Abstract-- Proton conducting polymer blend electrolyte based on PVP-PVC- CH₃COONH₄ were prepared for different compositions by solution cast techniques. The prepared films are studied by different techniques. The XRD study tells the amorphous nature of the polymer electrolyte. The FTIR studies prove the complex formation between the polymer and salt. DSC measurements show decrease in $T_f$ with increasing salt concentration. The conductivity of the polymer electrolyte is determined by AC impedance spectroscopy analysis. A maximum conductivity 9.14x10⁻² Scm⁻¹ at room temperature has been observed for the composition of 70PVP:30PVC:0.3 Mwt% of CH₃COONH₄. The dielectric behaviors are studied.

Key Words-- PVP, Proton Conducting, Conductivity analysis, Electrolyte.

I. INTRODUCTION

A solid polymer electrolyte is consisting of ionic salts dissolved in an appropriate polymer, which enables proton conduction at room temperature in the solid state. The solid polymer electrolyte is designed to show both high proton conductivity, while their characteristic varies depending on the composition of the host polymer. Proton conducting polymer electrolytes are important material because of its application for the development of fuel cells, solid state batteries, sensors and electrochemical devices [1-3]. The advantages of polymer blends are that properties of the final product can be modified to the requirement of applications, which cannot be attain alone by one polymer. However, the film properties depend on the miscibility of blend. The polymer –polymer miscibility possibly from any one of the interactions such as hydrogen bonding, dipole-dipole forces and charge transfer for homo polymer mixtures [4-9].

Polyvinyl pyrrolidone (PVP) deserves a particular awareness among the conjugated polymers because of its good environmental stability, easy processability, moderate electrical conductivity and wealthy physics in charge transport mechanism. Polyvinyl chloride (PVC) is flexibly thermoplastic with good mechanical strength and also possesses very good flame retardant properties among general commercial plastics [10-13].

PVP, PVC, CH₃COONH₄ and their blend samples are prepared by solution cast technique from room temperature, and the majority of the solvent was slowly evaporated at 30°C. To removal the residual solvent, all the films obtained were further desiccated in a vacuum at 50°C for 1 week. Prepared polymer electrolytes have been studied using FTIR, XRD and AC impedance measurements respectively. In the previous study the maximum ionic conductivity was found 8.12x10⁻³ Scm⁻¹ [21] for PVA - PVP blend with ammonium acetate polymer electrolyte.

II. EXPERIMENTAL TECHNIQUE

Films of pure PVP and films of pure PVP with PVC in the molar ratio 90:10, 80:20, 70:30, 60:40 have been prepared by solution cast technique using DMF as the solvent initially. The conductivity has been determined for the above films. From the above compositions, 70:30 ratio has better conductivity compared to other ratios. Hence 70%PVP: 30%PVC have been chosen for the present study.

Films of pure PVP, 70%PVP: 30%PVC and films of 70%PVP: 30%PVC with Ammonium acetate in the molar ratios 0.1, 0.2, 0.3 have been prepared by solution cast technique using DMF as a solvent. The solutions of PVP, PVC and with ammonium acetate were stirred well 10 to 12 hours to obtain a homogenous solution and then cast on to polypropylene dishes and evaporated slowly at room temperature.

III. RESULT AND DISCUSSION

A. XRD Analysis

Figure (i) show the XRD pattern of pure PVP, 70%PVP: 30%PVC and 70%PVP: 30%PVC doped with NH₄COONH₄ having different mole ratios. It has been observed from fig (i) that the broad peaks between 12-15° and 19-24° can be associated with the amorphous nature of pure PVP [14-19]. The relative intensity of the broad peaks decreased when adding 30%PVC and further decreased with increase of CH₃COONH₄ concentration. The results observed from the XRD measurements recommend that the crystalline of PVP/PVC has been demolished by the addition of ammonium acetate. Thus the X-ray diffraction examines clearly exposes the complex formation between the dissociated salt and the polymer matrices. The high amorphous nature was observed for the composition of 70%PVP: 30%PVC: 0.3Mwt% of CH₃COONH₄.

B. FTIR Analysis

FTIR spectroscopy has been used to identify the functional groups. Figure (2) shows FTIR of Pure PVP, 70PVP:30PVC and 70PVP:30PVC blend with different molar weight percentage Ammonium acetate (CH₃COONH₄). From the figure the observed band around 640 cm⁻¹ has been attributed to C-H bend of pure PVP, this peak shifted to 543 cm⁻¹, 592 cm⁻¹, 562 cm⁻¹, 536 cm⁻¹ for 70PVP:30PVC , 70PVP:30PVC:0.1 Mwt%, 70PVP:30PVC:0.2 Mwt%, 70PVP:30PVC:0.3 Mwt% of CH₃COONH₄ respectively. C-O stretching peak observed at 1221.58 cm⁻¹ for pure PVP and shifted to 1217.49 cm⁻¹ for 70PVP:30PVC. This peak was not found in salt concentration with 70PVP:30PVC. The observed band at 1641.28 cm⁻¹ has been attributed for pure PVP. The above peak was shifted to 1690cm⁻¹ and 1638.82 cm⁻¹ for 70PVP:30PVC, 70PVP:30PVC:0.1 Mwt% of CH₃COONH₄.
The band at 2026.78 cm\(^{-1}\) has been attributed to free SCN for pure PVP. This peak shift at 2058.22 cm\(^{-1}\) was due to fee SCN -1 ion aggregates for 70PVP:30PVC:0.3 Mwt% of CH\(_3\)COONH\(_4\). This peak shifted to 2065.94 cm\(^{-1}\) for 70PVP:30PVC.

N-H stretching peak has been observed at 3397.07 cm\(^{-1}\) for pure PVP and it was shifted to 3297.07 cm\(^{-1}\), 3362.27 cm\(^{-1}\), 3362.27 cm\(^{-1}\), 3378.39 cm\(^{-1}\), 3390.53 cm\(^{-1}\) for adding 30%PVC and increased concentration of CH\(_3\)COONH\(_4\).

C. DSC Analysis

The Figure (3) showed DSC graph of pure PVP, PVP: PVC and PVP: PVC: CH\(_3\)COONH\(_4\).

The glass transition temperature of PVP was 160°C [17] and PVC was 81°C. The Glass transition temperature (Tg) values of the PVP-PVC blend was 200°C. The addition of CH\(_3\)COONH\(_4\) to the PVP: PVC blend decreases with glass transition temperature of polymer blend from 200°C to 55°C, 53°C, 51°C for 0.1 MWT%, 0.2 MWT%, 0.3 MWT% of CH\(_3\)COONH\(_4\) respectively. The Tg decreased with increasing CH\(_3\)COONH\(_4\) concentration. This was due to chain flexibility which reflected by Tg. This decrease in Tg attributed to the plasticizing effect [17, 20]. The low glass transition temperature causes the higher segmental motion of the Polymer electrolyte. Addition of ammonium acetate concentration, the observed Tg values decreased drastically. This may due to the softening of the polymer blend by the addition of salt, which is beneficial for easy proton transport [21].

IV. CONDUCTIVITY STUDIES

The variation in the frequency –dependent AC conductivity spectra for the polymer blend electrolyte Pure PVP, 70%PVP: 30%PVC and 70%PVP: 30%PVC: X CH\(_3\)COONH\(_4\) (X=0.1, 0.2, 0.3 Mwt %) at room temperature as shown in the figure (4). The plateau region was not observed for pure PVP and pure blend. From figure, salt doped composition shows three regions– Low frequency dispersion region, frequency independent plateau region, and the high-frequency dispersion region. Low-frequency dispersion is due to electrode-electrolyte or space charge polarization effects [22]. In the low frequency region, extra charge accumulation takes place at the electrode –electrolyte interface, most important to a decrease in the number of mobile ions and conductivity. The frequency-independent plateau region is associated with the DC conductivity of the polymer blend electrolytes. This conductivity value has been allotted to the bulk conductivity of the sample. The \(\sigma_0\) value was calculated and tabulated in table (3). In the high-frequency region, the conductivity increases with the frequency. The mobility of charge carriers is higher in the high-frequency region [23]. As the concentration increases, the high frequency dispersion is shifted towards the higher-frequency side, and the conductivity was found to be increased. The pure PVP exhibit higher conductivity than 70%PVP: 30%PVC blend electrolytes. This observed decrease in conductivity by the addition of PVC is due to increase in crystalline nature. A maximum conductivity 9.14x10\(^{-5}\) S cm\(^{-1}\) was found for the composition of 70%PVP: 30%PVC: 0.3 Mwt% of CH\(_3\)COONH\(_4\).

V. DIELECTRIC ANALYSIS

Dielectric loss is a direct measure of energy dissipated and generally includes the contribution from the Ionic transport as well as from the polarization of a charge or a dipole [24]. The dielectric behavior of any polymeric system may be described by the real and imaginary parts of the complex permittivity \(\varepsilon^*\) which is defined by the relation

\[ \varepsilon^* = \varepsilon'(\omega) - j\varepsilon''(\omega) = 1 / j\omega C_0 Z^* \]

Where real \(\varepsilon'(\omega)\) and imaginary \(\varepsilon''(\omega)\) components are the storage and loss of energy in each cycle of the applied electric field. The log \(\omega\) vs. \(\varepsilon'\) and \(\varepsilon''\) plots for pure PVP, 70%PVP: 30%PVC, 0.1, 0.2, and 0.3 Mwt% CH\(_3\)COONH\(_4\) doped with 70% PVC: 30%PVC are shown in Figure (5 & 6). The dielectric constant is very large at lower frequencies due to free charge motion within the material [25]. High values have been explained by the presence of space charge effects, contributed by the accumulation of charge carriers near the electrodes [26]. At higher frequencies, \(\varepsilon'(\omega)\) was found to be relatively constant with frequency. The dielectric loss is larger at low frequency. The dielectric loss occurs as a result of collisions among the mobile charge carriers.

VI. CONCENTRATION-DEPENDENT CONDUCTIVITY:

At room temperature, ionic conductivity of 70PVP:30PVC with different molar weight percentage of the CH\(_3\)COONH\(_4\) polymer electrolyte is shown in Figure (7). It has been found that the conductivity increased with increase in CH\(_3\)COONH\(_4\) 0.1MWT%, 0.2MWT% and 0.3MWT%. This is due to the increase in the mobile charge carriers [19] and also to the increase in the amorphous nature of the polymer electrolyte, which reduces the energy barrier, thereby facilitating the fast ion transport [27]. However, decreasing conductivity is observed in the composition of 70PVP:30PVC.

CONCLUSION

Proton conducting polymer electrolytes based on poly (N-vinyl pyrrolidone) (PVP), Polyvinyl chloride (PVC) and CH\(_3\)COONH\(_4\) with different composition have been prepared by solution cast technique. The amorphous nature of polymer electrolytes has been confirmed from the XRD studies. The complex formation between the polymer and the salt has been confirmed by FTIR analysis. The DSC studies show that the glass transition temperature (Tg) decreases with the addition of salt. The highest ionic conductivity has been found to be 9.14x10\(^{-5}\) S cm\(^{-1}\) for the composition of 70PVP:30PVC:0.3Mwt% of CH\(_3\)COONH\(_4\).

A. Order Of Figures And Tables

Figure 1: XRD patterns of Pure PVP & PVP: PVC doped with CH\(_3\)COONH\(_4\)
Figure 2: FTIR Spectrum for PVP & PVP: PVC doped CH$_3$COONH$_4$

Figure 3: DSC thermo grams for PVP&PVP: PVC doped with CH$_3$COONH$_4$

Figure 4: Conductance Spectra PVP&PVP: PVC doped with CH$_3$COONH$_4$

Figure 5: Variation of $\varepsilon'$ vs log $\omega$

Figure 6: Variation of $\varepsilon''$ vs log $\omega$

Figure 7: Conductivity and concentration of Ammonium acetate at room temperature

Table 1: Peak position and their assignment for PVP-PVC blend with CH$_3$COONH$_4$

<table>
<thead>
<tr>
<th>S.No</th>
<th>Wave number cm$^{-1}$ Pure PVP</th>
<th>70%PVP:30PV C</th>
<th>70%PVP:30PVC:Mwt% of CH$_3$COONH$_4$</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>1</td>
<td>640</td>
<td>543</td>
<td>592</td>
<td>562</td>
</tr>
<tr>
<td>2</td>
<td>1221.58</td>
<td>1295</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>1641.28</td>
<td>1638</td>
<td>1690</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>2026.78</td>
<td>2065.94</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>3397.22</td>
<td>3297.07</td>
<td>3362.27</td>
<td>3378.39</td>
</tr>
</tbody>
</table>
Table 2: The glass transition temperature for PVP & PVC: 
PVC doped with CH₃COONH₄

<table>
<thead>
<tr>
<th>Composition</th>
<th>Glass Transition Temperature (Tg) °C</th>
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<tbody>
<tr>
<td>Pure PVP</td>
<td>160°C</td>
</tr>
<tr>
<td>70PVP:30PVC</td>
<td>200°C</td>
</tr>
<tr>
<td>70PVP:30PVC:0.1</td>
<td>55°C</td>
</tr>
<tr>
<td>70PVP:30PVC:0.2</td>
<td>53°C</td>
</tr>
<tr>
<td>70PVP:30PVC:0.3</td>
<td>51°C</td>
</tr>
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Table 3: Conductivity values of the polymer complexes at room temperature.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Ionic Conductivity (σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PVP</td>
<td>3.7245x10⁻⁸Scm⁻¹</td>
</tr>
<tr>
<td>70PVP:30PVC</td>
<td>8.4657x10⁻⁸Scm⁻¹</td>
</tr>
<tr>
<td>70PVP:30PVC:0.1Mwt%NH₄SCN</td>
<td>4.56x10⁻⁸Scm⁻¹</td>
</tr>
<tr>
<td>70PVP:30PVC:0.2Mwt%NH₄SCN</td>
<td>6.02x10⁻⁸Scm⁻¹</td>
</tr>
<tr>
<td>70PVP:30PVC:0.3Mwt%NH₄SCN</td>
<td>9.14x10⁻⁸Scm⁻¹</td>
</tr>
</tbody>
</table>

References