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VIBRATIONAL AND OPTICAL STUDIES ON AMMONIUM NITRATE DISPERSED TRI-BLEND POLYMER ELECTROLYTES

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Abstract

Synthesis and characterization of new materials for various electrochemical applications pave way for technological improvement. In the present study, proton conducting solid polymer electrolytes based on Polyvinylalcohol [PVA], Polyacrylonitrile [PAN], and Polyvinylidenefluoride [PVdF] are synthesized using di-methylformamide (DMF) as solvent. The complex formation between the polymers and the ammonium nitrate is confirmed by using Fourier transform infrared spectroscopic technique. The optical studies are made by using UV-Visible spectroscopic technique and the band gap energies are evaluated.

Introduction

In conventional electrochemical appliances like batteries, liquid electrolytes are used. Research work is carried on to replace the liquid electrolytes by ion conducting solid polymer electrolytes to have better durability, flexibility and long life time[1]. Many methods are used to improve the conductivity of such electrolytes[2]. One such method is blending of polymers by which the physical and chemical properties of the polymer chains can be changed so that the conductivity is improved. Some blend polymer systems have been studied and reported [3-5]. When the electrical nature of a single polymer doped with salt is compared with a blend polymer doped with the salt it is found that the conductivity is increased [6-7]. So, the present study is aimed at analyzing proton conducting tri-blend polymer electrolytes. To the best of author's knowledge, there is no report on tri –blend polymer based on Polyvinylalcohol [PVA], Polyacrylonitrile [PAN], Polyvinylidenefluoride [PVdF] dispersed with ammonium nitrate [NH_4NO_3]. PVA has excellent film forming ability, high tensile strength and flexibility. PAN is a resinous, fibrous, rubbery organic polymer which posses good mechanical strength. PVdF has low weight, low chemical corrosion resistance and heat resistance. In literature survey, the NH_4NO_3 is a good proton donor.

Experimental Techniques

Synthesis of Electrolytes

In the present work, the preparation of tri-blend polymer electrolyte dispersed with ammonium nitrate is done by using solution casting method. Blend polymer electrolytes are prepared with PVA (M.wt.1,25,000), PAN (M.wt.1,25,000), PVdF (M.wt.5,30,000) of various composition and ammonium nitrate using di-methylformamide (DMF) as solvent. The polymers are separately dissolved in DMF at 80^0C is then mixed and stirred. Then ammonium nitrate is added and stirred till the mixture becomes homogeneous. Then it is poured in the petri dish and kept in vacuum oven for solvent evaporation at 70^0C for 2 days. After the complete evaporation of the solvent the stand alone films were carefully removed from the petri dishes and sealed in an air tight cover. Polymer blend (0.9PVA: 0.08PAN: 0.02PVdF by weight) is denoted by PPP. Proton conducting Polymer blends with compositions 100% PPP – 0 % NH_4NO_3, 95 % PPP – 5 % NH_4NO_3, 90 % PPP – 10 % NH_4NO_3,85 %PPP – 15% NH_4NO_3, 80 % PPP – 20 % NH_4NO_3, 75% PPP – 25% NH_4NO_3 by molecular weight are thus synthesized.

Characterization of Electrolytes

In order to study the Vibrational, and Optical properties of the blend polymer electrolytes, they are characterized by FTIR and UV-Visible spectroscopy respectively.

- FTIR- To study the complex formation between the polymer and salt. The FTIR spectra for polymer electrolytes have been recorded in the transmission mode using a SHIMADZU-IR AFFINITY-1 spectrophotometer in the frequency range (400 - 4000 cm^{-1}).
- UV-Visible Spectroscopy- To find the band gap energy of the polymer electrolytes. The UV-Vis absorption measurements were carried out at room temperature using a Perkin Elmer Lambda 40 UV-Vis spectrometer in the range 300 to 750 nm with a resolution of 4nm

Results and discussions

Fourier Transform Infrared Analysis

FTIR has been used to study the complex formation between the polymer and the salt. FTIR is also used to study the interaction between cations, anions, solvents and polymers. This interaction is determined by the shift in the IR spectrum as well as the alteration in band shapes and the intensities of internal vibrational modes. Figure 1 represents the FTIR spectra of blend polymer electrolyte and blend polymer electrolyte dispersed with different concentrations of NH_4NO_3. The vibrational frequencies and their assignments are tabulated in Table 1.

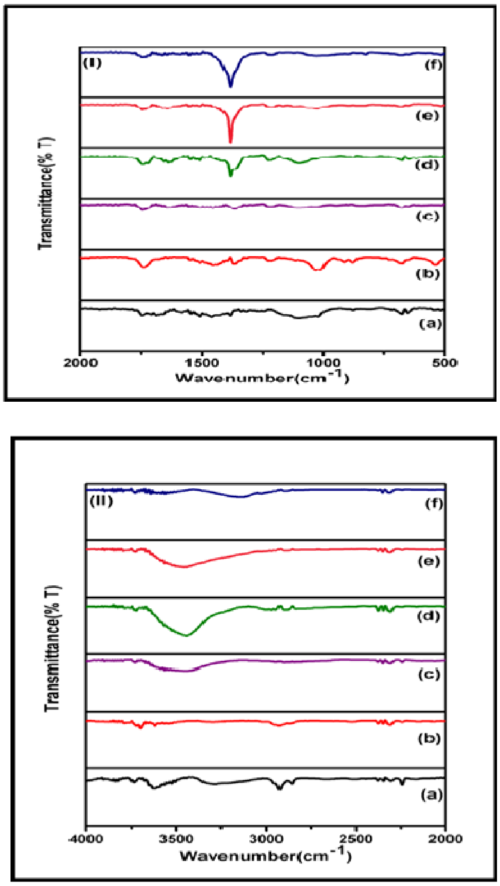


Figure 1. FTIR spectrum of (a) 100% PPP: 0% NH_4NO_3 (b) 95% PPP: 5% NH_4NO_3(c) 90% PPP: 10% NH_4NO_3 (d) 85% PPP: 15% NH_4NO_3 (e) 80% PPP: 20% NH_4NO_3(f) 75% PPP: 25% NH_4NO_3 (I) in the regions 2000-500cm^{-1},(II) in the regions 4000-2000cm^{-1}

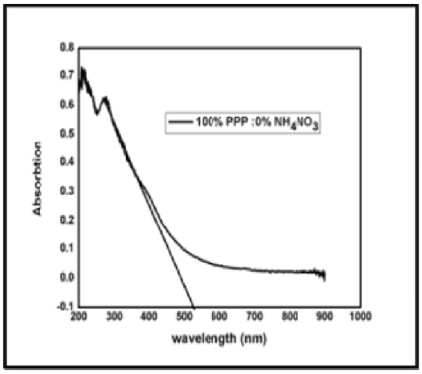
Table 1 Vibrational frequencies observed in the FTIR spectra of blend polymer electrolytes

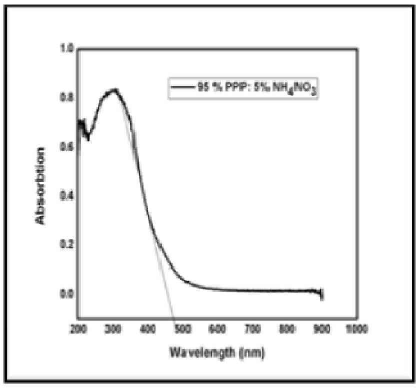
Wave number (in cm^{-1}) of composition PPP: NH_4NO_3 =						Assignment
100:0	**95:5**	**90:10**	**85:15**	**80:20**	**75:25**	
1102.24	1116.16	1104.17	1102.24	1119.26	1124.95	C-F Stretching
1211.98	1216.03	1228.57	1228.57	1215.07	1216.03	C-N Stretching
1378.47	1370.33	1364.73	1382.87	1383.83	1383.83	N-O Stretching
1459.05	1454.23	1454.23	1465.90	1470.16	1477.40	CH_2 bending
1746.42	1740.64	1745.46	1743.53	1745.46	1743.99	C=O Stretching
2243.06	2244.82	2243.53	2244.23	2242.15	2243.47	C ≡N Stretching
2308.12	2309.6	2309.6	2309.6	2310.56	2310.83	C-H sym.Stretching
3619.17	3620.14	3442.7	3446.56	3478.38	3139.01	O-H Stretching

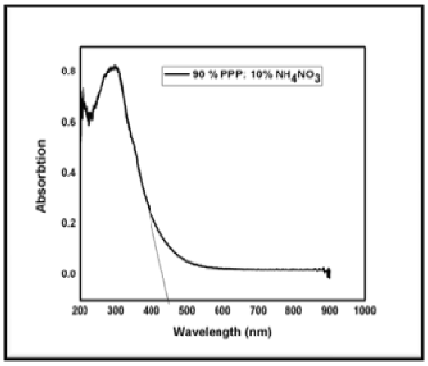
From Table 1, the shifting of peaks can be observed by comparing with the peaks of pure blend polymer (PPP). The peak observed at 1102 cm^{-1} is ascribed to C-F stretching of PVdF. This peak has been found to be shifted to higher wave number in the NH_4NO_3 dispersed polymer electrolytes. The broad peak observed at 1211 cm^{-1} is ascribed to C-N stretching of DMF. It indicates the presence of the solvent in the polymer electrolytes. The peak observed at 1309 cm^{-1} is ascribed to N-O stretching of DMF and this peak is shifted and becomes sharp when the salt concentration is increased. The peak observed at 1459 cm^{-1} which is ascribed to CH_2 bending of PAN, PVA, PVdF has been found to be changed in the NH_4NO_3 dispersed polymer electrolytes. The sharp peak observed at 1746 cm^{-1}ascribed to C=O stretching of PVA [8] is found to be shifted to lower wave number in the NH_4NO_3 dispersed polymer electrolytes. The weak peak observed at 2243 cm^{-1} corresponding to C≡N stretching of PAN [9] is found to be shifted to higher wave number in the NH_4NO_3 dispersed polymer electrolytes. A shallow peak is observed at 2309 cm^{-1}which corresponds to C-H symmetric stretching gets shifted in salt dispersed polymer electrolytes with the reduction of intensity [10]. Shift in the peak values appearance of new peak confirms the interaction of ions with polymer matrix. The above result confirms the complex formation between the polymer matrix and the salt.

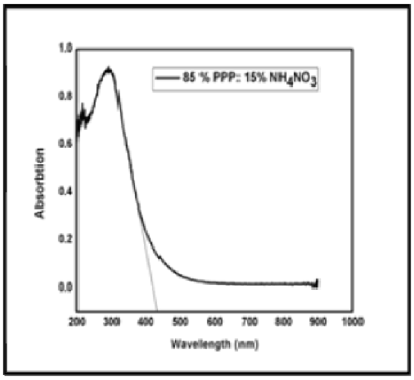
UV-Visible Spectral Analysis

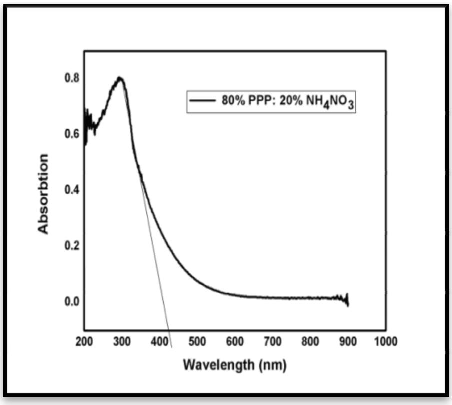
In optical studies, to investigating the band structure of materials the measurement of the absorption spectra is the most direct and simplest method [11]. In the absorption process an electron is excited from a lower to higher energy state by absorbing a photon of known energy in the transmitting radiation. The changes in the transmitted radiation can decide the types of possible electron transitions. Fundamental absorption refers to band-to-band or exciton transition. Moreover the fundamental absorption clears itself by a rapid rise in absorption, known as absorption edge, which can be used to determine the optical band gap.











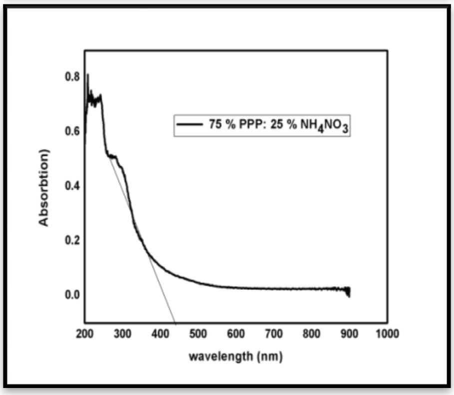


Fig 4.3.9 (I) UV-Visible Spectra forblend polymer electrolyte dispersed with different concentration of NH_4NO_3

(i) UV-Vis spectral analysis (Einstein method):

Fig 4.3.9 (I) represents the UV-Visible spectra for blend polymer electrolyte (PPP) and blend polymer electrolyte dispersed with different concentration of NH_4NO_3.The band gap energy is calculated using the Einstein relation [12]

E_g=hc/λ--------------(8)

Where, E_g is the band gap energy, h is the Planck's constant, c is the Velocity of light, λ is interpreted as the wavelength corresponding to sharp rise in absorption. The X- intercept of the tangent drawn at the sharp absorption region of the spectrum is the absorption edge.

(ii) UV-Vis spectral analysis (Tauc method):

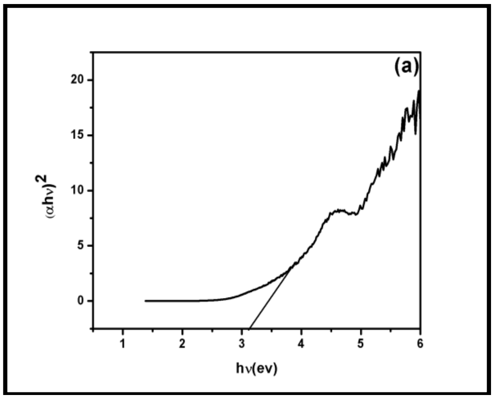
The absorption coefficient (α) on the photon energy (hv) in the band edge spectral region for a direct transition is given by the Tauc Model [13]

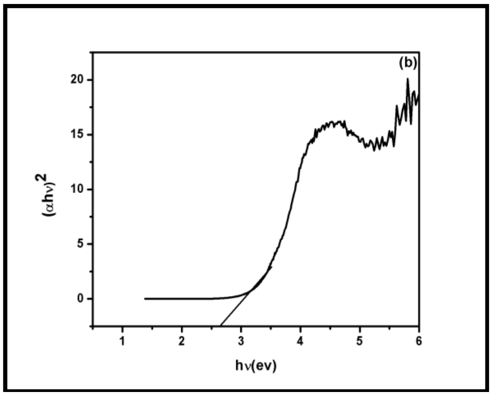
$(\alpha hv)^2 = A(Eg - hv)$--------(9)

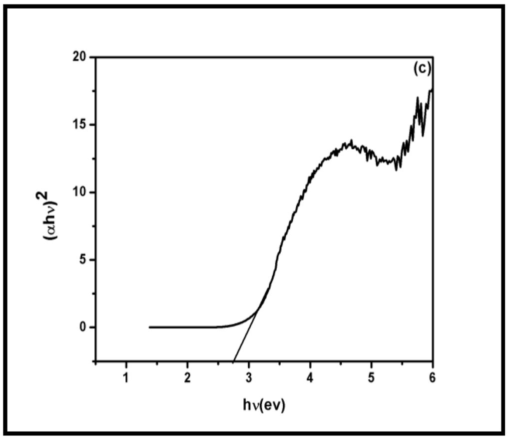
- where 'α' is the absorption coefficient,
- 'h' is the Planck's constant,
- 'v' is the frequency of light,
- E_g is the band gap of the solid and

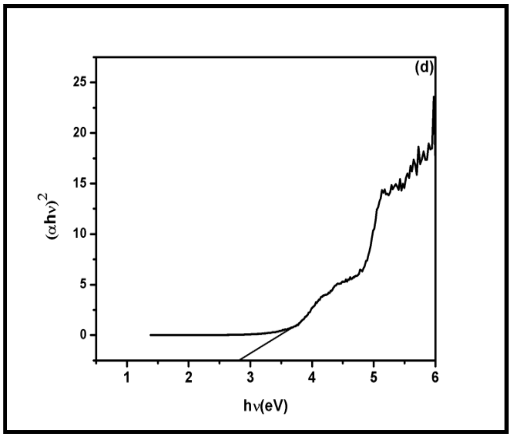
- 'A' is the constant.

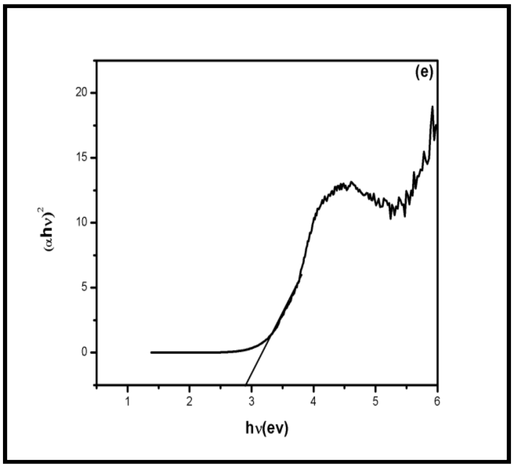
A plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for pure PPP and PPP dispersed with different concentration of NH_4NO_3 is shown in figure 4.3.9. The band gap energy is calculated from the plot by extrapolating the straight line portion of the curve to zero absorption coefficient value.











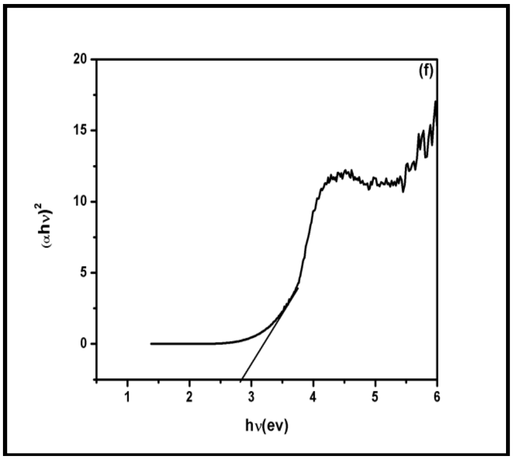


Fig 4.2.9 (II) UV-Visible Spectra of(a) 100% (PPP): 0% NH_4NO_3 (b) 95% (PPP): 5% NH_4NO_3(C) 90% (PPP): 10% NH_4NO_3(d) 85% (PPP): 15% NH_4NO_3(e) 80% (PPP): 20% NH_4NO_3 (f) 75% (PPP): 25%NH_4NO_3

Table 4.6 Band gap Energy of synthesized polymer electrolytes

Sample	Band gap Energy E_g (eV)	
	Einstein Equation	Tauc Equation
100% PPP : 0% NH_4NO_3	3.12	3.12
95% PPP : 5% NH_4NO_3	2.63	2.63
90% PPP : 10% NH_4NO_3	2.77	2.77
85% PPP : 15% NH_4NO_3	2.86	2.87
80%PPP: 20% NH_4NO_3	**2.93**	**2.92**
75% PPP : 25% NH_4NO_3	2.85	2.85

It is observed that, the band gap energy is decreased with the addition of NH_4NO_3. As the salt concentration is increased, the band gap energy increased and it is maximum for 20%NH4NO3 dispersed blend polymer electrolyte which suggests that, the electron conductivity is minimum in the 20% salt dispersed system.

References

1. Kumudu Perera and M. A. K. L. Dissanayake, Conductivity variation of the liquid electrolyte, EC: PC: $LiCF_3SO_3$ with salt concentration,Sri Lankan Journal of Physics, 7(2006) 1-5.
2. C.C. Yang, G .M. Wu, Study of Microporous – PVA/PVC composite polymer membrane and its application to MnO_2 Capacitors, Mater. Chem. Phys. 114 (2009) 948.
3. X.Lu,RA.Weiss, Devolpoment of miscible blends of polyamide and manganese sulfonated polystyrene using specific interaction, Macromolecules 24 (1991) 4381.
4. J.L.Acosta, E.Morales, Synthesis and characterization of polymethylalkoxysiloxanes solid polymer electrolytes, Solid State Ionics 85 (1996) 85-90.
5. Sandoval, C.Castro, L.Gargallo, D.Radic, J.Freire, Specific interaction in blends containing Chitosan and functionalized polymers, Polymer 46 (2005) 10437.
6. S.Nithya, S.Selvasekarapandian, S.Karthikeyan, D.Vinothpandi, C.Sanjeeviraja, Proton Conducting polymer electrolyte based on PAN, Indian Journal of Applied Research 3 (2013) 2249.
7. S.Sivadevi, S.Selvasekarapandian, S.Karthikeyan, N.Vijaya, F.Kingslin Mary Genova,C.Sanjeeviraja, H.Nithya, Iwai Junichi Kawamura, Proton conducting polymer electrolyte based on PVA-PAN blend doped with Ammonium Nitrate,Int.J.Electroact .Mater.1(2013) 64-70
8. S.Sivadevi, S.Selvasekarapandian, S.Karthikeyan, C.Sanjeeviraja, H.Nithya, Iwai Junichi Kawamura, Proton conducting polymer electrolyte based PVA-PAN blend doped with Ammonium Thiocyanate, Ionics (2014).
9. G.Hirankumar, Ph.D thesis entitled, Characterisation of solid polymer electrolytes based on poly (vinyl alcohol) submitted to Bharathiyar university, Coimbatore, India (July 2005).
10. Kopitzke RW, Linkous CA, Anderson HR, Nelson GL, Conductivity and water uptake of aromatic – based proton exchange membrane electrolytes, J.ElectrochemSoc,147 (2000) 1677.
11. P.Bacelon, J.Corset, C.De Loze, J.Solution Chem. 9 (1980) 129
12. Ali Akbar Yoursefi, Influence of Polymer Blending on crystalline structure of Polyvinylidene Fluoride, Iranian Polymer Journal 20 (2011) 109-121.