Microstructural and Electrical Properties of PVP-CH₃COONa Polymer Films

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Abstract
PVP based polymer electrolyte films are prepared by dissolving sodium acetate with different wt% compositions using solution cast technique. The structural surface and its roughness of the samples were analyzed by SEM studies for the resolution of 10μm. Optical absorption and its energy bandgap values were studied. The lowest energy bandgap value has been found for the composition 80PVP: 20CH₃COONa at 3.47 eV. DC ionic conductivity was done on lab made conductivity four probe method. Maximum ionic conductivity has been observed for the composition 80PVP:20CH₃COOK and it is found to be 2.31×10^{-5} S/cm at 373 K.

Keywords: Solid polymer electrolyte, Solution cast technique, SEM, Optical absorption and DC ionic conductivity

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Introduction

In the present scenario, an attractive attention has been made towards solid polymer electrolytes due to their vast advantages and also their low production cost, excellent structural, thermal and electrochemical properties. Solid polymer films have taken a revolutionary development in the fields of batteries, fuel cells and humidity sensors [1]. Solid polymer films are prepared by doping inorganic salt in the host polymer. The mechanism of solid polymer electrolytes and their advantages were reported by Wright and Armand in 1970s. Due to the advantages of solid polymer electrolytes, they have taken a new development role in the application field of energy storage devices. The physical and electrochemical studies of polymer electrolytes bring a new revolution in the fields of energy storage applications [2]. The work on these polymer electrolytes, has received great interest which leads a new way to the researches for the development of applications of new energy devices [3, 4].

Polyvinyl pyrrolidone (PVP) was chosen because of its wide properties, besides it possesses high performance in electrochemical stability [5, 6]. Most of the researchers have focused on PVP based solid polymer electrolytes because it shows good electrochemical performance of the cell such that it can be used in many potential applications [7]. It is also used as an electrochromic display material in microelectronics as well as in pharmaceuticals as a binary agent [8, 9]. Inorganic salt like potassium acetate is used as dopant material to the host polymer in order to enhance the ionic conductivity. Rao et al. presented their results in their earlier studies [10-36]. In the present investigation, solid polymer films were prepared with different wt% composition ratios of PVP-CH₃COONa in order to improve the ionic conductivity of the composite films.

Experimental

All the chemicals such as PVP polymer with an average molecular weight (M.W: 36,000), sodium acetate (CH₃COONa) 98% were used for the preparation of solid polymer films. All the chemicals used in the present investigation were purchased from Sigma Aldrich, India. Double distilled water was used as a common solvent in this process. All the chemicals were dried under vacuum oven at 40 °C for 1 hour. Later the precursor materials of PVP polymer and sodium acetate were weighed properly in different wt% concentrations PVP: x wt% CH₃COONa (where x = 5, 10, 15 and 20). This homogeneous mixture was added to 20 ml double distilled water and kept continuous stirring for 24 Hrs. Later it was poured into polypropylene dishes and allowed to evaporate the solution slowly in a hot air oven to remove the moisture and solvent solution. Finally the obtained samples were placed in vacuum desiccator.

Results and Discussion
SEM Analysis

SEM micrographs of [PVP-CH₃COONa]: x% were shown in **Figure 1(a-e)**. SEM image of pure PVP has been shown in Figure 1(a) and the remaining images represent the different compositions of [PVP-CH₃COONa]: x%. The images revealed the morphological features of the surface with little agglomerations are shown in Figure 1(b), (c) and (d). But at higher wt% composition, smooth surface on the films has been observed for the composition (80:20) wt% which was shown in Figure 1(e). This might be due to the complete solubility of CH₃COONa salt in the PVP matrix which in turns the amorphous nature [37-39]. This reveals that the complete dispersion of salt in PVP polymer matrix system.

UV-Visible Spectroscopic Studies

UV-Vis spectroscopy is an important tool which plays a key role to measure the optical bandgap in an energy level. The excitations of atoms in energy levels have been measured by the optical absorption spectroscopy [40]. In an energy level when a photon is absorbed at certain wavelength it undergoes the transition from lower to higher energy level called absorption process [41, 42]. UV-visible spectroscopy of the prepared solid polymer films were analyzed in the wavelength ranging from 200 to 800 nm is shown in **Figure 2**. An excitation peak has been identified at 386.45 nm in the wavelength region. This decrement in the wavelength may be due to the dopant of inorganic salt in the host polymer. The optical bandgap of absorption coefficient (α) is calculated by the following equitation,

$$I = I_o \exp(-\alpha x) \qquad (1)$$

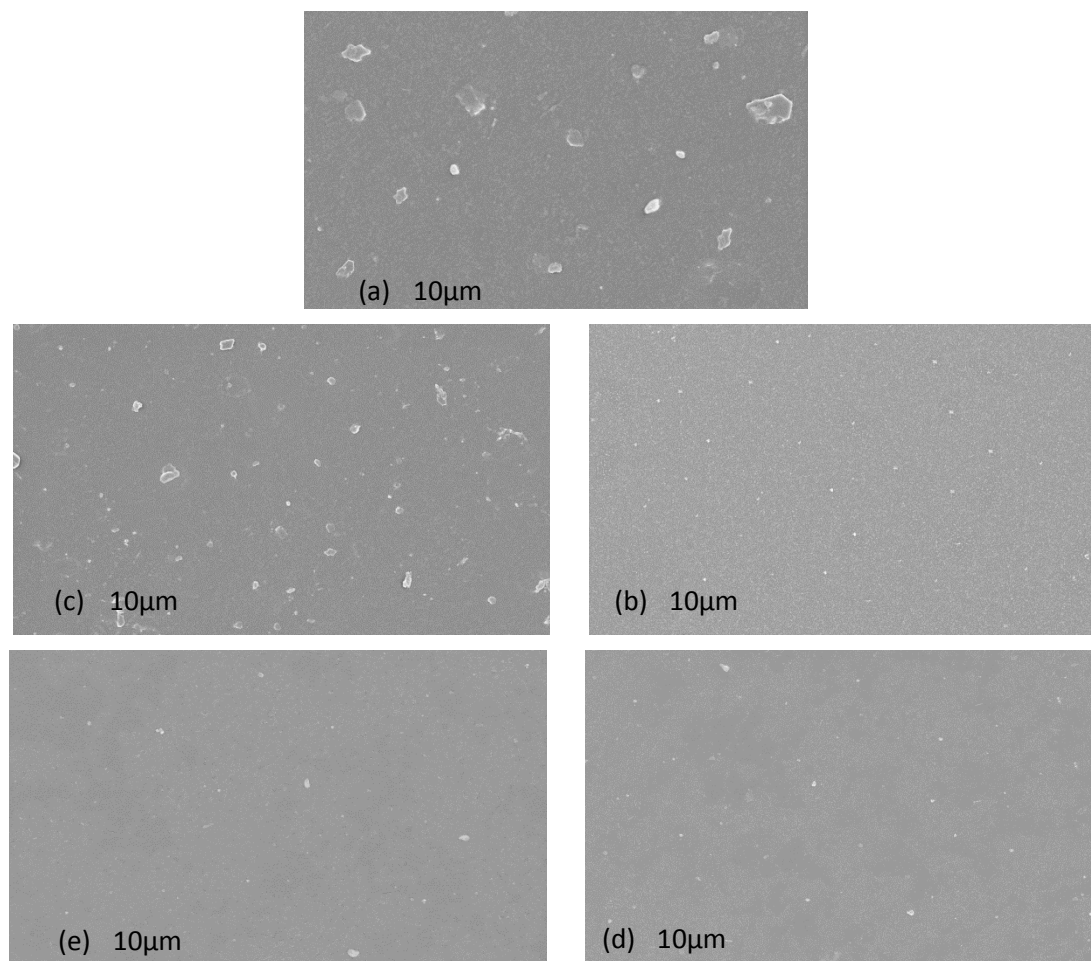where 'α' is the absorbance and 'x' is the thickness of the film.

Figure 1 (a), (b), (c), (d) and (e): SEM images for solid polymer electrolyte films
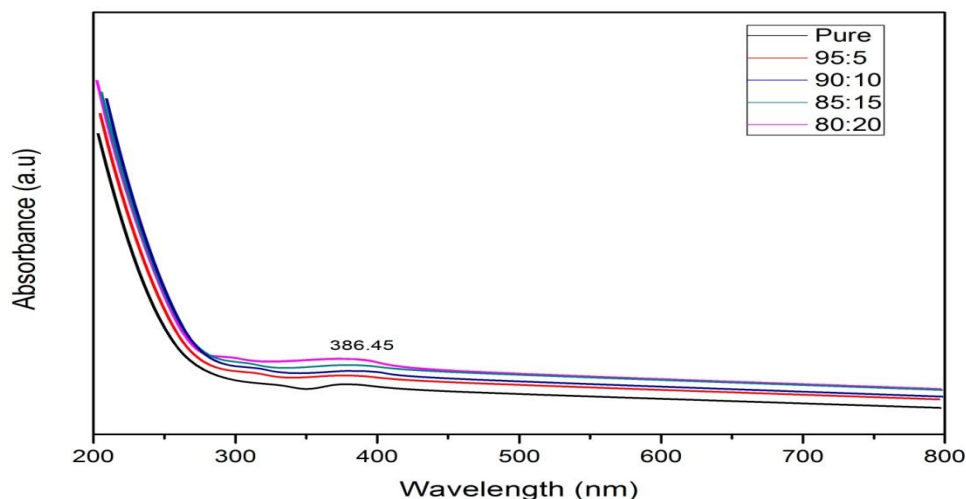
Figure 2 Optical absorption spectra of solid polymer electrolyte films

By plotting a graph between α and hυ, the absorption coefficient values can be calculated and the values are seen at 3.8, 3.71, 3.69, 3.65 and 3.61 eV.

From the obtained values, it is clear that the dissolution of salt is completely attained in polymer chains in a host lattice. Thus the activation energy is decreased with increase of ionic conductivity, on doping with CH_3COONa salt to the polymer. The direct and indirect bandgap values shifted to lower energies.

Direct bandgap energy values are calculated by the following relation,

$$\alpha h\upsilon = C \, (h\upsilon - E_g)^{1/2} \tag{2}$$

where E_g is the energy bandgap, C is a constant value.

Indirect bandgap values are calculated from the graph by plotting $(\alpha h\upsilon)^{1/2}$ vs hυ as shown in **Figure 3** and the direct bandgap values are found to be at 3.65, 3.61, 3.55, 3.49 and 3.47 eV.

Indirect energy bandgap values can be calculated by the following relation,

$$\alpha h\upsilon = A \, (h\upsilon - E_g - E_p)^2 + B \, (h\upsilon - E_g - E_p)^2 \tag{3}$$

where A and B are constants. Indirect bandgap values are at 3.68, 3.63, 3.58, 3.55 and 3.51 respectively.
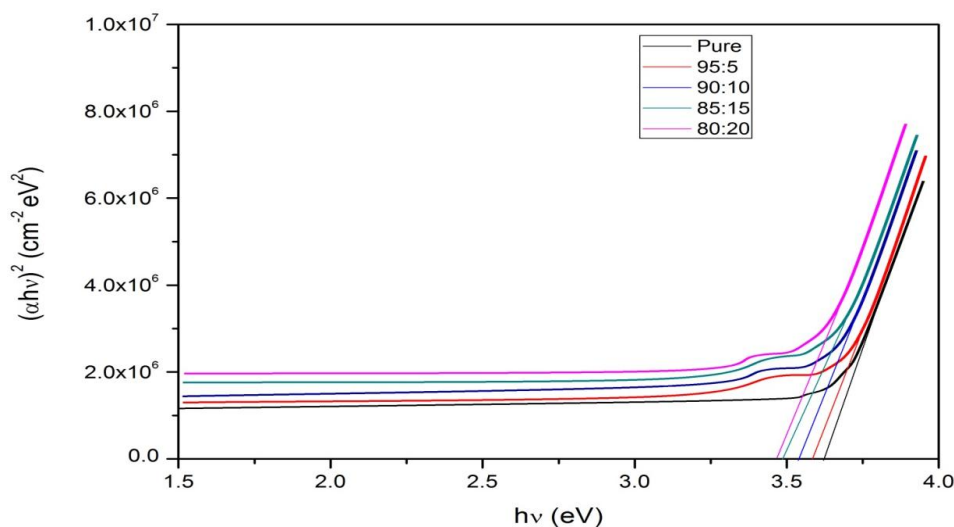

Figure 3 $(\alpha h\upsilon)^2$ vs hυ absorption spectra of solid polymer electrolyte films

From the obtained values, the energy bandgap values are found to decrease continuously with increasing doping wt% concentration of CH_3COONa in the host PVP polymer. When compared with the wt% compositional ratios, the lowest bandgap value has been found for (80:20) wt% compositional ratio. This compositional ratio could enhance the high ionic conductivity.

DC Ionic Conductivity

The DC ionic conductivity of the prepared polymer electrolyte films with different wt% compositional ratios is shown in **Figure 4**. From the literature survey, the ionic conductivity of pure PVP is found to be 1.02×10^{-9} Scm^{-1} at room temperature is confirmed from the DC ionic conductivity plot and is shown in Figure 4. From the plot, it is observed that by increasing the wt% concentration of CH_3COONa in the host PVP polymer, the higher ionic conductivity was obtained for the compositional ratio 80PVP:20CH_3COONa and it is found to be 2.13×10^{-5} S/cm at 373 K. The increase in conductivity with respect to the temperature has been observed from the conductivity plot.
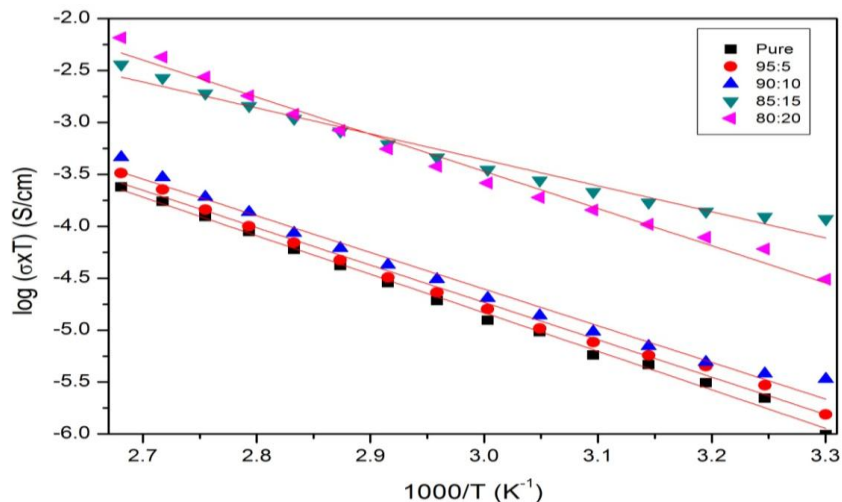

Figure 4 DC ionic conductivity of solid polymer electrolyte films

At high ionic conductivity point, the semicrystalline phase is converted into amorphous phase which results in the enhancement of ionic conductivity [43-45]. The ionic conductivity was calculated by using the following relation,

$$\sigma_{dc} = (i \times l)/(V \times A) \qquad (4)$$

Where i is the current, l is the thickness of the film, V is the applied voltage and A is the area of cross section of the film.

The calculated DC ionic conductivity values are shown in **Table 1**.

Table 1 Ionic conductivity of solid polymer electrolytes

Solid polymer electrolyte films	Conductivity at room temperature (Scm^{-1})	
Pure PVP	1.02×10^{-9}	1.13×10^{-8}
PVP:CH_3COONa (95:5)	3.11×10^{-8}	3.06×10^{-7}
PVP:CH_3COONa (90:10)	4.07×10^{-8}	4.11×10^{-7}
PVP:CH_3COONa (85:15)	1.20×10^{-7}	5.13×10^{-6}
PVP:CH_3COONa (80:20)	6.21×10^{-7}	2.13×10^{-5}

Conclusions

Solid polymer films have been prepared with different wt% ratios of PVP-CH_3COONa by solution cast technique. The structural surface and its roughness of the samples were analyzed by SEM studies for the resolution of 10 μm. UV-visible spectroscopy is used to determine the optical energy bandgap values. The lowest energy bandgap value has been found for the composition 80PVP: 20CH_3COONa at 3.47 eV. The maximum ionic conductivity was found to be 2.13×10^{-5} S/cm at 373 K for the compositional ratio 80PVP:20CH_3COONa from the DC ionic conductivity measurements.

References

[1]   Wright PV, Br Polym J 1975, 7, 319.
[2]   Fenton DE, Parker JM, Wright PV, Polym 1973, 14, 589-592.
[3]   Armand MB, Ann Rev Mater Sci 1986, 16, 245-261.

[4]   Wang X, Zhi L, Muellen K, Nano Lett 2008, 8, 323-327.
[5]   Guo S, Dong S, Wang E, ACS Nano 2010, 4, 547-555.
[6]   Zhang L, Shi GJ, Phys Chem C 2011, 115,17206-17212.
[7]   Li N, Cheng W, Ren K, Luo F, Wang K, Fu Q, Chin, J Poly Sci 2013, 31, 98-109.
[8]   Lin L, Deng H, Gao X, Zhang S, Bilotti E, Peijs T, Fu Q, Poly Int 2013, 62, 134-140.
[9]   Gao X, Zhang S, Mai F, Lin L, Deng Y, Deng H, Fu Q J Mater Chem 2011, 21, 6401-6408.
[10]   Rao M C, Hussain O M, J Alloys Compd 2010, 491(1), 503- 506.
[11]   Rao M C, J Crys Growth 2010, 312(19), 2799- 2803.
[12]   Rao M C, Optoelect Adv Mater (Rapid Commu) 2011, 5, 85-88.
[13]   Muntaz Begum Sk, Rao M C, Ravikumar R VS S N, Spectrochim Acta Part A Mol Biomol Spec, 2012, 98, 100-104.
[14]   Rao M C, J Optoelect Adv Mater 2011, 13, 428-431.
[15]   Rao M C, Hussain O M, Eur Phys J Appl Phys, 2009, 48(2), 20503.
[16]   Muntaz Begum Sk, Rao M C, Ravikumar R VS S N, J Inorg Organometa Poly Mater 2013, 23(2), 350-356.
[17]   Rao M C, J Optoelect Adv Mater 2010, 12, 2433-2436.
[18]   Rao M C, Optoelect Adv Mater (Rapid Commu) 2011, 5(5-6), 651-654.
[19]   Rao M C, J Optoelect Adv Mater 2011, 13(1-2), 72-75.
[20]   Rao M C, Optoelect Adv Mater (Rapid Commu), 2012, 6, 511-515.
[21]   Prasad P V, Ramachandra Rao K, Rao M C, J Mol Struc 2015, 1085, 115-120.
[22]   Rao M C, J Optoelect Adv Mater 2011, 13, 78-81.
[23]   Rao M C, Muntaz Begum Sk, Optoelect Adv Mater (Rapid Commu) 2012, 6, 508-510.
[24]   Rao M C, Int J ChemTech Res, 2014, 6(3), 1904-1906.
[25]   Rao M C, Optoelect Adv Mater (Rapid Commu) 2010, 4, 2088-2091.
[26]   Muntaz Begum Sk, Ravindranadh K, Rao M C, Ravikumar R V S S N, AIP Conf Proc 2013, 1536, 27-28.
[27]   Rao M C, AIP Conf Proc 2016, 1728(1), 020077.
[28]   Ravindranadh K, Rao M C, AIP Conf Proc 2016, 1728(1), 020079.
[29]   Ravindranadh K, Rao M C, AIP Conf Proc 2016, 1536(1), 219-220.
[30]   Rao M C, AIP Conf Proc 2016, 1536(1), 215-216.
[31]   Rao M C, Optoelect Adv Mater (Rapid Commu) 2012, 6, 245-248.
[32]   Rao M C, Optoelect Adv Mater (Rapid Commu) 2016, 10, 889-892.
[33]   Rao M C, Muntaz Begum Sk, AIP Conf Proc 2012, 1447, 613-614.
[34]   Ravindranadh K, Rao M C, Int J ChemTech Res 2016, 9(4), 598-603.
[35]   Rao M C, AIP Conf Proc 2012, 1447, 613-614.
[36]   Rao M C, AIP Conf Proc 2013, 1536, 27-28.
[37]   Di CA, Wei DC, Yu G, Liu YQ, Guo YL, Zhu DB, Adv Mater 2008, 20, 3289-3293.
[38]   Owens BB, Smyrl WH, Xu JJ, J Power Sources 1999, 150, 81-82.
[39]   Pandey GP, Agrawal RC, Hashmi SA, J Solid State Electrochem 2012, 15, 2253-2264.
[40]   Yang XF, Wang GC, Wang RY, Li XW, Electrochem Acta 2010, 55, 5414-5419.
[41]   Gregory TD, Hoffmann RJ, Winterton RC, J Electrochem Soc 1990, 137, 775-780.
[42]   Liew CW, Ramesh S, J Mater Res 2012, 27, 2996-3004.
[43]   Stoller MD, Park S, Zhu Y, An J, Ruoff RS, Nano Lett 2008, 8, 3498-3502.
[44]   Shahenoor Basha SK, Ranjit Kumar B, Veera Bhadra Reddy K, Rao MC, Chem Sci Rev Lett 2017, 6(22), 832-837.
[45]   Kojima Y, Usuki A, Kawasumi M, Okada A, Fukushima Y, Karauchi T, Kamigaito OJ Poly Sci 1993, 31, 1775-1778.