Nanotechnology Perceptions
ISSN 1660-6795
www.nano-ntp.com

Investigation Of AC Conductivity And Optical Characteristics Of PVA Films Doped With Ammonium Iodide

Beede Suneelkumar[1] , Vinodkumar Rathod[2] , Manjunatha B[3]

[1] *Associate professor Department of studies in PG & UG Chemistry,*
Government First Grade College, SHAHAPUR, India
[2] *Associate Professor Department of Physics Government College (Autonomous) Kalaburgi,*
Karnataka, India
[3] *Department of Physics Govt. Women first grade college Jewargi Colony Kalaburagi,*
Karnataka, India

This study explores the AC conductivity and optical properties of polyvinyl alcohol (PVA) films doped with ammonium iodide (NH_4I). The films were synthesized using the solution casting method, and their electrical and optical behaviours were analyzed through impedance spectroscopy and UV-Vis spectroscopy, respectively. The results indicate that NH_4I doping significantly enhances the AC conductivity of PVA films, suggesting improved ion transport mechanisms. Optical analysis reveals a reduction in the energy band gap with increasing dopant concentration, confirming alterations in the electronic structure. These findings highlight the potential applications of NH_4I-doped PVA films in electronic and optoelectronic devices.

KEYWORD: Polyvinyl alcohol (PVA), ammonium iodide (NH_4I).,XRD

INTRODUCTION

Polyvinyl alcohol (PVOH, PVA, or PVAl) is a water-soluble synthetic polymer. Polyvinyl alcohol has excellent film forming, emulsifying and adhesive properties. It is also resistant to oil, grease and solvents. It is odorless and nontoxic [1]. It has high tensile strength and flexibility, as well as high oxygen and aroma barrier properties. However these properties are dependent on humidity, in other words, with higher humidity more water is absorbed. The water, which acts as a plasticiser, will then reduce its tensile strength, but increase its elongation and tear strength [2]. Polyvinyl alcohol (PVA) is a widely used polymer in various applications due to its excellent film-forming ability, water solubility, and biocompatibility. To enhance its electrical and optical properties, PVA can be modified by doping with different salts and additives. Ammonium iodide (NH_4I) is an interesting dopant because of its ionic nature, which can influence the conductivity and optical characteristics of PVA-based films [3-4].The study of AC conductivity in polymer films is crucial for understanding their potential applications in electronic and energy storage devices, such as capacitors, batteries, and sensors. Similarly, the optical properties of these films, including absorption, transmittance, and band gap energy, are essential for applications in optoelectronic devices [5-9]. Investigating the impact of NH_4I doping on these characteristics can provide insights into the suitability of these materials for such applications [10].

Objectives

The primary objectives of this study are:

1. To analyze the AC conductivity of PVA films doped with ammonium iodide at different frequencies and temperatures.
2. To investigate the optical properties, including absorption spectra and optical band gap, of the prepared films.
3. To understand the correlation between the electrical and optical characteristics of NH_4I-doped PVA film[11]

Sample preparation

Poly vinyl alcohol (average mol.wt = 85.000 – 1.24.000), Ammonium iodide (144.94g/mole) and Dimethyl sulphoxide (78.13g/mole). Have been used for the preparation of polymer electrolytes. Various molar ratios of PVA: NH_4I (95:05, 90:10, 85:15, 80:20, 75:25 and 70:30) have been prepared by solution casting technique. In this technique, appropriate quantities of PVA and NH_4I in aprotic solvent. DMSO (dried and distilled before usage) are stirred continuously for several hours until a homogeneous solution has been obtained. The obtained solution is then casted in glass plates and is subjected to drying (70^0c for 5 days) in a vacuum chamber. Thick films of micrometer thickness range have been obtained.After the completion of different concentrations of NH_4I doped PVA solutions and NH_4I doped PVA films are subjected to characterization like UV visible, IR studies, conductivity, XRD analysis [12-13].

Results and Discussion:

X-Ray Diffraction studies:

The XRD pattern of PVA and PVA: NH_4I polymer electrolytes have been shown in fig . A broad peak around 24.46^0 has been observed in the XRD pattern of salt free PVA. However in the salt added system, the peak has been found to increase in broadness and decrease in intensity. Then clearly showsthe increased amorphous nature of the PVA film with increase in salt concentration.X-ray diffraction (XRD) analysis of Ammonium Iodide (NH_4I) helps in identifying its crystalline structure, phase purity, and possible structural changes**.** Based on standard data, here's how its XRD pattern can be understood[14].

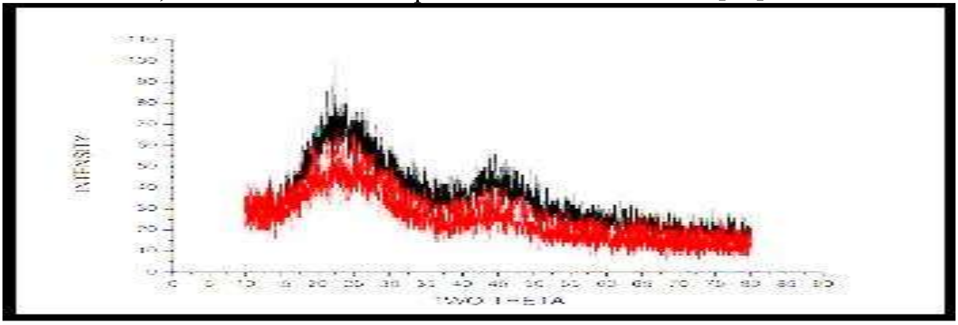

Figure: The XRD pattern of PVA and PVA: NH_4I

Scanning electron microscopy (SEM): Figure presents the SEM micrographs of the pure and composite samples, captured at a magnification of 1000×, illustrating their surface morphology [15].The prepared sample showed morphology with randomly distributed micro-sized round shaped particles with uniformity on the surface as well as a few agglomerations Smooth & Homogeneous if NH_4I is well dispersed in PVA.The SEM image these particle are nonporous, shape of the granular agglomerates also these particles are organised or interconnecting[16]. At higher doping levels, NH_4I may lead to phase separation or crystal growth Due to variations in material composition, areas with higher NH_4I concentrations may appear brighter or darker in SEM images[17].

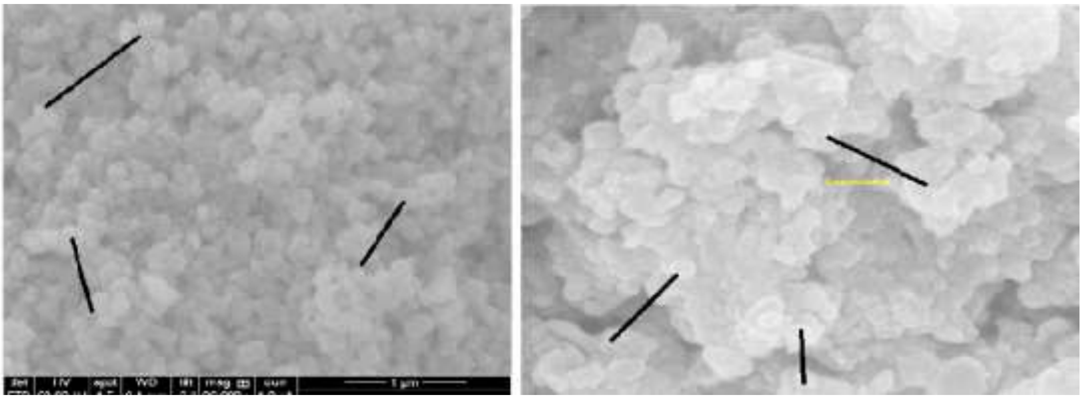

Figure: The SEM image of PVA and PVA: NH_4I

DCconductivity

The temperature-dependent DC electrical conductivity was investigated to understand the charge transport mechanism in the polymer composites. The variation in DC conductivity with temperature for the pure and composites is presented in Figure[18]. Conductivity increases as temperature rises. The scale suggests values between 2.0×10^{-2} to $\sim1.2\times10^{-1}$ S/cm.These likely represent two different samples or conditions. The black curve has higher conductivity at higher temperatures. The red curve follows a similar trend but with slightly lower values. A notable jump in conductivity occurs beyond 140-160°C. This could indicate a phase transition, polymer softening, or ion mobility enhancement. Beyond 180°C, conductivity increases rapidly. This suggests a higher carrier mobility or structural modifications in the material. The initial increase in the values of conductivity is due to the extended chain length of sample due to which the charge carriers can hopp between the favourable localized sites. The decrease in the values of conductivity of all the wt% of the composite is due to partial blocking of charge carriers. Further, gradual increase in conductivity is noticed due to thevariationin distribution of the sampleparticles incomposite [19].

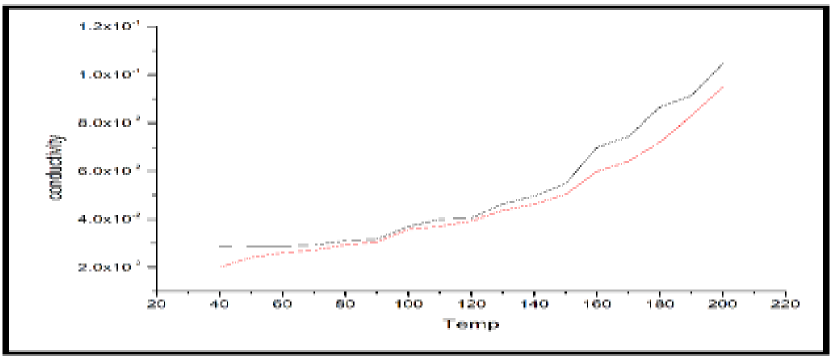

Figure: The DC conductivity of PVA and PVA: NH_4I

A.Cconductivity;

The A.C conductivity for the common polymer is changes with the frequency according to the following formula (Joshi & Sinha, 2007)[20].

$$\sigma_{ac}(\omega)=\sigma_t-\sigma_{d\tau}=A\omega^s$$

This figure show the variation of conductivity as a function of frequency **(**Freq) for a given material. This type of analysis is typically performed in AC impedance spectroscopy to understand charge transport mechanisms in materials like polymer electrolytes, ionicconductors, or semiconductors**.** Conductivity values range from 1.0×10^{-4} to ~4.0×10^{-4} S/cm. Higher conductivity means more charge carriers are moving efficiently. Conductivity increases significantly as frequency rises beyond ~10^4 Hz (10 kHz). This is due to the hopping of charge carriers, especially in materials like polymer electrolytes [20].

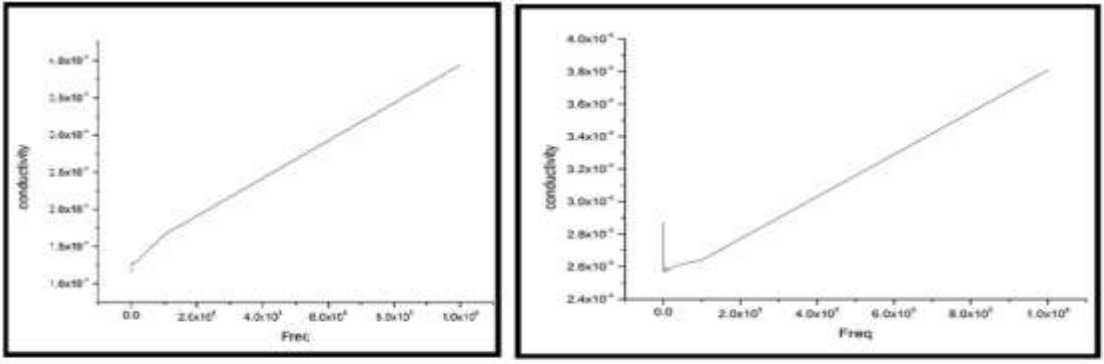

Figure: The AC conductivity of PVA and PVA: NH_4I

Optical studies of UV-Visible Spectroscopy:

UV-Vis spectroscopy measures the absorbance or transmittance of a material as a function of wavelength (typically 200–800 nm).. Absorbance occurs due to electronic transitions in molecules, where electrons move from a lower to a higher energy state (e.g., valence band to conduction band in semiconductors). The absorbance follows Beer-Lambert's Law: $\mathbf{A = \varepsilon Cl}$

where:

A = Absorbance, E=Molar absorptivity, C = Concentration ,l = Path length

This graph represents the UV-Visible absorption spectrum, showing how the material absorbs light at different wavelengths. The X-axis represents wavelength (nm)**,** while the Y-axis represents absorbance. The initial sharp rise in absorbance suggests a strong absorption in the UV region**.** This indicates the presence of electronic transitions in the material. The point where the absorbance rises sharply marks the absorption edge. It is related to the optical band gap (Eg) of the material. The absorption edge shifts based on doping levels, material composition, and defects.The point where the absorbance rises sharply marks the absorption edge. It is related to the optical band gap (Eg) of the material. The absorption edge shifts based on doping levels, material composition, and defects. After the sharp rise, the absorbance increases gradually in the higher-wavelength region This suggests some light scattering or extended absorption features.The absorption shift indicates doping-induced changes in the polymer structure. The presence of NH_4I may lead to an increased charge carrier density[21-23]..

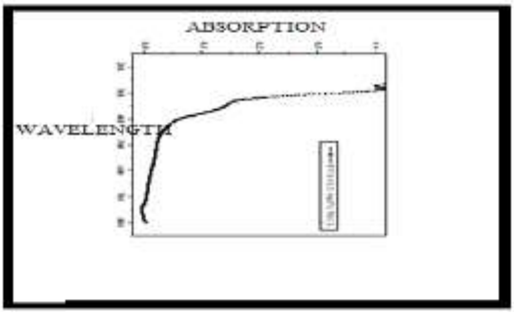

Figure: PLOT ABSORPTION V/S WAVWLENGTH

CONCLUSION:

In this study, PVA:NH_4I composite films were successfully prepared and characterized using various techniques, includingXRD, SEM, DC conductivity, AC conductivity, and UV-Vis spectroscopy. The results provide valuable insights into the structural, morphological, electrical, and optical properties of the prepared films. X-ray diffraction results confirmed the semi-crystalline nature of PVA, with the incorporation of NH_4I leading to a decrease in crystallinity. The broadening of peaks suggests an increase in amorphous regions, which is beneficial for ion transport. Scanning Electron Microscopy revealed homogeneous surface morphology, indicating good dispersion of NH_4I within the PVA matrix. The microstructure suggests the formation of interconnected ionic pathways, which enhance the conductivity of the material. The temperature-dependent DC conductivity measurements showed an increase in conductivity with temperature, confirming the thermally activated transport mechanism. The improvement in conductivity is attributed to the increased amorphous nature and enhanced ion mobility. Frequency-dependent conductivity analysis exhibited a power-law behavior, indicating the contribution of both ionic and electronic charge carriers. The increase in AC conductivity with frequency suggests the dominance of hopping conduction mechanisms Optical absorption studies revealed a shift in the absorption edge, indicating modifications in the band structure due to NH_4I doping. The calculated optical bandgap (Eg) decreased with NH_4I content, suggesting enhanced charge carrier density and improved conductivity.

References:

1. DizaoLi, JiabinZou, CongyuanWei, YankaiZhou, LipingWang, WeifengZhang, GuiYu. Small-moleculesemiconductorscontainingdithienylacrylonitrileforhigh-performanceorganicfield-effecttransistors. JournalofMaterials Chemistry C**2019**, 7 (37), 11457 11464. https://doi.org/10.1039/C9TC03726H
2. T.Ananthakumar,S.Malathi,C.V.MythiliandM.Jeyachandran,"Structural,MorphologicalandOpticalProperties of Zinc Oxide Nanoparticles by Polymer Capping", International Journal of ChemTech Research, Vol.11No.08,(2018), pp. 48-57.
3. L. Spanhel and M. A. Anderson, "Semiconductor clusters in the sol-gel process: quantized aggregation, gelation, andcrystal growthin concentratedzincoxide colloids",J.Am. Chem.Soc. Vol. 113,no. 8, (1991),pp. 2826–2833.
4. T. K. Kundu, N. Karak, P. Barik and S. Saha, "Optical Properties of Zno Nanoparticles Prepared by ChemicalMethod Using Poly (VinylAlcohol) (PVA) as Capping Agent", Int. J. Soft Comp. Eng. (IJSCE) vol. 1, (2011), pp. 19-24.
5. M. Thirumavalavan, K. L. Huang and J. F. Lee, "Preparation and Morphology Studies of Nano Zinc Oxide ObtainedUsingNativeandModifiedChitosans", Materials,vol.6,no. 9,(2013), pp.4198-4212. 5.Y.L.Wu,A. I.Y.Tok,F. Y.C. Boey, X. T. Zeng and X. H. Zhang, "Surface modification of ZnOnanocrystals", Appl. Surf. Sci. vol. 253, no. 12,(2007),pp. 5473–5479.
6. B. Bochev, G. Yordanov, H. Yoshimura and C. Dushkin, "Synthesis of ZnOnanocrystals in the presence of differentadditives," in Nanoscience and Nanotechnology, Proceedings of National Conference, Bulgaria,Sofia, (2011), pp. 25–26.
7. I M. Joni, A. Purwanto, F. Iskandar and K. Okuyama, "Dispersion Stability Enhancement of Titania Nanoparticles inOrganicSolventUsinga BeadMillProcess", Ind.Eng. Chem.Res. vol. 48,no.15, (2009),pp.6916–6922.
8. M.Kaur,K.L.SinghandP.Kumar,"EffectofPVAcappingontheopticalandstructuralpropertiesofhydrothermallysynthesizedZnSnanocrystals",Int. J.ITEng.Appl.Sci. Res.vol.2, no.1,(2013), pp.20–24.
9. I M. Joni, R. Balgis, T. Ogi, T. Iwaki and K. Okuyama, "Surface Functionalization for Dispersing and StabilizingHexagonal Boron Nitride Nanoparticle by Bead Milling", Colloids and Surfaces A: Physicochem. Eng. Aspects, vol.388, no. 1-3, (2011),49– 58.
10. I M. Joni, T. Ogi, A. Purwanto, K. Okuyama, T. Saitoh and K. Takeuchi, "Decolorization of beads-milled TiO2nanoparticlessuspensioninan organicsolvent", Adv.PowderTechnol.vol. 23,no.1,(2012), pp.55–63.
11. Jipa, I. M. et al. Effect of gamma irradiation on biopolymer composite films of poly(vinyl alcohol) and bacterial cellulose. Nucl. Instrum. Methods Phys. Res. B 278, 82–87 (2012).
12. Azmi, S. et al. Reinforcement of poly(vinyl alcohol) hydrogel with halloysite nanotubes as potential biomedical materials. Soft Mater **15**, 45–54 (2017).
13. Khiar, A. S. A. &Arof, A. K. Conductivity studies of starch-based polymer electrolytes. Ionics (Kiel) **16**, 123–129 (2010).
14. Karthikeyan, A., Vinatier, P. &Levasseur, A. Study of lithium glassy solid electrolyte/electrode

interface by impedance analysis. Bull. Mater. Sci. **23**, 179–183 (2000).

15. Mahadeva1 ,Manjunatha B2 , Nagajyoti3 , Manjula V.T3 , SHRUTI Gogi1 , VAISHALI N BIRGE1 , Sangshetty Kalyane1* "The Study Investigates the Preparation, Structural, Electrical and LPG Sensing Properties of Composite Material Comprising Nickel Oxide -Doped Polyaniline" Nanotechnology Perceptions 20 No. S8 (2024), ISSN 1660-6795, 851–861.
16. Rahul Jabnoor , Manjunatha B , M V N AmbikaPrasad , ArunkumarLagashetty, VijaykumarBasavarajappa , SangshettyKalyane "Synthesis, characterisation and AC conductivity study of PANI/α-Fe2O3 nanocomposites", IOP Conf. Series: Materials Science and Engineering 1221 (2022) 012001 IOP Publishing doi:10.1088/1757-899X/1221/1/012001
17. Arya, A. & Sharma, A. L. Structural, electrical properties and dielectric relaxations in Na^+ -ion-conducting solid polymer electrolyte. J. Phys. Condens. Matter **30**, 165402 (2018).
18. Shruti Gogi1, Manjunatha B2, Mahadeva1, Arunkumar Lagashetty3, Sangshetty Kalyane1* Preparation, Structural, Electrical and LPG Sensing Properties Study of Zinc Oxide Doped Polyaniline Composite (PnZnO), Nanotechnology Perceptions 20No.S6(2024), ISSN 1660-6795 253–265,http://www.nano-ntp.com
19. Aziz, S. B., Abdullah, O. G. &Rasheed, M. A. A novel polymer composite with a small optical band gap: New approaches for photonics and optoelectronics. J. Appl. Polym. Sci. **134**, 21 (2017).
20. B T Vijaykumar, B Manjunatha, RamabaiNarasimhachar, Mahadevi, Reshma, B Bharati ,,m BasavarajaSannakki " Studies on Structural, Morphological, Electrical And Gas Sensing Properties of the Polyaniline/ Bismuth Oxide (PANI/Bi2O3)Composites"Letters in High Energy Physics ISSN: 2632-2714,
21. Hassen, A., el Sayed, A. M., Morsi, W. M. & El-Sayed, S. Influence of Cr_2O_3 nanoparticles on the physical properties of polyvinyl alcohol. J ApplPhys 112, 093525 (2012).
22. El-Bana, M. S., Mohammed, G., el Sayed, A. M. & El-Gamal, S. Preparation and characterization of PbO/carboxymethyl cellulose/polyvinylpyrrolidonenanocomposite films. Polym. Compos. 39, 3712–3725 (2018).
23. M.C. Arenas et al.Electrical and morphological properties of polyaniline–polyvinyl alcohol in situ nanocompositesCompos. B Eng.(2014).
24. Arya, A. & Sharma, A. L. Structural, electrical properties and dielectric relaxations in Na^+ -ion-conducting solid polymer electrolyte. J. Phys. Condens. Matter **30**, 165402 (2018).