

Optical Characterization of Polyvinyl alcohol - Ammonium Nitrate Polymer Electrolytes Films

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Abstract

Polyvinyl alcohol – Ammonium Nitrate polymer electrolyte films were prepared by casting method. UV-Vis Double Beam Spectrophotometer in the wavelength range (190-1100) nm were used to investigate the optical properties. The optical constants such as, transmission spectra, refractive index, extinction coefficient, real and imaginary parts of the dielectric constant, optical band gaps, and optical conductance are found. It was found that the energy band gaps are decreased upon the increase of salts concentration. The values of the width of the tails of localized states in the forbidden gap of the films obtained from Urbach plots are varied from 0.64 to 1.16 eV. The real and imaginary part of dielectric constant of the polymer electrolyte films increases with increasing NH₄NO₃ concentration. The dielectric constant shows decreases abruptly in the wavelength (235-260) nm, and finally becomes constant with increase wavelength.

Keywords: optical energy band gap; optical conductance; refractive index; extinction coefficient.

1. Introduction

Polymer electrolytes recently have been a subject of great interest due to theoretical interest as well as practical importance for the development of electrochemical devices, such as rechargeable batteries, capacitors and sensors [1].

Generally, the addition of inorganic salts into a polymer matrix can improve its conductivity. It was found that metallic salts with Polyvinyl Alcohol (PVA) can improve the electrical conductivity, optical absorption and of the refractive index [2]. Polyvinyl Alcohol (PVA) exhibits adhesive and good film-forming properties. So an intense research has been focused both from a fundamental point of view in understanding the mechanism of ion transport and also from the application point of view in enhancing the performance of devices based on polymer electrolytes [3]. The present work aims to study the effect of Ammonium Nitrate (NH₄NO₃) on the optical properties of PVA.

2. Experimental details

Different compositions of Polyvinyl alcohol (PVA) Ammonium Nitrate (NH₄NO₃) films have been prepared by solution techniques, using different weight ratios of NH₄NO₃ (0, 5, 10, 15, 20, and 25) wt%. The solution of PVA and NH₄NO₃ is obtained by dissolving them in distilled water at 350 K, and the solution is stirred well using magnetic stirrer for one hour, until highly homogenous polymer solution was formed. These homogenous solutions were casted in a glass dish (diameter of 5 cm). The whole assembly was placed in a dust free chamber and the solvent was allowed to evaporate slowly in open air at room temperature for a week. The thickness of the films were in the range of (0.045-0.10) mm.

3. Theoretical method

The ratio of radiant power transmitted (P) by a sample to the radiant power incident (P_0) on the sample is called the transmittance T :

$$T = \frac{P}{P_0} \quad (1)$$

but, $P = P_0 e^{-\alpha t}$

$$T = e^{-\alpha t} \quad (2)$$

Where t is the sample thickness, and α is the optical absorption coefficient, which calculated from absorbance (A), and thickness of the films by [4, 5]:

$$\alpha = 2.303 \left(\frac{A}{t} \right) \quad (3)$$

If T is the Transmittance and A is the absorbance of the films, then, the reflectance of the films has been calculated as follows [6]:

$$R = 1 - (T + A) \quad (4)$$

The refractive index (n), and extinction coefficient (k), of the film, are calculated using [7, 8]:

$$n = \frac{[1 + \sqrt{R}]}{[1 - \sqrt{R}]} \quad (5)$$

$$k = \frac{\alpha\lambda}{4\pi} \quad (6)$$

Where λ is the wavelength of the incident light.

The optical energy gap (E_g) calculated from the relationship:

$$\alpha(\nu) = B \frac{(h\nu - E_g)^r}{h\nu} \quad (7)$$

Where $h\nu$ is the photon energy, B is a constant and r is the power factor and that takes **0.5, 2, 1.5, and 3**, for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively.

The dielectric constant can be obtained theoretically, since it was related to the absorption coefficient. The real part (ϵ_r) and the imaginary part (ϵ_i) of the dielectric constant, was obtained using relation [8]:

$$\epsilon_r = n^2 - k^2 \quad (8)$$

$$\epsilon_i = 2nk \quad (9)$$

The imaginary part of dielectric constant, represents loss factor or energy absorbed. So the complex dielectric constant (ϵ^*) is expressed as [9]:

$$\epsilon^* = \epsilon_r - i \epsilon_i \quad (10)$$

4. Results and Discussion

4.1. FTIR spectrum:

The infrared (IR) spectrophotometer (Perkin-Elmer 833) was used for recording the IR spectra in the wave number range **500 – 4000 cm^{-1}** at a resolution of **4 cm^{-1}** . FTIR absorption spectra of pure PVA film and it's with different concentrations of NH_4NO_3 are shown in Fig.1.

The broad band observed between **3200 – 3500 cm^{-1}** are refers to the intermolecular hydrogen bonding and **-OH** stretching vibration (region I). The vibrational band between **2800 – 3000 cm^{-1}** is associated with the **C – H** stretching from alkyl groups (region II), and the absorption peaks between **1690 – 1750 cm^{-1}** (region III) are due to the stretching **C = O** and **C – O** from acetate group remaining from PVA [10,11].

The **C – H** stretching band of pure PVA has been shifted to higher wavenumber in doped polymer electrolytes up to **20% NH_4NO_3** , whereas beyond this concentration the band was shifted to the lower wavenumber. This may be due to the interaction of anion with molecular complex species [2]. Thus the NO_3^- ion may be dominant up to **20% NH_4NO_3** concentration, and it may be decreased beyond that concentration as a result of the due to the formation of ion aggregates, which decrease the number of mobile charge carriers.

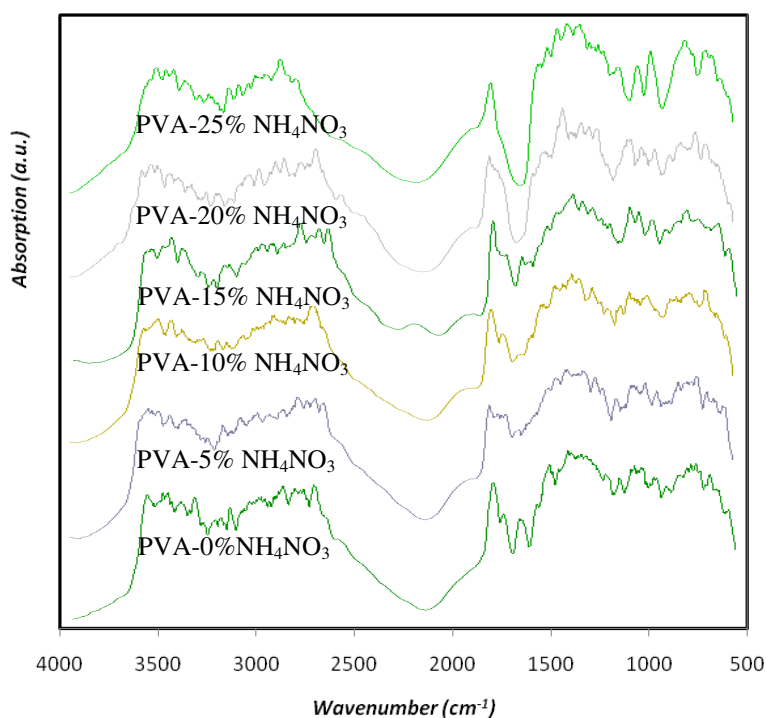


Fig.1: IR absorption spectra of PVA films filled with various filling level of NH_4NO_3 .

4.2. Optical Absorbance Spectra:

A Perkin-Elmer Lambda 25 UV–Visible spectrophotometer device was used to measure the absorption spectra of the samples in the wavelength range (190–1100) nm. The optical absorbance against the wavelength in the wavelength range (190–500) nm is shown in Fig.2.

The absorbance spectrum shows a sharp increase in absorption at wavelength near to the absorption edge of the threshold wavelength for onset of absorption. The energy corresponding to this region determines the band gap of the samples [12]. The addition of salt to PVA greatly increased the absorption edge in the wavelength range (190–230) nm. It was observed that the absorption edge shifts towards higher wavelength with NH_4NO_3 concentration increase.

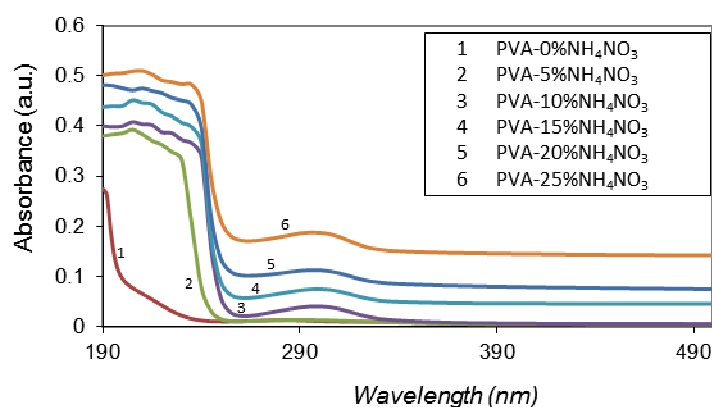


Fig.2. Absorption Spectra of PVA- NH_4NO_3 polymer electrolyte films.

4.3. Optical Transmittance Spectra:

The optical transmittance spectra of the samples in the wavelength range (190–500) nm, is shown in Fig.3. A shift in the optical absorption edge to low wavelengths (blue shift) is appeared for the polymer electrolyte samples.

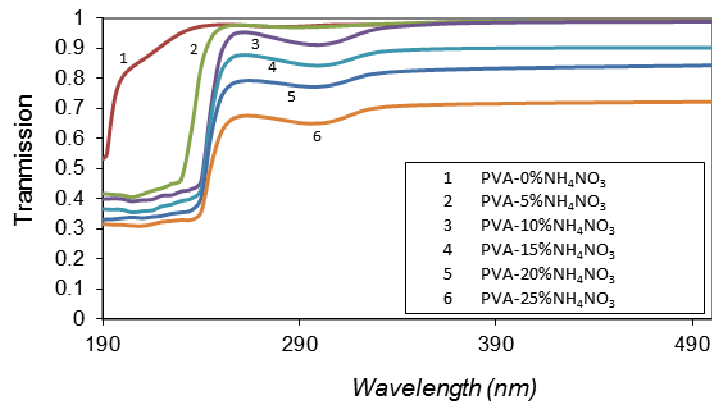


Fig.3. Transmittance Spectra of PVA-NH₄NO₃ polymer electrolyte films.

The optical transmittance at wavelength $\approx 190\text{nm}$ for pure PVA was nearly 78%, while it was 50% for other samples. The optical transmittance was increased with wavelength up to 98% for all films beyond 240nm.

4.4. Refractive Index:

The refractive index and extinction coefficient was plotted as a function of wavelength as shown in Fig. 4&5, respectively. The refractive index of polymer electrolyte samples was almost constant in low wavelength, and then decreased with increasing wavelength, after that it again becomes constant. Overall the Ammonium Nitrate (NH₄NO₃) concentration caused the increase in refractive index, especially in the UV range. The refractive index of the polymer electrolyte samples increase up to 2.6 and then it remain constant.

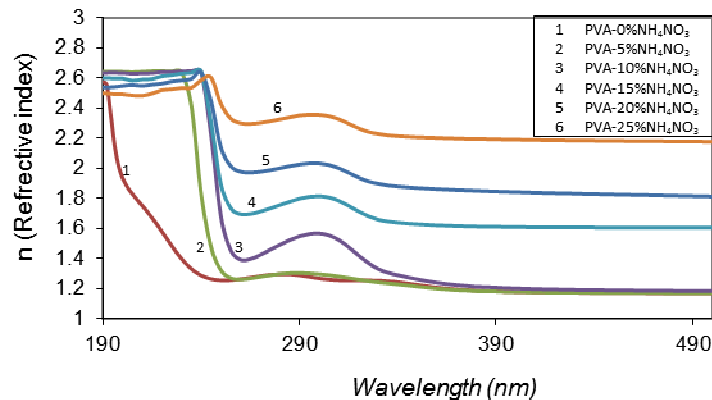


Fig.4. Refractive Index versus wavelength of PVA-NH₄NO₃ polymer electrolyte films.

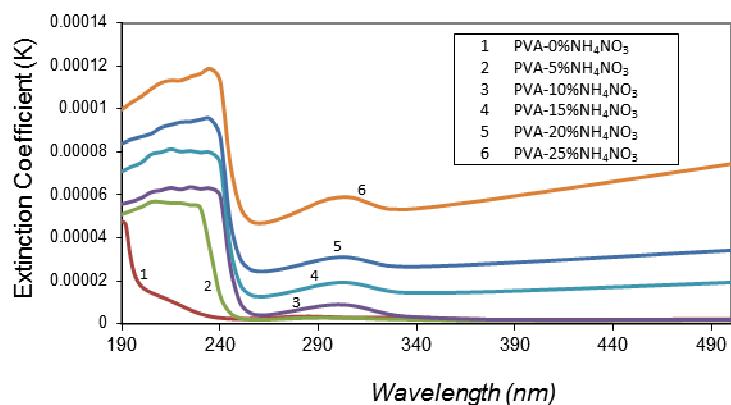


Fig.5. Extinction coefficient versus wavelength of PVA-NH₄NO₃ polymer electrolyte films.

4.5. Optical band gaps:

A plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for PVA-NH₄NO₃ polymer electrolyte films is shown in Fig.6. From the graph, the values of the direct band gap energies are evaluated. Extrapolation the straight line portion of the curves to zero absorption coefficient value gives the energy band gap value. The linear nature of the plots at the absorption edge confirms that PVA-NH₄NO₃ polymer electrolyte have a direct band gap. It can also be seen from the figure that the energy gap for pure PVA film was equal to 6.3 eV, and it is decreased by increasing NH₄NO₃ concentration, the values are summarized in Table I. the coefficient B in equation (7) was obtained from the $(slope)^2$ of the linear region of the plot.

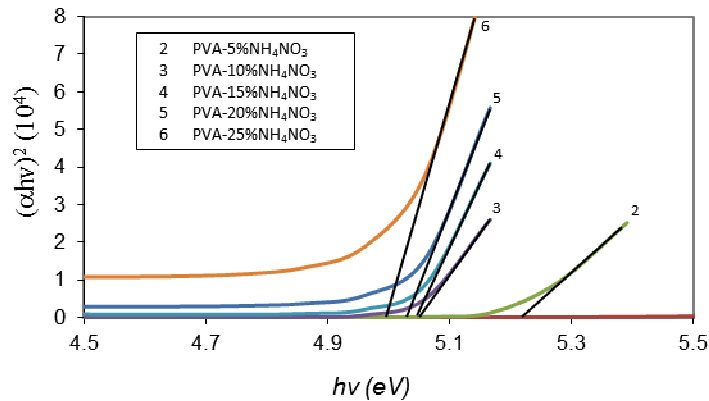


Fig.6. Variation of $(\alpha h\nu)^2$ as a function of photon energy of PVA-NH₄NO₃ polymer electrolyte films.

In 1953 F. Urbach introduces a relation which can be used for materials that absorption coefficient ($\alpha < 10^4 \text{ cm}^{-1}$) and an exponentially change against energy, the relation was used by other researchers [13-15]:

$$\alpha(\nu) = \alpha_0 \exp\left(\frac{h\nu}{\Delta E}\right) \quad (11)$$

where α_0 is a constant, and ΔE is an energy characterizing the degree of disorder introduced by the defects, dangling bond, and grain boundaries and hence it is interpreted as the width of the tails of localized states in the forbidding gap. The value of ΔE is calculated from the slope of the linear part of the curves and also listed in Table I. The decreases in the width of the tails of localized states of films are observed due to the increase of NH₄NO₃ concentration.

Table I: The variation of E_g , ΔE , and B versus NH₄NO₃ concentration.

NH ₄ NO ₃ concentration	E_g (eV)	ΔE (eV)	B ($\text{cm}^{-1}\text{eV}^{1/2}$)
0%	5.5812	0.3816	277.7928
5%	5.2228	0.9417	378.3266
10%	5.0428	1.1378	458.7884
15%	5.0357	1.1650	496.7671
20%	5.0286	0.8898	648.8247
25%	5.0035	0.6400	772.2559

4.6. Optical Conductance:

The optical conductance (σ) is obtained using the relation [12],

$$\sigma = \frac{anc}{4\pi} \quad (12)$$

Where c is the velocity of light in the space; n is the refractive index and a is the absorption coefficient.

Fig.7 shows the variation of optical conductivity of PVA- NH₄NO₃ films, as a function of photon energy. The conductivity of pure PVA is constant up to 5.0eV of photon energy, after that it increases with increase in photon energy, while the optical conductivity of PVA: NH₄NO₃ samples are found to decrease with increasing photon energy. The NH₄NO₃ concentration caused the increase in optical conductivity, which is due to high absorbance of polymer electrolyte films. The increase in optical conductance, and decrease in band gap energy of polymer electrolyte with increase of NH₄NO₃ concentration, can be attributed to the increase in number of mobile charge carriers and also to the increase in amorphous nature of the polymer electrolyte [2,3].

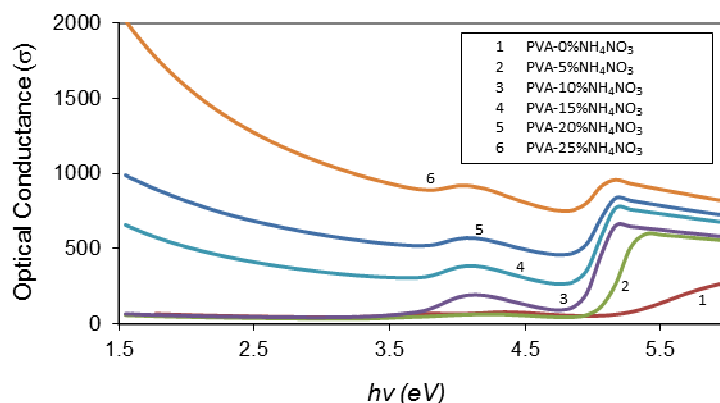


Fig.7. Optical conductivity of PVA-NH₄NO₃ polymer electrolyte films.

4.7. Dielectric Constant:

The real and imaginary parts of the dielectric constant of pure PVA and PVA: NH₄NO₃ samples, as a function of wavelength are illustrated in Fig.8. The real and imaginary part of the dielectric constant increases slowly with NH₄NO₃ concentration. At higher wavelengths the dielectric parameter are almost constant.

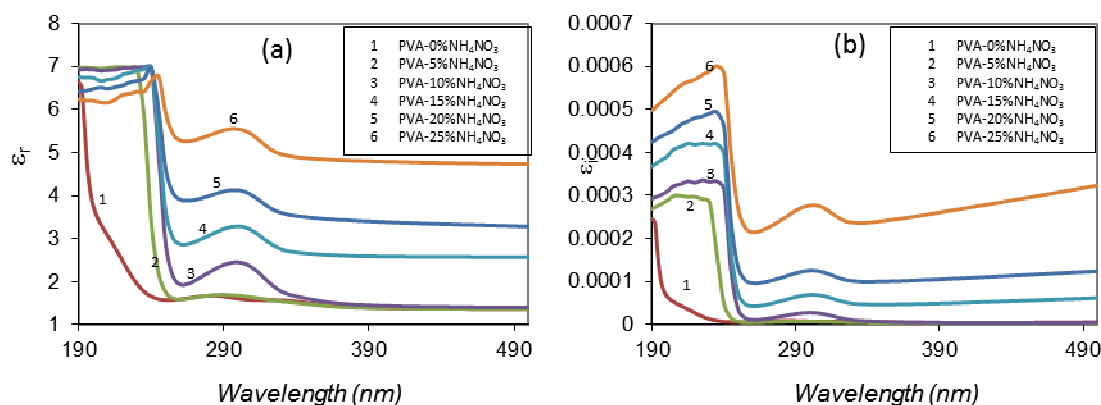


Fig.8. (a) Real part ϵ_r' and (b) Imaginary part ϵ_r'' of dielectric constant as a function of NH₄NO₃ concentration.

5. Conclusions

PVA based polymer electrolyte films with different concentration of ammonium nitrate NH₄NO₃ has been prepared using solution casting technique. The values of the direct optical band gaps decreased from 6.33eV for pure PVA to 5.00eV for 25% NH₄NO₃ concentration. The increase in optical conductance, and decrease in energy band gap of polymer electrolyte with increase of NH₄NO₃ concentration, was attributed to the increase in number of mobile charge carriers and also to the increase in amorphous nature of the polymer electrolyte. The optical constants such as, extinction coefficients, refractive index, real and imaginary dielectric constants and optical conductance are found to depend on the NH₄NO₃ concentration in the PVA film.

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