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Effect of Nanofiller on FTIR, DSC and DC Conductivity Studies of PVP Based Polymer Films

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Abstract
Nanocomposite polymer films (NCPs) are prepared by doping of potassium acetate (CH_3COOK) in polymer of polyvinyl pyrrolidone (PVP) by dispersing aluminium oxide (Al_2O_3) by different weight percentile ratios using solution cast technique. The obtained NCPs' films were characterized and reported. Complex analysis between NCs and host polymer was confirmed by FTIR. DSC analysis states the glass transition temperature, T_g=33.51°C at which the phase transformation changes from glassy to rubbery amorphous phase. The maximum ionic conductivity was found to be 2.02×10^{-3} S/cm for the prepared film PVP:CH_3COOK:Al_2O_3 (80:20:1%). With the proposed wt% ratios of polymer films, solid polymer battery has been fabricated and the discharge characteristics of the cell were studied.

Keywords: *Nanocomposite polymer films (NCPs), solution cast technique, FTIR, DSC, ionic conductivity, discharge characteristics*

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INTRODUCTION

In present day, researchers have made remarkable efforts on nanocomposite polymer films (NCPs) because of their excellent characteristic nature as well as good potential at physical, chemical and magnetic properties. Due to their long durability at electrochemical performances, NCPs have been used in many potential applications such as secondary batteries, electrochemical cells and sensors [1]. Nowadays, the energy consumption is the main source for the mankind for household purposes. To overcome these problems, a wide interest has taken place on electrolyte materials for the development of batteries and energy storage devices. Nanocomposite polymer films based batteries exhibit several advantages like easy film formation and flexibility and also possess good physical and mechanical stability over liquid electrolytes based batteries. Since liquid electrochemical cells have lot of disadvantages such as unstable at ambient temperatures, overflow of liquid when excess charged, rust formation at electrodes etc. [2]. Although the battery technology has improved for the past few years, the search for new materials, having better performance with high energy density and extended cycles of rechargeability, started [3]. However the uses of non-toxic and non-hazardous materials have not yet been systematically developed. In view of that, the scientists have been focused on potassium based secondary batteries. Since potassium based rechargeable batteries give the high potential and electrochemical performances, they can be treated as the alternative source to lithium and sodium rechargeable batteries [4, 5].

In the present study, polyvinyl pyrrolidone (PVP) is taken as the host polymer due to its excellent characteristics. PVP is mostly used in electronic and pharmaceutical industries due to its many potential applications. It is used as electrochromic display material in microelectronics. Potassium acetate is widely used in the preparation of electrolyte membranes for long life batteries. It is used as a complex agent in the electrolyte of dye-sensitized solar cells. Since CH_3COOK can easily dissolve in organic solvents due to their low dissipation lattice constants and having large ionic orientations. Aluminium oxide (Al_2O_3) is used as nanofiller in the preparation of polymer electrolytes to improve mechanical behavior and degree of roughness of the films because aluminium ions produce vacancies in which drifting of ions takes place freely gives rise to the ionic conductivity.

EXPERIMENTAL WORK

The chemicals such as PVP with molecular weight (M.W: 36,000 g/mol), potassium acetate (CH_3COOK) 98% purity; and aluminium oxide (Al_2O_3) were purchased from Sigma Aldrich chemicals, India. The films were prepared by using solution casting technique with doping of inorganic salt (potassium acetate) along with adding nanofiller in the host PVP polymer and labeled as different ratios (95:5:1), (90:10:1), (85:15:1) and (80:20:1). In the preparation process, double distilled water is used as a solvent. The proposed wt% ratios of chemicals are taken in beakers with solvent and allowed to stir for 48 h to get complete complexation. After that the solution was poured in dishes and kept in a hot air oven at 60°C. Later, the prepared films were placed in a vacuum desiccator.

RESULTS AND DISCUSSION

FTIR Studies

FTIR spectra of the prepared nanocomposite polymer films were analyzed in the wave numbers ranging from 450 to 4000 cm^{-1} which is shown in Figure 1. The broadening peak appeared in the spectra between 3100 and 3700 cm^{-1} relates to O=H band. This may be attributed to the redistribution of K^+ ions and ionic pairs associated with the hydroxyl group (O-H) of polymer matrix and oxygen atom in Al_2O_3 which is formed due to the complexation in the PVP-CH_3COOK polymer electrolyte.

The peaks observed at 944.5, 1105.7 and 1569.2 cm^{-1} are addressed to C-O bending, C-O stretching and C=O vibrations of the prepared PVP film [6, 7]. As increasing the dopant concentration in the host polymer, the widths of the spectral bands and the variations in the peaks have been observed at 570, 1204 and 2819 cm^{-1}. As the potassium salt is added in the polymer, the peak of the vibrational band becomes widened and slightly shifted because of the interaction between potassium-ions and carbonyl group of PVP. This results in the decrement in the transparency of the prepared films.

DSC Analysis

The DSC curves of the pure PVP and nanodoped polymer films with different wt% concentrations (95:5:1), (90:10:1), (85:15:1) and (80:20:1) were shown in Figure 2. It is observed from the DSC curve that the T_g of pure PVP has been observed at 35.75°C. Upon adding the wt% of salt concentration and by adding the Al_2O_3 (1%) to the PVP polymer, the phase formation of T_g decreased to lower value which is observed to be at 35.52, 35.06, 34.69 and 33.51°C. From the DSC curve, it is observed that the lowest Tg is found at 33.51°C for the sample with 80:20:1 wt% compositional ratio.

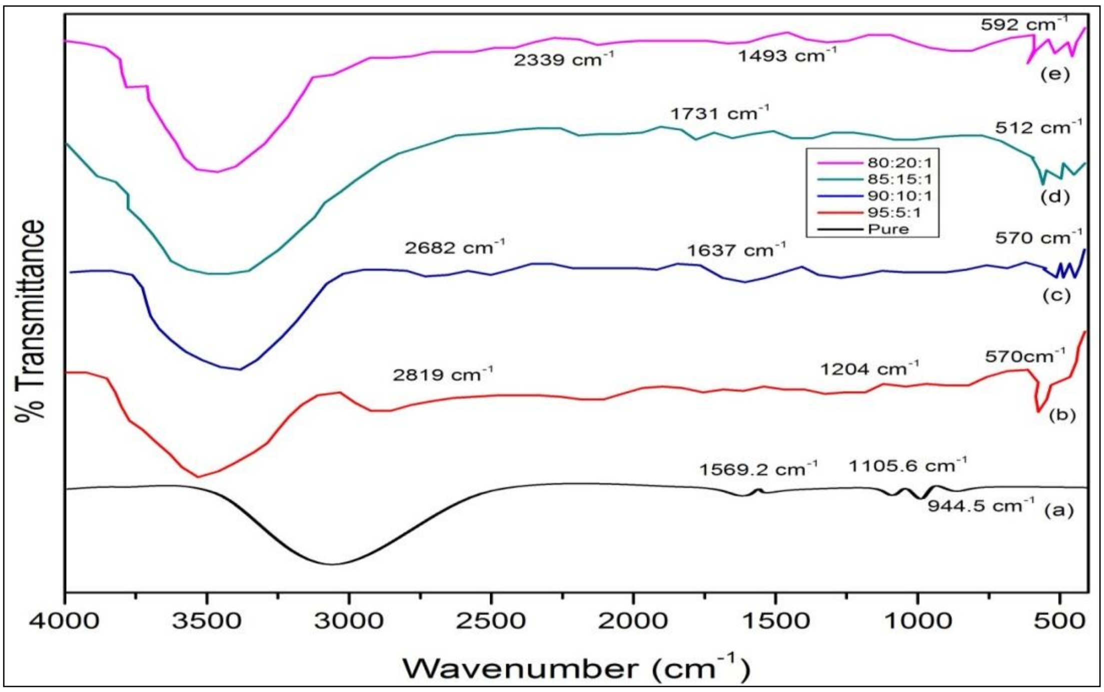

***Fig. 1:** FTIR Spectra of Nanocomposite Polymer Electrolyte Films.*

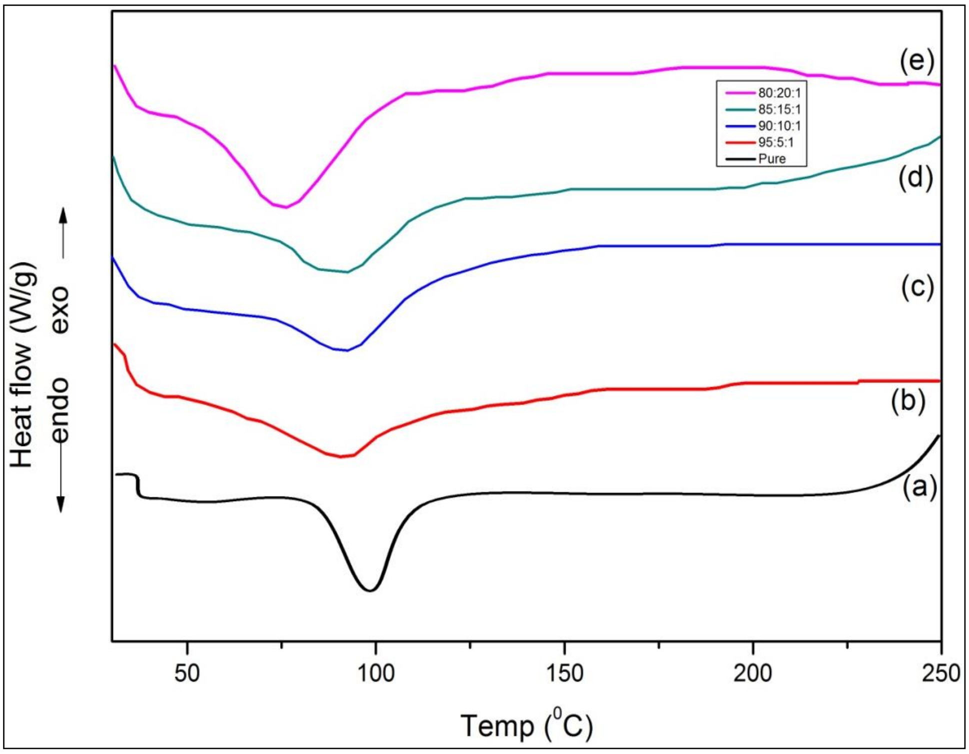

***Fig. 2:** DSC Spectra of Nanocomposite Polymer Electrolyte Films.*

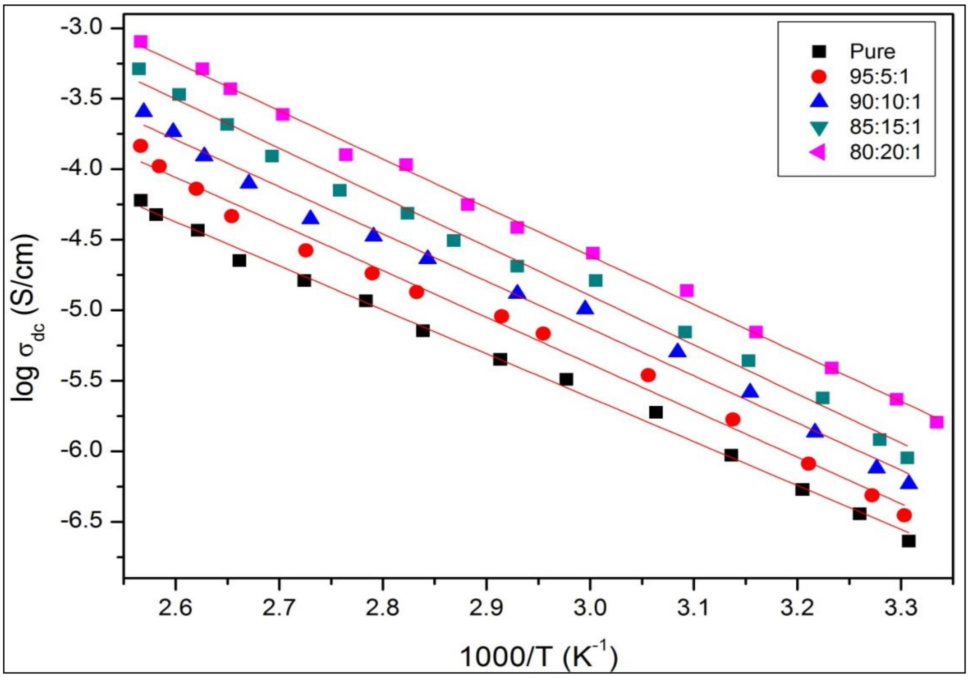

***Fig. 3:** DC Ionic Conductivity of Nanocomposite Polymer Electrolyte Films.*

The shifting of glass transition phase may be due to the plasticization phase in the polymer film. This plasticization creates the free spaces in the matrix where the ions are drifted freely; as a result, the ionic conductivity increases [8–11]. From the DSC curve, it is observed that the lowest T_g is found at 33.51°C for the sample with 80:20:1 wt% compositional ratio. During the dissociation phase, the potassium ions are interlinked with the polymer chains and due to the free flow of K^+ ions, the ionic conductivity occurs in the electrolyte films. The nanofiller is added to the proposed wt% ratio to improve the ionic conductivity rapidly.

DC Ionic Conductivity Studies

Ionic conductivity measurements of different wt% compositional ratio of the films were measured by using DC conductivity setup and the readings were noted on Keithley electrometer model 6514, which is shown in Figure 3.

By applying the temperature to the NCPs' films, the ionic conductivity value enhances, which is clearly observed from the graph. The conductivity value of pure PVP is 1.02×10^{-9} Scm^{-1} at room temperature and its value increases sharply to 1.13×10^{-8} Scm^{-1} at 373 K and for the other samples found to be 2.10×10^{-5}, 3.52×10^{-5}, 2.13×10^{-4} and 2.02×10^{-3} S/cm with 5, 10, 15 and 20% with CH_3COOK respectively. On comparison of the conductivity values, the high conductivity was found for Al_2O_3 doped nanofiller polymer film with 80:20:1% wt% ratio. The conductivity was calculated by using the formula:

$$\sigma_{dc}=(i\times l)/(V\times A) \quad (1)$$

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 increase in conductivity with temperature is explained by Arrhenius plots. At a certain point, the ionic conductivity is abruptly increased. This may be due to the change of phase from semi-crystalline to amorphous phase. This could acquire faster internal modes, for which bond rotation produces segmental motion of ions which leads to increase in the ionic conductivity [12, 13]. DC ionic conductivity and its values are shown in Table 1.

Table 1: *DC Conductivity of Nanocomposite Polymer Electrolyte Films.*

Nanocomposite Polymer Films	Conductivity at RT (Scm^{-1})	Conductivity at 373 K (Scm^{-1})
Pure PVP	1.02×10^{-9}	1.13×10^{-8}
$PVP:CH_3COOK:Al_2O_3$ (95:5:1%)	4.21×10^{-8}	2.10×10^{-5}
$PVP:CH_3COOK:Al_2O_3$ (90:10:1%)	3.01×10^{-6}	3.52×10^{-5}
$PVP:CH_3COOK:Al_2O_3$ (85:15:1%)	2.31×10^{-5}	2.13×10^{-4}
$PVP:CH_3COOK:Al_2O_3$ (80:20:1%)	6.35×10^{-5}	2.02×10^{-3}

Fabrication of Solid State Battery

NCPs based solid state battery is prepared at room temperature. In this configuration, the diffusion of ions takes place through potassium metal which acts as anode and the replacement of ions is done through mixture of iodine, electrolyte traces and carbon powder which act as cathode material, where the charge carriers take place freely and hence the ionic conductivity increases [14, 15]. The discharge performance of NCP's solid state battery is shown in Figure 4.

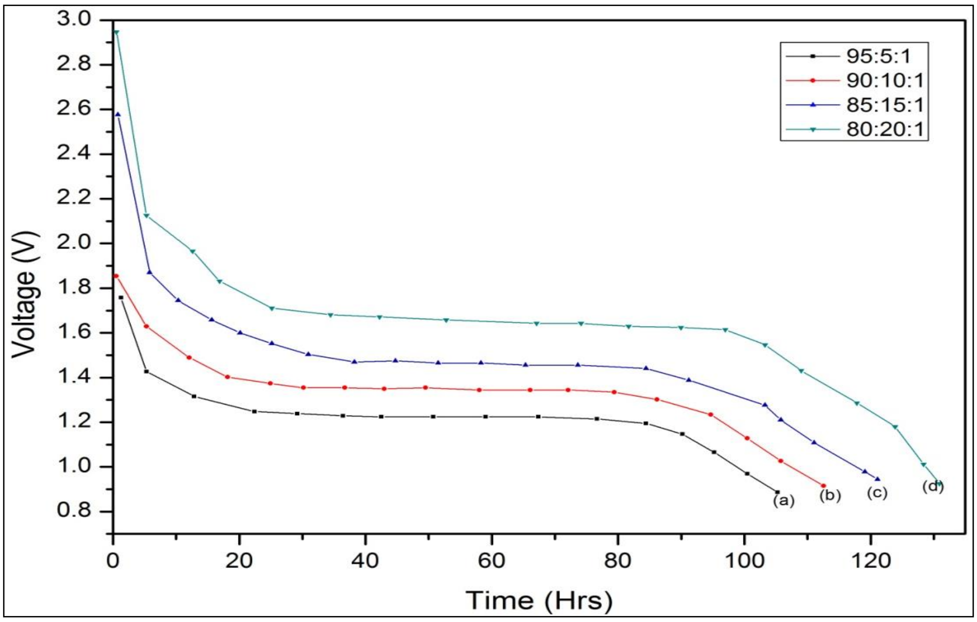

Fig. 4: *Discharge Performance of NCP's Solid State Battery.*

During discharge process, the decrement in the voltage for all the cells has been observed; this may be due to the polarization and thin layer like formation of inorganic salt at the electrode surfaces. On comparison, the solid state battery with the composition of (PVP: CH_3COOK + Al_2O_3) (80:20:1) exhibits discharge time up to 135 h than the other cells.

CONCLUSION

Nanocomposite polymer films are prepared by doping potassium acetate in host polymer of polyvinyl pyrrolidone with dispersing aluminium oxide by different wt% compositional ratios using solution cast technique. Complex analysis between NCs and host polymer was confirmed by FTIR. The peaks observed at 944.5, 1105.7 and 1569.2 cm^{-1} are addressed to C-O bending, C-O stretching and C=O vibrations of the PVP film. DSC analysis revealed the glass transition temperature, T_g=33.51°C at which the phase transformation changes from glassy to rubbery phase on heating. From the wt% composition studies, the higher value of ion conductivity for composition 80PVP-20 CH_3COOK+1% Al_2O_3 was found to be 2.02×10^{-3} Scm^{-1}at 373 K.

REFERENCES

1. Wright PV. *Br Polym J*. 1975; 7: 319p.
2. Armand MB, Chabango JM, Duclot MJ. In: Vashishta P, Mundy JN, Shenoy GK, editors. *Fast Ion Transport in Solids*. North-Holland, Amsterdam: 1979; 131p.
3. Fenton DE, Parker JM, Wright PV. *Polym.* 1973; 14: 589p.
4. Subba Reddy Ch V, Sharma AK, Narasimha Rao VVR. *Ionics*. 2004; 10(1–2): 142p.
5. Venkata Subba Rao C, Ravi M, Raja V, *et al. Iran Polym J*. 2012; 21: 530p.
6. Selvasekarapandian S, Hema M, Kawamura J, *et al. J Phys Soc Jpn Suppl A.* 2010; 79: 163p.
7. Sreekanth T, Jaipal Reddy M, Subba Rao UV. *J Power Sources.* 2001; 93: 268p.
8. Owens BB, Smyrl WH, Xu JJ. *J Power Sources*. 1999; 150: 81p.
9. Pandey GP, Agrawal RC, Hashmi SA. *J Solid State Electrochem.* 2012; 15: 2253p.
10. Yang XF, Wang GC, Wang RY, *et al. Electrochem Acta.* 2010; 55: 5414p.
11. Gregory TD, Hoffmann RJ, Winterton RC. *J Electrochem Soc.* 1990; 137: 775p.
12. Liew CW, Ramesh S. *J Mater Res.* 2012; 27: 2996p.
13. Rajendran S, Sankar Babu R, Siva Kumar P. *J Membrane Sci.* 2008; 315: 67p.
14. Naresh Kumar K, Sreekanth T, Jaipal Reddy M, *et al. J Power Sources.* 2001; 101: 130p.
15. Chandra A, Agrawal RC, Mahipal YK. *J Phys D: Appl Phys.* 2009; 42: 1p.

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