Research Article

Structural, Thermal, and Electrical Properties of PVA-Sodium Salicylate Solid Composite Polymer Electrolyte

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Structural, thermal, and electrical properties of solid composite polymer electrolytes based on poly (vinyl alcohol) complexed with sodium salicylate were studied. The polymer electrolytes at different weight percent ratios were prepared by solution casting technique. The changes in the structures of the electrolytes were characterized by XRD, which revealed the amorphous domains of the polymer which increased with increase of sodium salicylate concentration. The complexion of the polymer electrolytes were confirmed by FTIR studies. Thermal gravimetric analysis (TGA) was used to study the thermal stability of the polymer below 523 K. The decomposition decreases with increasing sodium salicylate concentration. The conductivity and dielectric properties were measured using an impedance analyzer in frequency range of 20 Hz to 1 MHz and narrow temperature range of 303 to 343 K. The conductivity increased with increase of sodium salicylate concentration and temperature. The dielectric constant and dielectric loss increased with the increase in temperature and decreased with the increase in sodium salicylate concentration.

1. Introduction

Solid composite polymer electrolytes (SCPEs) have been extensively studied in the recent years due to their importance and their potential applications in electrochemical devices such as batteries, sensors, super capacitors, and fuel cells [1–4]. Most SCPEs consist of a host polymer to provide high dielectric strength and good mechanical stability and an inorganic salt that supplies ionic carriers to cause electrical conductivity [4, 5]. They have unique properties which include film forming property, flexibility, light weight, fairly easy processability, elasticity, and high ionic conductivity. Examples of polymer electrolyte systems intensively studied were poly (ethylene oxide) (PEO) [6], poly (vinyl chloride) (PVC) [2], and poly (vinyl alcohol) (PVA) [2, 7].

One of such SCPE was a composite of PVA and Sodium Salicylate (SS), which is the subject of the present study. Among the polymers, PVA was especially attractive and was chosen as a polymer host since it is stable both thermally and environmentally, nontoxic, water soluble, and has good film-forming capacity [5]. Literature survey revealed that the ion transport studies of PVA doped with sodium salt polymer composite were scarce. In the present study, the structural, vibrational, thermal stability, and electrical studies of PVA polymer complexed with SS at different weight percent ratios were carried out by XRD, FTIR, TGA, and AC impedance measurements, respectively.

2. Materials and Methods

The glassy transparent host PVA polymer (Mw = 88,000 g/mol) at 88% hydrolyzed and sodium salicylate salt (HOC₆H₄COONa) were purchased (product of Acros, US) and used directly without further purification. The PVA was dissolved in deionized water at 90°C before adding SS salt which acts as an ionic dopant for the SCPEs. The SCPE films were prepared by solvent casting technique on the glass plates. Thick films of SCPEs between 80 to 220 μm of PVA-SS composite were prepared at different weight percent PVA-SS ratios (90:0, 80:20, 70:30, 60:40, and 50:50).

The XRD analysis was carried out using Phillips X’pert X-ray diffractometer with Cu-Kα radiation source at ambient temperature. The input voltage and current were 40 kV and
30 mA, respectively. The XRD patterns were recorded for 2θ measurements from 5 to 60 degrees and the scanning times took approximately about 20 minutes. FTIR measurements were performed on a Perkin Elmer Spectrum 100 FTIR-instrument with a resolution of 2 cm\(^{-1}\). The measurements were taken over a wave number range of 280 to 4000 cm\(^{-1}\). Thermogravimetric analysis (TGA) was performed using Perkin Elmer TGA Instrument. Sample of about 2 to 12 mg was placed in the specimen holder and initial mass was recorded and heating rate was set at 10 °C/min and the measurements were carried out in ambient atmosphere air from 35 to 500 °C.

A series of conductivity and dielectric measurements on the SCPE samples of different weight percent PVA:SS ratios were carried out over a frequency range of 100 Hz to 1 MHz from the ambient temperature to 343 K using computer-controlled LCR meter (HP4284 A). Each film sample was sandwiched between two circular metal electrodes with the surface area of 4.90 × 10\(^{-4}\) m\(^2\).

3. Results and Discussion

3.1. X-Ray Diffraction Analysis. Figure 1 presented XRD analysis for pure PVA and PVA-sodium salicylate composite with different compositions of sodium salicylate. It was found that the XRD pattern of pure PVA showed a broad peak around 2θ corresponding to semicrystalline nature of pure PVA [6, 8]. In the present study, a decrease in intensity and an increase in broadness of the diffraction peak of pure PVA were observed with increase of sodium salicylate concentration. This result could be due to the disruption of the PVA crystallinity which revealed the amorphous nature of the PVA-sodium salicylate polymer composites. This amorphous nature results in greater ionic diffusivity with high conductivity for other systems [8, 9]. A previous study reported that the intensity of XRD pattern decreases with increase of amorphous nature by addition of dopant [10]. This has established a correlation between the height of the peak and the degree of crystallinity. No new peaks corresponding to sodium salicylate were observed which indicate a complete dissolution of salt in the PVA polymer matrix.

3.2. FTIR Analysis. A FTIR spectroscopy was used to identify the compound and investigate the complexation and interactions in the polymer matrices. The FTIR spectra of pure PVA and PVA doped with 20, 40, and 50 wt% of SS are shown in Figure 2. After comparing the spectra of pure PVA with PVA-SS composites, several changes in the spectral features were observed and tabulated in Table 1. The peak centered at 3294 cm\(^{-1}\) assigned to the stretching vibration of hydroxyl groups (O–H) of pure PVA [6, 8] was shifted to 3309, 3338, and 3399 cm\(^{-1}\), respectively, in 20, 40, and 50 wt% SS in PVA-SS electrolyte system, which indicates the specific interaction in the polymer systems. In addition to this, the C–H stretching of CH\(_2\) which showed absorption at 2934 cm\(^{-1}\) in pure PVA [6, 8, 9] was shifted to 2930, 2935, and 3066 cm\(^{-1}\) in 20, 40, and 50 wt% SS, respectively. The peak at 1723 cm\(^{-1}\) corresponding to C=O stretching of PVA [4, 8, 9] was shifted to lower wave numbers in the 10, 20, and 30 wt% SS but it disappeared in 40 wt% SS system. The peak at 1427 cm\(^{-1}\) corresponds to C–H bending of pure PVA [6, 8]. This peak is shifted to 1451, 1454, and 1461 cm\(^{-1}\), respectively, in 20, 40, and 50 wt% SS systems. The vibration of CH\(_2\) group was found at 1372 cm\(^{-1}\) corresponding to C–H wagging in pure PVA [6] and it was shifted to higher wave numbers in the complexed systems. Also, the peak at 1329 cm\(^{-1}\) that corresponds to C–H wagging of pure PVA is absent in PVA-SS complexed systems. The C–C stretching vibration of PVA [8] appearing at 1249 cm\(^{-1}\) was shifted to lower wave numbers in the 10, 20, 30, and 50 wt% SS, respectively, in 20, 40, and 50 wt% SS systems. The vibration peak at 1084 cm\(^{-1}\) in pure PVA [6, 8, 9] was shifted to 1085 cm\(^{-1}\) in 20 wt% SS electrolyte systems. For 40 wt% SS system, C–O stretching occurred at 1080 cm\(^{-1}\). This clearly showed that the interaction between the SS dopant salt and PVA in the polymer composite does not only arise from O–H group but also from C–O group of pure PVA. The vibration peak appearing at 836 cm\(^{-1}\) assigned to C–H rocking mode of PVA [6, 9] was shifted to 848, 851, and 857 cm\(^{-1}\), respectively, in 20, 40, and 50 wt% SS complexed electrolyte systems. The shift of this wave number may be due to the interaction of proton in the salt with the carbonyl oxygen of PVA [2]. Also, new peaks at between 1425 cm\(^{-1}\) and 1628 cm\(^{-1}\) which were found in the polymer complex systems of 10, 20, 30, and 40 wt% SS could be attributed to the carboxylate moiety (COO\(^{-}\)) of sodium salicylate [11]. Hence, from the FTIR analysis, the complex formation of PVA polymer, and SS salt was confirmed.

3.3. TGA Analysis. The thermal stability of the solid composite polymer electrolytes is an important parameter to guarantee acceptable performance in electrochemical devices. Figure 3 shows TGA and differential gravimetric analysis (DTG) thermographs of PVA and PVA-SS composite polymer electrolytes with various SS compositions at a heating rate of 10°C/min and in the temperature range of room temperature to 500°C. A derivative weight loss
Table 1: FTIR band assignments of PVA-SS solid composite polymer electrolytes. The peaks assigned to PVA shifted to higher wavenumbers by increasing SS concentration.

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Pure PVA</th>
<th>PVA : SS 90 : 10</th>
<th>PVA : SS 80 : 20</th>
<th>PVA : SS 70 : 30</th>
<th>PVA : SS 60 : 40</th>
<th>PVA : SS 50 : 50</th>
<th>Band assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3294</td>
<td>3298</td>
<td>3309</td>
<td>3338</td>
<td>3399</td>
<td>3402</td>
<td>O–H groups</td>
<td></td>
</tr>
<tr>
<td>2934</td>
<td>2932</td>
<td>2930</td>
<td>2935</td>
<td>3066</td>
<td>3066</td>
<td>C–H stretching</td>
<td></td>
</tr>
<tr>
<td>1723</td>
<td>1722</td>
<td>1723</td>
<td>1721</td>
<td>—</td>
<td>—</td>
<td>C = O stretching</td>
<td></td>
</tr>
<tr>
<td>1427</td>
<td>1425</td>
<td>1451</td>
<td>1454</td>
<td>1461</td>
<td>1467</td>
<td>C–H bending</td>
<td></td>
</tr>
<tr>
<td>1372</td>
<td>1378</td>
<td>1379</td>
<td>1381</td>
<td>1373</td>
<td>1372</td>
<td>C–H wagging</td>
<td></td>
</tr>
<tr>
<td>1249</td>
<td>1253</td>
<td>1252</td>
<td>1254</td>
<td>1287</td>
<td>1286</td>
<td>C–C stretching</td>
<td></td>
</tr>
<tr>
<td>1084</td>
<td>1085</td>
<td>1085</td>
<td>1085</td>
<td>1080</td>
<td>1140</td>
<td>C–O stretching</td>
<td></td>
</tr>
<tr>
<td>944</td>
<td>944</td>
<td>946</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>C–H stretching</td>
<td></td>
</tr>
<tr>
<td>836</td>
<td>843</td>
<td>848</td>
<td>851</td>
<td>857</td>
<td>856</td>
<td>C–H rocking</td>
<td></td>
</tr>
</tbody>
</table>

curve can be used to tell the point at which weight loss is most apparent. TGA and DTG curves of PVA and PVA-SS composite polymer electrolytes revealed three main weight loss regions. The initial weight loss for pure PVA occurred at a temperature region of 36 to 145°C with a sharp peak at 81°C in the DTG curve ($T_{\text{max,1}} = 81^\circ\text{C}$), due to the evaporation of physically weak and chemically strong bound H$_2$O from the polymer matrix [12–14]. The weight loss of this membrane was about 5.8 wt%. It was also observed that the major weight losses have occurred in the range of 178 to 368°C ($T_{\text{max,2}} = 321^\circ\text{C}$). This is due to the degradation of side chain (O–H) of PVA and the weight loss corresponding to this stage was about 45 wt%. Finally, the peak of the third stage temperature range between 370 and 473°C ($T_{\text{max,3}} = 413^\circ\text{C}$). This may correspond to the cleavage of C–C backbone of PVA polymer or commonly called carbonation [1, 13, 14], with a weight loss of 30 wt%.
The PVA-sodium salicylate solid composite polymer electrolytes of various compositions of sodium salicylate (10, 20, and 30 wt%) also exhibited three major processes of weight losses for all the prepared samples shown in Figures 3(b)–3(d). The first region at a temperature range of 35 to 180°C observed was associated with the loss of H₂O molecules. The weight loss was about 7.1 to 10.3 wt%. The major weight losses were observed in the range of 177 to 338°C which may be due to the structural decomposition of the polymer systems and their complexes [12]. In this project, the decomposition of PVA and sodium salicylate may occur at this stage. The weight loss which corresponds
to this stage was about 49–59 wt%. The peak of the third stage at 350–500°C was due to the cleavage of the backbone of PVA polymer and the weight loss was about 5–15 wt%. The decompositions of the samples as well as percentage weight loss were given in Table 1. It should be mentioned that the peaks of the first decomposition step were less intense and shifted towards higher temperature with increasing SS compositions, while the peak temperature of the second decomposition step decreases with increasing SS concentrations. Table 2 showed the value of weight loss was irregular for the first and second decomposition with increasing SS concentrations. However, the value of weight loss for the third decomposition step and the total weight loss decreases with increasing SS concentrations. Therefore, it could be concluded that the thermal stability of polymer electrolyte system improved due to the addition of SS salt.

3.4. Electrical Conductivity. Figures 4(a) and 4(b) show the conductance spectra for PVA-sodium salicylate composite electrolytes of various concentrations of sodium salicylate at 303 K and for the PVA-50 wt% sodium salicylate sample at various temperatures up to 343 K. The conductance spectrum consists of two distinct regions: the low frequency dispersion region, followed by the frequency independent plateau region. Low frequency dispersion was due to electrode-electrolyte or space charge polarization effects [1] and the frequency independent plateau region was connected with the DC conductivity of solid composite polymer electrolytes. In the low frequency region, more charge accumulation occurred at the electrode and electrolyte interface, leading to a decrease in the number of mobile ions and conductivity. The mobility of charge carriers was higher in the high-frequency region; hence the conductivity increases with frequency as reported earlier [9, 15]. In Figure 4(a), the results showed that the conductivity increases with an increase in sodium salicylate concentration throughout the measured frequency region due to the enhancement of the mobility of charge ions and the larger number of charge carriers.
Table 2: TGA and DTG data for the solid composite polymer electrolytes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Start</th>
<th>End</th>
<th>$T_{max}^{a}$</th>
<th>Partial</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PVA</td>
<td>36.3</td>
<td>143.7</td>
<td>80.9</td>
<td>5.8</td>
<td>86.4</td>
</tr>
<tr>
<td>PVA: SS 90:10</td>
<td>36.6</td>
<td>164.7</td>
<td>87.8</td>
<td>9.8</td>
<td>83.5</td>
</tr>
<tr>
<td>PVA: SS 80:20</td>
<td>36.5</td>
<td>161.4</td>
<td>95.9</td>
<td>10.3</td>
<td>81.7</td>
</tr>
<tr>
<td>PVA: SS 70:30</td>
<td>35.5</td>
<td>155.2</td>
<td>83.1</td>
<td>10.1</td>
<td>75.4</td>
</tr>
<tr>
<td>PVA: SS 60:40</td>
<td>37.6</td>
<td>170.1</td>
<td>90.9</td>
<td>9.7</td>
<td>76.7</td>
</tr>
<tr>
<td>PVA: SS 50:50</td>
<td>36.1</td>
<td>180.4</td>
<td>131.4</td>
<td>7.2</td>
<td>72.1</td>
</tr>
</tbody>
</table>

$^a$Peak temperature of DTG.

Figure 6: DC conductivity of PVA-sodium salicylate solid composite polymer electrolyte at ambient temperature for different SS concentrations.

Figure 7: The relationship between $\ln \sigma_{dc}$ and $1000/T$ of PVA-sodium salicylate solid composite polymer electrolyte for different SS concentrations.

can be connected to the bulk conductivity of the polymer electrolytes [9] and the low frequency spike was due to the blocking electrode [7]. In Figure 5(a) it was found that with increase in concentration of sodium salicylate, the semicircle disappeared suggesting that only the resistive component prevailed [8]. However, the semicircle disappeared at high frequencies in the system at 50 wt% sodium salicylate as was shown in Figure 5(b). This is caused by the increase in the number of charge carriers due to dopant salt composition which reduces the bulk resistance and increase the electrical conductivity.
3.5. Dielectric Properties. Figure 8(a) shows the variation of $\varepsilon'$ with frequency for different temperatures from 303 K to 353 K for pure PVA and PVA-sodium salicylate composite electrolytes. It can be seen that the $\varepsilon'$ values decrease as frequency increases from 1 Hz to 1 MHz. This could be explained due to the dipoles which were not able to follow the variation field at higher frequencies [8]. The $\varepsilon'$ increases towards low frequencies may be due to dielectric orientation polarization [16] and space charge polarization [7].

In Figure 8(a) it can be seen that $\varepsilon'$ increases with the increase of temperature for PVA and PVA-sodium salicylate polymer electrolyte system. For polar and nonpolar material, the variation of $\varepsilon'$ with temperature was different. In general, polar polymer has high $\varepsilon'$, dependent on temperature. But in the case of nonpolar polymer, $\varepsilon'$ is independent of temperature [8]. The $\varepsilon'$ increases with increase in temperature of polar material due to facilitation in orientation of dipoles [17] and increasing mobility of charge carriers which tend to move freely as the temperature increase.

The same trend can be observed for the imaginary part of dielectric permittivity of the polymer system. Figure 8(b) shows the variation of dielectric loss $\varepsilon''$ with frequency for all samples at different temperatures. The figure shows that the $\varepsilon''$ decreases as frequency increases. It can also be seen that as temperature increases, the value of $\varepsilon''$ increases. This is due to the contribution of mobility of free ions which increase with their kinetic energy and thermal energy.

Generally, the dielectric constant and dielectric loss shows a considerable increase when the temperature is increased may be due to polarization effect. The electron exchange interaction results in a local displacement of the electron in the direction of an electric field, which determines the polarization of the PVA-Sodium salicylate. The space charge polarization is governed by the numbers of space charge carriers with the rise in temperature the numbers of carriers increase resulting in an enhanced builtup space charge polarization and hence increase in dielectric properties. In other words, increasing the dielectric loss by increasing temperature is owing to the hopping of the charge...
carriers in the localized state and also due to the excitation of charge carriers to the states in the conduction band.

4. Conclusion

The solid composite polymer electrolyte of PVA-sodium salicylate was prepared by solution casting technique. The structure revealed the amorphous domains of the polymer which increased with increase of sodium salicylate concentration. The complexation and thermal stability were examined by FTIR and TGA, respectively. The conductivity and dielectric values were determined using ac impedance method. The conductivity increased with increase of sodium salicylate concentration and temperature. The dielectric constant and dielectric loss increased with the increase in temperature and decreased with the increase in sodium salicylate concentration. The PVA-50 wt% sodium salicylate possesses highest conductivity, low activation energy, high amorphous nature and high thermal stability, and is suitable for application in electrochemical devices.

References


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