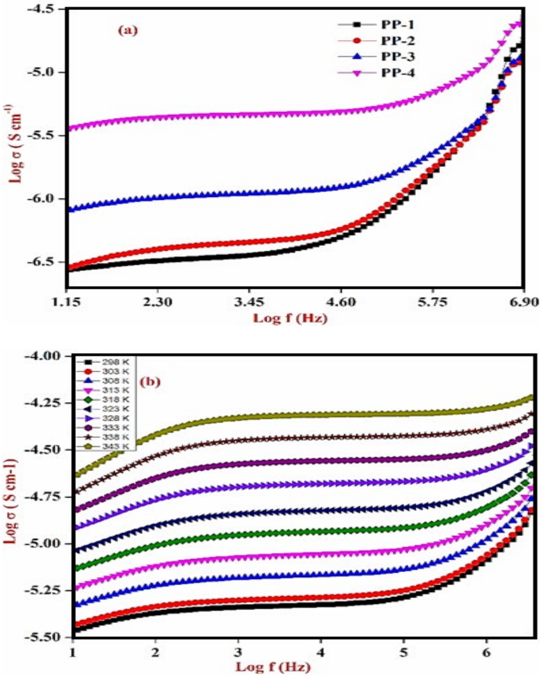

Fig. 4(a). Frequency dependent conductivity of PP-1 to PP-4 systems (b) at different temperatures of PP-4 system

Jonscher's power law describes the variation of conductivity with frequency is given by

$$\sigma(\omega)= \sigma_0+A\omega^n \tag{1}$$

Where A is constant, n is a frequency exponent, The conductivity at a certain frequency is denoted by $\sigma(\omega)$ and σ_0 is the frequency-independent conductivity at lower frequency, which is equivalent to the DC ionic conductivity. The frequency-dependent A.C conductivity of blend composite systems is depicted in Fig. 4(a) between 298 K and 343 K. There are three types of dispersion areas, corresponding to the space charge at low frequency, the saturation at mid frequency, and the dipole-dipole interactions of charged particles at high frequency respectively[32,33]. From the figure, it can be noticed that as the sample composition changes, the plateau region changes and the maximum plateau length is observed for PP-4 system which could be due to the availability of large number of free charge carriers at this composition comparted to other samples. Fig. 4(b) illustrates the electrical conductivity of a PP-4 sample between 298 K and 343 K, and follow the three characteristic dispersion regions[34-36]. As the temperature rises, the conductivity with frequency also increases due to thermally activated mechanisms.

Loss tangent

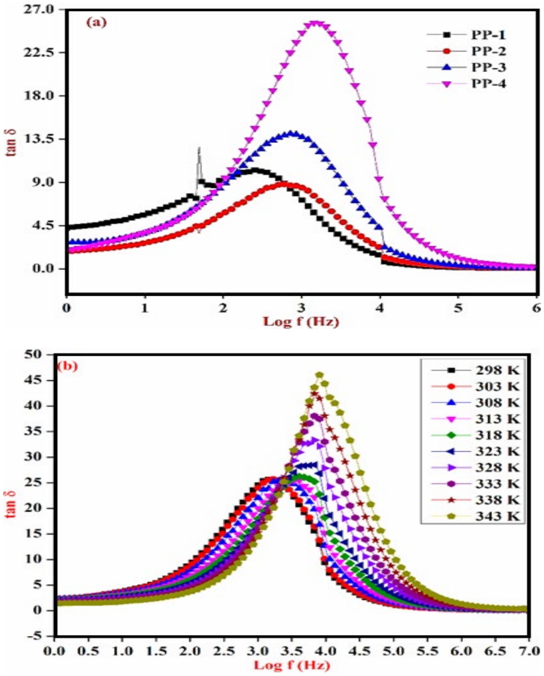

Fig. 5(a). Variation of tan δ with frequency of PP-1, PP-2, PP3 and PP-4 systems at 298 K b) PP-4 at different temperatures

Figure 5(a) illustrates how the loss tangent varies with frequency of all the blend systems. It is observed that by changing the polymer ratio, the peak moves to the high-frequency area, and the PP-4 system is observed to have the large shift towards high frequency. The shift towards to the high-frequency zone demonstrates that the decrease in relaxation when mobile ions are linked with rapid segmental motion[37]. Fig. 5(b) shows that the loss tangent of PP-4 system at various temperatures. The shift in the dispersion is noticed towards high frequency region and increase in its intensity signifies decrease in relaxation time with temperature. The peak shift moves to high frequencies, when the temperature rises is standard phenomenon in dielectrics[38].

Dielectric studies

A material's complex dielectric constant*, which varies with frequency, is expressed as

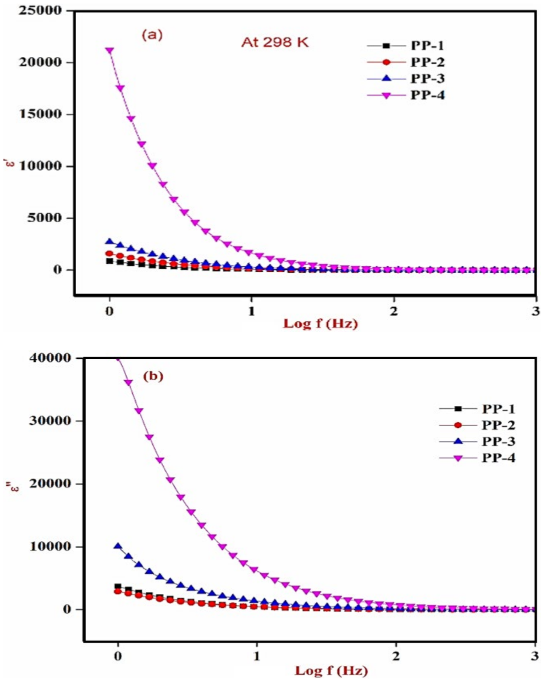

Fig. 6(a) & (b). Change of dielectric constant & dielectric loss with frequency of PP-1, PP-2, PP-3 and PP-4 at 298 K 6(c) & (d) PP-4 at several temperatures

$$\sigma^* = \varepsilon'(\omega) - j\,\varepsilon''(\omega) \quad (2)$$

Figure 6(a) & (b) describe the frequency-dependent dielectric constant and dielectric loss of all blend systems at room temperature It has been seen that both ε' and ε" behaves the same with frequency. The values of εε' and ε" are steeper at very low frequency due to space charge polarization and decreases exponentially with frequency due to absence of dipolar polarization. Finally attains to a negligibly small values at very high frequency. The dielectric relaxation shows similar behaviour except that its value is finite and constant at high frequencies. It is identified that PP-4 system showing the highest value of at 1Hz when differ to all other systems. At this frequency the large value dielectric constant could be due to presence of all polarizations but dominated by space charge polarization. The dielectric constant is lower at intermediate frequencies due to space charge and the presence of orientational polarisations[39,40]. As PVP content increases the permittivity increases and it is maximum for PP-4 system which could be due to presence of large number of free ions. Maximum dielectric loss for PP-4 is seen at a frequency of 1Hz and decreases with increase in frequency, reaches a saturation point at very high frequencies (above around 10MHz). Dielectric loss at low frequencies can be understood in terms of the polarisation phenomenon at the electrode/electrolyte interface. High measurable value of ε" is due to the enormous amount of free flow of charges in the system and there will be sufficiently of time for charges to accumulate at the interface before the electric field is altered. A maximum dielectric loss is observed for the PP-4 system at ambient temperatures compare to all other systems. In the high-frequency area, charges did not accumulate at the interface[41-42].

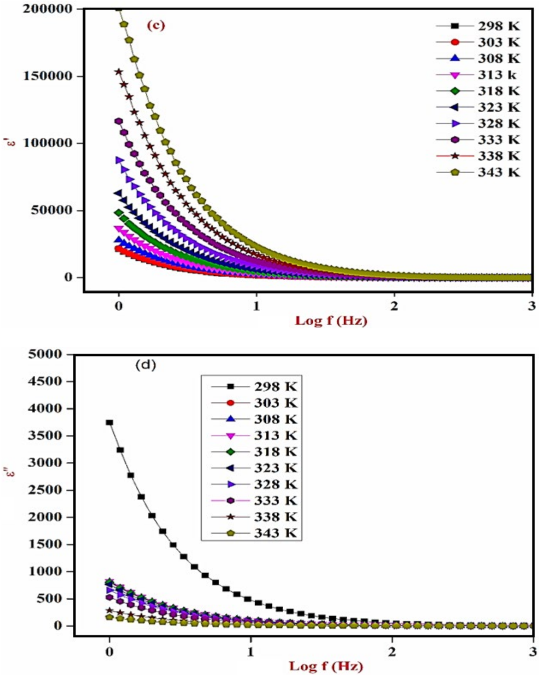

Fig. 6(c) and (d) represent the temperature dependent dielectric constant and dielectric loss of PP-4 sample. The values of ε' rise with temperature due to increased free ion movement[43-45].

DC Ionic Conductivity

Figure 7 shows the variation of conductivity due to ions versus inverse of temperature in between 298K–343K for all blend electrolyte systems. The ionic conductivity has been evaluated using the equation $\sigma = t/AR_b$, where t is the thickness, A is the area of cross section and R_b is the bulk resistance of the sample. It is observed that as the quantity of PVdF decreases, the ionic conductivity increases. The highest conductivity obtained for PP-4 system is 4.332×10^{-5} S/cm at

298K, this could be due to decreased crystallinity and increased amorphous nature[46,47]. A larger PVdF ratio in electrolytes leads to high viscosity, which in turn lowers the movement of the charge carriers and there by limits the conductivity[48].

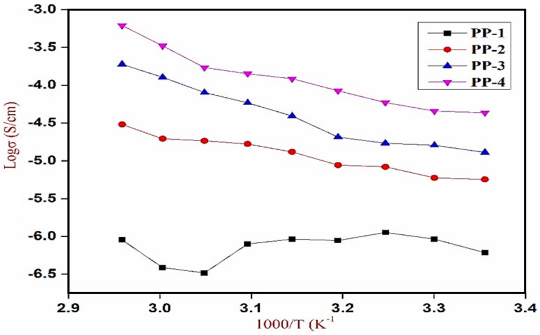

Fig. 7. Arrhenius plot: Log σ Vs 1000/T.

CONCLUSION

Polymer electrolytes films complexed with $NaClO_4$ are prepared from PVP and PVDF using a solution cast process. The smooth surface morphology of the PP-4 system is clearly illustrated using SEM Technology. DSC analysis revealed the lowest melting temperature for a blend of 80 wt% PVP+20 wt% PVDF+4 wt% $NaClO_4$ (or) PP-4 system in the range of temperatures from 298°C to 343°C. The Arrhenius rule can be applied to describe the changes in ionic conductivity with temperature and it was discovered that the blend systems PVP & PVDF in 80:20 composition produces excellent conductivity values.

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Conflicts of Interest

The authors certify that they do not have any competing interests to declare.

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